Remote sensing of sea surface Sun-induced chlorophyll fluorescence: consequences of natural variations in the optical characteristics of phytoplankton and the quantum yield of chlorophyll $a$ fluorescence

M. BABIN, A. MOREL and B. GENTILI

Laboratoire de Physique et Chimie Marines, Université Pierre et Marie Curie and CNRS BP 8, F 06230 Villefranche-sur-Mer, France

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Abstract. The rate of Sun-induced chlorophyll $a$ fluorescence (SICF) observed at sea surface is determined by chlorophyll $a$ concentration, incident irradiance, and optical and fluorescence properties of the phytoplanktonic population. In this study, the impact of natural variations in the two latter on the use of remotely sensed SICF to determine ocean surface chlorophyll $a$ concentration, is assessed using a simple parameterization of phytoplankton optical properties and a model describing the variations in the quantum yield of chlorophyll $a$ fluorescence as a function of environmental factors, such as excess irradiance and nutrient limitations. It is shown that (1) variations in the optical properties of phytoplankton are the main cause of non-linearity in the relationship between SICF and chlorophyll $a$ concentration, (2) the extent of spatial variations in the rate of fluorescence per unit chlorophyll $a$ concentration and irradiance, at the level of a typical sensor scene, prevents the use of a linear relationship between SICF and chlorophyll $a$ concentration even at local scales and (3) the optical properties of the ocean surface layer play an important role in modifying the SICF signal. Nevertheless, the parameterizations presented in this paper may represent a reasonably sound approach for a meaningful use of SICF in view of detecting the chlorophyll $a$ concentration within the upper layer of the ocean. Interestingly, it is also shown that the detection threshold of SICF could be significantly lower than the one currently expected.

1. Introduction

The use of in vivo fluorescence excited by artificial light sources to monitor the concentration of phytoplankton chlorophyll $a$ in sea water was introduced 30 years ago by Lorenzen (1966). The simultaneous discovery and identification of the Sun-induced chl $a$ fluorescence emission peak in the upward light stream measured at sea surface (Morel and Prieur 1977, Neville and Gower 1977), thereafter studied by Gordon (1979), Kishino et al. 1984a, Topliss and Platt (1986) and Dirks and Spitzer (1987), led Neville and Gower (1977) to extend this technique to airborne remote sensing of Sun-induced chl $a$ fluorescence (SICF). Following the successful application of SICF airborne remote sensing (Gower and Borstad 1981, Doerffer 1981), the European Space Agency (ESA) started up the development of an ocean colour sensor which includes appropriate channels for the detection of SICF (MERIS; MEdium Resolution Imaging Spectrometer). Launching of MERIS is expected for 1999. MODIS (MODe rate resolution Imaging Sensor) planned by NASA for launch at the end of the 1990s, will have a similar capability.

The measurement of SICF from space seems promising, especially in coastal
(Case 2) waters where fluorescence can provide a signal specific of chl $a$, while the standard blue-to-green reflectance ratio technique fails. Nevertheless, before any quasi-quantitative results can be expected from this technique, some basic problems in the interpretation of SICF detected from space have to be considered and ruled out. One of these is the retrieval of the relatively weak SICF signal through the set of radiances detected at the spacecraft level. To solve this problem, radiative transfer models are currently developed to predict the influence of oceanic and atmospheric optical properties on SICF (Fischer and Kronfeld 1990, Fischer and Schlüssel 1990). The crucial problem, however, is the non-conservative character of in vivo chl $a$ fluorescence, which is largely affected by the physiological response of phytoplankton to environmental factors such as the light and nutrient concentration. As a result, the relationship between fluorescence and chl $a$ concentration (from hereafter denoted [chl $a$]) is highly variable, as well as site- and time-dependent (see Falkowski and Kiefer 1985).

The lack of knowledge on the behaviour of SICF has prevented its applicability to remote sensing from being clearly assessed. Firstly, the range of [chl $a$], possibly accessible to SICF remote sensing techniques, has not been rigorously established. As a first approximation, Doerffer (1993) estimated that the detection threshold could be about 1 mg m$^{-3}$. Waters containing more than 1 mg chl $a$ m$^{-3}$ would occupy c. 2 per cent of the world ocean surface, and would be responsible for less than 8 per cent of global ocean primary production (Antoine et al. 1996). In this context, the contribution of SICF remote sensing would be highly mitigated, even in coastal waters, as [chl $a$] can also be found here lower than 1 mg chl $a$ m$^{-3}$. However, as chlorophyll-specific phytoplankton light absorption capabilities seem to be higher in low-[chl $a$] waters (e.g., see Bricaud et al. 1995 and Cleveland 1995), SICF remote sensing may perhaps allow detection of [chl $a$] lower than 1 mg m$^{-3}$. This point deserves study.

The second aspect of SICF remote sensing applicability that has to be considered is the depth from which fluorescence can be detected above sea surface. Chlorophyll $a$ fluorescence, with an emission maximum around 685 nm, is strongly absorbed by the water itself; therefore the fluorescence signal emerging from sea surface originates from the very upper layer, and thus originates from only a minute fraction of the whole water column chl $a$ content. This constraint, although being much less severe for the colour ratio techniques (e.g., blue-to-green ratio), is typical of ocean colour remote sensing. To circumvent this limitation, empirical algorithms have been developed to predict the water column integrated chl $a$ content from the concentration within the first optical depth determined through a colour ratio technique (Morel and Berthon 1989). In regard to chl $a$ fluorescence, the limited depth from which SICF can be remotely detected involves additional consequences. Near surface phytoplankton actually experience the most acute physiological stresses due to excessive irradiance (and possibly nutrient limitation). To what extent these stresses can affect the fluorescence response and therefore any quantitative relationship between fluorescence and [chl $a$] remains to be determined.

Finally, the applicability of SICF remote sensing to large-scale monitoring must be explored. If we acknowledge that the relationship between algal fluorescence and [chl $a$] is highly space-dependent, regional calibrations could represent a solution. Nevertheless, at which scale such calibration could be applied is to be examined.

The first objective of the present study is to identify the most significant factors that govern the behaviour of SICF. After these factors are introduced into a
biophysical model, the second objective is to assess, through a sensitivity analysis, their impact on SICF in the marine environment. Finally, the applicability of SICF remote sensing on a large scale is examined through a case study.

2. Background

The rate of chlorophyll a fluorescence \( F \); mol quanta m\(^{-2}\) s\(^{-1}\) emitted by a thin seawater layer of thickness \( dz \), can be expressed as:

\[
F = PAR[chl \, a] \bar{a}^* Q_a^*(685) \phi_F dz
\]

where \([chl \, a]\) is the concentration of chl a within this layer (mg m\(^{-3}\)), \( \bar{a}^* \) is the mean absorption coefficient of algae expressed per unit of chl a [m\(^2\) (mg chl a\(^{-1}\))], \( Q_a^*(685) \) is a dimensionless factor accounting for intracellular reabsorption of fluorescence within the emission spectral band (centred on 685 nm), and \( \phi_F \) is the quantum yield of fluorescence [mol quanta emitted (mol quanta absorbed)\(^{-1}\)]. \( PAR \) is the photosynthetically available radiation (mol quanta m\(^{-2}\) s\(^{-1}\)), defined as the scalar irradiance \( \bar{E}(\lambda) \) integrated between 400 and 700 nm. Note here that, in the particular case where only a fraction of fluorescence emission is detected within a narrow spectral window, the spectral range of exciting radiations to be considered should not overlap with the detection window.

In equation (1), the independent variables that experience the largest variations in the marine environment are \( PAR \) and \([chl \, a]\). In the first metres of the water column, \( PAR \) varies mostly according to the sun elevation, from 0 to about 2000 \( \mu \)mol quanta m\(^{-2}\) s\(^{-1}\); \([chl \, a]\) goes from less than 0.03 in oligotrophic waters to more than 30 mg m\(^{-3}\) in eutrophic ones. Therefore, \( F \), when normalized to \( PAR \), is largely determined by the variations of \([chl \, a]\), to the extent that the three other terms in equation (1) remain sufficiently stable. This is the rationale for using the signal of natural chl a fluorescence to estimate \([chl \, a]\) through remote sensing techniques, given that \( PAR \) can generally be fairly well estimated using models or other sensor channels information. Indeed, \( F/PAR \) can in some circumstances explain up to 80 per cent of \([chl \, a]\) natural variations (e.g., Lorenzen 1966, Kiefer et al. 1989, Chamberlin et al. 1990). Nevertheless, because the product \([\bar{a}^* Q_a^*(685) \phi_F]\) is also largely variable in the natural environment (Kiefer 1973, Loftus and Seliger 1975, Slovacek and Hannan 1977, Heaney 1978, Falkowski and Kiefer 1985), the overall accuracy of \([chl \, a]\) determinations from \( F/PAR \), is of c. \pm 50 per cent (Parsons et al. 1984). To reduce these uncertainties, the natural variability of \([\bar{a}^* Q_a^*(685) \phi_F]\) must be understood and its cause more precisely known; thereby, a predictive parameterization, based on variables measurable by remote sensing, could be achieved with the aim of improving the \([chl \, a]\) determination.

3. Natural variability of the optical components of SICF

3.1. Chlorophyll-specific absorption coefficient of algae, \( \bar{a}^* \)

In natural lighting conditions, the operational coefficient is expressed as:

\[
\bar{a}^* = \int_{400}^{700} a^*(\lambda) \bar{E}(\lambda) d\lambda \left( \int_{400}^{700} \bar{E}(\lambda) d\lambda \right)^{-1}
\]

where \( a^*(\lambda) \), the chl a-specific in vivo absorption coefficient of phytoplankton [m\(^2\) (mg chl a\(^{-1}\))] is weighted by the in situ irradiance spectrum, \( \bar{E}(\lambda) \). For a hypothetical solution of pure chl a, the \( a^*(\lambda) \) spectrum is a constant; according to Beer's law, the absorption coefficients \([a(\lambda); m^{-1}]\) of such a solution is a linear function of the
chl a concentration, with \( a^*(\lambda) \) representing the slope. For algae, \( a^*(\lambda) \) is always enhanced by the contribution of accessory pigments also present within algal cells (other chlorophylls, carotenoids and phycobilins). Therefore, as the relative pigment composition, \( a^*(\lambda) \) is highly species-dependent (see for example, the review by Prézelin and Boczar 1986). Additionally, because pigments are packaged into cells, molecular self-shading brings \( a^*(\lambda) \) to decrease from its maximal value \( [a^*_\text{sol}(\lambda)] \); spectral absorption coefficients by the same pigments when not embedded within the cells] to lower values as the intracellular pigment content \( (c_i) \) and cell diameter \( (d) \) increase (Duysens 1956). For this phenomenon, generally denoted as ‘package effect’, a simple mathematical formulation was given by Morel and Bricaud (1981) for spherical cells.

In marine environment, \( a^*(\lambda) \) was recently found to be roughly inversely correlated with [chl a] (Carder et al. 1991, Babin et al. 1995, Bricaud et al. 1995). This observation suggests that, in natural oceanic environments, (1) the proportion of accessory pigments relative to the chl a content increases with decreasing [chl a], and (2) variations in [chl a] seem to mainly result from variations in \( c_i \) and \( d \), rather than in cell number per unit volume.

Using a set of 815 \( a^*(\lambda) \) spectra gathered from oceanographic campaigns conducted in the Gulf and Estuary of the St. Lawrence River (Canada), the Pacific Peruvian upwelling, the Sargasso Sea, the western tropical Atlantic and the Mediterranean Sea, the relationship between \( a^*(\lambda) \) and [chl a] was examined by Bricaud et al. (1995). At the wavelength of maximum absorption by chl a (i.e., 440 nm), [chl a] was found to explain 77 per cent of \( a^*(\lambda) \) natural variations. In the present study, we computed \( \tilde{a}^* \) using equation (2) for each of the same 815 \( a^*(\lambda) \) spectra and applying an irradiance spectrum typical of sea surface (figure 10 in Babin et al. 1993). Firstly, it was found that \( \tilde{a}^* \) vary over almost one order of magnitude (figure 1(a)). Secondly, [chl a] explains 67 per cent of \( \tilde{a}^* \) variations (figure 1(b)), and according to the data distribution, \( \tilde{a}^* \) can be expressed as a function of [chl a] using the following expression:

\[
\tilde{a}^* = 0.0161 [\text{chl a}]^{-0.257}
\]  

so that \( \tilde{a}^* \) would vary from 0.007 to 0.04 m²(mg chl a)

3.2. The reabsorption factor, \( Q_a^*(685) \)

Because the red chl a absorption band partly overlaps its fluorescence band (see figure 2), the fluorescence emission is partly reabsorbed before escaping the cell. The fraction of fluorescence that is not reabsorbed at 685 nm is determined by the dimensionless factor \( Q_a^*(685) \) (Collins et al. 1985), which theoretically varies between 0 and 1. For a variety of phytoplankton species \( Q_a^*(685) \) was found to change from 0.66 to 1 (Collins et al. 1985).

According to Morel and Bricaud (1981), \( Q_a^*(685) \) can be expressed as:

\[
Q_a^*(685) = \frac{a^*(685)}{a^*_\text{sol}(685)}
\]  

At 685 nm, \( a^*(\lambda) \) mostly reflects the contribution of chl a, especially when measured over a baseline linearly joining \( a^*(660) \) and \( a^*(700) \) to remove the contribution of accessory pigments (see table 1 in Bricaud and Stramski 1990). Therefore, \( a^*_\text{sol}(685) \) can be assumed to equal the value typically obtained for a solution of chl a when accounting for the spectral shift occurring in vivo (see Bidigare et al. 1990). In
Figure 1. (a) Frequency distribution of the mean absorption coefficient of algae expressed per unit of chl a ($\bar{a}^*$), obtained at different locations in the world oceans (see Briceaud et al. 1995). (b) Relationship between $\bar{a}^*$ and chlorophyll a + pheopigment concentration.

acetone, $a_{sol}^*(685)$ is found to equal $c.0011 \, \text{m}^2/\text{(mg chl a)}^{-1}$. Using this value, $Q_{av}^*(685)$ was computed via equation (4) for the 815 absorption spectra of Briceaud et al. (1995). The results show that $Q_{av}^*(685)$ varies widely for natural conditions at sea (figure 3(a)); a large part of these variations, however, is believed to result from residual absorption by accessory pigments (not entirely removed with the adopted base line) as well as from some technical errors which are expected to be larger, for
these data, in spectral regions where absorption is low (see Bricaud et al. 1995). These uncertainties explain the presence of \( Q_\alpha^*(685) \) values exceeding 1, the theoretical upper limit (Morel and Bricaud 1981). Nevertheless, \([chl\alpha]\) explains 43 per cent of \( Q_\alpha^*(685) \) variations (figure 3(b)), and as a first and rough approximation, \( Q_\alpha^*(685) \) could be expressed through the following expression:

\[
Q_\alpha^*(685) = 0.549[chl\alpha]^{-0.173}
\]  

(5)

When using equation (5), \( Q_\alpha^*(685) \) increases from 0.3 to 1.0 for \([chl\alpha]\) values decreasing from 30 to 0.03 mg m\(^{-2}\). It must be stressed that, in this first approximation, the full width of the chl\(\alpha\) emission band (c. 25 nm) is not accounted for.

4. **Natural variability of the quantum yield of chl\(\alpha\) fluorescence, \(\phi_F\)**

4.1. **Current knowledge**

The maximal value of the *in vivo* (i.e., in living cells) quantum yield of chl\(\alpha\) fluorescence would reach 0.05 quanta emitted (quanta absorbed)\(^{-1}\) (see Latimer et al. 1956, Clayton 1980, Kishino et al. 1984b, Falkowski and Kiefer 1985, Krause and Weis 1991, Ahn et al. 1992).

In particular cases, for instance when studying diel variations, the relative change in \(\phi_F\) can be inferred from measurements of \(F/PAR\) \([chl\alpha]\). Because, on a diurnal basis, the algal optical properties \((a^*, Q_\alpha^*)\) are not expected to vary largely (Stramski and Reynolds 1993), variations in \(F/PAR\) \([chl\alpha]\) have to be mainly ascribed to variations in \(\phi_F\). Note here that fluorescence measurements performed using an artificial (constant) excitation source in a stable marine system provide numbers equivalent to \(F/PAR\) \([chl\alpha]\). Kiefer (1973) reported 4-fold diurnal variations in the ratio \(F/PAR\) \([chl\alpha]\) with minimal values around noon. Loftus and Seliger (1975) observed a day to night variability spanning over a factor of up to 8, and a daily variability of c. 20 per cent due to irradiance variations related to cloud occurrence.
Sea surface Sun-induced fluorescence

Figure 3. (a) Frequency distribution of the reabsorption factor of algae [$Q_a^*(685)$], obtained at different locations in the world oceans (see Bricaud et al. 1995). (b) Relationship between $Q_a^*(685)$ and chlorophyll $a$ + pheopigment concentration.

Such daily variations were also shown by Abbott et al. (1982). Figure 4 illustrates diel variations in the rate of in vivo chl $a$ fluorescence measured at two different sites in the Pacific Ocean. It can be seen that, in this highly stable systems, $F/PAR$ [chl $a$] varies over a factor of about 2.5 in opposition to the solar irradiance (N. Metzl, pers. comm.). These three examples provide a gross indication of the range of diurnal variations in $\phi_P$ at given sites, i.e., for given phytoplankton assemblages, and nutrient
Figure 4. Diel variations in the rate of chl a fluorescence and the total downward irradiance measured on 10–11 November 1994 at two different sites (8° 30′ S and 7° S–150° W) in the Pacific Ocean. Fluorescence was measured continuously using an artificial (constant) light source on seawater pumped at 5 m. The chl a concentration was constant for both sampling periods at about 0.1 mg m⁻³.

and hydrological conditions. For lack of data, the absolute natural variability of $\phi_F$ in the marine environment must rather be understood using a model of light utilization by the photosynthetic apparatus; this model will rest on the most recent results about light and nutrient effects on the functional components of this apparatus.

4.2. Organization of the photosynthetic apparatus and basic processes

In vivo fluorescence of chl a is essentially associated with the light reactions of photosynthesis. The light reactions are promoted by discrete entities denoted ‘photosynthetic unit’ (PSU) (see Rabinowitch and Govindjee 1969). At the supramolecular level, one PSU is composed of two ‘photosystems’ (PSI and PSII) and a chain of electron carriers. Each photosystem incudes light harvesting antenna and a reaction centre (RCI and RCI). The antenna consist of chl a and accessory pigments (other chlorophylls, carotenoids and phycobilins), the composition of which is specific of the photosystem (PSI or PSII), of the algal taxon, as well as of physiological status. The reaction centres are made of a dimer of specialised chl a. RCI and RCI are serially included within the electron carrier chain.

The energy of two photons, one reaching each of the RC, initiates the transfer of one electron from water to NADP⁺ through the electron carrier chain. The latter is organized, in terms of redox potential, in a way (the ‘Z’ scheme) that allows a strong reductant (NADP⁺) to be reduced (increase in free energy) but prevent back reactions; the function of the PSU is analogous to a battery charger. Of special interest for the understanding of chl a fluorescence is the functioning of PSII given that, in vivo, this photosystem is the main source of emission (c. 95 per cent; see Owens 1991). The sequence of a successful photochemical event begins, at the level of the PSII, by the transfer to RCI of the energy of a photon (exciton) once it has been absorbed by the antenna. This step is followed by charge separation; RCI
reduces the first electron acceptor, a phaeophytin (I). In turn, I− reduces the second electron acceptor, a special form of plastoquinone (Q). RCII⁺ is then reduced by the primary donor (Z), which finally oxidizes water. The Z–RCII–I–Q sequence returns to its initial state when Q− is oxidized by a plastoquinone (PQ). PQ, which is present in the electron transport chain as a mobile pool, works in parallel and thus acts as a buffer. When the PQ pool is fully reduced, Q is blocked in its reduced state as back reaction is prevented by the redox gradient, and the RC is said to be ‘closed’. By analogy, the RC is said to be ‘open’ when Q is oxidized (see also the detailed description given by Kolber and Falkowski 1993).

4.3. Origin and regulation of fluorescence emission in PSII

In vitro, a photosystem reaches an excited state through absorption of a photon, and goes back to its ground state essentially through photochemistry, re-emission of a photon by fluorescence or through radiationless dissipation. According to the model of Schatz et al. (1988) as re-formulated by Kiefer and Reynolds (1992), the quantum yields of fluorescence and photochemistry can be expressed as:

\[ \phi_f = A \psi_{cso} \psi_{sto} \sum_{n=1}^{\infty} (\psi_{cso} \psi_{cro})^n \]  \hspace{1cm} (6a)

\[ \phi_f = A \psi_{f0} \sum_{n=1}^{\infty} (\psi_{cso} \psi_{cro})^n + (1 - A) \psi_{f0} \sum_{n=1}^{\infty} (\psi_{css} \psi_{crs})^n \]  \hspace{1cm} (6b)

where \( \psi_{cs}, \psi_{st}, \psi_{cr} \) and \( \psi_f \) are the probabilities for charge separation at the level of the reaction centre (RC reduces I), charge stabilization at the level of Q (I reduces Q), charge recombination at the level of the reaction centre (I back reduces RC), and fluorescence in the antenna, respectively. \( A \) represents the fraction of open reaction centre. The subscripts ‘o’ and ‘s’ denote open (Q oxidized) and close (Q reduced) states, respectively. Figure 5 illustrates the model of Schatz et al. (1988) and provides the values attributed to all probabilities, according to Kiefer and Reynolds (1992). Equations (6a) and (6b), where the sums account for the electron

![Figure 5. Schematic view of the model of Schatz et al. (1988) (see text).]
travelling back and forth between the reaction centre and the acceptor I, converge to:

\[ \phi_p = \frac{A \psi_{cso} \psi_{sto}}{1 - \psi_{cso} \psi_{cro}} \]  

\[ \phi_F = \frac{A \psi_{Fo}}{1 - \psi_{cso} \psi_{cro}} + \frac{(1 - A) \psi_{Fs}}{1 - \psi_{css} \psi_{crs}} \]  

(7 a)  

(7 b)

4.4. Photochemical quenching of fluorescence

Photochemical 'quenching' of fluorescence refers to the decrease of fluorescence emission resulting from the photochemical activity. In the above model, photochemical quenching is expressed by \( A \), the fraction of open reaction centres. Of course, \( A \) is a function of \( PAR \) and decreases as irradiance increases. At steady state, \( A \) is also a function of the effective cross-section of photosystem II (\( \sigma_{PSII} \)), and of the minimal time for electron transport from water to \( CO_2 \) (\( \tau_{CO_2} \); Falkowski and Kiefer 1985). According to the target theory (e.g., Dubinsky et al. 1986), \( A \) follows a Poisson probability such that (Falkowski and Kiefer 1985):

\[ A = \exp(-\sigma_{PSII} \tau_{CO_2} PAR) \]  

(8)

Equation (8) can also be written as (see Cullen 1990):

\[ A = \exp(-PAR/E_k) \]  

(9)

where \( E_k \), which merges variations in both \( \sigma_{PSII} \) and \( \tau_{CO_2} \), is the irradiance at which \( A = 1/e \), so that 63 per cent of the reaction centres are closed. The latter formulation is particularly convenient because a large amount of \( E_k \) measurements have been published in the past.

4.5. Non-photochemical quenching

Non-photochemical quenching of fluorescence refers to decreases in fluorescence induced by factors other than photochemistry. In the marine environment, at least three such factors are known to be significant: (1) photodamage due to excessive light, (2) nutrient limitation and (3) intracellular accumulation of non-photosynthetic pigments. These factors are expected to be particularly effective near the sea surface and, thus, of special interest when modeling remotely sensed SICF.

4.6. Photodamage to photosystem II

Photodamage to reaction centres happen at the high irradiances, as at midday and near the surface. Photodamage may consist of an inactivation of the reaction centres produced by the accumulation of active forms of oxygen (\( O_2 \) and singlet oxygen, \(^1O_2\)) (reviewed by Demmig-Adams and Adams 1992). Inactivated reaction centres would act as thermally quenching traps (Cleland et al. 1986, Weis and Berry 1987) and their fluorescence yield would be approximately that of open reaction centres (Krause and Weis 1991). On this basis, equation (7 b) can be re-written as:

\[ \phi_F = \frac{[1 - f(1 - A)] \psi_{Fo}}{1 - \psi_{cso} \psi_{cro}} + \frac{f(1 - A) \psi_{Fs}}{1 - \psi_{css} \psi_{crs}} \]  

(10)

where \( f \) is the fraction of reaction centres that remains functional (activated), \( f \) is a function of the rate constants for inactivation and re-activation (repair) of photosystems, \( K_i \) and \( K_r \), respectively. As proposed by Kok (1956) (quoted in Neale 1987),
when photosystems are suddenly exposed to a constant high irradiance, time-variations of $f$ can be expressed as:

$$\frac{df}{dt} = -K_i \sigma_{PSII} PAR f + K_r (f_0 - f) \quad (11)$$

where $f_0$ is the initial value of $f$. The equilibrium being reached when $df/dt = 0$, $f$ can be expressed as:

$$f = \frac{K_r f_0}{K_i \sigma_{PSII} PAR + K_r} \quad (12)$$

following a decreasing hyperbolic curve with increasing irradiance. The expression of photodamage through $f$ happens because $K_i$ is generally greater than $K_r$ (see Vincent 1990).

In the marine environment, it can be expected that $K_r$, as being most probably related to enzymatic reactions, will depend on temperature. Moreover, because of variations of $PAR$ with time, mostly related to sun elevation and vertical mixing in the surface layer of the water column, a true equilibrium is unlikely to be truly found. Nevertheless, empirical formulation of $f$ has been proposed, assuming that $K_i$ is small enough relative to irradiance temporal variations and, thus, that $f$ is near equilibrium. According to Neale and Richerson (1987):

when $PAR \leq E_T$

$$f(PAR) = 1$$

and when $PAR > E_T$

$$f(PAR) = \exp[-\beta (PAR - E_T)] \quad (13)$$

where $\beta$ [(\text{\mu mol quanta m}^{-2} \text{s}^{-1})^{-1}] is the photodamage parameter and $E_T$ (\text{\mu mol quanta m}^{-2} \text{s}^{-1}) is the irradiance threshold for the occurrence of photodamage.

4.7. Nutrient limitations

Several laboratory experiments revealed that nitrogen and iron limitation induces a depression of photochemistry in marine phytoplankton (Cleveland and Perry 1987, Kolber et al. 1988, Herzig and Falkowski 1989, Greene et al. 1992). Nutrient limitation would have a photodamage-like effect on photosystem II (Greene et al. 1992), i.e., it would decrease $f$ and, thereby, affect fluorescence. Direct measurements of $f$ using 'pump and probe' fluorometry confirmed these results at sea (Kolber et al. 1990, Falkowski et al. 1991, Geider et al. 1993, Greene et al. 1994, Babin et al. in press). At different location of the world oceans, a relationship was observed between the concentration of nitrate (NO$_3$) and $f$ (Kolber et al. 1990, Falkowski et al. 1991, Geider et al. 1993). This relationship (see figure 5(b) in Geider et al. 1993) could conveniently be represented by a Michaelis–Menten function with a half saturation nitrate concentration of about 0.15 \text{\mu mol m}^{-3} (typical of open ocean, those of coastal water being generally more than 10 times higher) and an intercept at $f(NO_3) \sim 0.5$. The intercept represents a minimum value which could be explained by regenerated sources of nitrogen (ammonium and urea), still present when nitrates are all consumed.

Photodamage and nutrient limitation both having an effect on $f$, the latter can
be expressed in equation (10) as:
\[ f = f(PAR) \times f(NO_3) \] (14)

It is worth noting that, at sea, the surface concentration of nitrate is often correlated to surface temperature (Kamykowski and Zentara 1986). Therefore, sea surface temperature measurements from remote sensors such as Advanced Very High Resolution Radiometer (AVHRR) have already been used to derive maps of surface nitrate concentration (Sathyendranath et al. 1991). It could open the perspective of estimating \( f(NO_3) \) from a remote sensing technique, at least in some areas, for which oceanographic knowledge can support a nitrate–temperature correlation.

4.8. Intracellular accumulation of nonphotosynthetic pigments

All pigments of the chlorophyll and phycobilin families transfer absorbed quanta to chl\( a \) with nearly a 100 per cent efficiency. Among carotenoids, some, being considered as 'photosynthetic' pigments, also have a 100 per cent transfer efficiency, while some others, considered as 'nonphotosynthetic' pigments, dissipate absorbed quanta as heat (see Clayton 1980). When plants are exposed to high irradiances, the intracellular content of nonphotosynthetic carotenoids generally increases relative to that of true photosynthetic pigments. Therefore, nonphotosynthetic carotenoids are believed to play a photoprotective role in plants (see the review of Demmig-Adams and Adams 1992).

The presence of photoprotectant pigments (in particular zeaxanthin and diatoxanthin) in photosystem II would increase the rate constant of radiationless dissipation (Demmig-Adams 1990, Olaizola and Yamamoto 1994; reflected by an increase in \( \psi_D \)) and correlative depress the quantum yields of fluorescence (reflected by a decrease in \( \psi_F \)) and photochemistry (reflected by a decrease in \( \psi_{cs} \)) (see figure 5; discussed in Kiefer and Reynolds 1992). Nevertheless, it is not yet known what relationship governs the changes in radiationless dissipation followed by the appearance of photoprotectant pigments. As an indication, Bilger and Björkman (1990) observed, for sun-adapted leaves of Hedera canariensis (Algerian Ivy), that the accumulation of zeaxanthin lowered the yield of fluorescence in open and closed reaction centres, by 50 and 72 per cent, respectively.

To account for the presence of photoprotectant pigments, equation (10) can be rewritten as:
\[ \phi_F = \frac{PP_o[1 - f(1 - A)]\psi_{Fs}}{1 - \psi_{cs}\psi_{cro}} + \frac{PP_s f(1 - A)\psi_{Fs}}{1 - \psi_{css}\psi_{crs}} \] (15)

where \( PP_o \) and \( PP_s \) are parameters accounting for the presence of photoprotectant pigments,

\[ A = \exp(-PAR PP_o/E_T) \] (16a)

and, when \( PAR \leq E_T/PP_o \)
\[ f(PAR) = 1 \] (16b)

and, when \( PAR > E_T/PP_o \)
\[ f(PAR) = \exp[-\beta(PAR - E_T/PP_o)] \] (16c)

During Polish–Russian research expeditions conducted between 1978 and 1991 in various regions of the world oceans, Wozniak et al. (1992) compiled c. 1500
vertical profiles of pigment concentrations. A striking feature in their results is the significant inverse relationship that exists between the relative concentrations of chl-a and total carotenoids (see figure 6); both experience a large range of variation (by a factor of 4 and 2.5, respectively), while the chl-b and chl-c relative concentrations appear much less variable. A threshold occurs around [chl-a] = 0.5 mg chl-a m^{-3}, below which the relative concentration of chl-a and total carotenoids dramatically decreases and increases, respectively. Thus, it seems that the relative concentration of total carotenoids is generally low in waters with high [chl-a] (eutrophic and mesotrophic waters), whereas it is generally high in waters with low [chl-a] (oligotrophic waters). Moreover, in the first case, carotenoids would be mainly photosynthetic while, in the second case, they would be non-photosynthetic (see Babin et al. in press). These observations are likely to be related to the shallow surface mixed layer (relative to the euphotic layer) often occurring in oligotrophic systems, where phytoplankton undergo acclimation to high irradiances. On the basis of the results of Wozniak et al. (1992), the carotenoid abundance could be inferred from chl-a concentration by partitioning waters into two groups. Phytoplankton in high-[chl-a] waters could be considered as adapted to moderate irradiance, while in low-[chl-a] waters algae could be assumed as being sun-adapted, at least near the surface.

On these bases, realistic values could be assigned to PP_a and PP_s. To set such values, however, one has to consider the peculiarity of low-[chl-a] waters in terms of phytoplankton species composition. In these waters, the phytoplankton population is generally dominated by prokaryotic tiny species. Prokaryotes contain zeaxanthin but do not operate a cycle such as that described above. In prokaryotes, zeaxanthin would neither have a photosynthetic (light harvesting) nor an active photoprotection role. Nevertheless, the presence of zeaxanthin has to be considered in the present SICF model as it has been found to contribute for as much as 66 per cent of phytoplankton absorption near surface in oligotrophic waters (Babin et al. in press).

![Graph showing relationship between pigment concentration and Chl-a concentration](image)

Figure 6. Relationship between the relative concentration (%) of different algal pigments and chlorophyll a concentration (redrawn from Wozniak et al. 1992). Relative concentrations (weight:weight) are obtained by normalizing to total pigment.
In this case, zeaxanthin light absorption would simply increase and decrease $\tilde{a}^*$ and $\phi_F$, respectively, by the same (albeit opposite) extent. Since the contribution of zeaxanthin to phytoplankton light absorption is statistically included in our parameterisation (equation (3)), its contribution to $\phi_F$ has to be accounted for. This can be done by assigning the same appropriate value to $PP_o$ and $PP_s$ in equation (15). In equations (16a) and (16c), however, the application of $PP_o$ and $PP_s$ parameters is not rigorously necessary in the case of prokaryotic phytoplankton, although it may statistically account for the natural variations in $E_k$ and $E_T$ (see below).

5. Sensitivity analysis

In the previous section, the main physiological factors and stresses affecting the rate of fluorescence in the marine environment have been identified and incorporated into a SICF model. In this section, a sensitivity analysis is presented, using equations (1), (3), (5) and (15), to assess their respective impact on SICF. Numerical simulations of SICF were performed by applying the following assumptions. The extrema values of $\phi_F$ were set according to Kiefer and Reynolds (1992):

$$\phi_F \{A = 1\} = \frac{\psi_{F_o}}{1 - \psi_{css} \psi_{cro}} = 0.02 \text{ emitted quanta (absorbed quanta)}^{-1} \quad (17)$$

and

$$\phi_F \{A = 0\} = \frac{\psi_{F_s}}{1 - \psi_{css} \psi_{crs}} = 0.05 \text{ emitted quanta (absorbed quanta)}^{-1} \quad (18)$$

Over 722 measurements performed over the world's oceans, $E_k$ (equation (9)) was found to average 52 Wm$^{-2}$ (see Lewis et al. 1985) (between 200 and 250 $\mu$mol quanta m$^{-2}$s$^{-1}$). In the present simulation, it was set at 300 $\mu$mol quanta m$^{-2}$s$^{-1}$, which can be assumed to be a typical value for most of surface waters (see, for instance, surface values in Cullen et al. 1992, Schofield et al. 1993 and Babin et al. in press). During an experiment conducted at Lake Titicaca (Peru/Bolivia), Neale and Richerson (1987) found $\beta$ (equation (13)) and $E_T$ to average $1.22 \times 10^{-3}$ (SD = $0.25 \times 10^{-3}$, $n = 6$) and 593 (SD = 138, $n = 12$), respectively, when sampling at various depths and different times of the day. These values were adopted for the present simulation. Except if otherwise stated, $PP_o$, $PP_s$ and $f(NO_3)$ were given a value of 1.

Figure 7 shows the variations of the $F/(PAR \ [chl \ a])$ ratio as a function of $[chl \ a]$ and for different $PAR$ values. Indeed $F/(PAR \ [chl \ a])$ is the useful 'calibration factor' for any conversion of in vivo chl $a$ fluorescence into $[chl \ a]$. In the range of 0.03–30 mg chl $a$ m$^{-3}$, and for given $PAR$ values, the variability of the optical terms in equation (1) [namely $\tilde{a}^*$ and $Q_8^*(685)$] brings $F/(PAR \ [chl \ a])$ to vary over a range of 20:1, with the highest values found at low $[chl \ a]$. For a given $[chl \ a]$, it can be seen also that the variations in $\phi_F$ resulting from changes in $PAR$, may induce about a 2-fold variability in the calibration factor $F/(PAR \ [chl \ a])$.

Figure 8(a) shows the variations of $\phi_F$ and sea surface $PAR$ as a function of sub-satellite pixel latitude along the operational trajectory of MERIS at winter and summer solstices, as well as at equinox. To compute $PAR$, sun elevation was determined using the Orbit Generator program developed by ACRI (Sophia-Antipolis, France). Then total energy just above the surface and in absence of clouds, computed using the model of Tanrê et al. (1979) for a standard atmosphere, was converted into $PAR$ just below surface, as described in Morel (1991). The parabola-like
variations of PAR at the sub-satellite point are a function of the latitude, and also of the local time. As MERIS crosses the equator around 10:00 in descending mode, the high latitude zones in the Northern Hemisphere are seen later in the morning (and even in the afternoon), whereas at high latitude in the Southern Hemisphere, the sensor overflies early in the morning. The quantum yield of fluorescence ($\phi_F$), which never reaches its maximal value [0.05 emitted quanta (absorbed quanta)$^{-1}$] because of photodamage, experiences along this trajectory less than a 2-fold change. Its latitude-dependent pattern incurs significant zonal translations during the year. Therefore, the latitude of maximal (at low PAR) and minimal (at high PAR entailing maximal photodamage) values are variable. Compared to the zonal PAR distribution, the corresponding $F$ pattern (computed for 0.3 mg chl a m$^{-3}$ in figure 8(b)) is strongly flattened because of photodamage. It follows that the fluorescence signal varies within a rather narrow range ($\sim$ 20 per cent) over a wide latitude range ($\pm$ 45 degrees), whereas it decreases abruptly at higher latitudes. Seasonal translations of the $F$ zonal pattern are also predictable (figure 8(b)). These results emphasise problems to be encountered when trying to directly perform global scale monitoring and temporal series of remotely sensed SICF. Also, the detection threshold of the sensor may represent a particular constraint at high latitudes, especially when considering the seasonal translations of the $F$ zonal pattern.

Figure 9(a) shows the variations of $\phi_F$ and PAR with sub-satellite pixel latitude when accounting for the effects of nutrient limitation and non-photosynthetic pigments. Nutrient limitation was simulated by attributing to $f$(NO$_3$) a value of 0.5, which is an upper limit for oligotrophic waters (e.g., Falkowski et al. 1991, Babin et al. in press). As a result, $\phi_F$ is depressed by 10 to 25 per cent and its variability is restricted within 0.023–0.033. The effect of photoprotectant pigments was simulated by giving $PP_o$ and $PP_s$ values of 0.5 and 0.28, respectively. These values seem typical of quenching related to xanthophylls in plants well adapted to high irradiance (see $F'_o$ and $F'_m$ quenching in Demmig-Adams 1990, Bilger and Björkman 1990, Olaizola and Yamamoto 1994). Let us note that such a simulation of the non-photosynthetic
pigment effect is admittedly highly simplified. As a result, $\phi_F$ is strongly depressed and restricted within the range of 0.0125–0.0135. When adding both nutrient limitation and photoprotectant effects, as expected in oligotrophic waters (see above), $\phi_F$ become nearly constant around 0.011 and the fluorescence signal (figure 9(b)) is reduced by a factor of about 3 with respect to the initial case (neither nutrient nor photoprotection effect). These predictions, which would be valid only for oligotrophic waters, show the respective weights of the physiological and environmental factors on SICF.

6. A case study
In order to simulate SICF in realistic conditions, we based our analysis on a Coastal Zone Colour Scanner (CZCS) scene obtained on 10 February, 1980, off the
Figure 9. Variations in (a) $\Phi_F$, $PAR$ and (b) $F$ as a function of sub-satellite pixel latitude along the operational trajectory of MERIS, for some selected days of the year, with nutrient limitation and non-photosynthetic pigment effects accounted for through equation (15). An integration depth of 1 m was applied for $F$ calculation.

Mauritanian coast, and converted into a surface $[chl\ a]$ map (figure 10(a)) according to methods described in Bricaud and Morel (1987) and André and Morel (1991). The $[chl\ a]$ range covered by this scene goes from 0.04 to more than 10 mg m$^{-3}$. The
Figure 10. (a) CZCS (Coastal Zone Colour Scanner) scene obtained on 10 February 1980, off the Mauritanian coast, converted into a surface chlorophyll map. (b) Spatial distribution of $L_p$ (TOA) when $PAR$ equals 1700 $\mu$mol quanta m$^{-2}$ s$^{-1}$ and when accounting for vertical attenuation of $PAR$ and $F$ (see equations (18) to (27)). (c) Spatial distribution of the ratio $F$/$PAR$ [chl $a$]. Black pixels along the coastline represent turbid-water mask; white pixels are for clouds (or land).
region was selected in correspondence with the area covered by a research cruise that took place in June 1992 (French JGOFS EUMELI program). During this expedition, we visited three fixed stations located in the eutrophic (coast; 20° 32' N, 18° 35' W), mesotrophic (18° 30' N, 21° 02' W) and oligotrophic (open ocean; 21° 02' N, 31° 08' W) zones included in the CZCS scene. At each site, the following variables were measured: [chl a], f(NO₃), accessory pigments concentrations and the maximum quantum yield of carbon fixation (Babin et al. in press). f was measured using the pump and probe fluorometric method (Kolber and Falkowski 1993). f(NO₃) is taken to be the f value measured in the surface mixed layer below the first optical depth. The main features emerging from these measurements, of interest in support to the present study, are as follows:

1. f(NO₃) decreases at surface from 0.7, at the eutrophic site, to 0.55, at the mesotrophic site, or to 0.47 at the oligotrophic site;
2. high amount of non-photosynthetic pigments (mainly zeaxanthin) were observed only at the oligotrophic site;
3. at this site, measurements showed that the presence of non-photosynthetic pigments strongly depressed (by 66 per cent) the maximum quantum yield of carbon fixation, which suggests a parallel depression of fluorescence.

6.1. Assumptions made for the application of the fluorescence model

In order to include the above information into a simulation of SICF based on the CZCS scene, the eutrophic, mesotrophic and oligotrophic areas were tentatively delineated in terms of [chl a] as following:

- eutrophic when [chl a] ≥ 2 mg m⁻³;
- mesotrophic when 0.5 ≤ [chl a] < 2 mg m⁻³;
- and oligotrophic when [chl a] < 0.5 mg m⁻³.

f(NO₃) was given values of 0.7, 0.55 and 0.47 in the eutrophic, mesotrophic and oligotrophic areas, respectively. PPₐ and PPₜ were both given values of 1 in the eutrophic and mesotrophic areas, while, in the oligotrophic area they were both given the value of 0.34. These parameters were also applied in equations (16a) and (16c) to account for the variations actually observed for E₉ and suspected for E₇. Figure 11 shows how F varies, in these conditions, as a function of PAR and [chl a]. It can be seen that, at low irradiiances, F heavily depends on the PAR value and conversely it tends to depend almost exclusively on [chl a] at higher irradiiances. For the present CZCS scene, located between 14 and 28° N, the variations of PAR with latitude were therefore neglected (see PAR variations as a function latitude in figures 8(a) and 9(a)). Note that the variation range of [chl a] for given irradiances is more than 5 times larger than that of F.

6.2. Attenuation of the fluorescence signal throughout the upper layer

At a given depth, z, the exciting radiation is \( \hat{E}_{PAR}(z) \) (scalar irradiance; mol quanta m⁻² s⁻¹) with:

\[
\hat{E}_{PAR}(z) = \hat{E}_{PAR}(0) \exp(-K_{PAR}z)
\]

where \( \hat{E}_{PAR}(0) \) is scalar irradiance at surface and \( K_{PAR} \) (m⁻¹) is the vertical attenuation coefficient for \( \hat{E}_{PAR}(z) \). The layer at \( z \) with a thickness \( dz \) re-emits \( \hat{E}_F \)
\( F (\mu \text{mol quanta m}^{-2}\text{s}^{-1}) \)

Figure 11. Contour plot showing the variations of \( F \) as a function of both \( \text{PAR} \) and chlorophyll \( a \) concentration.

(mol quanta m\(^{-2}\)s\(^{-1}\)) in an isotropic way (and over \( 4\pi \) sr) according to:

\[
\dot{E}_F(z) = \dot{E}_{\text{PAR}}(z)[\text{chl}a]a^*Q^*(685)\phi_F dz
\]

In any direction (and in an upward vertical direction for instance) the radiance due to fluorescence, \( L_F(z) \) (mol quanta m\(^{-2}\)s\(^{-1}\)sr\(^{-1}\)), is:

\[
L_F(z) = \dot{E}_F(z)/4\pi
\]

Along the vertical path from \( z \) to surface, \( L_F(z) \) is attenuated and becomes \( L_F(z \rightarrow 0) \), with:

\[
L_F(z \rightarrow 0) = L_F(z) \exp[-c(685)z]
\]

where \( c(685) \) is the beam attenuation coefficient at 685 nm. In the diffuse transmission process, however, radiation scattered out from the direction considered is partly compensated by reintegration of the scattered radiation from the adjacent directions. If the compensation was complete, the attenuation coefficient would reduce to \( a(\lambda) \), the absorption coefficient. Therefore, just below the surface, all the \( L_F(z \rightarrow 0) \) originating from the various depths have to be summed up according to:

\[
L_F(0) = \int_0^\infty L_F(z) \exp[-\kappa(685)z] dz
\]
with $a < \kappa < c$. To the extent that at 685 nm, most waters act as a strong absorbing medium and a weak scattering one, $\kappa$ is closer to $a$ than to $c$ (note also that at this wavelength $a$ and $c$ are close).

Assuming that $[chl\ a]$, $a^*$ and $Q_a(685)$ are constant with depth in the upper layer of the water column, then $c(685)$ is constant. In a first approximation, $K_{PAR}$ can also be considered as constant with depth. Additionally, as in general $c(685) \gg K_{PAR}$, the $\phi_F$ variations throughout the detection depth can be neglected, so that $L_F(0)$ simply becomes:

$$L_F(0) = \hat{E}_{PAR}(0)[chl\ a]\bar{a}^*Q_a^*(685)\phi_F \left( \frac{1}{4\pi} \int_0^\infty \exp\{-[K_{PAR} + \kappa(685)]z\} dz \right)$$

$$= \hat{E}_{PAR}(0)[chl\ a]\bar{a}^*Q_a^*(685)\phi_F \left( \frac{1}{4\pi} \frac{1}{K_{PAR} + \kappa(685)} \right)$$

(24)

According to Morel (1988), $K_{PAR}$ can be empirically related to $[chl\ a]$ as follows:

$$K_{PAR} = 0.121[chl\ a]^{0.428}$$

(25)

This expression, valid for a $K_{PAR}$ coefficient averaged over the euphotic depth, leads to an underestimate of the $K$ coefficient typical of the very upper layer where red radiations are strongly attenuated. Nevertheless, because chl $a$ fluorescence is mostly excited by blue and green radiations, equation (25) remains appropriate for the problem described here.

The absorption and scattering coefficients of seawater ($a$ and $b$) can also be expressed as a function of $[chl\ a]$, according to Morel (1991) and Prieur and Sathyendranath (1981):

$$a(685) = 0.475 + 0.0252[chl\ a]^{0.65}$$

(26)

and, according to Gordon and Morel (1983) and neglecting the molecular scattering

$$b(685) = 0.3[chl\ a]^{0.62}(550/685)$$

(27)

Finally, the attenuation coefficient is expressed as

$$c(685) = a(685) + b(685)$$

(28)

Therefore, $1/[K_{PAR} + c(685)]$ or $1/[K_{PAR} + a(685)]$ can be easily computed from the sole knowledge of $[chl\ a]$. To get an estimation of the thickness of the surface layer from which 90 per cent of the fluorescence signal originates $(z_{90})$ and for a nadir viewing observation, it suffices to solve:

$$\int_0^{z_{90}} \exp\{-[K_{PAR} + \kappa(685)]z\} dz = 0.9 \int_0^\infty \exp\{-[K_{PAR} + \kappa(685)]z\} dz$$

which leads to:

$$z_{90} = \frac{2.3}{K_{PAR} + \kappa(685)}$$

(29)

The lower and upper estimates of this depth are obtained by replacing $\kappa$ by $c(685)$ or $a(685)$, respectively. For slant directions, $z_{90}$ has to be reduced roughly by using the cosine of the viewing angle. Figure 12 shows that $z_{90}$ goes from 4.4–4.6 m when $[chl\ a] = 0.03$, to 0.7–1.8 m when $[chl\ a] = 30$ mg m$^{-3}$, where the lowest values are more realistic.
Figure 12. Depth of the water column ($z_{90}$) from which 90% of the fluorescence signal originates, as a function of chlorophyll $a$ concentration. The two curves represent the lower and upper limits of the actual variations for a nadir-viewing detection, and Case 1 waters (see text).

Figure 13 shows how $F$ varies, when accounting for attenuation in the surface layers, as a function of PAR and $[chl\,a]$. It can be seen that, when compared to variations in figure 11, the $F$ variations are narrower. In this case, when $PAR = 2000\, \text{mol quanta m}^{-2}\text{s}^{-1}$, the range of variation in $F$ (20:1) is 50 times lower than that of $[chl\,a]$ (1000:1).

6.3. Spatial variations in fluorescence properties

Figure 10(b) shows the spatial distribution of $L_F$ at nadir when PAR is uniformly set to $1700\, \mu\text{mol quanta m}^{-2}\text{s}^{-1}$. It is derived using our SICF model, as stated just above, and when accounting for attenuation within the surface layer (equation (24)) and for the width (5 nm) of a channel centred at 682 nm. Note that with such a rather narrow channel, the energy received represents only 15 per cent of the total energy emitted by fluorescence. The fluorescence signal is estimated at the top of the atmosphere [$L_F(\text{TOA})$] by assuming a transmission factor through the sea–atmosphere interface of 0.53 for radiances (Austin 1974), and a diffuse transmission factor across the atmosphere of 0.9. $L_F(\text{TOA})$ is expressed as W m$^{-2}$ sr$^{-1}$ $\mu$m$^{-1}$.

In the CZCS scene, the variation range of $[chl\,a]$ is about 40 times higher than that of $L_F(\text{TOA})$. This result demonstrates that, at the level of a typical satellite scene, the relationship between SICF and $[chl\,a]$ is far from being linear. The spatial pattern of the $F/(PAR\,[chl\,a])$ ratio is highly contrasted (figure 10(c)), which prevents even local calibration of a linear $F$ vs. $[chl\,a]$ relationship from being useful. Note also in figure 10(b) the weak difference in $F$ between the areas where $[chl\,a]$ is around 1 mg m$^{-3}$ and those where $[chl\,a]$ is markedly lower than 1 mg m$^{-3}$. This result further supports the idea that the chl $a$ fluorescence may hopefully be detectable at relatively low concentrations (i.e., below 1 mg m$^{-3}$).
Figure 13. Contour plot showing the variations of \( F \) as a function of \( PAR \) and chlorophyll \( a \) concentration when accounting for vertical attenuation of \( PAR \) and \( F \) (see equations (18) to (27)).

6.4. Detection threshold

Figure 14 shows how \( L_p(\text{TOA}) \) emerging from nadir (and computed as in figure 13) varies as a function of \([chl a]\), for a moderate solar irradiance (\( PAR = 1000 \text{ \( \mu \)mol quanta m}^{-2} \text{s}^{-1} \)) and when accounting for attenuation within the surface layer (equation (24)). According to the technical specifications presently announced for MERIS and MODIS, their noise equivalent radiance (\( \text{NE\Delta L} \)) around 682 nm would be of 0.043 and 0.008 W m\(^{-2}\) sr\(^{-1}\) \( \mu \)m\(^{-1}\), respectively. According to our results, the corresponding \([chl a]\) values would be of 0.07 and 0.45 mg m\(^{-3}\), respectively (figure 14). It is assumed that, at 682 nm, the atmospheric corrections are nearly perfect given the proximity of the near IR channels used for atmospheric corrections. This assumption is reinforced by the fact that residual error in atmospheric correction mostly disappears when subtracting a baseline to derive the fluorescence line height. The digitization of the signal (12 bits) in MERIS and MODIS will not, conversely to CZCS, affect the detection threshold as the signal-to-digit ratio is lower or equal to the specified \( \text{NE\Delta L} \).

This ideal scenario suggests a detection limit lower than the one expected by Doerfler (1993). The high \( F/(PAR \ [chl a]) \) ratio for low-\([chl a]\) waters would explain this result, which is further supported by observations of fluorescence reflectance spectra measured in highly oligotrophic waters (see figure 15). However, a realistic
estimation of the SICF detection limit has to account for other causes of uncertainty as, for instance, the adoption of a reliable baseline.

7. The use of SICF to estimate primary production

The estimation of oceanic primary production at global scale \( P \), generally expressed in terms of areal carbon assimilation rate (e.g., mol C m\(^{-2}\) s\(^{-1}\)), is an essential product to be derived from remotely sensed \([chl\ a]\) maps. For this task, several models have been developed which are solely based on the useful variables measured by remote sensing, i.e., \( PAR \) and sea surface \([chl\ a]\) (e.g., Platt and Sathyendranath 1988, Morel 1991). These models are generally operated with constant values for the optical and photosynthetic parameters of algae, which represents a significant limitation for their predictive capability (e.g., Berthon and Morel 1992).

By analogy with equation (1), primary production can be expressed as:

\[
P = PAR[chl\ a]a^{*}\phi_{p}dz
\]

where \( \phi_{p} \) is the quantum yield for carbon fixation. When combining equations (1) and (30):

\[
P = F\phi_{p}[\phi_{p}Q_{a}^{*}(685)]^{-1}
\]

To the extent that the \( \phi_{p} [\phi_{p}Q_{a}^{*}(685)]^{-1} \) term would be constant, the primary production could be directly estimated from \( F \). This approach, originally proposed by Kiefer et al. (1989), has been used on moorings and for \textit{in situ} fluorescence profiling systems. Although it is limited by the high natural variability of the

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Figure 15. Reflectance \( (E_\alpha/E_\lambda) \) spectra measured at surface in the Pacific Ocean during November 1994. Chl \( a \) concentration was 0.14 mg m\(^{-3}\) at 1\(^{\circ}\)N and 0.05 mg m\(^{-3}\) at 16\(^{\circ}\)S. (a) displays the total visible spectrum on a log scale while (b) shows only the spectral range in the vicinity of the chl \( a \) fluorescence emission on a linear scale.
$\phi_P \left[ \phi_P Q^*_P(685) \right]^{-1}$ term (see discussion in Kiefer and Reynolds 1992), it accounts for the first-order determinants of primary production, namely PAR and $[chl a]$, and therefore it represents an efficient approach for intensive, albeit approximate, in situ monitoring.

Besides the variability of the $\phi_P \left[ \phi_P Q^*_P(685) \right]^{-1}$ term, however, the application of Kiefer's approach to remotely sensed SIFC comes up against different problems. Firstly, the fluorescence signal that can be detected from a spaceborne sensor originates from less than the first attenuation depth (equation (29)), while carbon fixation by algae occurs within a layer extending over about the first 5 optical depths. The $P$ vertical profile is generally non-uniform and essentially varies as a function of PAR and $[chl a]$. Secondly this signal is instantaneous, i.e., it only corresponds to a short time period of the day. Therefore, $P$ has to be predicted for the rest of the day essentially as a function of PAR. Given these limitations, also encountered to a lesser extent when using the blue-to-green ratio, and the fact that most of optical and biological parameterization in primary production models are based on $[chl a]$, the interpretation of the SIFC signal in terms of $[chl a]$ presently remains a reasonable way of using the remotely detected SIFC signal.

8. Concluding remarks

The possibility of deriving chl $a$ concentration directly from Sun-induced in vivo fluorescence rests on the assumption of a constant $F/(PAR \ [chl a])$ ratio. Since the study of Lorenzen (1966), this assumption has been widely applied in the field of oceanography to map the chlorophyll patchiness in surface waters. Paradoxically, this ratio is well known to be highly variable when considering full temporal and spatial scales involved in the natural marine environment. The main sources of its variability are (1) taxonomic specificity, (2) illumination conditions and (3) nutritional status. In the present study, we presented a tentative parameterization of the $F/(PAR \ [chl a])$ ratio in order to evaluate and, eventually, support the use of SIF to derive $[chl a]$ maps from space. In this model, taxonomic specificity is indirectly accounted for through varying optical inherent properties of algae. Light conditions are accounted for through the $\phi_F$ variations, which are related to photochemical and nonphotochemical quenching processes. Finally, nutritional status is also considered through its impact on $\phi_F$. This model, which aims at being as general as needed for remote sensing applications, is based on the more recently published values for the optical and physiological parameters. It does not claim, however, to encompass all complexities and specific behaviours to be locally encountered in the real ocean.

Optical parameters, as well as photochemical quenching and photodamage are satisfactorily parameterized. The reliability of our model, however, is mainly limited by the lack of precise knowledge about the actual limits of variation in $\phi_F$ in the marine environment. In addition, the relationships between fluorescence and nutrient limitation and photoprotectant pigments, are still poorly documented, even if photoprotectant pigments can be suspected to form a more significant source of variability in $F$, compared to nutrient limitation.

Few studies have shown that, at local scale, a linear relationship between SIFC and $[chl a]$ may exist (e.g., Fischer and Kronfeld 1990). Nevertheless, this can be true when observations are made over a narrow range of $[chl a]$. According to the present study, this relationship turns out to be strongly nonlinear. Even on a local scale any 'calibration' of a linear and permanent relationship therefore remains questionable. The unexpected consequence of the nonlinearity in the SIFC vs. $[chl a]$
relationship is that the range of variation in $F$ is much smaller than the one in $[\text{chl}a]$. Therefore, a detection threshold for SICF technique of about 1 mg m$^{-3}$, as proposed by Doerffler (1993), is likely pessimistic as the SICF signal for waters where $[\text{chl}a] < 1$ mg m$^{-3}$ appears to be significant and detectable (figure 15). Thus, SICF remote sensing technique could also apply to oceanic (Case 1) waters, in addition to Case 2 waters.

From the present study, two major recommendations can be stated for future studies on SICF: firstly, a reliable parameterization of $\phi_F$ variations remains to be achieved. To succeed in this way, the relationship between $\phi_F$, and nutrient and non-photosynthetic pigment concentrations has to be more thoroughly documented at sea. The possible effect of other factors such as temperature (Chamberlin and Marra 1992, Lizotte and Priscu 1994) should also be considered. In this context, the possibility of using SICF as an indicator of phytoplankton physiological state, as proposed by Doerffler (1993), could be examined seriously. Secondly, a full simulation of the SICF signal to be measured by sensors such as MERIS and MODIS has to be performed. Such a simulation will allow, for instance, the assessment of the limitation which results from the existence of the oxygen absorption band around 686 nm, and to find a practical way of quantifying the fluorescence signal above a ‘baseline’ provided by contiguous channels, in relation to the position of these channels.

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### Glossary of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Significance</th>
<th>Units</th>
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<tr>
<td>[chl a]</td>
<td>concentration of chlorophyll a in the water body</td>
<td>mg m(^{-3})</td>
</tr>
<tr>
<td>(\text{PAR}, \bar{E}_{\text{PAR}})</td>
<td>photosynthetically available radiation</td>
<td>mol quanta m(^{-2})s(^{-1})</td>
</tr>
<tr>
<td>(\bar{a})</td>
<td>mean absorption coefficient of algae expressed per unit of chl a</td>
<td>m(^2) (mg chl a(^{-1}))</td>
</tr>
<tr>
<td>(\bar{\lambda})</td>
<td>wavelength</td>
<td>nm</td>
</tr>
<tr>
<td>(a^* (\lambda))</td>
<td>chl a-specific in vivo absorption coefficient of phytoplankton</td>
<td>m(^2) (mg chl a(^{-1}))</td>
</tr>
<tr>
<td>(Q^*_S(685))</td>
<td>fraction of fluorescence that is not reabsorbed within the phytoplanktonic cell at 685 nm</td>
<td>dimensionless</td>
</tr>
<tr>
<td>(a^*_{\text{mol}})</td>
<td>chl a-specific absorption coefficient by all pigments when not embedded within the cells</td>
<td>m(^2) (mg chl a(^{-1}))</td>
</tr>
<tr>
<td>(F)</td>
<td>rate of chlorophyll a fluorescence</td>
<td>mol quanta m(^{-2})s(^{-1})</td>
</tr>
<tr>
<td>(P)</td>
<td>rate of carbon fixation</td>
<td>mol C m(^{-2})s(^{-1})</td>
</tr>
<tr>
<td>(\phi_F)</td>
<td>quantum yield of fluorescence</td>
<td>mol quanta emitted (mol quanta absorbed(^{-1}))</td>
</tr>
<tr>
<td>(\phi_P)</td>
<td>quantum yield of photosynthetic carbon fixation</td>
<td>mol C (mol quanta(^{-1}))</td>
</tr>
<tr>
<td>(\bar{E}(\lambda))</td>
<td>scalar irradiance</td>
<td>mol quanta m(^{-2})s(^{-1})</td>
</tr>
<tr>
<td>(c_i)</td>
<td>intracellular pigment content</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>Symbol</td>
<td>Significance</td>
<td>Units</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>(d)</td>
<td>cell diameter</td>
<td>m</td>
</tr>
<tr>
<td>(\psi_x)</td>
<td>probability for: (x = cs) charge separation at the level of the reaction centre (RC reduces I)  (st) charge stabilization at the level of (Q) (I reduces (Q)) (F) fluorescence in the antenna (cr) charge recombination at the level of the reaction centre (I back reduces RC)</td>
<td>dimensionless</td>
</tr>
<tr>
<td>(A)</td>
<td>fraction of open reaction centre</td>
<td>dimensionless</td>
</tr>
<tr>
<td>(\sigma_{PSII})</td>
<td>effective cross-section of photosystem II</td>
<td>(\text{Å}^2)</td>
</tr>
<tr>
<td>(\tau_{CO_2})</td>
<td>minimal time for electron transport from water to CO(_2)</td>
<td>s</td>
</tr>
<tr>
<td>(E_k)</td>
<td>irradiance at which (A = 1/e)</td>
<td>(\text{mol quanta m}^{-2}\text{s}^{-1})</td>
</tr>
<tr>
<td>(f)</td>
<td>fraction of reaction centres that remains functional (activated)</td>
<td>dimensionless</td>
</tr>
<tr>
<td>(\beta)</td>
<td>photodamage parameter</td>
<td>((\mu\text{mol quanta m}^{-2}\text{s}^{-1})^{-1})</td>
</tr>
<tr>
<td>(E_T)</td>
<td>irradiance threshold over which the occurrence of photodamage is onset</td>
<td>(\text{mol quanta m}^{-2}\text{s}^{-1})</td>
</tr>
<tr>
<td>(PP_o, PP_s)</td>
<td>parameters accounting for the presence of photoprotectant pigments</td>
<td>dimensionless</td>
</tr>
<tr>
<td>(L_F)</td>
<td>radiance due to fluorescence</td>
<td>(\text{mol quanta m}^{-2}\text{s}^{-1}\text{sr}^{-1})</td>
</tr>
<tr>
<td>(L_F(\text{TOA}))</td>
<td>radiance due to fluorescence reaching the top of the atmosphere</td>
<td>(\text{W m}^{-2}\text{s}^{-1}\text{sr}^{-1})</td>
</tr>
<tr>
<td>(\hat{E}_F)</td>
<td>scalar irradiance due to fluorescence</td>
<td>(\text{mol quanta m}^{-2}\text{s}^{-1})</td>
</tr>
<tr>
<td>(c(\lambda))</td>
<td>beam attenuation coefficient</td>
<td>(\text{m}^{-1})</td>
</tr>
<tr>
<td>(K_{PAR})</td>
<td>vertical attenuation coefficient for (\hat{E}_{PAR})</td>
<td>(\text{m}^{-1})</td>
</tr>
<tr>
<td>(z)</td>
<td>depth</td>
<td>m</td>
</tr>
<tr>
<td>(z_{90})</td>
<td>thickness of the surface layer from which 90% of the fluorescence signal originates</td>
<td>m</td>
</tr>
</tbody>
</table>