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ATBD 2.9 — PIGMENT INDEX RETRIEVAL IN CASE 1 WATERS

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1. Introduction

1.1 Definition of Case 1 waters

Case 1 waters are defined as waters for which phytoplankton and their associated materials (such as debris, heterotrophic organisms and bacteria, excreted organic matter) control the optical properties (Morel and Prieur, 1977 ; Gordon and Morel 1983). To the extent that the quantification of these materials (living and inanimate) was operationally made through the determination of a single pigment, i.e. chlorophyll *a*, it can be said that the optical properties of such case 1 waters depend only on the chl *a* concentration, which actually is not true and is only a verbal short cut. The chlorophyll *a* is denoted [Chl]; divinyl Chl-*a* and chlorophyllid-*a* are included in "Chl", when the determination of pigments are made via HPLC technique.

This dependence of optical properties on [Chl] is not a linear one, as it should be for a simple 2-component system obeying the Beer-Lambert-Bouguer law. The reasons for the non-linearity and, in addition, for the natural "noise" around the non-linear mean relationship, are well identified. Among them, and not exhaustively, the major ones are:

- The varying detritus-to-chl *a* ratio; for instance a regression analysis shows that the particulate organic carbon concentration (quantifying all biogenous materials) is roughly varying as the square root of [Chl] (Morel, 1988). The heterotrophic bacteria concentration also follows such a statistical relationship (Cole et al., 1988), with implications for the optical properties (mainly for the scattering coefficient), as discussed in Stramski and Kiefer (1991) and Morel and Ahn (1991).
- The varying pigments-to-chl *a* ratio in algal cells; all pigments (various chlorophylls, carotenoids, phycobilins) contribute to the formation of the absorption coefficient of the algal cells and thus of water bodies; they are not, however, in constant proportion relatively to Chl (see for instance Wozniak et al., 1992).
- The packaging effect (Kirk, 1975; Morel and Bricaud, 1981); the resulting absorption of a given amount of pigment present in algal cells depends on both the size of these cells and their internal concentration in pigment; as a consequence the "Chl-specific absorption coefficient" of algae (absorption per unit of Chl) is not a constant, as it should be if chl *a* was a "dissolved" absorbing substance (Bricaud et al., 1995; 1998). Actually, this Chl-specific coefficient increases when the algal concentration in the water body decreases, in other words, for increasing "oligotrophy". In such tropic regimes, the algal population is generally represented by tiny species, leading to a reduced packaging effect; the converse occurs (large cells, strong packaging effect) in eutrophic regimes.
- The relative proportions of algae and of endogenous "yellow substance" (i.e., locally formed dissolved organic compounds) are not regularly varying along with [Chl]. These proportions likely depend on the algal community, its age, as well as on the season (because of the photodegradation of the yellow substance). Therefore noise is added to the non linear character of the relationship between the absorption coefficient of the water body and its [Chl] concentration.
- The light backscattering efficiency and its spectral dependency; backscattering coefficients of a water body are governed by water molecules and by particles, particularly by the submicron detrital and unidentified particles, rather than by the large phytoplanktonic cells; this rather unknown compartment appears to be variable in relative importance and optical properties (Koike

et al., 1990; Morel and Ahn, 1991). Various parameterizations of the backscattering coefficient as a function of the Chl concentration have been proposed in the recent years (Gordon et al., 1988; Morel, 1988; Haltrin and Kattawar, 1991). None of them has been fully and directly validated up to now.

1.2 Departure from Case 1 waters: various Case 2 waters

In coastal zones influenced by land drainage or by sediment resuspension, the optical properties depart from those in Case 1 waters because of the presence of at least two additional components, (separate or simultaneous), which generally are not correlated with [Chl], namely:

- the colored dissolved organic matters of terrigenous origin, collectively named "yellow substance", or "Gelbstoff" or "Gilvin", or CDOM (colored dissolved organic matter);
- the mineral particles and various suspended sediments.

Note that human activity, urban discharges and industrial wastes can add supplementary components to the natural components above. Disregarding these additional perturbations, the "natural" Case 1 and 2 waters can be conceptually organized according to the triangular diagram in Fig. 1 (adapted from Prieur and Sathyendranath, 1981).

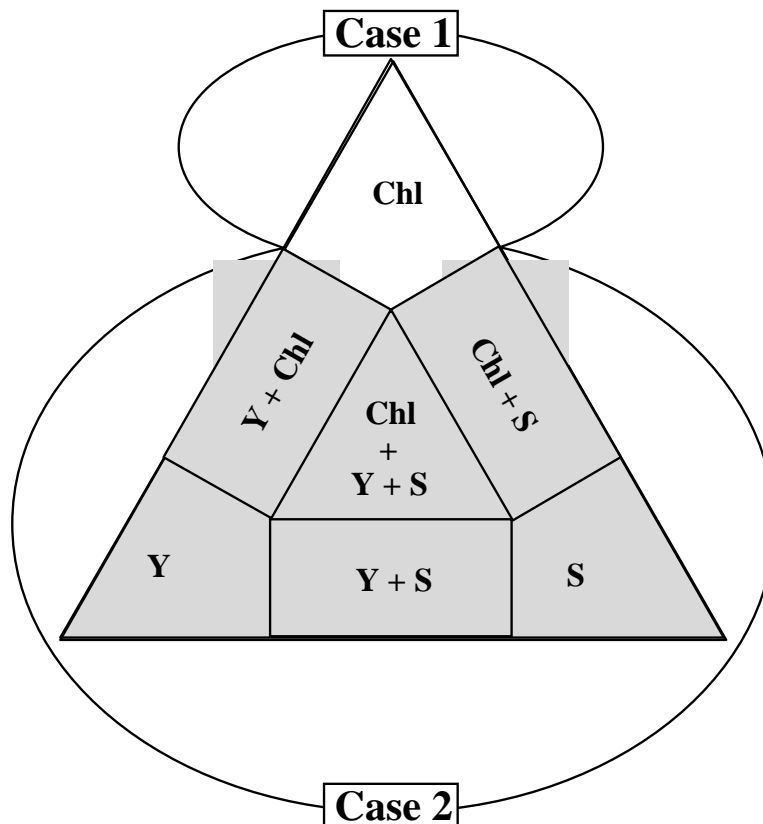


Figure 1. Partitioning of seawater into optical main optical classes.

The 3 tips (denoted Chl, Y and S) represent the Chl-dominated waters, (i.e. the "true Case 1 waters"), the yellow substance-dominated Case 2 waters, and the sediment dominated Case 2 waters,

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respectively. The central part of the triangle represents Case 2 waters with various mixtures of optically active substances. It is worth noting that the two kinds of Case 2 waters are strongly differing in regards to their optical properties. The yellow substance-dominated waters are essentially absorbing (thus with extremely low reflectances), whereas the sediment-dominated Case 2 waters are strongly scattering bodies, with high reflectances.

In Case 1 waters, and depending on the trophic regime, the chlorophyll concentration may vary over about 3 orders of magnitude, starting from values near 0.02 mg m^{-3} and up to 20 mg m^{-3} (or more), in waters ranging from oligotrophic, to mesotrophic, and to eutrophic ones.

1.3 Geographical distribution of Case 1 / Case 2 waters

Case 2 waters are restricted to coastal zones. The shelf zone (0-200 m) represents 7.5 % of the whole ocean (including all adjacent and inner seas) or only 3.1 % (when excluding these seas). Only a part of the shelf zone is a candidate for generating Case 2 waters because many arid coasts, without rivers, do not deliver those components typical of Case 2 waters, and also because resuspension of sediments (by the action of waves and tides) does not occur when the bottom depth exceeds 30-50 m. From these geographical and hypsometric considerations, it can be concluded that 2 to 5 % (at the most) of the world ocean are possibly belonging to Case 2 waters. This small relative number does not prejudice of their interest, for obvious human and economical reasons (such as recreational, defense, fisheries, or fish farming)

Case 1 waters are typical of the open ocean, which, in no way, means that such waters are uniform. The chl *a* concentration ranges from very low values ($\sim 0.02 \text{ mg m}^{-3}$) in vast oligotrophic zones (as subtropical gyres) up to high values, 5 - 30 mg m^{-3} , in more restricted upwelling areas (e.g. off Peru, Mauritania, Benguela...), or during the short blooming period in moderate and high latitude ocean. The chl *a* concentration to be detected from space spans over 3 orders of magnitude, while the mean concentration for the entire ocean, when spatially and temporally averaged, lies around $0.20 \text{ mg (chl } a) \text{ m}^{-3}$. Roughly speaking, for 10% of the world ocean, [Chl] is below 0.05 mg m^{-3} , and again for 10%, [Chl] is above 0.4 mg m^{-3} , and [Chl] exceeds 1 mg m^{-3} for 1% of the total area (see e.g., Antoine et al. 2005).

Blooms of coccolithophorids may occur in the open ocean with typical high reflectance values (caused by the strong backscattering efficiency of the cells covered by calcite plates, and to the numerous detached calcite liths). Such waters meet the formal criterion for classification as Case 1 waters (no terrestrial influence). They, however, are of milky-turquoise appearance, and look like turbid, sediment laden, waters (they have been called “anomalous Case 1 waters –Gordon et al., 1988). Their location, if clearly offshore, can remove the ambiguity concerning their interpretation. Other peculiar situations can be encountered in the open ocean, e.g. trichodesmium blooms (Subramanian et al. 1999), phaeocystis, or synechococcus blooms (Morel, 1997), leading to strong deviations from the case 1 normal properties.

Biophysical models for Case 1 waters

For the remote sensing problem two germane approaches have been adopted, relying either on reflectance at null depth, $R(0^-)$, or on the normalized water-leaving radiance, introduced by Gordon and Clark (1981), $[L_w]_N$ (see Appendix for definitions, notations and symbols). They are linked through

$$[L_w]_N = \frac{F_o \mathfrak{R}_o}{Q_o} R(0^-) \quad (1)$$

In turn $R(0^-)$, an apparent optical property, is linked to two inherent optical properties (*sensu* Preisendorfer, 1961), namely to the absorption and backscattering coefficients of the water body, a and b_b respectively, through

$$R(0^-) = f_1 \frac{b_b}{a} \quad (2)$$

where f_1 , by approximation often set at 0.33 (Morel and Prieur, 1977), actually is a varying number (say between 0.3 and 0.5) depending on both the illumination conditions above the surface (the sun position in a clear sky), and the water properties (related to the chl a concentration) — Figure 2 (redrawn from Morel & Gentili, 1993) provides instances of such f_1 -variations throughout the visible spectrum.

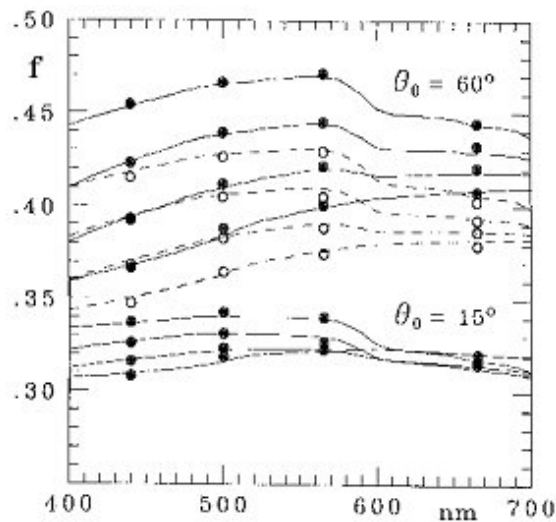


Fig.2 - Values of the f factor as a function of the wavelength for an overcast sky (dashed curves and white circles) and for direct Sun with $\theta_0=60^\circ$ or 15° (solid curves and black dots). For each illumination condition, the four curves correspond, from bottom to top, to waters with increasing chlorophyll concentration (0.03 , 0.1 , 0.3 , and 1 mg m^{-3}).

Morel and Gordon (1980) pointed out three different approaches for using and interpreting measurements of spectral radiance (or irradiance) and for estimating the concentrations of optically active constituents of the water, in particular those expected to be present in Case 1 waters: an analytical method, a semi-empirical method and a totally empirical method. They are briefly summarized below.

1. a fully **analytical method** can be, in principle, envisaged by taking advantage of the additivity principle which strictly applies when dealing with inherent properties (such as a and b_b). By using this analytical way, the optical coefficients are split into their partial components, as for instance (the wavelength dependency is omitted for brevity)

$$b_b = b_{bw} + b_{b\phi} + b_{bd} + \dots = b_{bw} + b_{b\phi}^* [\text{Chl}] + b_{bd}^* [d] + \dots \quad (3)$$

$$a = a_w + a_y^* [y] + a_d^* [d] + a_\phi^* [\text{Chl}] + \dots \quad (4)$$

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These partial components account for the main contributors to backscattering and absorption in Case 1 waters ; the subscripts w , φ , y and d stand for pure water, phytoplankton, endogenous yellow substance (created by algal decay and excretion) and associated detritus including bacteria ; the bracketed terms mean "concentration" in each substance and the starred quantities are the specific absorption or backscattering coefficients; for instance, a^*_φ is the specific absorption of algae, i.e. the value of the coefficient when $[Chl]$ is 1 mg m^{-3} . This rigorous approach presently comes up against the absence of precise knowledge of the specific coefficients (they actually are known to be variable), and also against the absence of tight relationships between the concentrations, which only could allow an accurate model to be developed as a function of a unique variable (namely the chl a concentration). Approximate models, however, have been proposed along these lines and used (see below).

2. a **semi-empirical approach** is also possible and actually is more realistic according to the present state of knowledge. It keeps the principle of expressing the ratio b_b/a but simplifies the full expansions given in Eqs. 3 and 4. The backscattering term thus becomes simply

$$b_b = b_{bw} + F_{bb} [Chl] \quad (5)$$

the algal and detrital contributions to the backscattering coefficient are merged into a certain function (F_{bb}) of the chl a concentration. In a similar way, a becomes

$$a = a_w + F_a [Chl] \quad (6a)$$

where mean relationships (for Case 1 waters) between the concentrations $[d]$ and $[y]$, and $[Chl]$ are implicit, and merged within the F_a function.

Because spectrally detailed absorption has not been determined routinely at sea, the absorption coefficient is replaced by the diffuse attenuation coefficient for downwelling irradiance, K , a parameter much more documented. Thus Eq. 6a is modified according to (note that this expression is incorrect as the K coefficients are not additive; it is only a convenient approximation)

$$K = K_w + F_k [Chl] \quad (6b)$$

In counterpart, the K coefficients must be manipulated in view of deriving a before entering into Eq. 2 (see Morel, 1988, Morel and Maritorena, 2001). Alternatively, in the Gordon et al.'s method (1988), K is entered without modification, at the expense of modifying the coefficient f_1 so that Eq. 2 is to be written

$$R = f_3 \frac{b_b}{K} \quad (7)$$

where f_3 is more varying than f_1 , because $f_3 = f_1 K/a$, and K/a (always > 1) increases when the zenith sun angle increases.

3. Historically, the first approach which was attempted (and extensively used for CZCS), was the **purely empirical one**. It has consisted in directly relating field measurements of $R(\lambda)$, or $[L_w(\lambda)]_N$, to the chl a (plus pheopigments) concentration determined in the upper part of the water column. The distribution in a log-log plot of the data concerning "C" (= Chl a + pheo a) and the ratio $R(445) / R(550)$ strongly suggested a linear relationship (see Fig. 3, redrawn from Gordon and Morel, 1983) and the regression techniques led to statistical equations, thereafter utilized as predictive algorithms of the power form like:

$$C = A [R(445) / R(550)]^B \quad (8)$$

where A and B come from a linear regression analysis on the log-transformed quantities (see e.g. Table 2 in Gordon and Morel, 1983); other wavelengths are equally possible when forming a ratio as above. However the above "blue-to-green" ratio is the most sensitive compared to any other ratio, because its value spans over the most extended range (from >10 to 0.5 when C varies from 0.02 to 20 mg m⁻³). The compatibility between such empirical algorithms (which necessarily fail at very low and high concentration) and the results of the semi-analytical approach has been studied very early (Fig 4). For extremely low chlorophyll content, the ratio of the reflectances at two wavelengths (440 and 560 nm in Fig. 4, redrawn from Gordon-Morel, 1983) tends toward a limit which is imposed by the optical properties of pure water (about 18); conversely, at very high chlorophyll concentration, the ratio would be governed by the optical properties of algal cells (and would tend toward ~0.3 depending on the dominant algal species). The existence of these two limiting value imposes a sigmoidal form to the curve representing R as a function of C in a log-log representation. Recent empirical relationships (O'Reilly et al., 1998) account for this double curvature and make use of polynomial expressions in the log-log plane, instead of the old Eq. 8, which can only describe the linear (central) portion of the curve in Fig. 4.

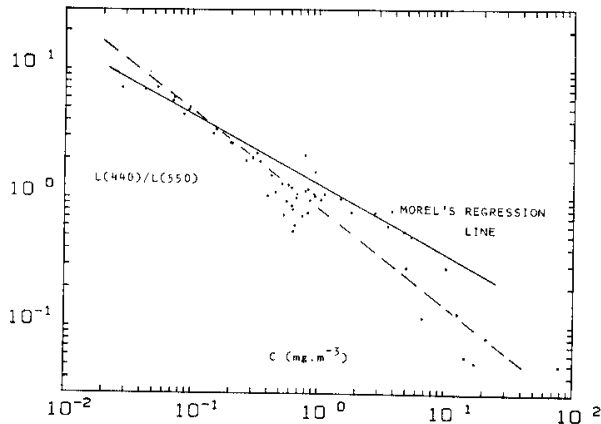


Figure 3a. Radiance ratio, $L_n(440)/L_n(560)$, plotted vs. pigment concentration (Clark's data, 1981) and regression line (dashed line). Morel's regression line comes from Fig. 3b (and represents the algorithm 3, Table 2).

Figure 3a.

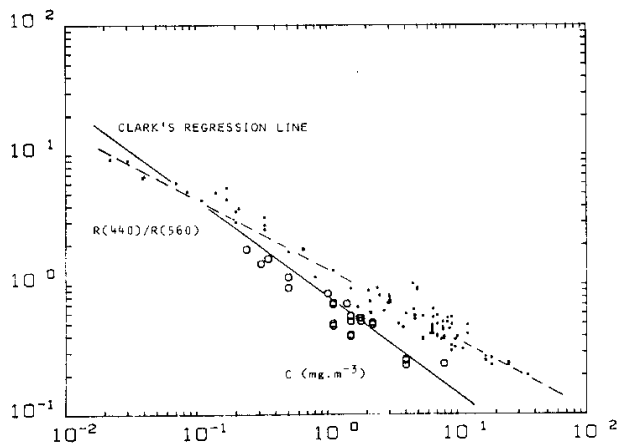


Figure 3b. Reflectance ratio, $R(440)/R(560)$, plotted vs. pigment concentration. With respect to a previously published figure (Morel, 1980), 27 additional data have been included. These additional data were obtained around Vancouver island (C-Fox experiment), some of them in eutrophic waters. By using an exclusion test ($\rho > 0.91C^{-0.575}$) to select only Case 1 waters, and then performing the regression analysis, the relationship $C = 1.71\rho^{-1.82}$ ($r^2=0.954$ $N=92$) is obtained (dashed line), which does not significantly differ from algorithm 3, Table 2. Clark's regression line comes from Fig. 3a (and algorithm 5, Table 2).

Figure 3b.

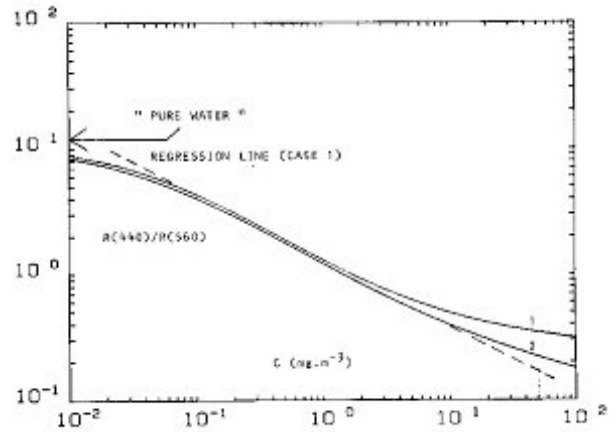


Figure 4. The dashed line represents the regression $\rho=1.437C^{-0.556}$ (i.e., the inverted algorithm3). The upper and lower curves represent the variations of ρ according to the prediction of improved models (see text) with respect to models previously used. The arrow indicates the limiting value $\rho=11.9$ for pure water (when C tends to zero).

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2. Algorithm Description

2.1. Theoretical Description

2.1.1. Physics of the Problem and historical developments

Semi-empirical approach: models and subsequent algorithms

The purely empirical models, consisting of inverting a statistical relationship established between a ratio of spectral reflectances and [Chl], do not provide any understanding of the optical properties involved in the remote sensing problem. They do not lend themselves to improvement. The entirely analytical approach, still very uncertain, has to be kept for advanced research and products. **Semi-empirical approach** is well adapted for future evolution, and presently can be used for routine production of an operational pigment index for Case 1 waters (see 3.1.2 and 3.2.4). Validation of such models is feasible by comparing their predictions and in situ measurements. Such an inter-comparison/validation exercise has been conducted in January 1997 by NASA/SEABAM. Seventeen algorithms have been under evaluation, and the results were published (O'Reilly et al., 1998).

Various models were developed based on semi-empirical approaches; two of them are briefly described below.

M88 Model

This model, was presented in every details elsewhere (Morel, 1988); it can be summarized as follows. The backscattering coefficient is parameterized as the sum of the backscattering coefficient by water molecules and the backscattering coefficient for all particles (algal and non-algal)

$$b_b(\lambda) = b_{bw}(\lambda) + 0.30 [\text{Chl}]^{0.62} \left[0.002 + 0.02 \left(\frac{1}{2} - \frac{1}{4} \log_{10}[\text{Chl}] \right) \left(\frac{550}{\lambda} \right) \right] \quad (9)$$

The exponent 0.62 accounts for the non-linear increase of scattering with increasing chl *a* concentration. The bracket expresses the backscattering efficiency, and also varies decreases with increasing chl *a*. The wavelength dependency (λ^{-1}) which actually applies to the scattering coefficient, is inserted into the bracket.

The semi-analytical expression for *a* is replaced by similar expression making use of the K coefficients (cf. Eq. 6b)

$$K(\lambda) = K_w(\lambda) + \chi(\lambda) [\text{Chl}]^{e(\lambda)} \quad (10)$$

where $K_w(\lambda) = a_w(\lambda) + b_{bw}(\lambda)$ and the $\chi(\lambda)$ and $e(\lambda)$ are tabulated values (ibid.). Note that when [Chl] = 1, the $\chi(\lambda)$ spectrum is a "chl *a*-specific" attenuation coefficient. The shape of this spectrum, however, is not constant when Chl is varying to the extent that the exponents $e(\lambda)$ — ranging from 0.600 to 0.708 — are not spectrally constant. This feature differentiates this model from other ones, where the spectral shape of algal absorption was considered as invariable.

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It is worth noting that the algal contribution expressed by the second term in Eq. 10 actually (albeit implicitly) includes the optical effect of any natural material (detritus, bacteria, dissolved colored matter...) associated and co-varying with the Chl concentration in Case 1 waters. It is one among the reasons why this term is not linear with respect to [Chl], nor spectrally constant in shape.

The transformation of K into R is iteratively made according to the following scheme.

1 st loop: R is computed according to

$$R(\lambda) = (0.33) \frac{b_b(\lambda)}{U_1 K(\lambda)} \quad \text{with } U_1 = 0.75 \text{ (whatever the wavelength)} \quad (11)$$

Then, by using the exact relationship which links a , K and R,

$$a = K \left(1 - R + \frac{1}{K} \frac{dR}{dz} \right) \frac{\mu_d \mu_u}{R \mu_d + \mu_u} \quad (12)$$

transformed into

$$a(\lambda) = K(\lambda) \frac{0.90 [1 - R(\lambda)]}{1 + 2.25 R(\lambda)} = K(\lambda) U_2(\lambda) \quad (13)$$

and with the R value produced at the issue of the first loop, a set of $U_2(\lambda)$ values can be produced; then Eq. 13 is re-operated with $U_2(\lambda)$ replacing U_1 , etc.. Steady values of $R(\lambda)$ are always obtained within 3 loops in this process.

G88 Model

"A semi-analytical radiance model of ocean color" has been described by Gordon et al in 1988 (also known under the acronym SARMOG). Following considerations expressed in Gordon and Morel (1983), the backscattering coefficient is decomposed into

$$b_b(\lambda) = b_{bw}(\lambda) + \alpha(\lambda) [\text{Chl}]^{\beta(\lambda)} \quad (14)$$

The phytoplankton + detritus term relatively decreases for increasing [Chl] (the $\beta(\lambda)$ values are 0.22, 0.35 and 0.36 at $\lambda = 443, 520$ and 550 nm respectively). The values resulting from this formulation are not far from those obtained via Eq. 9, but are not coinciding. The compatibility between the various expressions recently proposed for the backscattering efficiency remain to be studied.

As in M88, the K coefficients are used. They are modeled according to Baker and Smith (1982) as

$$K(\lambda) = K_w(\lambda) + k_c(\lambda) [\text{Chl}] \exp \left[\left[k_c'(\lambda) \log_{10} \frac{[\text{Chl}]}{\text{Chl}_0(\lambda)} + 0.01 [\text{chl}]^2 \right] \right] \quad (15)$$

where the 3 parameters k_c , k_c' , and Chl_0 are dependent on λ and tabulated in Baker and Smith (1982). Again $K(\lambda)$ depends on [Chl] in a nonlinear manner; the relative amounts of algae and of detritus (not explicitly accounted for) vary with the chl a concentration, forcing the total coefficient to be a

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nonlinear function of [Chl]. An additional term for yellow substance can be included; absorption is modeled according to: $a_y(\lambda) = a_y(\lambda_0) \exp[-0.014(\lambda - \lambda_0)]$ (Bricaud et al., 1981)

and a_y is transformed into K_y through

$$K_y = a_y / \cos \theta_0 \quad (16)$$

where θ_0 is the in-water solar zenith angle.

Conversely to the previous M88 model, the K values are not retransformed into a values, thus the final G88 model is expressed in a way derived from Eq. 7, except that R is replaced by $[L_w]_N$ (see Eq. 1). Finally it takes the following form

$$[L_w]_N(\lambda) = \frac{f_3 \mathfrak{R}_o}{Q_o} \frac{b_b(\lambda)}{K(\lambda)} F_o \quad (17)$$

It has been shown elsewhere (Gordon, 1986) that the global factor ($f_3 \mathfrak{R}_o/Q_o$) amounts to 0.11 with a rms error of 20% (according to Monte Carlo simulations) and is kept constant in the model formulation.

2.1.2. General Description of the "Pigment Algorithm" for MERIS

A detailed description of the algorithms providing not only the pigment index, but also the reflectances and/or normalized water-leaving radiances at all visible wavelengths is given in DPM 2.9. The way of removing the bidirectional effects is explained in Morel et al. (2002), and follows the recommendations provided in Chapter 13 of the NASA/TM 2002 report (Ocean Optics Protocols for satellite ocean color sensor validation, Revision 3, Volume 2; Chap 13: "Normalized water-leaving radiance and remote sensing reflectance : Bidirectional reflectance and other factors", by A. Morel and J.L. Mueller). Here is only presented the principle for retrieving the "pigment index". It stems from the semi-empirical approach presented in Morel (1988). This previous study has been revisited (Morel and Maritorena, 2001), and the present algorithm accounts for these new developments.

This new model (MM01), is designed only for oceanic (Case 1) waters, and is thus explicitly dependent on the sole chlorophyll concentration. The input quantities are either physical constants (for pure water), or are expressed as a function of Chl. Only the main features of the new model are recalled below.

The spectral IOPs of optically pure sea water, namely the absorption, $a_w(\lambda)$, (new values from Pope and Fry, 1997) and scattering, $b_w(\lambda)$, coefficients, as well as the molecular phase function (Morel, 1974) are known, and used as such.

The particle scattering coefficient b_p and Chl as simultaneously measured at sea are related, in a statistical sense (revised relationship of Loisel and Morel, 1998). The expression now in use is

$$b_p(560) = 0.416 [\text{Chl}]^{0.766} \quad (18)$$

The spectral dependence of this coefficient is expressed as a power law, λ^v , where the exponent, v , varies from -1 to 0 (when Chl increases from 0.02 to 2 mg m^{-3}), and then becomes constant ($= 0$) for larger concentrations. The variation is expressed as

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$$v = (1/2) (\log_{10} [\text{Chl}] - 0.3) \quad \text{when } 0.02 < [\text{Chl}] < 2 \text{ mg m}^{-3}$$

$$\text{and } v = 0 \quad \text{when } [\text{Chl}] > 2 \text{ mg m}^{-3} \quad (19)$$

The shape of the phase function of this particulate matter is also made varying with Chl, but is not wavelength dependent (see Fig 3 in Morel et al., 2002). As a result, the backscattering probability is spectrally neutral, and decreases from 1.2% down to 0.2% when Chl increases from 0.01 up to 100 mg m⁻³, according to

$$0.002 + 0.01 (0.5 - 0.25 \log_{10} [\text{Chl}]) \quad (20)$$

The data bank of simultaneous determinations of Chl and $K_d(\lambda)$ has been increased compared to that used in Morel 1988. Therefore, by accounting for these new data, the relationships between $K_{\text{bio}}(\lambda)$ and Chl (Eq. 10) have been refined; the slightly modified coefficients, $\chi(\lambda)$ and exponents $e(\lambda)$, are available (Morel and Maritorena, 2001) and used in the revised model. Note that, by using $K_d(\lambda)$, there is no need to make hypotheses about the relative proportions of particle absorption and dissolved colored matter absorption, nor about the change in these proportions as a function of Chl. Indeed, the effects of both kinds of absorbers are cumulated in the formation of $K_d(\lambda)$. The transformation of this apparent property $K_d(\lambda)$ into an inherent one, namely $a(\lambda)$ is iteratively made as before (Eq. 12 and 13).

The last needed IOP is the Raman scattering coefficient, actually the fractional absorption that leads to a (trans-spectral) re-emission by water molecules. The value adopted is $2.6 \cdot 10^{-4} \text{ m}^{-1}$ (at 488 nm) with a spectral dependency expressed as λ^{-5} (Bartlett et al., 1998). The effect of Raman emission on reflectance is not negligible when Chl is low and for wavelengths beyond 590 nm (see Morel and Gentili, 2004, their Fig. 9 for quantitative information). The “algal pigment algorithm” in Case 1 waters (see below) does not use these wavelengths. The fluorescence by phytoplankton around 685 nm is another kind of emission, which is separately examined in the particular case of reflectance just beneath the surface, but not in the frame of the present pigment algorithm. Finally, with the absorption and backscattering coefficients modeled as a function of [Chl] as described above, the Equation 2 is operated to produce the spectral reflectance $R(\lambda, [\text{Chl}])$.

Proposition for an algorithm providing the algal pigment index in Case 1 water from ratio of reflectance (band ratio)

This proposition (see also definition and constraints in 3.2.4) consists in using the variation of the ratio

$$\rho_{i,j} = R(\lambda_i) / R(\lambda_j) \quad (21)$$

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along with the Chl *a* concentration. These variations, $\rho_{ij}([\text{Chl}])$ are then inverted to constitute the retrieval algorithm under a polynomial form as follows

$$\log_{10}[\text{Pigment index}] = \sum_{x=0}^n A_x (\log_{10} \rho_{i,j})^x \quad (22)$$

The log transform of the pigment concentration is well adapted to cope with the 3 orders of magnitude change expected for this quantity. The wavelengths to be considered are

- for λ_j , the green wavelength available with MERIS, is $\lambda_5 = 560$ nm
- and for λ_i , one of the three wavelengths in the blue and blue-green part of the spectrum, namely

$\lambda_2 = 443$ nm, $\lambda_3 = 490$ nm, and $\lambda_4 = 510$ nm are available

Two examples (reproduced from Morel and Maritorena, 2001, denoted MM-01) are shown in Figure 5. The curves are produced by the MM-01 reflectance model, whereas the symbols represents field data which include simultaneous pigment determination and spectral reflectance measurements. It is important to note that these reflectance data (and their ratios) are not used in the development of the model. In other words, and as said above, the model is not an empirical one, i.e. a best fit of the reflectance ratios as a function of Chl (as are OC2 or OC4, in use with SeaWiFS, and OC3M in use with MODIS), but is a semi-analytical one.

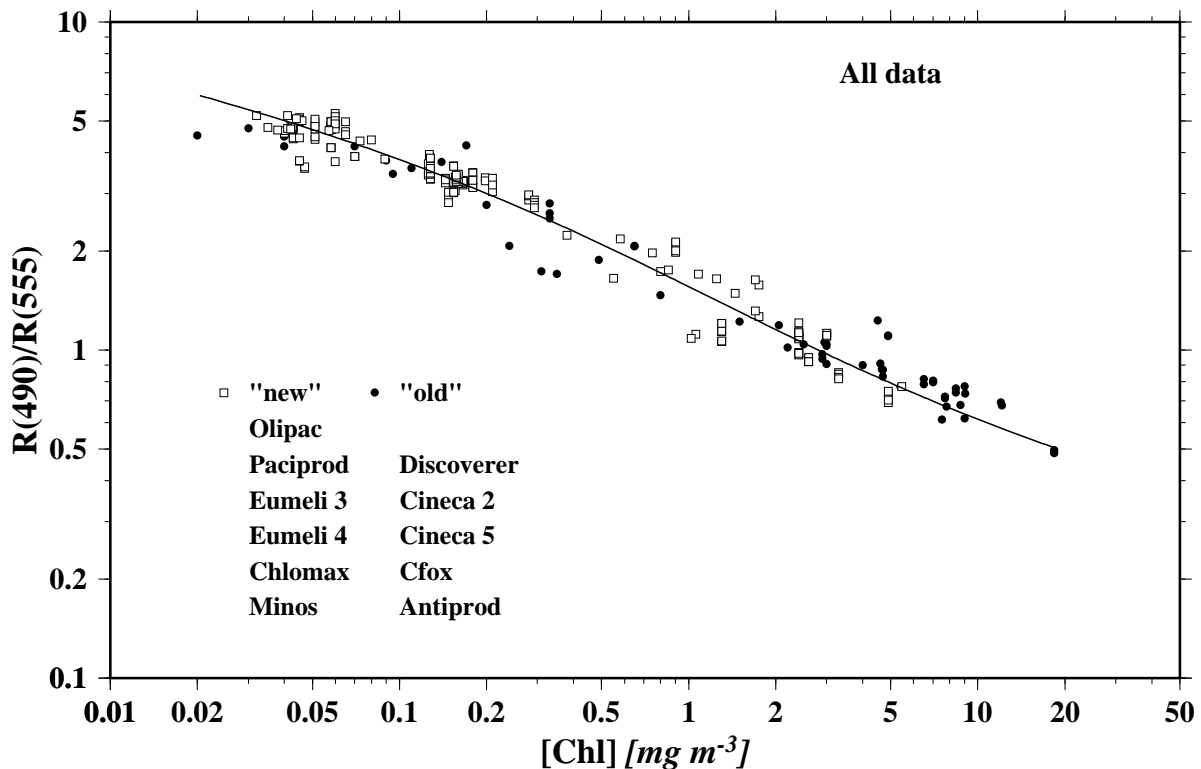
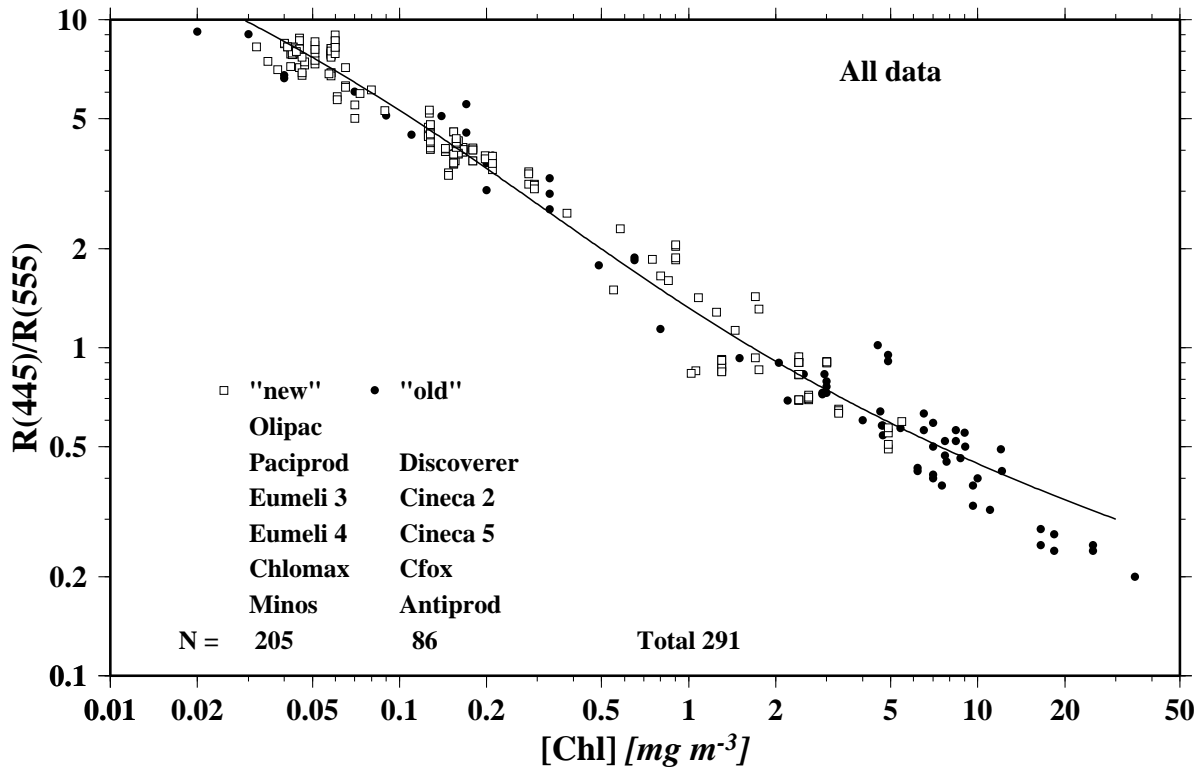


Figure 5. These Figures show for two couples of wavelengths the ratio of reflectances as a function of the pigment concentration. The curves correspond to a semi-analytical approach, which makes use of the newly published values for the spectral absorption by pure water (Pope and Fry, 1997). The closed and open symbols represent field measurements of the same quantities. Note that the development of the semi-analytical model is independent from these reflectance measurements, which are used for validation (reproduced from Morel and Maritorena,2001).

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Updated proposition: the OC4Me algorithm

In the hyperspectral reflectance model (MM-01), the dataset used to statistically derive the relationships (Eq.10) included simultaneous field values of $K_d(\lambda)$ and $[Chl]$ that were determined before the year 1996; the resulting $\chi(\lambda)$ and $e(\lambda)$ values were tabulated in the above referenced paper.

New couples of $K_d(\lambda)$ and $[Chl]$ values were determined during several recent cruises, Prosope(1999), Bencal(2002), Aopex(2004) and Biosope(2004). These data have been added to the previous dataset, and the statistical analysis $K_d(\lambda) \leftrightarrow [Chl]$ was run again on this increased dataset. As a result, the $\chi(\lambda)$ and $e(\lambda)$ values are slightly modified (available on internet at oceane.obs-vlfr.fr, cd pub/morel, file `e_chi_kw_2006`). Therefore the reflectance model, unchanged in its structure, but fed with these new values, provides slightly modified reflectance values, compared to those in MM-01. These updated $R(\lambda) \leftrightarrow [Chl]$ relationships lead to modified ratios of reflectance, ρ_{ij} , or band ratios, which are the basis of the algorithm (see Eqs. 21 and 22).

The agal-1 pigment retrieval will be performed by using normalized reflectance values, denoted $R_0(\lambda)$, which are the hypothetical $R(\lambda)$ values to be observed were θ_s , the sun-zenith angle, equal to zero.

In the relationship which express the reflectance as a function of the absorption (a) and backscattering (b_b) coefficients (Reference Model, Eq. 49')

$$R(\lambda) = f(\lambda) [b_b(\lambda) / a(\lambda)]$$

$f(\lambda)$ must take the particular (and minimal) values, $f_0(\lambda)$, corresponding to $\theta_s = 0$ (note that the f values are not spectrally neutral) These values have to be introduced to obtain the appropriate $R_0(\lambda)$ values, and then the $(\rho_{ij})_0$ ratios to be introduced into the algorithm. (Note that $f_0(\lambda)$ for clear skies is also weakly depending on the atmospheric turbidity, i.e. on τ_a , the aerosol optical thickness; this dependence is ignored and τ_a is set equal to 0.1 at 550 m). Therefore the algorithm (Eq. 22) must be formulated in terms of $(\rho_{ij})_0$ ratios.

$$\log_{10}[\text{Pigment index}] = \sum_{x=0}^n A_x [\log_{10}(\rho_{i,j})_0]^x$$

This OC4Me algorithm applies on the ratios of exactly normalized reflectances (the $R_0(\lambda)$ defined above). Its polynomial structure (4th order) includes 5 coefficients (the A_0 to A_4 coefficients) as follows

$$0.4502748 \quad -3.259491 \quad 3.522731 \quad -3.359422 \quad 0.949586$$

It is graphically presented in Fig. 6. Practically, the three possible ratios $(\rho_{2,5})_0$, $(\rho_{3,5})_0$, $(\rho_{4,5})_0$ can be combined into a unique polynomial, which is the envelope of the three curves. The automatic switching procedure consists of using the maximum value among the three ρ values, so that

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$$\log_{10} [Pigment\ index] = \sum_{x=0}^n A_i [\log_{10} Max\ \rho_0]^x$$

with $Max\ \rho_0 = \max [(\rho_{2,5})_0, (\rho_{3,5})_0, (\rho_{4,5})_0]$

The switching between $(\rho_{2,5})_0$ and $(\rho_{3,5})_0$ occurs for $Chl \sim 0.54\ mg\ m^{-3}$; and between $(\rho_{3,5})_0$ and $(\rho_{4,5})_0$ for $Chl \sim 2.2\ mg\ m^{-3}$. The use of the maximal ratio combined within a unique polynomial was also adopted for the OC4V4 algorithm of SeaWiFS (the wavelengths are not the same, as $\lambda_5 = 555\ nm$), and for the OC3M algorithm of MODIS (with only 3 wavelengths, 443, 488, and 550 nm, and thus 2 ratios).

Practical use of the above algorithms when remote sensed radiances are used as inputs

At his stage, it is assumed that the measured radiances (TOA) have been "perfectly" corrected for the atmospheric contribution, so that the water-leaving radiances, $L_w(\lambda)$, are accurately known. The problem examined below lies in the bi-directional character of these radiances. In other words, for a given Chl value (in Case 1 waters), L_w varies with the geometrical conditions, namely the viewing angle, the zenith-sun angle and the azimuth difference (θ_v , θ_s , and $\Delta\phi$, respectively). In addition, these variations are depending on the relative proportions of scattering (b) and absorption (a) in forming the total attenuation coefficient ($c = a + b$); they also depend on the relative proportions of the molecular scattering, b_w , and the particle scattering, b_p , in forming the (total) scattering coefficient ($b = b_w + b_p$). These relative proportions are, in Case 1 waters, governed by the chlorophyll concentration, so that the bidirectional effect can be predicted from the model. This model has been tested by comparing its predictions with field measurements (Morel, Voss and Gentili, 1995; Voss and Morel, 2005), over a large range of chlorophyll concentrations, by using a radiance distribution camera system (Voss and Chapin, 1992).

Therefore, the expected outputs of the processing, namely the pigment index, is already needed when the processing is started. The only conceivable solution is in the development of an iterative process (Morel and Gentili, 1996), which results in the production of exactly normalized water-leaving radiances, $[L_w]_N^{ex}$, i.e. free from the bidirectional variations. The correction is made through the use of the (f/Q) factor, and this factor is tabulated (5-D) as function of the geometrical parameters (θ_v , θ_s , and $\Delta\phi$), of λ , and of Chl. (see also Morel and Mueller, 2002). The ratio of the corrected radiances at two wavelengths (equal to the ratio of reflectances at the same wavelengths) can be used in Equation 22 to derive the pigment index value.

The acronym used to designate the algorithm for MERIS is OC4Me (with the convention that Me is kept for MERIS and Mo for MODIS).

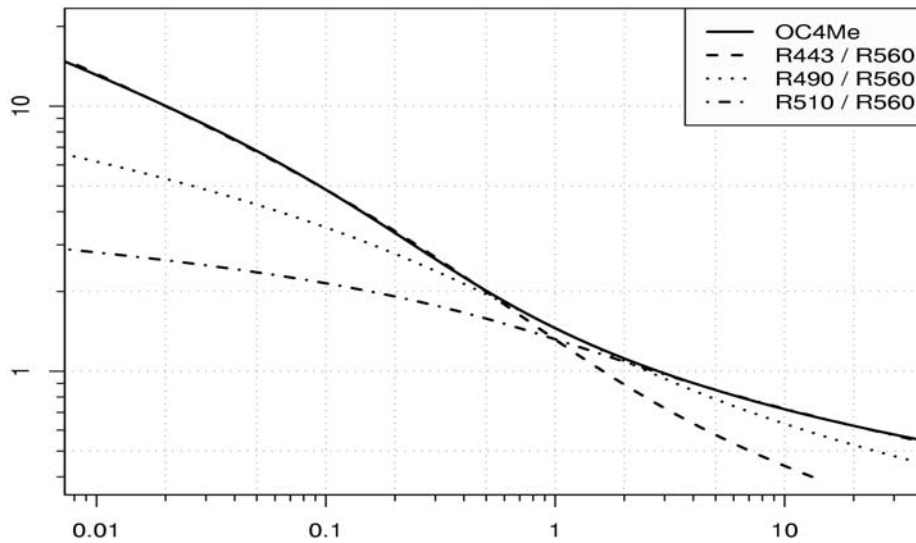


Figure 6. The three reflectance ratios $(\rho_{2,5})_0$, $(\rho_{3,5})_0$, $(\rho_{4,5})_0$ (as indicated), as a function of the algal pigment concentration, $[Chl]$ (mg m^{-3}). They are derived from the revised reflectance model and when each reflectance takes its (minimal) value when the sun is at zenith (with f_0 (λ), corresponding to $\theta_s = 0$). The envelope for the three curves correspond to the maximum band ratio, and its polynomial best fit provides the algorithm OC4Me

2.1.3. Error Budget Estimates

The f/Q tables can be prepared in such a way that the interpolations are possible with an accuracy better than 1%. The iterative process, even if restricted to two loops, does not introduce significant deviations according to simulations effected in the worst cases. The polynomial expressions operated when computing the pigment index are accurate to any level desirable.

Therefore, the error budget, in a numerical sense, is extremely favorable, as purely numerical error can be reduced at a controlled level. The actual error budget, which limits the final realized accuracy, is out of control, as the computations rest on hypotheses and semi-analytical models, previously developed from statistical analyses. In essence, such models depict "average" situations, from which natural conditions may randomly depart.

2.2. Practical Considerations

2.2.1. Calibration and Validation

There is no internal way for a validation; only field measurements, simultaneously dealing with optical properties of water bodies and their pigment concentrations can constitute a calibration/validation of the processing, as well as the tool for improvement of bio-optical models. The calibration/validation of the entire processing (atmospheric corrections included) must also include atmospheric determinations. Protocols for the whole series of such needed measurements (both

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oceanographic and atmospheric optical measurements) have already been prepared under the auspice of NASA (a series of Reports Ocean Optics Protocols for satellite ocean color sensor validation).

The presently available way of testing the efficiency of marine algorithms consists of comparing the results of the semi-analytical model (in terms of ρ plotted as a function of [Chl]), with experimental determinations at sea of [Chl] and spectral values of reflectance, allowing ρ to be derived for appropriate wavelengths. Such a comparison is displayed in Fig.7, only based on recent field data (posterior to the development of the model, and the proposition of the OC4Me algorithm).

2.2.2. Quality Control and Diagnostics

To the extent that the quality tests related to the atmospheric correction are successful, and that "positive" water-leaving radiances are obtained, the derivation of a pigment index is always possible. At this stage there is no possibility of detecting a failure, as an imperfect atmospheric correction, leading to positive, albeit wrong, water-leaving radiance cannot be identified per se. This means that only external quality control, based on image structure analysis combined with oceanographic knowledge, or based on comparison with other sensors data, is able to detect non-plausible pigment concentrations.

2.2.3. Exception Handling

All waters identified as Case 2 waters, and belonging to sediment-dominated or yellow substance dominated case 2 waters, are not amenable to the above algorithm. If the algorithm is still applied, it generally leads to a considerable overestimate of the pigment content. Therefore, a discrimination between Case 1 and Case 2 waters have to be first achieved. This is possible regarding the sediment-dominated Case 2 waters, through the enhancement of the reflectance in the channel at 560 nm; the consideration of the bidirectional effect is needed for this discrimination (see Morel and Belanger, 2006). The identification of yellow-substance dominated Case 2 waters (for which the channel 1 at 412 nm was intended for) remains an elusive target.

All zones contaminated by sun glint, even weak, may provide wrong results, because the additional signal at all wavelength affects the value of the ρ_{ij} ratios.

2.2.4. Output Product

Operational Definition of a Pigment Product in Case 1 waters

When defining such a product there are several constraints, in order

1. to ensure a continuity with the CZCS-type "chlorophyll", or at least to warrant a simple and meaningful convertibility between the "new" and "old" products; to ensure a coherence with the SeaWiFS-type "pigment" product; to ensure a compatibility of the products of the various sensors and Agencies;
2. to minimize the ambiguities about the meaning of the proposed product by defining its very nature and significance in reference to oceanographic knowledge;

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3. to provide a product useful for subsequent applications (such as algal biomass description, primary production assessment, carbon cycle, marine ecology...);
4. to dispose of a simple algorithm to derive the product;
5. to develop this algorithm on the basis of ratio technique(s), less sensitive to various biases (radiometric shift, inaccurate atmospheric correction, residual bi-directional effects ...).

As a consequence of the above constraints, as they are presently identified and understood, only one routine product is proposed (Algal-1). More specific products (such as absorption and backscattering coefficients), relying on more complex algorithms, are beyond the scope of the present definition and form a category of "advanced" products, still requiring research. Such a research is based on the use of "water-leaving" radiances in the various channels, or on similar products provided by other sensors (SeaWiFS, MODIS) or/and on field data.

The above constraints deserve some comments :

Concerning 1

The need for a continuity and internal consistency is obvious in the frame of a continuous monitoring of the ocean, which is the rationale for all the new ocean color sensors to be launched. Such a consistency is strongly encouraged by the JGOFS community as stated in the "Report of the JGOFS Remote Sensing Task Team" (J.A. Yoder *ed.*, SCOR 1995, and IOCCG report #1, 1998)

Concerning 2

The issue of ambiguities is less trivial than generally recognized. The CZCS pigment, often denoted "C", was considered as the sum of chl *a* + pheopigments concentrations, where pheopigments (degraded products from chl *a*) appeared in this definition essentially because of experimental deficiencies in discriminating pheopigments from chl *b*. It is now acknowledged that the pheopigments concentration is much lower than previously (and wrongly) believed.

Saying "chlorophyll concentration" is equally erroneous (see discussion page 67 in Gordon and Morel, 1983). If chl *a* is absorbing in the blue part of the spectrum (the γ - Soret band at 440 nm), the broad absorption in this spectral region, detectable from space, is also and sometimes predominantly due to other algal pigments (other chlorophylls and carotenoids, either photosynthetic or photoprotectant). Therefore the less contestable appellation which is proposed is "algal pigment index" (rather than chlorophyll concentration), even if the unit will necessarily remain mg m^{-3}

- This unit is consistent with the bio-optical models which also relate the global properties, and the blue-to-green ratios in particular, to the Chl *a* concentration, without ignoring that other materials and pigments are involved in the formation of the optical properties (their nonlinear character with respect to [Chl] partly reflects this complexity — see discussion above).

Concerning 3

If for algal biomass evolution and repartition, the pigment index as defined is a convenient descriptive tool, for quantitative predictions concerning, for instance, the oceanic primary production, some drawbacks still subsist. To the absorption measured from space must be associated a "useful"

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absorption by algae only, and complications then arise when photoprotectant pigments are in a significant amount. Very likely progress will be made to solve such issues.

Concerning 4 and 5

Blue-to-green ratios techniques provide the desirable continuity with the CZCS- SeaWIFS-MODIS products and simultaneously are the most straightforward and sensitive ones which can be presently envisaged for routine production. Some inevitable inaccuracies (originating from the processing and correction scheme) which affect in the same direction the spectral marine information, partly cancel out by the virtue of taking the ratio of two signals.

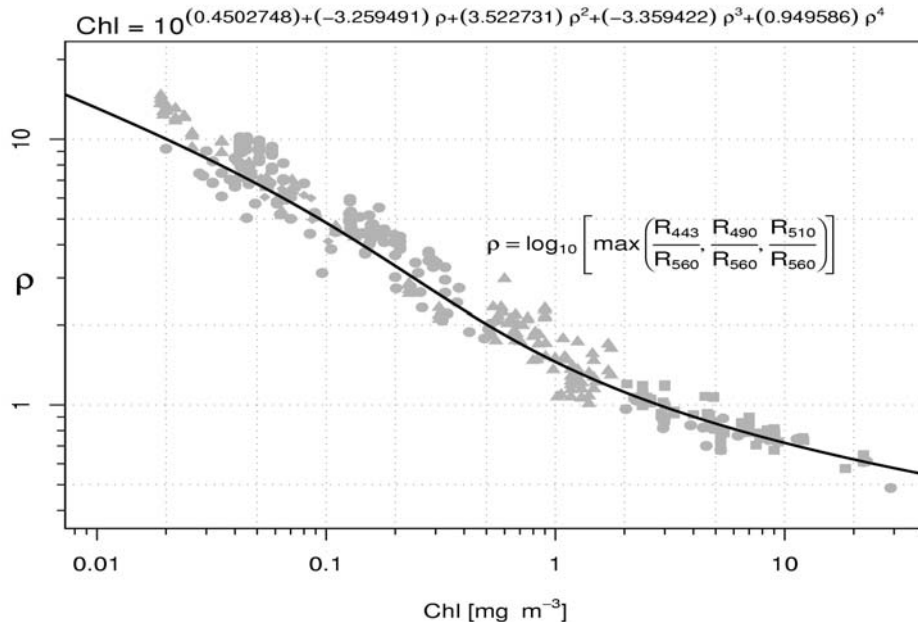


Figure 7. The envelope corresponding to the algorithm OC4Me is reproduced from Fig. 6a; all the data in the LOV bank (reflectances and [Chl]) are plotted for comparison. As in Fig. 5, these determinations were not used in the development of the semi-analytical model leading to OC4Me.

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4. Appendix 1

Notation	Definition	Units
a,b	absorption and scattering coefficients	(m ⁻¹)
b _b	backscattering coefficient	(m ⁻¹)
K	attenuation coefficient for downwelling irradiance, normally written as K _d ; the subscript d is here omitted.	(m ⁻¹)
R(0 ⁻)	reflectance at null depth (0 ⁻), defined as the ratio of upwelling irradiance, E _u , to downwelling irradiance, E _d , (both just beneath the surface).	dimensionless
[L _W] _N	normalized water-leaving radiance, defined as the radiance measured by a nadir-viewing instrument if the sun is at zenith, in absence of any atmospheric loss, and when the earth is at its mean distance from the sun.	W m ⁻² nm ⁻¹ sr ⁻¹
L _W (0 ⁻ ,nad)	upwelling radiance, originating from nadir, and at null depth (0 ⁻).	W m ⁻² nm ⁻¹ sr ⁻¹
Q _o	ratio E _u (0 ⁻) / L _W (0 ⁻ ,nad)	sr
F _o	extraterrestrial irradiance	W m ⁻²
R _o	term accounting for all the reflexion and refraction effects = $\frac{(1 - \bar{\rho})(1 - \rho)}{(1 - FR) n^2}$ its value is about 0.529	dimensionless
Subscripts	w, φ, y, d stand for water, phytoplankton, yellow substance and detritus, respectively.	

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ATBD 2.9 — MERIS DATA PRODUCT SUMMARY SHEET

Product Name: Algal pigment index in Case 1 waters
Product Code: MERIS.PIGIND
Product Level: 2
Description of the product: algal pigment concentration based on a blue-to-green ratio technique. This product quantifies the concentration in all the pigments responsible for blue absorption, among which chlorophyll *a* is a peculiar one, and even if the sole chl *a* (according to tradition and routine measurements) is used as unit

Product Parameters:

Coverage: global
Packaging: half-orbit
Units: mg (chl *a*) m⁻³
Range: 0.01 - 30 mg m⁻³
Sampling: pixel-by-pixel
Resolution: relative ± 13% (10 classes per decade)
Accuracy: **TBC**
Geo-location Requirements: 1 pixel
Format: 16 bits/sample
Appended Data: location, flag, mask, quality index
Frequency of generation: 1 product per orbit
Size of the Product: **TBD**

Additional Information:

Identification of bands used in algorithm: 2, 3, 4, and 5
Assumptions on MERIS input data: water-leaving radiances
Identification of ancillary and auxiliary data:
Assumptions on ancillary and auxiliary data: