Light scattering and chlorophyll concentration in case 1 waters: A reexamination

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Abstract

An analysis is presented based on a large dataset (N = 2,787) made up of recent measurements of the beam attenuation coefficient at 660 nm and of the chlorophyll concentration by using the SeaTech transmissometer and the high-pressure liquid chromatography technique, respectively. This analysis, restricted to case 1 waters, aims at reassessing a previous nonlinear relationship established between the particle scattering coefficient, b_p (very close to the particle attenuation coefficient, c_p), and the chlorophyll concentration, [Chl]. As a first result, nonlinearity is fully confirmed over the whole range of oceanic chlorophyll concentration (about 3 orders of magnitude). Despite more accurate measurements, the scatter in this relationship remains large and is actually comparable to that observed within the old dataset. Rather than establishing a single relationship between c_p (or b_p) and [Chl] for the entire upper water column, the deep layer and the near-surface layer (important for remote-sensing application) have been studied separately. This separation has led to two distinct expressions. A more appropriate parameterization is thus proposed when dealing specifically with, and modeling, the near-surface layer. As a consequence, a modified criterion is also suggested with a view to identifying turbid case 2 waters.

Understanding or predicting the propagation of radiant energy within a water body requires that the boundary conditions (at the interface and bottom) and the inherent optical properties (IOP) within the medium are both known or prescribed. Strictly speaking, these properties (IOP) within the medium are both known or prescribed. Strictly speaking, these properties comprise the absorption coefficient, α, and the volume scattering function β(θ); the scattering coefficient, b, derives from β(θ) by integrating over the whole space, and the attenuation coefficient, c, represents the sum of α and b. These last three coefficients are expressed as m^{-1}. The IOP result from the presence in a water body of colored dissolved organic substances and of scattering as well as absorbing particulate matter.

In the open ocean, far from notable terrigenous influence, these optically active materials are locally and permanently formed through various processes along the trophic chain. These oceanic waters are commonly referred to as case 1 waters (Morel and Prieur 1977). For historical and practical reasons, the index usually adopted to specify the bio-optical state (Smith and Baker 1978) of a water body is its chlorophyll concentration, hereafter simply denoted as [Chl] (expressed in mg m^{-3}). This adoption acknowledges that in many oceanic environments, and in case 1 waters by definition, phytoplankton with their associated and derivative products play a major role in determining the IOP. As a result, optical modeling of case 1 waters requires that relationships between the IOP and [Chl] are available for the whole range of possible variations in [Chl]. In the upper layers of these waters, [Chl] may vary from nearly zero (i.e., -0.02 mg m^{-3}) up to 20 mg m^{-3} or even more from oligotrophic to eutrophic situations. The present study deals with recent field measurements specifically performed in case 1 waters and aims at reexamining the relationships between the scattering coefficient and [Chl]. The scattering coefficient, or more accurately its varying part, denoted b_p (the constant part originates from the scattering of water molecules), results from the presence of all kinds of suspended matter, such as autotrophic, small heterotrophic living organisms, as well as from detritus of various sizes. Among these particles, only phytoplanktonic cells bear chlorophyll (some of their predators may also). Importantly, [Chl] is a descriptor of only one fraction of the particle population; therefore, trying to relate b_p to [Chl] admittedly induces some inevitable uncertainties.

Based on previous field determinations in the tropical Atlantic and Pacific Oceans and on their statistical analyses, a first empirical relationship was presented (Morel 1980) and then slightly modified after additional data were included (Gordon and Morel 1983). This relationship, for case 1 waters only (with 659 pairs of data), was established for the particle scattering coefficient, b_p, determined at the wavelength 550 nm, and for [Chl] spanning about three orders of magnitude. The relationship was

OMEX data were made available with the originators’ permission from the EU-MAST OMEX 1 Programme by the British Oceanographic Data center (BODC). The HPLC chlorophyll measurements for this project were undertaken by R. Barlow and R. F. C. Mantoura at the Plymouth Laboratory. They are gratefully acknowledged for having made their data available to us. The transmissometer data for the same cruise were calibrated and quality controlled by the BODC. We thank R. Lowry for his help in the control of, and access to, these data. The BOFS data, published on a CD-ROM, were also produced under the BODC, and are duly appreciated here. The HPLC data for the EUAMELI and OLIPAC (French JGOFS) cruises and those (unpubl.) for the MINOS campaign were performed by H. Claustre with the collaboration of J. C. Marty, C. Cailliau, and F. Vidussi. We thank them for these data. We also thank H. Claustre for helpful suggestions and discussions on a first draft of this paper: Substantial help with fieldwork and maintenance-calibration of the transmissometers used during the French cruises were provided by D. Tadliez, who is gratefully thanked. We acknowledge and thank our colleagues who worked at the two U.S. JGOFS-WOCE time-series and during the EqPac cruises or were involved in the related databanks—these colleagues rendered this study feasible through their continuous effort. This work is a contribution to the French JGOFS Programme "Prosop."
As far as we know, the above expression, commonly employed to estimate the coefficient $A$, which is on average 0.30 within the upper oceanic layer, may vary between 0.12 and 0.45 to account for the lowest and highest particle scattering coefficients found at various depths in waters satisfying the criterion for belonging to case 1 waters (see Fig. 5a in Gordon and Morel 1983). The first important result of this previous study was the finding of the nonlinear character of this relationship. The second result was the lack of tightness in this relationship, as expressed by the wide possible variations in $A$. As far as we know, the above expression, commonly employed in bio-optical studies and models, has never been reassessed since, except by Voss (1992), who examined a set of 50 data and provided another (albeit similar) relationship between $c_\lambda$ and $[\text{Chl}]$, which will be examined later.

The data on which Eq. 1 rests were obtained in the 1970s and were not derived from simultaneous determinations. Indeed, the scattering coefficient was measured with a profiling calibrated instrument, whereas samples for chlorophyll determinations were taken separately during classical hydrocasts using Niskin bottles. The chlorophyll (and pheophytin) determinations were then carried out either spectrophotometrically (Jeffrey and Humphrey 1975) or by the fluorimetric technique (Holm-Hansen et al. 1965), which have potential errors when Chl $b$ is present (Gibbs 1979); in particular, such errors may lead to an artifactual overestimate of pheopigment concentration.

The varying chlorophyll-specific scattering coefficient of phytoplanktonic species (Morel 1987), as well as the variable contribution of heterotrophs and detritus, provides some explanations of the nonlinearity and variability in Eq. 1 (Morel and Alni 1991). It is plausible, however, that the scatter in the original figure of Gordon and Morel originates, at least in part, from the nonuniformity of the measurements of the two parameters. Some inconsistencies in the $[\text{Chl}]$ determinations owing to changes in methods and experimenters are also likely. Reducing the persisting uncertainties in Eq. 1 and improving the predictive skill of this expression is desirable, if feasible, as weaknesses when modeling case 1 waters originate to a large extent from the approximate character of this relationship.

The vertical profile of the attenuation coefficient, $c$, at a wavelength of 660 nm, is now routinely measured in a continuous way by using transmissometers, such as the SeaTech transmissometer (Bartz et al. 1978). At this wavelength, and once the attenuation by pure seawater has been subtracted, the particle attenuation coefficient is chiefly (≈97%; see below) due to particle scattering. The transmissometer can be attached to a CTD sensor equipped with a rosette sampling device, so that perfect coincidences between optical measurement and sampling are now achievable. More accurate determinations of the Chl $a$ (and divinyl-Chl $a$) are presently possible (and actually recommended; cf. JGOFS protocols) by using high-pressure liquid chromatography (HPLC). Therefore, the validity of the above relationship can be reexamined more accurately than was possible 20 years ago.

### Data and methods

Several datasets, consistent in terms of methodologies (SeaTech transmissometer and HPLC), have been considered for the present reexamination. Relevant information is summarized in Table 1. The locations where these measurements have been carried out, all in case 1 waters, are displayed in Fig. 1. They include two permanent time-series stations, at the BATS and HOTS sites (near Bermuda and Hawaii, respectively; Kar. and Michaels 1996), as well as stations occupied during specific cruises in the Mediterranean Sea and in the tropical Pacific and Atlantic Oceans. The EUMELI cruises (Fig. 1) were planned to study eutrophic, mesotrophic, and oligotrophic regimes (hence the acronym), and the locations of the three stations were selected accordingly (Morel 1996). The eutrophic site (E site, 140 km of the coast) is located close to the permanent Mauritanian upwelling, the oligotrophic site (O site) in the North Atlantic gyre (1,400 km offshore), and the mesotrophic site (M site) in an intermediate position (400 km offshore).

The $[\text{Chl}]$ range encompassed by these data extends from 0.01 mg m$^{-3}$ to 4.5 mg m$^{-3}$; these values were observed between the surface and a depth of 200 m (see Table 1). The $[\text{Chl}]$ quantity is actually the sum of the concentrations in Chl $a$ and divinyl-Chl $a$ (when present), whereas pheopigment concentrations, generally found to be insignificant, are not included in $[\text{Chl}]$. The highest $[\text{Chl}]$ values were

### Table 1. Relevant information concerning the data used in this study ($N_{\text{all}}$, subset of data "seen" by a satellite-borne sensor; $N_{\text{all}}$, subset of data within homogeneous layers; $N_{\text{all}}$, all data).

<table>
<thead>
<tr>
<th>Cruise</th>
<th>$N_{\text{all}}$</th>
<th>Chl range (mg m$^{-3}$)</th>
<th>$N_{\text{all}}$</th>
<th>Chl range (mg m$^{-3}$)</th>
<th>$N_{\text{all}}$</th>
<th>Chl range (mg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apr–Jul 1989—1990</td>
<td>BOFS</td>
<td>77</td>
<td>0.511-3.770</td>
<td>149</td>
<td>0.275-3.770</td>
<td>280</td>
</tr>
<tr>
<td>Jan–Jun—Sep 1995</td>
<td>OMEX</td>
<td>32</td>
<td>0.202-1.490</td>
<td>91</td>
<td>0.113-1.490</td>
<td>204</td>
</tr>
<tr>
<td>Oct 1991</td>
<td>EUMELI 3</td>
<td>26</td>
<td>0.070-0.350</td>
<td>33</td>
<td>0.070-0.350</td>
<td>145</td>
</tr>
<tr>
<td>Jun 1992</td>
<td>EUMELI 4</td>
<td>45</td>
<td>0.037-2.010</td>
<td>65</td>
<td>0.043-4.330</td>
<td>158</td>
</tr>
<tr>
<td>Feb–Mar 1992</td>
<td>EqPac</td>
<td>32</td>
<td>0.062-0.251</td>
<td>96</td>
<td>0.062-0.276</td>
<td>473</td>
</tr>
<tr>
<td>Nov 1994</td>
<td>OLIPAC</td>
<td>63</td>
<td>0.030-0.202</td>
<td>113</td>
<td>0.030-0.230</td>
<td>331</td>
</tr>
<tr>
<td>Jun 1996</td>
<td>MINOS</td>
<td>103</td>
<td>0.032-0.138</td>
<td>148</td>
<td>0.032-0.217</td>
<td>513</td>
</tr>
<tr>
<td>1991—1995</td>
<td>HOTS</td>
<td>25</td>
<td>0.0550-0.113</td>
<td>81</td>
<td>0.055-0.138</td>
<td>308</td>
</tr>
<tr>
<td>1989—1993</td>
<td>BATS</td>
<td>32</td>
<td>0.018-0.330</td>
<td>74</td>
<td>0.018-0.330</td>
<td>375</td>
</tr>
<tr>
<td>1989—1996</td>
<td>Total</td>
<td>435</td>
<td>0.018-3.770</td>
<td>850</td>
<td>0.018-4.530</td>
<td>2,787</td>
</tr>
</tbody>
</table>

$$b_\lambda(550) = A[\text{Chl}]^{0.62},$$

(1)
systematically observed at the E site occupied during the EUMELI cruise No. 4 (Morel 1996). High values were also commonly observed at the M site and during the spring bloom in the North Atlantic, at the BOFS and OMEX stations (Lowry et al. 1994). The lowest values (i.e. <0.1 mg m\(^{-3}\)) belong to two categories—they were observed either in deep samples in mesotrophic, eutrophic, and bloom situations, or in the upper layers, when oligotrophic conditions prevailed. Such conditions were permanently encountered in the oligotrophic EUMELI site, the HOT site, in the Eastern Mediterranean Sea in June, in the OLIPAC and EqPac stations outside of the equatorial divergence (see Fig. 2), and in the BATS site (most of the time, except in early spring). Mesotrophic conditions, with intermediate [Chl] values, between 0.1 and 1 mg m\(^{-3}\) in the upper layer, are also included in the datasets. They were observed at the mesotrophic EUMELI site, near the equator in the Pacific Ocean (EqPac, OLIPAC), anywhere in the eastern North Atlantic, near Bermuda in spring, and in some locations in the western Mediterranean Sea. In total, for all locations and all depths, 2,787 pairs of [Chl] data have been gathered (Table 1).

A general feature, typical of oligotrophic situations, is the existence of a deep chlorophyll maximum (DCM) that develops in the stratified portion of the water column below the nutrient-depleted mixed layer (see examples in Fig. 2). The [Chl] values in this DCM, generally in the range 0.25–0.50 mg m\(^{-3}\), are similar to those encountered within the near-surface layer in mesotrophic conditions. Because the [Chl] increase in the DCM generally reflects an increase in the chlorophyll content per cell (Kiefer et al. 1976; Cullen 1982; Pak et al. 1988; Kitchen and Zaneveld 1990), rather than an increase in the algal cells numbers (and thus in scattering particles), it seems judicious to consider separately the optical properties in such deep layers and those in the upper mixed layer. In addition, for remote-sensing applications, only the upper layers are involved, so that their optical properties, insofar they may differ from those in the whole euphotic layer, have to be specifically studied. The thickness (Z\(\text{m}\)) of such near-surface layers “seen” by a satellite-borne sensor is equal to one penetration depth (Gordon and McCluney 1975), i.e. a depth approximately equal to one-fourth of the euphotic depth (as adopted here). For the present dataset, the euphotic depth was either determined at sea or, in absence of measurement, computed by using the vertical chlorophyll profiles and the algorithms developed in Morel (1988) and Morel and Berthon (1989).

Therefore, in view of performing this separate analysis, a subset has been formed that includes only those data (N\(\text{m}\) = 435; see Table 2) that pertain to the Z\(\text{m}\) layer as defined above. Visual inspection of all [Chl] and c\(\text{p}\) profiles, together with the density profiles, has shown, not unexpectedly, that in most situations the [Chl] is essentially constant within the mixed layer and thus extends deeper than the satellite-sensed layer. Therefore, another subset has been formed that includes all the paired data belonging to these homogeneous layers with quasi-uniform chlorophyll profiles. This subset, which contains more couples (N\(\text{m}\) = 850; Table 2), obviously contains the 435 couples already selected for the previous subset. A third subset is composed of data pertaining to the deep layer, below the homogeneous layer (N\(\text{m}\) = 1,937).

In the present study, only discrete samples with HPLC determinations are considered for the statistical analysis. They are coupled with the attenuation coefficient determined at the same depth. Because the transmissometer has been...
Fig. 2. Selected examples of simultaneous nightly records of beam attenuation and chlorophyll fluorescence (no near-surface photoinhibition effect). For clarity, the scales differ between the panels. Ultra-oligotrophic situations are illustrated by panels A and B, with conspicuous DCM without impact (B) or with minute impact (A) on the attenuation profiles. The algal content in the near-surface layer is higher in P1 than in P2, and the DCM is less prominent, with the result of a quasi-uniform c profile from the surface down to the DCM. In the eutrophic situation (panel D), a tight correlation exists between the two plotted quantities. Temporal variations between the beginning and the end of the night, detectable on the c profiles, are not discussed in the present study.
operated in association with a fluorometer (FL 3000, SeaTech), most of the time, it is possible to convert the vertical profiles of fluorescence by algae into equivalent chlorophyll profiles, and then to compare these profiles with those of attenuation. Such a fluorescence-to-chlorophyll conversion can only be made by interpolating between those depths where the fluorescence signal has been calibrated through the HPLC determination. For the statistical analysis there is objectively no real gain in information when such an expanded and redundant dataset is created; nonetheless, for some figures displayed later, the comparative use of both continuous profiles can offer visual advantages.

After calibration and processing, the transmissometer provides the attenuation coefficient for natural water, which must be corrected for the attenuation by pure (particle-free) seawater to derive the particle attenuation coefficient, \( c_p \). With a view to eliminating the uncertainties resulting from imperfect calibrations, the value of \( c_p \), as observed at the bottom of the column investigated (at 200 or 250 m) where \([\text{Chl}]\) is nearly zero, has been considered as being representative of the \( c \) value for particle-free water. This value actually is always lower than 0.37 m\(^{-1}\) (see Fig. 2), and thus is never far from that of pure water (0.358 m\(^{-1}\); Bishop 1986), except at the E site (EUMELI No. 4, Fig. 2D). At site E, \( c \) remained slightly higher (0.39 m\(^{-1}\) on average), in agreement with a higher particulate organic carbon content at 200–250 m (~0.15 mg C m\(^{-2}\) vs. 0.05 at the M and O sites). By subtracting the local deep value, only the excess of attenuation that is related to the presence in the upper layers of chlorophyll-bearing particles and of their retinue is accounted for. The possible effects of dissolved absorbing substance or of local backscattering background (if any) are also greatly reduced by this procedure. Because measurements in OMEX stations were generally restricted to the upper 120 m, the factory-calibrated value (0.364 m\(^{-1}\)) was subtracted, which is safe since the calibration of the sensor was carefully checked (Lowry pers. comm.).

After the deep (or the calibrated) value is subtracted, the value of \( b_p \) and \( c_p \) are directly comparable, and then to estimate the contribution of absorption to the attenuation coefficient. The absorption coefficient for phytoplankton in natural seawaters with varying chlorophyll concentration has been studied (Bricaud et al. 1995); at 660 nm, this coefficient, \( a_p \), can be expressed as a function of [Chl] according to

\[
a_{\phi}(660) = 0.012[\text{Chl}]^{0.878}. \tag{2}
\]

A similar relationship for \( a_p \), the absorption coefficient by the total particulate matter retained on a GFF filter, has also been established (A. Bricaud pers. comm.):

\[
a_{\phi}(660) = 0.014[\text{Chl}]^{0.817}. \tag{3}
\]

Despite a rather low coefficient of determination (\( r^2 = 0.27 \)), this expression allows the effect of absorption to be roughly estimated. For the [Chl] range considered here, extending from 0.02 to 4.5 mg m\(^{-3}\), \( a_p \) would vary between 0.00057 and 0.048 m\(^{-1}\) according to Eq. 3. These values are negligible (<3%) compared to those of \( c_p \), amounting to ~0.03 and 1.5 m\(^{-1}\) for the same extrema in [Chl], as seen in Fig. 3A. Actually, these values are totally insignificant compared to the (natural as well as instrumental) fluctuations that affect the \( c_p \) values, as well as to the scatter seen in Fig. 3. Therefore...
fore, in what follows, \( c_p \) can be safely considered as equivalent to \( b_p \) and discussed as such.

Results and first analysis

All \( c_p \) values \((N = 2,787)\) are plotted vs. their associated [Chl] values in Fig. 3A. Specific symbols are used to discriminate the three vertically stratified subsets. The general disposition of the data in this graph resembles that previously found for the \( b_p \)-[Chl] relationship (Gordon and Morel 1983). The band (in Gordon and Morel’s fig. 5a) delimiting the domain where case 1 waters were confined is reproduced in Fig. 3B after having been slightly shifted down by a factor 0.83; this factor assumes a scattering spectral dependency expressed by \( \lambda^{-1} \). The upper and lower \( A \) values become 0.38 and 0.10, and the average value becomes 0.25, when corrected for the spectral shift from 550 to 660 nm. A \( \lambda^{-0.5} \) dependency, with a resulting factor of 0.91, as proposed by Voss (1992), could as well be used without appreciable impact.

From the examination of Fig. 3A (see also Table 2), and in reference to the previous findings, several important points emerge. For the whole dataset the general slope (i.e. the exponent) is slightly higher than that appearing in Eq. 1. Indeed, when all depths are pooled together, the regression analysis performed on the log-transformed data leads to

\[
c_p(660) = 0.189[\text{Chl}]^{0.751} \quad \text{(with } r^2 = 0.60 \text{ and } N_{\text{all}} = 2,787),
\]

and the coefficient (0.189) falls slightly below the previous \( A \) value (0.25, from Eq. 1). For the near-surface layer, limited by the depth \( Z_{\text{op}} \), the separate analysis results in

\[
c_p(660) = 0.407[\text{Chl}]^{0.705} \quad \text{(with } r^2 = 0.89 \text{ and } N_{\text{sat}} = 435),
\]

whereas for the homogeneous layer it becomes

\[
c_p(660) = 0.347[\text{Chl}]^{0.766} \quad \text{(with } r^2 = 0.88 \text{ and } N_{\text{hl}} = 850).
\]

These last two equations are not significantly different according to Fisher’s combined probability test. They are numerically very close, as Eq. 5 provides \( c_p \) values exceeding those from Eq. 6 by 2–20\% when [Chl] varies from 0.01 to 4 \( \text{mg m}^{-3} \). If the subset corresponding to the homogeneous layer is subtracted from the full dataset, only the deep values are kept (bottom line in Table 2), and the regression analysis for these data leads to

\[
c_p(660) = 0.124[\text{Chl}]^{0.601} \quad \text{(with } r^2 = 0.54 \text{ and } N_{\text{dt}} = 1,937).
\]

There is more scatter in this particular subset, in particular in the domain of extremely low chlorophyll concentrations where both [Chl] and \( c_p \) are less accurately determined (recall that \( c_p \) is known with an accuracy \( \pm 2 \times 10^{-3} \text{ m}^{-1} \)). The low coefficient (0.124) in this equation is not unexpected, for in deep waters the increase in cellular chlorophyll content, and thus a diminishing number of cells per unit of chlorophyll, may account for a relative reduction in scattering. A lesser proportion of other (nonalgal) accompanying particles could also contribute to this reduction.

Compared to the value of 0.62 in Eq. 1, the increase in the exponents appearing in Eq. 4, 5, and 6 essentially originates from the inclusion of the North Atlantic data (not represented in the Gordon–Morel previous analysis); in this
zone, most of the [Chl] values are >1 mg m\(^{-3}\), and \(c_p\) values are >0.5 m\(^{-1}\). Regression analyses restricted to the BOFS and OMEX data (subset 1 in Table 2) produce, regardless of the layer considered, exponents distinctly larger than those obtained for the other oceanic areas (subsets 2 and 3, which show exponents close to 0.62). The same statement holds true for the coefficients, notably higher for subset 1 than for other oceanic areas (subsets 2 and 3). Even outside of specific coccolithophore blooms (Ackleson et al. 1994), it is known that coccolithophorids and detached lells are episodically abundant in the North Atlantic (see e.g. Holligan et al. 1983; Jickells et al. 1996), and likely are at the origin of changes in optical coefficients as are those detected through separate regression analysis. The presence of such particulate calcite debris increases the scattering coefficient (Bricaud and Morel 1986; Balch et al. 1989), and even can create “anomalous” case 1 waters (Gordon et al. 1988), with extremely high scatterance and reflectance.

Subset 2 includes [Chl] values >1 mg m\(^{-3}\), which were observed at the eutrophic EUAMEL site and occasionally at the mesotrophic site (both at ~20°N; see map in Fig. 1). In these locations, the algal populations were dominated by diatoms (E site) or by cyanobacteria (M site) (Morel 1997). The \(c_p\) values determined in these relatively Chl-rich waters, but in low latitudes, remain below those found farther to the north. Accordingly, the coefficients and exponents for subset 2 are lower than those for subset 1, in particular when the \(Z_0\) layer is considered (see values in Table 2). The low value of the exponent found for the BATS and HOTS data, associated with a low coefficient of determination (subset 3 in Table 2), actually results from the clustering of all these data within a restricted range of values, centered on low [Chl] and \(c_p\) values where the signal-to-noise ratio is unfavorable (see Table 1).

The coefficients in Eq. 5 or 6, on one hand, and in Eq. 7, on the other hand, are compatible with the maximal and minimal values of \(A\) in Eq. 1. The agreement between these previous results and those presented here is clearly seen in Fig. 3b. The spreading of the points for all depths in Fig. 3A is definitely high (\(r^2 = 0.60\)). The band demarcating case 1 waters in Gordon and Morel’s figure (reproduced in Fig. 3B) has already acknowledged that \(c_p\) cannot be predicted from [Chl] within a factor better than 3 (actually +50%, -60% with respect to the mean). This factor is not at all reduced for the recent dataset. For the near-surface layer or the homogeneous layer, however, the scatter is considerably less and \(r^2\) is increased up to 0.88, so that the predictive ability is somewhat better and would correspond to a factor of -2 (instead of -3) when all depths have been confounded. It has been verified that such a lack of tightness does not result from having pooled diverse sources of data, because separate, cruise-by-cruise analyses do not provide improved (local) correlation and reduced scatter.

There was also a lot of scatter around the relationship obtained by Voss (1992), which was
\[
c_p(490) = 0.390[\text{Chl}]^{0.57}. \tag{8a}
\]
By using his spectral relationship, this equation can be rewritten for the 660-nm wavelength as
\[
c_p(660) = 0.314[\text{Chl}]^{0.57}, \tag{8b}
\]
which is also shown for comparison in Fig. 3B. The relationship of Voss consistently agrees with those found here for the homogeneous or near-surface layers, as well as with the upper limit indicated by Gordon and Morel, who stated (as a comment to their Fig. 5a) that “Surface waters are, in most cases, represented by points close to the upper limit.”

Another approach can be used to understand the link between \(c_p\) (or \(b_s\)) and the suspended particle content. Instead of [Chl], the particulate organic concentration, POC, can be adopted as being likely a better descriptor of the total (animate and inanimate) particle content for upper layers in case 1 waters. An almost linear relationship between \(b_s\) and POC was already suggested (Morel 1988) by the likeness of the exponents appearing in Eq. 1 and in another empirical relationship, which was established between POC and [Chl] and expressed as (eq. 25 in Morel 1988)
\[
POC = 90[\text{Chl}]^{0.57}, \tag{9}
\]
where POC is expressed in mg C m\(^{-3}\). Compared with Eq. 8b above, this expression suggests a perfect linear relationship between \(c_p\) and POC, and combined with Eq. 1, it provides the following quasilinear relationship:
\[
b_s(550) = B[\text{POC}]^{1.088}, \tag{10}
\]
where \(B\) is either 0.0090 or 0.0034 (in correspondence with the two extreme \(A\) values in Eq. 1). The two straight lines using these values (becoming 0.0075 and 0.0028 at 660 nm) are shown in Fig. 4 and compared to the data. Indeed, considerable (\(N = 642\)) paired data for both POC and \(c_p\) were collected during the BOFS and HOTS experiments. The data relevant to the upper homogeneous layer, as previously identified, are shown with distinct symbols. A regression for this subset (\(N = 297\) data) leads to a significant (\(r^2 = 0.92\)), almost linear relationship (also displayed in Fig. 4):
\[
c_p(660) = 0.0010[\text{POC}]^{1.17}. \tag{11}
\]
The compatibility between the previous expression (Eq. 10) and present data (leading to Eq. 11) is well ensured. The linear correlation established by Gardner et al. (1993) during a spring bloom in the North Atlantic, which was expressed as
\[
c_p(660) = 0.00264[\text{POC}], \tag{12}
\]
is also numerically equivalent within the scatter affecting the data.

Discussion and conclusions

The nonlinear character of the dependence of \(b_s\) (or \(c_p\)) on [Chl] within the whole chlorophyll concentration range and the noise in the correlation between these two quantities observed for surface waters are the main results that warrant further discussion. Both of these aspects are not disjoined. Linearity can only be expected if two obvious conditions are fulfilled. First, the relative size distribution and the particle chemical composition (which governs the refractive index) must remain unchanged; only the bulk seston concentration may vary, as if the same particle assemblage were more or less diluted. In such a case, \(c_p\) will be linearly correlated...
Fig. 4. Log-log plot of all the particulate organic carbon data (POC) and associated $c_p$ values, determined during the BOFS and HOTS experiments as indicated (note that they are not in the same range). The regression line computed (Eq. 11) for the homogeneous layer data only and the two lines corresponding to Eq. 10 (with its two coefficients, see text) are superimposed on the data. The correlation established by Gardner et al. (1993) (Eq. 12) is very close to the upper line.

with the volume or mass concentration. The slope in this linear relationship depends on the characteristics (size distribution, refractive index, and to a lesser extent shape) of the seston assemblage (see e.g. Baker and Lavelle 1984; Spinrad 1986). This slope changes from place to place, even if only deep waters are considered (Bishop 1986). Second, assuming that the first condition is satisfied, the linearity can be preserved in the relationships between $c_p$ and POC or [Chl] only if the POC-to-seston or the Chl-to-seston ratios (wt/wt) are constant.

Concerning the first condition, it is worth recalling what is the size range involved in the formation of the scattering coefficient in oceanic waters. By assuming particle size distributions of the Junge type, with exponents not far from $-0.4$ and a mean relative index of refraction close to 1.05, it follows that those particles having sizes between $0.5$ and $10$ $\mu$m are the main contributors ($>95\%$) to the formation of $b_p$ (see fig. 3-8 in Morel [1973], where the Junge exponent and the refractive index were varied within reasonable limits; see also Morel and Ahn 1991; Stramski and Kiefer 1991). To the extent that the particle-phase function remains rather steady in shape for various oceanic waters (Petzold 1972; Morel 1973; Mobley 1994), the size distribution and the refractive index cannot experience too large variations with respect to figures given above, so that the size range mentioned above is, at least roughly, valid in most circumstances. There is enough variability in particle optical characteristics, however, to impede the prediction of any ubiquitous relationship between $b_p$ and the particle load.

Concerning the second condition, and when using [Chl] as an index for constructing bio-optical models, the situation becomes even more complicated. In effect, the Chl-to-seston ratio is known to vary widely in oceanic waters. The proportions between algal and nonalgal compartments may change and actually do in a more or less regular manner; that is, when the chlorophyll content increases a relative decrease of the nonalgal material influence seems to be the rule (Gordon and Morel 1983; Gordon et al. 1988; Morel 1988). In addition, inside the sole algal compartment, the chlorophyll content per cell also varies widely. In effect, interspecific variability in cellular chlorophyll concentration is large, and intraspecific variation also occurs, in particular as a result of photoacclimation (see e.g. Falkowski 1980). Therefore, linear relationships between $c_p$ and [Chl] are not to be expected except in particular conditions. Even in a given location, as soon as all depths are considered, the linearity could be the rule only if the (algal and nonalgal) population remains qualitatively homogeneous vertically, which is not the most common situation (Kitchen and Zaneveld 1990), but may exist when vigorous vertical mixing occurs. Contrasted examples are provided in Fig. 5 by displaying $c_p$-[Chl] diagrams that are typical of various trophic conditions and hydrologic structures.

In mesotrophic and eutrophic environments with mixed layers thicker than the euphotic layer, as found during the EUMELI cruise No. 4 (Morel 1996), the well-mixed populations satisfy the conditions for linearity. This is reflected by $c_p$-[Chl] diagrams with a one-to-one slope and concomitant decrease in both quantities along with depth (Fig. 5F). The chlorophyll-specific particulate attenuation coefficient, $c_p$, defined as the ratio of $c_p$ to [Chl] (Mitchell and Kiefer 1988), is roughly constant in these examples and amounts to $0.04$ or $0.5$ $m^2 (mg Chl)^{-1}$. The algal populations in these two environments, however, differ; that is, they are diatom-dominated in the E site and cyanobacteria-dominated in the M site. In the North Atlantic BOFS stations (not shown in Fig. 5), 1:1 slopes are also derived for the upper layers, as can be anticipated from the high coefficient and exponent close to one (first line in Table 2). The $c_p$ values are similar to those in E and M sites ($<0.5$ $m^2 (mg Chl)^{-1}$). Within deeply mixed waters in the Drake Passage, with [Chl] typically between $0.5$ and $0.8$ mg m$^{-3}$, Mitchell and Holm-Hansen (1991) reported $c_p$ values of $0.35$ $m^2 (mg Chl)^{-1}$ in December January. In February March at the same location (also at another location within an active bloom), $c_p$ values were in the 0.1-0.2 $m^2 (mg Chl)^{-1}$ range. This decrease was attributed (Mitchell and Holm-Hansen 1991) to a chronic low-light adaptation of the algal population, with the con-
Fig. 5. For selected stations, diagrams showing how the quantities $c_p$ and [Chl] vary with depth. They are constructed either with the [Chl] values determined at discrete depths via HPLC (panels A and C) or (other panels) with the [Chl] profiles derived from the fluorescence profiles after HPLC calibration (only nightly profiles are used). These plots are similar to those in Kitchen and Zaneveld (1990), apart from the replacement of fluorescence by chlorophyll values. Note the change in scales for the eutrophic and mesotrophic stations (EUMELI 4). The straight lines drawn with a 1:1 slope correspond to discrete values of the chlorophyll-specific particle attenuation coefficient, $c_p^*$, expressed in m$^2$ (mg Chl)$^{-1}$ and with values as indicated.
sequence of a significant increase in chlorophyll per cell. Also in Antarctic waters (in the Bellingshausen Sea), Sagan et al. (1995) found $c_\text{e}^*$ values from 0.1 to 0.4 m$^2$ (mg Chl)$^{-1}$ inside an extensive phytoplankton bloom, whereas outside this area, values were between 0.4 and 0.9 m$^2$ (mg Chl)$^{-1}$. In the western Mediterranean Sea during a vernal bloom, $b_\text{e}^*$ ($c_\text{e}^*$) values of 0.22 m$^2$ (mg Chl)$^{-1}$ were observed in the upper layer (fig. 5B in Gordon and Morel 1983).

Situation from ultra-oligotrophic (Fig. 5A–D) to moderately oligotrophic (Fig. 5E) have in common a peculiarly shaped diagram (called A-shape in Kitchen and Zaneveld 1990). Between the surface and the DCM, a more or less extended horizontal segment develops. It begins with a cluster of data corresponding to the upper part of the mixed layer, where the $c_\text{e}^*$ values are $\sim$1 m$^2$ (mg Chl)$^{-1}$. Interestingly, similar values are found in the tropical Pacific and Atlantic Oceans, as well as in the Mediterranean Sea (MNOS cruise, not shown). Below this layer, [Chl] increases while $c_\text{e}$ (and the number of scattering particles) remains steady, so that $c_\text{e}^*$ progressively diminishes. The extremum in these diagrams always coincides with the DCM, and the associated $c_\text{e}^*$ values are close to 0.2 m$^2$ (mg Chl)$^{-1}$. Below the chlorophyll maximum and toward the deeper aphotic levels another linear segment takes place that follows a 1:1 slope. Such a linearity reflects a “mixing rule,” i.e. a downward progressive dilution of approximately the same particle assemblage (algal cells, heterotrophic bacteria, and detritus). At these depths, below the euphotic depth, the photoacclimation is almost reached, and thus the chlorophyll contents per cell vary only slightly. The $c_\text{e}^*$ values corresponding to these linear segments are steadily close to 0.1 m$^2$ (mg Chl)$^{-1}$ (slightly less in Mediterranean), in spite of a progressive replacement of prochlorophytes by pico-eukaryotes as predominant species (see e.g. Partensky et al. 1996; Claustre and Marty 1995). This general $c_\text{e}^*$ vertical pattern (typical of oligotrophic waters), as well as the high values near the surface, are perfectly put in evidence in the meridional sections of the identified microbial organisms, and thus produces results in a global nonlinear effect, reflected by exponents on the order of 0.7 that apply to [Chl]. This nonlinear biological effect essentially originates from the continuous and nonlinear change in the Chl-to-POC ratio, as a contrario, testified by the existence of a quasilinear relationship between scattering (or attenuation) and POC. Second, the very upper layer, involved in remote-sensing applications, or the homogeneous part of the mixed layer exhibits specific bio-optical properties, and thus produces relationships (Eq. 5 and 6) differing from that describing the deep layer (Eq. 7). The adoption, as done before, of a unique expression when modeling case 1 waters is certainly to be discouraged, in particular if scattering vertical structures are to be reconstructed from the vertical chlorophyll profiles. This point was rightly stressed by Kitchen and Zaneveld (1990), particularly for backscattering, but holds true also for scattering. For remote-sensing applications, the adoption of Eq. 5 is definitely thought to be a better choice over Eq. 1. This proposed expression leads to $c_p$ ($b_\text{p}$) values that are similar to those provided by Eq. 1 when systematically operated with its upper value. Eq. 5 appears more robust to the extent that $c_p$ can be predicted from [Chl] within a factor of 2 (instead of 3 with Eq. 1).

Finally, contrary to expectation, a less noisy relationship was not derived from the present data, despite methodological improvements in their determination. The natural variability at local and then at global scales prevents obtaining tighter relationships between optical properties and [Chl]. In this respect, it must be added that arctic and antarctic waters, with presumably low-light-adapted phytoplanktonic populations, could depart from the general trend and thus be in-

\begin{equation}
\begin{aligned}
(c_p)^{(660)} &= 0.65[\text{Chl}]^{0.80}. \\
\end{aligned}
\end{equation}
adequately described by the present expressions. Future improvements, including a regionalization of the predictive algorithms, still require additional measurements in various oceanic conditions.

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