

Determining the contribution of pigments and the nonalgal fractions to total absorption: Toward an improved algorithm

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Abstract

Three methods that estimate the algal and nonalgal contributions to the total particulate matter light absorption were analyzed against the experimental Kishino method in a wide variety of environments. We found that one method gave better overall correlations and slopes closer to 1 than did the other methods, but the method overestimated the nonalgal fraction when the nonalgal absorption to total particulate matter absorption proportion in the sample was low. As a result, a correction is suggested and results are compared with those of the other methods, showing that the combined use of the original algorithm and the correction do configure a suitable basis for differentiating the algal and nonalgal fractions using as input only the total particulate light absorption data.

Optical variability of oceans is controlled to a large extent by the amount of biogenic particulate matter present in the water column. Therefore, the role of phytoplankton and related detritus material in absorbing and backscattering light is of fundamental interest (Kirk 1983), an interest that has grown recently (Kishino et al. 1986; Schofield et al. 1991; Bricaud et al. 1995). Light-absorption spectra of phytoplankton populations are needed to develop bio-optical models and, together with photoirradiance curves, to determine the quantum yield of photosynthesis, which is an important component of primary production models (Bannister 1974; Bannister and Wiedemann 1984; Kishino et al. 1986; Morel et al. 1987; Lewis et al. 1988).

Two approaches—one experimental, the other mathematical—have been developed to partition the total particulate light absorption into algal and nonalgal fractions. Among the experimental methods cited in the literature, the simple pigment extraction method that Kishino and co-workers described in 1985 (using methanol as a solvent) has gained the greatest acceptance (Kishino et al. 1985). Tassan and Ferrari (1995) modified this method to extend the application to case 2 waters, where the standard method is not effective.

On the other hand, researchers have developed various algorithms to perform distinctions between algal and nonalgal fractions. Morrow et al. (1989) estimated the particulate algal and nonalgal light absorption in the Sargasso Sea

by using a two-component model. Bidigare et al. (1989) derived algal light absorption from HPLC analysis and compared measured total light absorption with the reconstructed phytoplankton light absorption. Roesler et al. (1989) implemented a model to resolve in situ phytoplankton light absorption from total particulate absorption, chlorophyll, and pheopigment concentration. Later, Bricaud and Stramski (1990) developed another procedure by using data from the Sargasso Sea and the Peruvian upwelling region to partition the total absorption coefficient into the contribution due to living algal cells and to the nonalgal particulate matter.

More recently, Hoepffner and Sathyendranath (1992) used a complex method to decompose the total absorption spectra into several Gaussian bands, each one reflecting absorption by different pigments (Hoepffner and Sathyendranath 1993). A unique, general, normalized absorption spectrum of phytoplankton, which the authors claimed to be representative of a wide variety of water masses, was used to discriminate between the detrital and the algal light absorption. Finally, Cleveland and Perry (1994) developed yet another method based on the measurement of Chl *b* and pheophytin to differentiate between nonalgal and algal absorption.

However, despite the fact that much work has been devoted in recent years to develop techniques to distinguish between algal and nonalgal light absorption, no attempt has yet been made to compare the suggested algorithms and to verify their usefulness. Such comparison is our main goal here. We use the restrictive criterion that the methods must provide estimates of the algal and nonalgal light absorption fractions using only the total particulate light absorption data as input. This can be justified since the need of one or more variables in addition to the total particulate light spectra restricts the usefulness of a method from both an in situ and a remote-sensing perspective. The methods of Morrow et al. (1989) (hereafter M-C-K), Bricaud and Stramski (1990)

Acknowledgments

Financial support from CYCIT (Spanish Commission of Science and Technology) projects AMB93-0129, ANT93-0997, AMB94-0739, AMB94-0746 and MAR91-0503 is gratefully acknowledged. This work was made possible thanks to a Spanish Ministry of Sciences contract to R.A.V. and a Xunta de Galicia grant to B.A. We also want to thank C. M. Duarte and two anonymous reviewers for useful criticisms of the manuscript.

(hereafter B-S), and Hoepffner and Sastryendranath (1993) (hereafter H-S) comply with this criterion and were therefore included in this analysis. The Bidigare et al. (1989) method, which uses the HPLC technique to estimate the phytoplankton light absorption component, and the Roesler et al. (1989) and Cleveland and Perry (1994) methods, which need measurements of chlorophyll and(or) pheophytin concentrations, did not comply with the criterion and were excluded from this comparison.

The selected models have different constraints when applied to determine the shape and magnitude of the algal- and nonalgal-specific absorption coefficients. The B-S method uses only selected points of the total particulate matter absorption spectra to reconstruct the phytoplankton absorption coefficient, whereas the H-S method uses a whole normalized average absorption spectrum. The latter approach seems in principle to be more constraining, and will introduce underestimations of the nonalgal fraction when the contribution by accessory pigments is high or when the packaging effect is very low. On the other hand, the M-C-K method was developed with a local dependency in mind, and it may be expected that its applicability will be a priori reduced when using a single set of parameters in a global perspective.

All three methods were tested in a wide variety of water masses, including the Bransfield Strait Antarctic waters, oceanic and inland waters of northwestern Spain, the Southern Atlantic Ocean, and coastal waters of the northwestern Mediterranean Sea. This analysis should help to identify the best algorithm overall and which conditions are better for a given method. Our second objective is to determine under which circumstances the best algorithm fails and try to enhance its results by suggesting a suitable correction.

Particulate light absorption sampling data were derived from a wide range of marine stations. The first set of data corresponds to an Antarctic cruise aboard the RV *Hespérides* in the Bransfield Strait during January–February 1994. The *Latitude I* (spring 1995) cruise, also the aboard the RV *Hespérides*, during March–April 1995 supplied data from many different depths and from a large latitudinal range, from Punta Arenas (Chile) to the Canary Islands (Spain). Nearshore waters from the northwestern Mediterranean Sea (Blanes) sampled during 1993 and 1994, as well as from northwestern Spain (La Coruña, during the spring season, and Ria de Vigo, during the fall season), increased the range of detritus/algal absorption and provided the remaining datasets.

Dual-beam Uvikon 750 and Jasco UV-VIS 7800 spectrophotometers were used during the *Latitude I* cruise and for the northwestern Mediterranean Sea datasets, respectively, to measure particulate matter absorption. In the remaining datasets the absorption spectra were determined with a Beckman DU650 single-beam spectrophotometer. A variable volume of seawater was filtered through a 25 mm glass fiber GF/F filter, and a modified opal-glass technique (Shibata 1958; Kiefer and SooHoo 1982; Mitchell and Kiefer 1988) was used to determine the optical density, $OD(\lambda)$, of the particles retained on the filter. An identical glass-fiber filter soaked in filtered seawater was used as a blank. The optical density at 750 nm was subtracted from $OD(\lambda)$ (Cleveland and Weidemann 1993) and the phytoplankton absorption coefficients [$a_p(\lambda)$] were estimated according to the relationship

$$a_p = \frac{2.3 \times OD(\lambda) \times s}{V \times \beta(\lambda)}, \quad (1a)$$

where V is the volume of filtered seawater, s the filtering area of the GF/F filter, and the β factor ($\beta(\lambda)$) was estimated according to Bricaud and Stramski (1990) as

$$\beta(\lambda) = 1.63 \times OD(\lambda)^{0.22}. \quad (1b)$$

Note that the subtraction of the optical density at 750 nm introduces a modification in the original B-S method. Bricaud and Stramski (1990) assumed that all the light absorbed at 750 nm corresponds to detritus, whereas our assumption implies that the total particulate light absorption is 0 at 750 nm. We used this modification to reduce the noise fluctuations of the baselines of the different spectrophotometers (see Cleveland and Weidemann 1993).

The light absorption by particulate detritus [$a_{kd}(\lambda)$] was estimated experimentally following the method of Kishino et al. (1985). The filter used in the determination of total particulate matter absorption was placed in 100% methanol for 30 min, soaked in filtered seawater to remove excess methanol, and scanned again in the 350–750-nm range by using the same spectrophotometer and timing schedule. We used an identical correction for volume, filter size, and β factor to obtain $a_d(\lambda)$ as that described for $a_p(\lambda)$. We also included the assumption of 0 light absorption at 750 nm.

The algal absorption coefficients [$a_{ph}(\lambda)$] were estimated by difference from $a_p(\lambda)$ (see notations):

$$a_{ph}(\lambda) = a_p(\lambda) - a_d(\lambda). \quad (1c)$$

Empirical determination of light absorption by detritus material (M-C-K method)

The M-C-K method uses a two-step procedure to estimate phytoplankton and detrital absorption from an individual $a_p(\lambda)$ spectrum. First, a multiple linear regression equation is used to characterize the nature of phytoplankton and detritus during a whole cruise (Eq. 2). The resulting slopes, A and B , actually represent the degree of coupling between the array of measurements for 570 and 675 nm and the measurements at all other wavelengths:

$$a_p(\lambda)_n = A(\lambda)[a_p(675)_n - 0.2a_p(570)_n] + B(\lambda)[a_p(570)_n - 0.07a_p(675)_n]. \quad (2)$$

Because we wanted to test the usefulness of the selected method as a whole, this algorithm was applied to all the regions by always using the same constants involved in Eq. 2.

In the second step, individual absorption spectra contributing to the regression analysis are partitioned by using a two-compartment model, which was solved for the two unknowns, parameters k_{ppl} and k_d by using a nonlinear (quasi-Newton) estimation technique:

$$\hat{a}_p(\lambda) = k_{ppl} \times A(\lambda) \times a_p(675) + k_d \times B(\lambda) \times a_p(570). \quad (3)$$

The particle absorption coefficients for phytoplankton [$am_{ppl}(\lambda)$] and for detritus [$am_d(\lambda)$] are then calculated from.

Notations

General symbols	
Wavelength (nm)	λ
Optical density (adimensional)	$OD(\lambda)$
Pathlength amplification (adimensional), water volume filtered (m^3), filter area (m^2)	$\beta(\lambda), V, s$
Light absorption coefficient by algal particles (m^{-1})	$a_{ph}(\lambda)$
Light absorption coefficient by total particulate matter (m^{-1})	$a_p(\lambda)$
Light absorption coefficient by nonalgal particles (m^{-1})	$a_d(\lambda)$
Light absorption coefficient by algal particles at 440 nm (m^{-1})	$a_{ph}(440)$
Light absorption coefficient by nonalgal particles at 440 nm (m^{-1})	$a_d(440)$
Degree of coupling between the 570 nm and all other wavelengths (adimensional)	$A(\lambda)$
Degree of coupling between the 670 nm and all other wavelengths (adimensional)	$B(\lambda)$
Various slopes and intercepts of the linear regression suggested	a, b, a_1, b_1
Kishino method (Kishino et al. 1985)	
Light absorption coefficient by nonalgal particles (m^{-1})	$ak_d(\lambda)$
Modeled light absorption coefficient by total particulate matter (m^{-1})	\hat{a}_p
Normalized light absorption coefficient by nonalgal particles (adimensional)	$ak_d'(\lambda)$
Light absorption coefficient by nonalgal particles at 440 nm (m^{-1})	$ak_d(440)$
Morrow et al. method (Morrow et al. 1989)	
Light absorption coefficient by nonalgal particles (m^{-1})	$am_d(\lambda)$
Light absorption coefficient by algal particles (m^{-1})	$am_{ph}(\lambda)$
Partitioning coefficient for phytoplankton (adimensional)	k_{ppd}
Partitioning coefficient for detritus (adimensional)	k_d
Bricaud and Stramski method (Bricaud and Stramski 1990)	
Light absorption coefficient by nonalgal particles (m^{-1})	$ab_d(\lambda)$
Normalized light absorption coefficient by nonalgal particles (m^{-1})	$ab_d'(\lambda)$
Light absorption coefficient by nonalgal particles at 440 nm (m^{-1})	$ab_d(440)$
Parameter of the equation (nm^{-1})	S
Parameter of the equation (m^{-1})	A
Hoepffner and Sathyendranath method (Hoepffner and Sathyendranath 1993)	
Light absorption coefficient by nonalgal particles (m^{-1})	$ah_d(\lambda)$
Light absorption coefficient by algal particles (m^{-1})	$ah_{ph}(\lambda)$
Exponent of the nonalgal estimation curve (nm^{-1})	q
Averaged normalised light absorption coefficient by algal particles at 440 nm (adimensional)	$a_{ph}^*(\lambda)$
Suggested modification	
Light absorption coefficient by nonalgal particles (m^{-1})	$a_{ph}^*(\lambda)$

$$am_{ph} = k_{ppd} \times A(\lambda) \times a_p(675) \quad (4)$$

$$0.99Ae^{-380S} - Ae^{-505S} = 0.99a_p(380) - a_p(505) \quad (6)$$

$$am_d = k_d \times B(\lambda) \times a_p(570). \quad (5)$$

$$Ae^{-580S} - 0.92Ae^{-692.5S} = a_p(580) - 0.92a_p(692.5). \quad (7)$$

By simplifying for A on the left side and dividing Eq. 6 by Eq. 7 we obtain

Empirical determination of light absorption by detritus material (B-S method)

$$\frac{0.99e^{-380S} - e^{-505S}}{e^{-580S} - 0.92e^{-692.5S}} = \frac{0.99a_p(380) - a_p(505)}{a_p(580) - 0.92a_p(692.5)}, \quad (8)$$

Bricaud and Stramski (1990) developed a simple empirical procedure to separate the total absorption spectra into the nonalgal and algal compartments. Their algorithm is based on the exponential shape of the detritus absorption curve and on their finding of a remarkably constant violet to green and yellow to red ratios of the $a_{ph}(\lambda)$ absorption curve, from which they derived a set of two equations (Eq. 6 and 7) that can be simplified and solved for factors S and A iteratively:

where S can be computed easily by using an iterative approach. After obtaining S (and A through substitution with either Eq. 6 or 7), $ab_d(\lambda)$ can be calculated with Eq. 9 (which is identical to equation 6A of B-S):

$$ab_d(\lambda) = Ae^{-S\lambda} + a_p(750) - Ae^{-750S}, \quad (9)$$

and $ab_{ph}(\lambda)$ is obtained by difference using Eq. 1c.

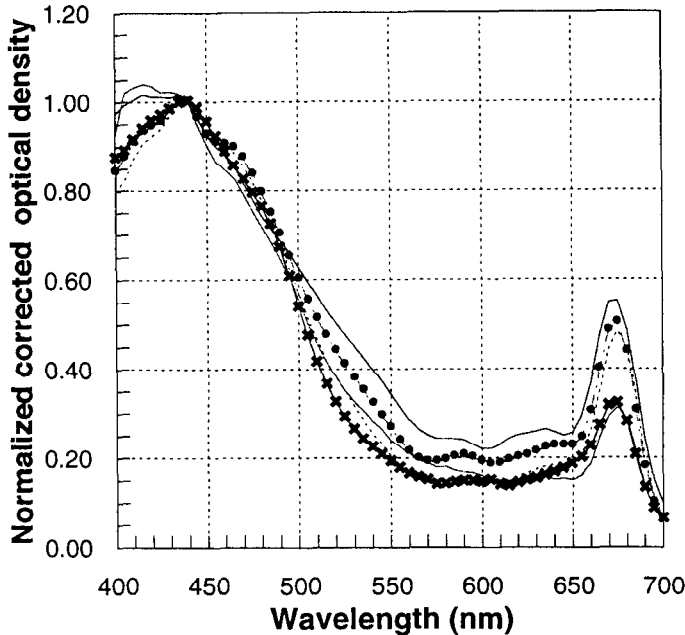


Fig. 1. Plot showing the normalized (to 440 nm) and corrected (subtracting the 750 nm value) mean optical densities for each region. —*—, Latitude; ·····, Bransfield; —, Ría de Vigo; —, Blanes; - - -, La Coruña.

Empirical determination of light absorption by nonalgal material (H-S method)

Hoepffner and Sathyendranath (1993) estimated the contribution of nonalgal particles and phytoplankton to total light absorption by using a nonlinear regression technique. Briefly, their model assumed that detrital matter absorbs light in a manner similar to that of yellow substances, and they expressed this relationship as an exponential function of the form

$$ah_d(\lambda) = ah_d(440)e^{[q(\lambda - 440)]}, \quad (10)$$

where q is the exponent of the nonalgal estimation curve.

By combining Eq. 1c and 10 the absorption of total particulate matter can be expressed as

$$a_p(\lambda) = ah_{ph}(\lambda) + ah_d(440)e^{[q(\lambda - 440)]}. \quad (11)$$

$ah_{ph}(\lambda)$ in Eq. 11 can be rewritten as the product of a normalized average absorption spectrum [$a_{ph}'(\lambda)$, computed as the average of ~ 100 spectra from the northwest Atlantic Ocean each normalized to 440 nm] and the absorption coefficient of phytoplankton at 440 nm:

$$a_p(\lambda) = ah_{ph}(440)a_{ph}'(\lambda) + ah_d(440)e^{[q(\lambda - 440)]}. \quad (12)$$

Obtaining $a_{ph}'(\lambda)$ from Table 1 of Hoepffner and Sathyendranath (1993) and given $a_p(\lambda)$ from field measurements, Eq. 12 was solved for the three unknowns parameters, i.e. $ah_{ph}(440)$, $ah_d(440)$, and q , using a nonlinear quasi-Newton estimation technique. The spectral absorption of pigments can then be estimated using

$$ah_{ph}(\lambda) = a_p(\lambda) - ah_d(440)e^{[q(\lambda - 440)]} \quad (13)$$

and $ah_d(\lambda)$ obtained by difference using Eq. 1c as usual.

The wide range of algal to nonalgal absorption of this dataset is ideal to test the contribution of nonalgal and algal particles to the total light absorption by using an empirical approach. The shapes and magnitudes of the spectra estimated for the different regions were quite similar, as depicted in Fig. 1. Some small differences among the Ría de Vigo and the other regions appeared, however, after normalizing (to 440 nm), correcting (subtracting the 750 nm value), and averaging (at each 5 nm interval) optical densities. That region showed larger values above 500 nm and differences at the lower (400–450 nm) and higher (660–680 nm) light (visible) range.

We therefore undertook a comparison of calculated $am_d(\lambda)$, $ab_d(\lambda)$ and $ah_d(\lambda)$ against the results estimated with measured $ak_d(\lambda)$, which yielded significant correlations for the three methods in the different regions; however, the best correlations overall were those given by the B-S method (Table 1). In regions with a high percentage of detritus [$\Sigma(a_p)/\Sigma(a_p)$], all three methods gave very significant results. However, when the percentage of detritus was low (e.g. Bransfield Strait, some regions of the *Latitude* cruise), results among methods differed greatly, but, again, the B-S method had the highest correlation coefficients. Also note that many of the detritus absorption spectra calculated with the H-S method in these low percentage detritus conditions

Table 1. Regression results (mean correlations and slopes) obtained by comparing measured $ak_d(\lambda)$ against the B-S, H-S, and M-C-K methods. Results in boldface indicate the best correlations obtained by a given method in a particular region (BL, Blanes; BS, Bransfield Strait; RV, Ría de Vigo; CO, La Coruña; LA, *Latitude* cruise). The quasi-Newton solving algorithm used by the H-S method sometimes gave negative values of parameter $a_d(440)$ (see text); therefore, its average correlations and slopes are not always computed with the same number of spectra (N) as the other methods.

Region	N	M-C-K method			B-S method			H-S method		
		r	Slope	Intercept	r	Slope	Intercept	r	Slope	Intercept
BL	43	0.972	0.635	-0.0009	0.987	0.981	0.0004	0.940	1.070	0.001
BS	41	0.727	0.179	-0.00008	0.948	1.239	0.0003	0.819	1.388	0.0003
RV	9	0.584	0.580	-0.0036	0.943	1.570	-0.0009	0.632	1.751	0.0822
CO	33	0.697	0.408	-0.0012	0.972	1.598	-0.0004	0.846	1.635	0.0003
LA	42	0.730	4.74	0.00392	0.766	0.678	-0.00004	0.679	0.780	0.00136
Total	168	0.742	1.308	-0.0004	0.923	1.213	-0.00013	0.783	1.325	0.0173

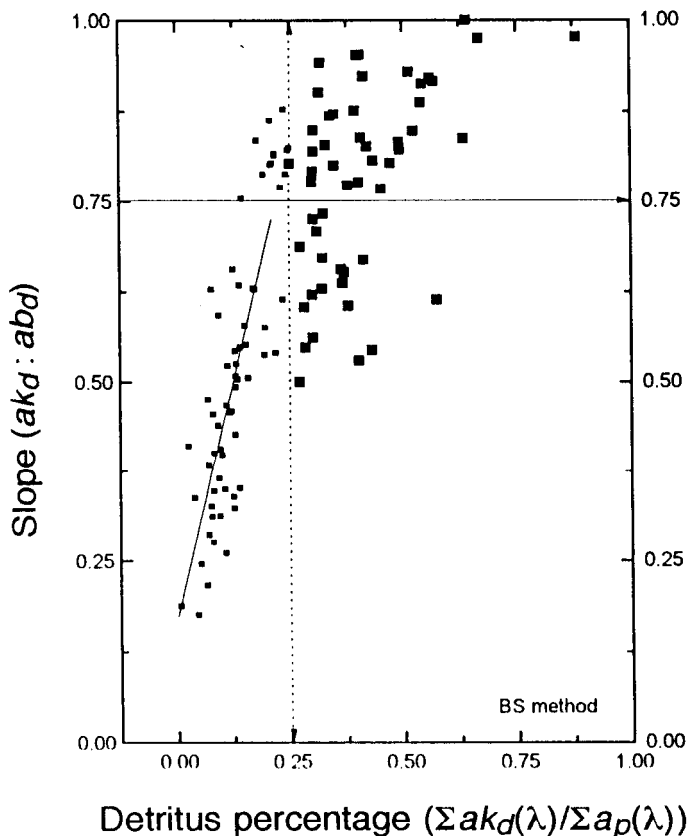


Fig. 2. Graph showing the ak_d/ab_d slope against the percentage of detritus for all analyzed spectra between 400 and 700 nm. The figure shows a good correspondence for points with $<25\%$ detritus, showing that the B-S method overestimates detritus in such circumstances.

were wrong, since $ah_d(440)$ values estimated with the quasi-Newton algorithm yielded negative values. In rare cases ($<1\%$ of the total) the B-S method also gave unreliable estimates of the detritus absorption spectra, but these cases were always related to spectra having very low (<0.2) optical density values. Previous research (Bricaud and Stramski 1990; Babin et al. 1993) has shown that when optical densities are low, the use of an equation such as 1b can provide unreliable estimates of the β function. As indicated by their slope and intercept values when performing a regression between spectral values of $ak_d(\lambda)$ against $ab_d(\lambda)$, $am_d(\lambda)$ or $ah_d(\lambda)$, the B-S and H-S algorithms generally overestimated detritus, whereas the M-C-K method always underestimated detritus.

In particular, the slope $ab_d(\lambda):ak_d(\lambda)$ was found to be linearly related to the overall percentage of nonalgal matter [$\Sigma ak_d(\lambda)/\Sigma a_p(\lambda)$], with r of 0.84 ($n=65$), when the nonalgal percentage is roughly $<25\%$ (Fig. 2). This relationship disappears at higher values of percent nonalgal absorption, for which the slope is closer to the expected value of 1. Hence, the B-S method tends to overestimate the nonalgal fraction when it accounts for $<25\%$. Most spectra with $\Sigma ak_d(\lambda)/\Sigma a_p(\lambda)$ of <0.25 were obtained in the La Coruña region, the Bransfield Strait, or, when present, from the deep chlorophyll maximum layers of the different regions, which seem

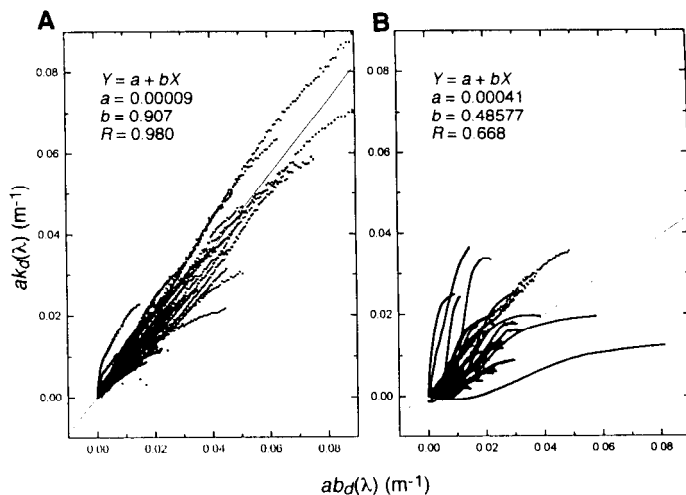


Fig. 3. Plot of the relationship between $ak_d(\lambda)$ and $ab_d(\lambda)$ for 91 spectra between 400 and 700 nm at a 1-nm interval and according to the percentage of detritus. At high percentages (>0.25 , panel A) the B-S method is a reliable estimate of $ak_d(\lambda)$, with a slope of 0.91 and a correlation coefficient of 0.98. When the percentage of detritus is low (<0.25 , panel B) B-S estimates gave a lower slope (0.49) and a poor correlation coefficient (0.69).

overall to be the worst regions to apply the B-S method. On the other hand, coastal waters are a priori better places for using the B-S method. This is confirmed by the much better relationship found between ab_d and ak_d using data only where the percent absorption by detritus is >0.25 ($r = 0.98$ slope = 0.91, intercept = 0.0009, $n = 71$) against the one obtained where the nonalgal fraction accounts for $<25\%$ of percent total particulate absorption ($r = 0.67$, slope = 0.49, intercept = 0.0004, $n = 97$) (Fig. 3).

There is therefore a need to improve the B-S algorithm in many oceanic waters. The first step we must consider is to distinguish between regions with low and high nonalgal percentage and to know where to apply either the B-S method alone or the B-S method and a correction. This is fortunately possible since, overall, the total amount of nonalgal matter estimated by the B-S method is linearly correlated to the total amount of nonalgal matter obtained with the Kishino et al. (1985) method:

$$\sum_{\lambda=400}^{700} ak_d(\lambda) = a + b \sum_{\lambda=400}^{700} ab_d(\lambda), \quad (14)$$

where a is -0.2250 and b is 0.81321 ($r = 0.92$, $n = 83$).

One possibility to obtain the $ak_d(\lambda)$ values is derived from Fig. 2: Eq. 14 can be used to calculate $\Sigma ak_d(\lambda)$ from $\Sigma ab_d(\lambda)$ and then obtain the slope $ak_d(\lambda)/ab_d(\lambda)$ to recompute the $ak_d(\lambda)$ values at each nanometer. This approach, perhaps simpler than the one that we describe below, proved to be less accurate.

Another possibility stands from the use of normalized $ab'_d(\lambda)$ values [$ab'_d(\lambda) = ab_d(\lambda)/ab_d(440)$] against normalized $ak'_d(\lambda)$ [$ak'_d(\lambda) = ak_d(\lambda)/ak_d(440)$] values, which do show strong linear correlations for all the regions considered, with a similar slope and ordinate (Fig. 4A):

$$ak'_d(\lambda) = a_1 + b_1 \times ab'_d(\lambda), \quad (15)$$

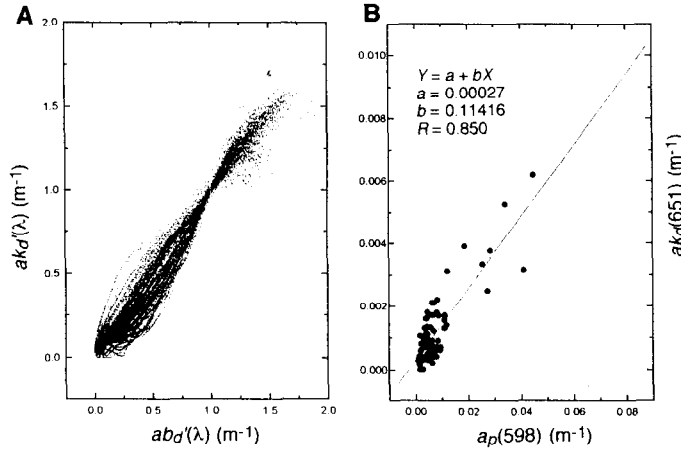


Fig. 4. Plot showing spectral-normalized values estimated with the B-S method ($ab_d(\lambda)$) against normalized experimental data obtained with the Kishino method ($ak_d(\lambda)$) for all the regions. In panel B, a good linear relationship is obtained when plotting $ak_d(651)$ against $a_p(598)$.

where a_1 is very close to zero b_1 equals 0.98 ($r = 0.98$, $n = 49,364$).

Assuming for instance that $ak_d'(\lambda)$ can be approximated with a general regression from $ab_d'(\lambda)$, it is only necessary to determine the slope between $ak_d(\lambda)$ and $ak_d'(\lambda)$ to successfully reconstruct the $ak_d(\lambda)$ spectra, since the intercept must be zero. However, estimating this slope [actually $ak_d(440)$] is not a straightforward process, even knowing that we need only one true $ak_d(\lambda)$ value at any wavelength. Several possible relationships between the $a_p(\lambda)$ values—or $a_p(\lambda)$ quotients at different λ —and $ak_d(\lambda)$ emerged with matrix correlation statistics for all the regions considered, but the best one overall related $a_p(598)$ to $ak_d(651)$ (Fig. 4B, and Eq. 16):

$$ak_d(651) = 0.0003 + 0.112a_p(598), \quad (16)$$

with r of 0.85 and n of 80. As a result, the slope $ak_d(440)$ can be computed by means of

$$ak_d(440) = \frac{0.112a_p(598) + 0.0003}{ak_d'(651)}. \quad (17)$$

Knowing $ak_d(440)$ allows us to estimate the remaining values at any other wavelength by using Eq. 18

$$a^*_{d'} = ak_d'(\lambda) \times ak_d(440). \quad (18)$$

Estimated results [$a^*_{d'}(\lambda)$] using this linear correction everywhere were compared against measured $ak_d(\lambda)$ in the different regions, obtaining much better slopes and similar or even better correlations than with the B-S method. When the correction was used (Table 2), the slope was improved from 0.76 to 1.00 in the Blanes area, from 0.48 to 1.02 in La Coruña, from 0.70 to 0.77 in inland waters (Ría de Vigo), and from 0.42 to 0.80 in the *Latitude 95* survey. The corrected slope only increased (from 1.07 to 1.26) in the Antarctic waters of the Bransfield Strait, whereas the intercept remained close to zero in all the cases. On the other hand, the correlation coefficients decreased only slightly, but kept their significance in the La Coruña region, kept their value at the Ría de Vigo region, and increased in the Bransfield Strait, Blanes, and in the *Latitude 95* survey. When the correction was not considered in detritus-poor regions, the B-S algorithm gave the best correlations in three cases, whereas the M-C-K and H-S methods performed better in one case each. In detritus-rich regions, where the linear correction should not be used, the B-S algorithm gave the best results overall, but shared with the H-S method in two cases.

Another test of the suitability of the proposed correction can be done by comparing the integrals of each nonalgal spectra (those coming from the correction, the B-S, H-S, and M-C-K methods) with the nonalgal matter integral obtained using the Kishino et al. (1985) method (Eq. 19):

$$\frac{\sum_{nm=400}^{700} (a_d - ak_d)}{\sum_{nm=400}^{700} ak_d}, \quad (19)$$

where $a_d(\lambda)$ can be $ab_d(\lambda)$, $a^*_{d'}(\lambda)$, $am_d(\lambda)$, or $ah_d(\lambda)$. Results (which can be converted to percentage difference by multiplying by 100) are summarized in Table 3, where it is shown that the proposed correction always gives much better results than does the B-S method. The correction algorithm also compared favorably to the H-S method in three of five sites, gave similar values at the La Coruña region, and yielded its

Table 2. Correlations and slopes between the corrected $a^*_{d'}(\lambda)$, the detritus obtained with the different methods, and ak_d as differentiated according to the percent detritus of each sample (n.a., not applicable; boldface indicates the best correlations obtained by a given method in a particular region).

Location (% detritus)	Slope (r)			
	M-C-K method	B-S method	H-S method	Our correction
Blanes (<0.25)	0.45(0.98)	0.76(0.95)	0.85(0.95)	1.00(0.98)
Blanes (>0.25)	0.83(0.96)	0.92(0.98)	1.08(0.98)	n.a.
La Coruña overall	0.52(0.80)	0.48(0.91)	1.17(0.75)	1.02(0.89)
Bransfield Strait (<0.25)	0.38(0.92)	1.07(0.82)	1.53(0.98)	1.26(0.98)
Bransfield Strait (>0.25)	0.32(0.90)	0.71(0.97)	0.70(0.95)	n.a.
Ría de Vigo (<0.25)	0.53(0.75)	0.70(0.96)	0.91(0.52)	0.77(0.96)
Ría de Vigo (>0.25)	0.44(0.44)	0.80(0.99)	0.89(0.93)	n.a.
<i>Latitude</i> cruise (<0.25)	0.47(0.34)	0.42(0.69)	0.50(0.54)	0.80(0.80)
<i>Latitude</i> cruise (>0.25)	0.28(0.36)	0.28(0.73)	0.43(0.71)	n.a.

Table 3. Mean (fractions) and relative errors obtained for the different methods using Eq. 19 and differentiating according to the percentage of detritus in each sample (best results, which are indicated in boldface, are those obtained when the mean is closer to 0; values for various methods are the means, with percent enclosed in parentheses; n.a. indicates not applicable).

Location (% detritus)	M-C-K method	B-S method	H-S method	Our correction
Blanes (<0.25)	2.63(75.2)	1.09(158.7)	1.02(167.6)	0.30(90.0)
Blanes (>0.25)	0.65(46.1)	0.24(108.3)	0.21(57.1)	n.a.
La Coruña overall	2.21(66.9)	1.88(65.9)	0.57(65.9)	0.62(114.5)
Brandsfield Strait (<0.25)	10.32(133.7)	2.18(141.3)	1.49(77.2)	1.93(79.8)
Brandsfield Strait (>0.25)	20.63(139.2)	0.87(154.0)	0.49(71.4)	n.a.
Ria de Vigo (<0.25)	0.33(84.8)	0.47(74.4)	0.69(15.9)	0.31(90.3)
Ria de Vigo (>0.25)	1.27(74.8)	0.22(4.5)	0.47(57.4)	n.a.
Latitude cruise (<0.25)	1.13(44.2)	1.52(101.3)	1.17(60.7)	0.81(114.8)
Latitude cruise (>0.25)	1.25(36.0)	0.41(61.0)	0.44(79.5)	n.a.

worst estimate (1.93) in the Brandsfield Strait. Interestingly, estimates coming from the B-S method when the correction was not applicable were comparable to those of the H-S method in two regions (Blanes region and *Latitude* cruise), they were better in one region (inland waters of north-western Spain), and were worse in also one region (Brandsfield Strait). The M-C-K method better approached the Kishino method at the Ría de Vigo region and in detritus-poor conditions.

The difference between the suggested correction and the B-S method can also be seen graphically, plotting $a^*_d(\lambda)$ together with $ak_d(\lambda)$ and $ab_d(\lambda)$ on a wavelength x -axis (Fig. 5). The $a^*_d(\lambda)$ curve remains closer to $ak_d(\lambda)$ compared to the B-S method, and as a consequence should also provide enhanced estimates of the algal absorption contribution, when the latter is computed by difference using Eq. 1c as it is usual.

Our results showed that the B-S method is useful and reliable to partition particulate absorption spectra into an algal and a nonalgal components, but its use is desirable when the percentage of nonalgal matter in the sample is >25%. In all other situations the B-S method tends to overestimate the nonalgal fraction when compared to the experimental method of Kishino et al. (1985) and needs a correction algorithm.

We suggest that the bias of the B-S method in detritus-poor waters can be related to the ratios used in computing the exponential detritus curve by the B-S method and, more specifically, to the ratio $a_{ph}(505)a_{ph}(380)$. Values obtained by calculating $a_{ph}(505)a_{ph}(380)$ (mean = 0.91, SD = 0.15) and $a_{ph}(580)a_{ph}(692.5)$ (mean = 0.90, SD = 0.13) including all the regions are similar to those cited by Bricaud and Stramski (1990), who gave $a_{ph}(505)a_{ph}(380) = 0.9$ (SD = 0.1) and $a_{ph}(580)a_{ph}(692.5) = 0.92$ (SD = 0.16). The main differences that appear in the $a_{ph}(505)a_{ph}(380)$ ratio can be traced to one region or conditions with particular low detritus characteristics (i.e. the Brandsfield Strait) when the spectra were analyzed individually. This therefore introduces some bias in the final estimation of the $ab_d(\lambda)$ curve. It would of course be possible to recompute the ratios proposed by Bricaud and Stramski (1990) using the available Kishino measurements, but this approach would be dependent on the region and

would thus lack the desired extended usefulness of our methodology.

Another issue remains on how different estimations of the pathlength amplification factor [$\beta(\lambda)$] can influence the linear correction suggested. Changing how this factor is estimated introduces important changes on many steps of the overall process. First, $a_p(\lambda)$ values are affected, and through them the $\Sigma a_p(\lambda)$ and the $\Sigma ak_d(\lambda)/\Sigma a_p(\lambda)$ proportion. We explored this possibility and recomputed $a_p(\lambda)$ using a different formula, this time the one suggested by Arbones et al. (1996). Results showed that the number of stations with a detritus percentage >0.25 increased significantly (by a factor 2). The correlation coefficient between $ak_d(651)$ and $a_p(598)$ remained highly significant, the intercept was again very close to zero, but the slope changed, increasing by ~20%. As a consequence, the correction proposed is strongly dependent on the way $\beta(\lambda)$ is computed and is inadequate if another pathlength amplification factor is used.

The weakest point of the suggested correction algorithm is more likely the estimation of $ak_d(651)$ from $a_p(598)$. In fact, we need to obtain only one "good" value of $ak_d(\lambda)$, since normalized $ak'_d(\lambda)$ can then be estimated with great accuracy. The correlation obtained for $ak_d(651)$ ($r = 0.85$), although significant at the 99% level, is not as high as one could desire. However, after trying all the possible combinations between $a_p(\lambda)$ and $ak_d(\lambda)$, and between $a_p(\lambda)$ ratios and $ak_d(\lambda)$ in the 400–700 nm range, it remains the best one that we could obtain globally for all the regions. The field remains open to those interested in obtaining a better approximation to one or more $ak_d(\lambda)$ values from the $a_p(\lambda)$ spectra, since the correlation obtained relating $ab'_d(\lambda)$ and $ak'_d(\lambda)$ is indeed very good. Also note that no significant differences were found when using $ab'_d(\lambda)$ directly in place of $ak'_d(\lambda)$ (i.e. in Eq. 17). Another related source of error in the suggested algorithm appears when the estimated $ak'_d(651)$ gives a near-zero value [because of its corresponding $ab'_d(651)$ value] and, as a consequence, Eq. 17 becomes undefined or gives unrealistically high values. In this rare case (<2% found in our datasets), one can either reject the spectrum (as we did) or assume a very small value for $ak_d(651)$.

The use of an empirical method such as the one described

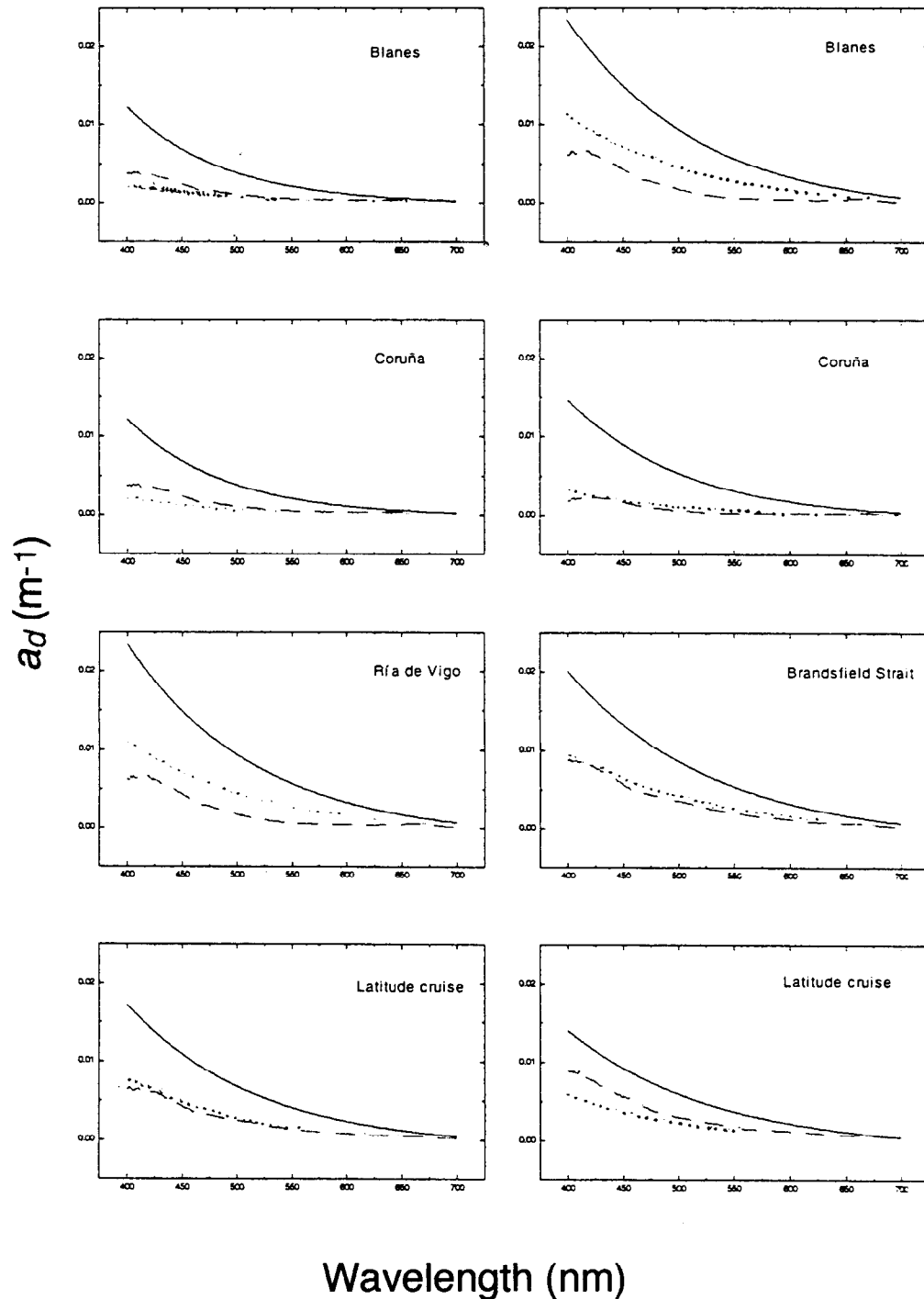


Fig. 5. Particulate absorption spectra comparing the nonalgal absorption spectra experimentally estimated (ak_d , ---) with the B-S method (ab_d , —) and the corrected B-S method (a_d^* ,) in different regions. Within each region, the spectra shown were taken at random.

has, in our opinion, crucial advantages over the experimental approach. Most of the advantages are related to saving time and work. In this case, moreover, the possibility of having an improved algorithm that can distinguish non algal and algal fractions from the total particulate matter spectra seems more appealing, since it is readily applicable to satellite measurements.

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Received: 9 February 1996

Accepted: 2 July 1997