Variability of the relationship between the particulate backscattering coefficient and the volume scattering function measured at fixed angles

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[1] The particulate backscattering coefficient b_{bp} is an inherent optical property that plays a central role in studies of ocean color remote sensing. Because of practical difficulties associated with measurements of the volume scattering function (VSF) over the whole backward hemisphere, b_{bp} is currently derived using fixed-angle backscattering sensors and applying a conversion factor for particulate backscattering, referred to as χ_p. The underlying assumptions of the fixed-angle approach are as follows: (1) in the green band, χ_p is fairly constant in the angular range 100°–150° and (2) for a fixed scattering angle, χ_p is wavelength-independent. In this study we investigated the variability of χ_p based on spectral measurements of the full VSF, both in situ and for algal culture in the laboratory. The in situ data used in our study were acquired in a coastal environment outside of phytoplankton blooms, whereas the laboratory data were representative for phytoplankton bloom conditions in oceanic waters. At 555 nm, χ_p was found to vary significantly in the angular range 100°–130°, and at 140°, χ_p was found to be weakly variable in nonblooming waters only. The spectral variability of χ_p was studied for the first time, and the spectral slopes of χ_p, measured in situ, were found to vary within ±6%. Under the assumption that $\chi_p(140°)$ is wavelength-independent, the induced error in the estimates of b_{bp} was found to be lower than 10%. The algal culture showed a much higher spectral variability in χ_p(±20%), which induced an error in the estimates of b_{bp} up to ±25.8%.

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1. Introduction

[2] Knowledge of the total backscattering coefficient b_b in natural waters is of primary importance for satellite remote sensing applications, because b_b is directly related to the signal exiting the ocean, the so-called sea surface reflectance or water-leaving radiance. Theoretically, the accurate way to calculate the backscattering coefficient is to integrate the volume scattering function (VSF), denoted by $\beta(\theta)$, over the backward hemisphere. Therefore a rigorous estimation of b_b requires measurements of the VSF over the full range of backward scattering angles, i.e., from 90° to 180°. Unfortunately, the theoretical way to compute b_b is rarely used because of practical difficulties related to the lack of appropriate instruments for direct measurements of the full VSF. Therefore an alternative method, based on measuring the VSF at a fixed scattering angle, was proposed to estimate b_b [*Oishi*, 1990; *Maffione and Dana*, 1997; *Boss and Pegau*, 2001]. On the basis of Mie calculations, *Oishi* [1990] showed that the relationship between b_b and β measured at a scattering angle of 120° was fairly constant. *Maffione and Dana* [1997] proposed to use the VSF at a scattering angle of 140°, and they introduced a dimensionless coefficient, the so-called conversion factor $\chi_t(\theta)$, which is defined as the ratio of the total backscattering coefficient b_b to the quantity $2\pi\beta(\theta)$. *Boss and Pegau* [2001] examined the separate contributions to the VSF of seawater due to scattering by particles and molecules. They showed that for scattering angles ranging from 115° to 123°, the conversion factor χ_p, which relates the particulate VSF, denoted by β_p, to the particulate backscattering coefficient b_{bp}, was nearly equal to the conversion factor χ_w, which relates the pure seawater VSF, denoted by β_w, to the pure seawater backscattering coefficient b_{bw}. However, for scattering angles larger than 130°, they suggested to remove the contribution of pure seawater from the total VSF, denoted by $\beta(\theta)$, prior to calculating b_{bp}. In any case, the previous studies [*Oishi*, 1990; *Maffione and Dana*, 1997; *Boss and Pegau*, 2001] agree on the fact that the relative variations of $\beta(\theta)$ are smallest in the middle range of scattering angles between 100° and 150°, and thus, that χ_p may be considered to be fairly constant in this angular range. In his empirical

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validations, *Oishi* [1990] used scant and often incomplete measurements of the VSF compiled from the literature [*Tyler and Richardson*, 1958; *Petzold*, 1972; *Kullenberg*, 1974; *Morel*, 1973], and *Boss and Pegau* [2001] used a restricted data set (44 samples) measured with a prototype volume scattering meter (VSM) [*Haltrin et al.*, 1996]. As suggested by *Oishi* [1990] and *Boss and Pegau* [2001], the invariance of χ_t or χ_p in the range of scattering angles from 100° to 150° needs to be empirically verified using a large number of new VSF measurements.

[3] In this paper, we analyze a significant number of in situ and laboratory measurements to obtain the conversion factor χ_p from VSFs measured over a wide range of scattering angles and at different wavelengths. The in situ data were obtained in a coastal environment, offshore the Crimea Peninsula in the Black Sea. The laboratory measurements were carried out on marine microalgal culture of different species. Because algal cultures follow a lognormal size distribution, analyses of their VSFs can be helpful to understand the variation of χ_p in natural waters during blooming conditions. The main objective of this paper is to analyze the natural variability of the relationship between b_b and $\beta(\theta)$, with particular emphasis on discussing the spectral variation of χ_p. This has not been investigated earlier because of the lack of appropriate measurements. As mentioned above, χ_p is currently assumed to be independent of the wavelength [*Oishi*, 1990; *Maffione and Dana*, 1997; *Boss and Pegau*, 2001; *Twardowski et al.*, 2001; *Vaillancourt et al.*, 2004], and the aim of our study is to test this hypothesis. Another objective is to quantify the errors induced in b_b by assuming that χ_p at a particular scattering angle is wavelength-independent.

2. Material and Methods

2.1. In Situ Volume Scattering Function (VSF) Measurements

[4] In situ measurements of the VSF were carried out by use of the VSM that recently was developed by the Marine Hydrophysical Institute (Ukraine) in cooperation with Satlantic Inc. (Canada) [*Lee and Lewis*, 2003]. Here we give a brief description of this VSM and refer to *Lee and Lewis* [2003] for more details. The VSM provides the VSF for scattering angles in the range between 0.6° and 177.3° with an angular resolution of 0.3°. A notable difference between traditional VSM concepts and that of *Lee and Lewis* [2003] is that the positions of the light source and the photo detector are fixed in the latter model. The measurement angle is changed by the rotation of a special periscope prism with three reflecting facets. The shape of the prism together with a particular geometrical design allows the scattered radiance to be detected over nearly the full angular range. When the measurement angle is equal to zero, the instrument also measures the beam attenuation coefficient *c*. To make it possible to measure spectral properties of $\beta(\theta)$ the VSM is equipped with a revolving wheel with three color filters with centre wavelengths at 443 nm, 490 nm, and 555 nm. The bandwidth of each channel is 10 nm.

[5] The VSM was calibrated using a solution of latex polystyrene microspheres with precisely known geometry and refractive index. Because the particles of the solution are nearly perfectly spherical, the VSF can be predicted with a high accuracy using Mie theory. The calibration constant of the VSM was estimated by the least squares method based on minimizing the difference between the logarithms of the measured and simulated VSFs. More details about the calibration procedure are given in *Chami et al.* [2005].

[6] The integration of $\beta(\theta)$ over the backward hemisphere provides the backscattering coefficient b_b, i.e.,

$$b_b = 2\pi \int_{\frac{\pi}{2}}^{\pi} \beta(\theta) \sin\theta d\theta. \quad (1)$$

The total conversion factor χ_t (θ) is defined as

$$\chi_t(\theta) = \frac{b_b}{2\pi\beta(\theta)}. \quad (2)$$

[7] In order to obtain the conversion factor χ_p for particulate scattering, the VSF for pure seawater was subtracted from the measurements of the total VSF through application of the coefficients provided by *Morel* [1974]. The correction for salinity was carried out according to the procedure given by *Boss and Pegau* [2001]. The conversion factor χ_p is defined as

$$\chi_p(\theta) = \frac{b_{bp}}{2\pi\beta_p(\theta)}. \quad (3)$$

2.2. Laboratory Measurements of the VSF

[8] The VSF measurements were carried out in the laboratory using the LABVSM instrument developed by *Zhao et al.* [2006], which worked according to the following principle. A Xenon lamp (LQX1000, LINOS Photonics GmbH) provided white light, which was guided through a liquid fiber and a collimator. The color of the light was selected using an interference filter (Andover Co., Salem, NH 03079) with transmittance peaks at the wavelengths 442 nm, 490 nm, and 550 nm. Each channel had a bandwidth of 10 nm. After passage through the collimator the beam was directed normally onto two concentric cylinders with glycerol in between them, and the sample was placed inside the inner cylinder. The diameters of the two cylinders were carefully chosen so as to avoid divergence of the beam. A silicone-based photodiode was used as detector. It could be positioned at any azimuth angle, and was tilted to a zenith position of 86° in order to avoid internal reflections of light in the sample container. The experimental setup was calibrated with polystyrene beads having a diameter of 2 μm. After the calibration, the VSF measurements were carried out in two steps, first in forward directions (3°–90°) and then in backward directions (90°–165°). A black reflecting surface, tilted 45° relative to the incident beam, was introduced in the sample container during measurements in backward directions. This was done to avoid reflected light from getting scattered in backward directions. Mie theory was used to extrapolate the VSF in the ranges 0°–3° and 165°–180°.

3. Results

3.1. Variation of the Conversion Factor at 555 nm in the Black Sea

[9] A field experiment, devoted to the characterization of the optical properties of particles, was carried out in a

Table 1. Angular Variation of the Mean χ_t Conversion Factor Measured in the Black Sea at 555 nm Together With the Relative Standard Deviation[a]

	θ								
	90°	100°	110°	120°	130°	140°	150°	160°	170°
χ_t	0.87	1.05	1.18	1.25	1.24	1.15	1.03	0.91	0.69
σ, %	5.1	4.3	4.6	4.4	4.0	3.7	4.1	5.2	11.0
χ_t Oishi	0.71	0.90	1.06	1.14	1.20	1.08	1.00	0.93	0.84
$\Delta\chi_t\chi_t$, %	22.5	16.7	11.3	9.6	3.3	6.5	3.0	−2.1	−17.9

[a]Standard deviation in %. Also shown are the values tabulated by *Oishi* [1990] and the relative difference (in %) between our results and Oishi's data, which is calculated as $\Delta\chi_t/\chi_t = (\chi_{tChami} - \chi_{tOishi})/\chi_{tOishi} * 100$.

coastal area of the Black Sea near the Crimea Peninsula during 3 weeks in the summer of 2002 [*Chami et al.*, 2005]. The optical measurements were performed on an oceanographic platform located 600 meters offshore from the southern coast of the Crimea Peninsula (44°23N and 33°59E). The analysis of the absorption and scattering properties of the particles was discussed in detail by *Chami et al.* [2005]. Here, we briefly report the main features of the field campaign. Water samples (132 in total) were collected at different depths (0, 4, 8, 12, 16, 20 m). The chlorophyll-*a* concentration varied from 0.45 to 2.1 mg m^{-3}. The nonalgal particles absorption contributed to the total particulate absorption by 40% up to 88% at 443 nm. The range of variation of the scattering coefficient b_p, backscattering coefficient b_{bp} and the backscattering ratio of the particles $\tilde{b}_{bp}$ ($\tilde{b}_{bp}$ is defined as the particulate backscattering coefficient divided by the particulate scattering coefficient) was 0.2–1 m^{-1}, 0.003–0.02 m^{-1} and 1.2–3.2% respectively. The average values of b_p, b_{bp} and $\tilde{b}_{bp}$ were 0.33 ± 0.11 m^{-1}, 0.006 ± 0.002 m^{-1} and 1.9% ± 0.3% respectively. We note that a significant variability (∼30 %) was observed in b_p and b_{bp} during the experiment. The strong variability observed in the optical properties of the particles was mainly ascribed to the intrusion of a new water body near the platform in the second half of the experiment resulting from important changes in the weather conditions (strong winds, currents reversal). The new water mass was characterized by colored mineral particles and by phytoplankton cells having a higher packaging effect. Our field data are thus relevant to study the natural variability of the conversion factors χ_t and χ_p.

[10] Table 1 shows the angular variation of the mean χ_t at 555 nm together with the relative standard deviation. It also shows the values published by *Oishi* [1990] and the relative difference between the results of our study and those of Oishi. A small variability, typically within ±5%, of the χ_t was observed during the field experiment for scattering angles smaller than 170°. *Oishi* [1990] found the smallest standard deviation at 120° and reported $\chi_t(120°)$ = 1.14 ± 10%. Our results give $\chi_t(120°)$ = 1.25 ± 4.4%, implying that our mean value corresponds to the upper limit of the interval of variation found by *Oishi* [1990]. Also in the angular range 90°–110°, our measurements were significantly higher (more than 10%) than Oishi's results. These differences will be discussed later.

[11] We applied the water removal approach of *Boss and Pegau* [2001] to study the influence of molecular scattering on the conversion factor. A comparison between χ_p and χ_t (Tables 1 and 2) shows that they were nearly equal (within 2%) for scattering angles smaller than 120°. The χ_t and χ_p curves cross each other at 110° with the following value: $\chi_t(110°) = \chi_p(110°)$ = 1.18 ± 5%. *Boss and Pegau* [2001] found that the equality between χ_t and χ_p occurs when χ_p and χ_w (χ_w is the conversion factor related to pure seawater only) are the same, which is verified in this study since $\chi_w(110°)$ is 1.16. Therefore at scattering angles between 90° and 110°, there is no need to know the contribution of the VSF of pure seawater $\beta_w(\theta)$ to $\beta(\theta)$ exactly. For scattering angles larger than 110°, χ_p departs significantly from χ_t (more than 3%) due to a larger influence of the pure seawater contribution to $\beta(\theta)$. This is so because the VSF for pure seawater $\beta_w(\theta)$ increases steadily with the scattering angle, whereas the VSF for particle scattering $\beta_p(\theta)$ usually decreases steadily as the scattering angle increases to 150°. Therefore to obtain a good estimate of the backscattering coefficient using the VSF measured at a fixed angle higher than 110°, one should remove the contribution from pure seawater to $\beta(\theta)$, in accordance with the recommendation of *Boss and Pegau* [2001].

[12] Figure 1 shows the angular variation of the mean χ_p and its standard deviation for the range of backward scattering angles from 90° to 177°. The variability in χ_p was found to be less than 6% for the majority of scattering angles (Table 2). Figure 1 also shows the values of χ_p measured by *Boss and Pegau* [2001] in a coastal shelf off New Jersey (United States). It should be emphasized that the instrument used by *Boss and Pegau* [2001] to measure the VSF was a previous generation of the VSM instrument used in this study, and thus, our and their instruments have a similar design and concept. The major difference between the two devices was the ability of our VSM to carry out spectral measurements, while the VSM used by *Boss and Pegau* [2001] worked at one single wavelength only (530 nm). Figure 1 shows important discrepancies between our values for χ_p and those of *Boss and Pegau* [2001] for scattering angles smaller than 140°. Thus in the angular range 90°–130°, the mean χ_p values measured in the Black Sea were much higher than those observed by *Boss and*

Table 2. Mean Values of χ_p at 555 nm Based on the VSM Measurements at Intervals of 10° from 90° to 170°[a]

	θ								
	90°	100°	110°	120°	130°	140°	150°	160°	170°
χ_p	0.84	1.03	1.18	1.29	1.29	1.21	1.08	0.94	0.70
σ, %	5.1	4.5	5.3	5.5	5.4	5.1	5.3	5.8	11.5
χ_p Boss and Pegau, %	0.71 ± 4.3	0.90 ± 2.6	1.03 ± 3.1	1.12 ± 4.2	1.17 ± 3.3	1.18 ± 3.5	1.13 ± 4.2	1.00 ± 6.4	0.62 ± 34.8
$\Delta\chi_p\chi_p$, %	18.3	14.4	14.6	15.2	10.2	2.5	−4.4	−6.0	12.9

[a]The relative standard deviation is also shown (in %). Also listed are the values tabulated by *Boss and Pegau* [2001] and the relative difference $\Delta\chi_p/\chi_p = (\chi_{pChami} - \chi_{pBoss})/\chi_{pBoss}) * 100$.

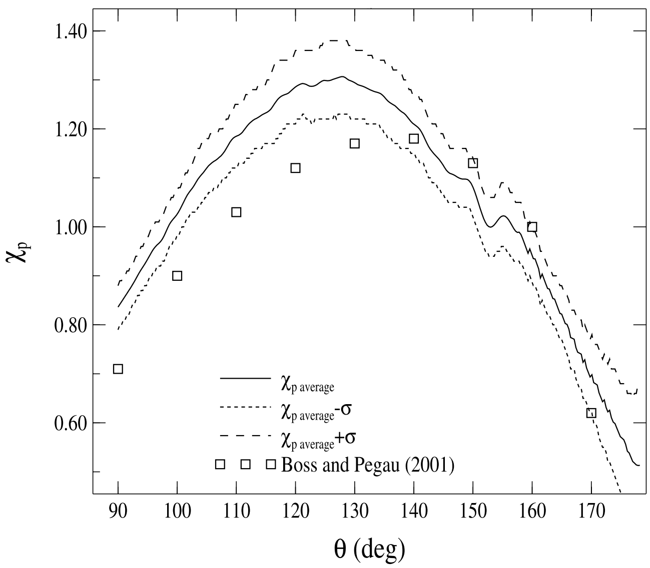

Figure 1. Mean angular variation and standard deviation σ of the conversion factor χ_p at 555 nm measured in the Black Sea. Also shown are the measurements tabulated by *Boss and Pegau* [2001].

Pegau [2001]. The relative difference has its maximum value at 90° (18%), and is always greater than 10% (Table 2), which is significant since the variability of χ_p observed in the measurements of *Boss and Pegau* [2001] was small (less than 4.3%). Therefore the conversion factor χ_p shows a high degree of variability in this range of scattering angles, implying that the use of a fairly constant value of $\chi_p(\theta)$ in the range 110°–130° to derive the particulate backscattering coefficient b_{bp} is not justified. This finding is in contrast to that inferred by *Oishi* [1990] or *Boss and Pegau* [2001]. On the other hand, the mean value of $\chi_p(140°)$ measured in our study (1.21 ± 5.1%) is in a good agreement with the value previously reported by *Boss and Pegau* [2001] ($\chi_p(140°)$ = 1.18 ± 3.5%). Furthermore, during our experiment the variability of χ_p with wavelength was close to its smallest value at a scattering angle of 140°. Therefore $\chi_p(140°)$ can be regarded as fairly constant, at least in nonblooming waters, in accordance with the theoretical predictions of *Maffione and Dana* [1997].

3.2. Variation of the χ_p Factor at 550 nm for Algal Culture of Phytoplankton

[13] Monospecific phytoplankton cultures representing 12 species from 5 marine algal classes were used in the present study (Table 3). The phytoplankton species were highly different in shape, external structure, and internal assemblage. The asphericity parameter of the algae, which is defined as the ratio between the long axis over the short axis, varied from 1.0 (for a spherical algae) to 22.9. *Emiliania huxleyi* and *Karenia mikomotoi* are nearly spherical in shape, whereas *Phaeodactylum tricornutum* and *Nitzchia longissima* are prolate ellipsoidal-shaped with very high asphericity parameters. The algae species *Chaetoceros wighamii* and *Skeletonema costatum* can be approximated as cylinders. The external structure of phytoplankton ranges from ''soft'' algae like ''naked'' *E. huxleyi* (here ''naked'' means that they have a low fraction of coccoliths cells, typically less than 15%) to more ''hard'' algae, such as Bacillariophyceae (with a SiO_2 cell wall), *Proteceratium reticulatum* (with a cell wall made of cellulose), and *E. huxleyi* covered by $CaCO_3$ platelets. The real part of the refractive index of the algae typically varies within the range from 1.02 to 1.09 [*Aas*, 1996].

[14] The species were preadapted to growth in continuous light (except for the algae class Dinophyceae), and they were grown in nutrition rich water at temperatures varying between 15 °C and 20 °C. Dinophyceae was grown during a light:dark cycle of 12 hours:12 hours. The growth medium was based on filtered seawater from a deep water intake at a depth of 100 m in the fjord located nearby the city of Bergen (Norway). This water is characterized by relatively stable temperature values, which are in the range 5°C and 10°C and a salinity varying from 33 to 35 PSU throughout the year [*Erga et al.*, 2003]. The seawater was autoclaved before supplementing it with Conway nutrition [*Walne*, 1966] or with the growth medium $IMR_{1/2}$ [*Eppley et al.*, 1967]. The temperature and light conditions (50–350 μmol quanta m^{-2} s^{-1}) were chosen to give optimum growth conditions for the algae. The algae cultures were regularly monitored using a light microscope and a Coulter counter to ensure that they were in a good physiological condition. The volume equivalent radius of each algal culture was measured using a light microscope or a Coulter Counter with aperture diameter of 50 or 100 μm (Table 3). For the algal cultures that were examined using Coulter Counter, we

Table 3. Characteristics of the Algal Culture Studied: Algal Class, Name of the Species, Asphericity Ratio, r_{mean}, and σ of the Lognormal Distribution[a]

Class	Name of the Species	Asphericity Ratio	$r_{mean} \pm \sigma$
Bacillariophyceae	*Chaetoceros wighamii*	1.5	3.81 ± 0.22
Bacillariophyceae	*Nitzchia longissima*	22.9	2.77 ± 1.61
Bacillariophyceae	*Phaeodactylum tricornutum*	8.3	1.96 ± 0.33
Bacillariophyceae	*Skeletonema costatum*	2.6	3.24 ± 1.34
Bacillariophyceae	*Thalassiosira nordenskioeldii*	1.7	4.31 ± 1.01
Dinophyceae	*Karlodinium micrum*	1.1	4.15 ± 1.61
Dinophyceae	*Karenia mikmotoi*	1.0	10.30 ± 1.74
Dinophyceae	*Proteceratium reticulatum*	1.2	12.10 ± 1.62
Prasinophyceae	*Tetraselmis* sp.	1.3	4.64 ± 1.03
Prymnesiophyceae	*Emiliana huxleyi*	1.0	2.46 ± 0.94
Prymnesiophyceae	*Emiliana huxleyi* (naked)	1.0	1.77 ± 0.24
Raphidophyceae	*Heterosigma akashiwo*	1.9	4.94 ± 1.06

[a]Two species of *Emiliana huxleyi* were studied; one was fully covered with coccoliths, and the other (referred to as ''naked'' *Emiliana huxleyi*) had a low fraction of coccoliths cells, typically less than 15%. Both r_{mean} and σ are in μm.

Table 4. Average Value of χ_p Calculated for All Phytoplankton Species at 550 nm at Intervals of 10° From 90° to 160°[a]

	θ							
	90°	100°	110°	120°	130°	140°	150°	160°
χ_p	0.76	0.87	0.99	1.13	1.35	1.30	1.30	1.31
σ, %	25.0	11.1	9.9	9.9	8.9	9.1	8.6	14.2

[a]The relative standard deviation is also given (in %).

found the size to follow a lognormal distribution. The asphericity parameter was measured using light microscope. The radii of the cells varied from 1.77 μm ("naked" *Emiliania huxleyi*) to 12.1 μm (*Proteceratium reticulatum*). Only cultures in the exponential growth phase were used in the experiments.

[15] The mean value and standard deviation of χ_p at 550 nm are listed in Table 4 for various scattering angles. For scattering angles smaller than 120°, the χ_p values were consistent with the data of *Boss and Pegau* [2001], while they differ significantly from the Black Sea data (more than 15%) (Figure 2). For scattering angles larger than 120°, the χ_p values for monospecific algal culture were found to be much higher than those for the measurements in the Black Sea or off the coast of New Jersey [*Boss and Pegau*, 2001]. As an example, χ_p(140°) averaged over all the algal culture was 1.30 ± 9.1%, which is 10% larger than the corresponding value obtained from in situ data. This mean value of χ_p(140°) was also 50% higher than that obtained from recent measurements by *Vaillancourt et al.* [2004] on phytoplankton cultures (0.82 ± 2%). The decrease of the mean value of χ_p as the backward scattering angle increases (θ > 150°), which was noticeable in the Black Sea data and in the data of *Boss and Pegau* [2001], is not observed in the laboratory measurements. The variability of χ_p was nearly twice as large for the monospecific algal cultures (~9%) as that obtained from the in situ measurements in the Black Sea or off the coast of New Jersey [*Boss and Pegau*, 2001].

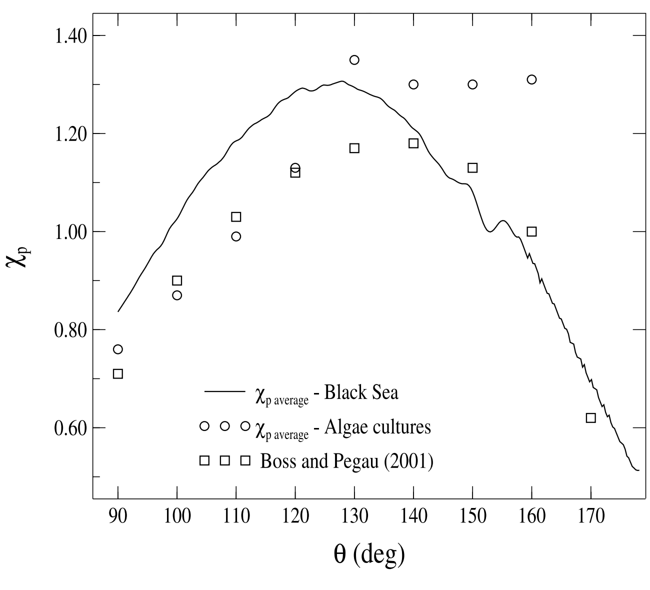

Figure 2. Comparison of the mean χ_p measured in the green band for data from algae cultures, from the Black Sea, and from *Boss and Pegau* [2001].

4. Discussion

4.1. Influence of the Size Distribution on χ_p

[16] To better understand the significant differences observed between the mean values of χ_p at 555 nm in the range 110°–130° obtained from in situ measurements in the Black Sea (section 3.1) and from previous studies [*Oishi*, 1990; *Boss and Pegau*, 2001], we carried out a series of calculations using Mie theory. We carried out computations for a realistic range of refractive index values and particle size distributions. The real part of the refractive index n_p at 555 nm was varied from 1.02 to 1.20, and the imaginary part n'_p was varied from 0 to 0.01. A Junge hyperbolic size distribution, which often is used for natural waters [*Bader*, 1970; *Carder et al.*, 1971; *Gordon and Brown*, 1972; *Boss and Pegau*, 2001], was applied as a first approximation to the particle size distribution. The Junge exponent ν of the distribution was varied from 3.2 to 5.0 in the simulations, and the minimum and maximum radii of the distribution were 0.01 μm and 40 μm, respectively.

[17] We obtained best agreement between measurements and computations (Figure 3) when the real and imaginary parts of the refractive index were n_p = 1.16, and n'_p = 0, respectively, and the Junge exponent ν was 4.2. The relative root mean square error (RMS) was 14.0% with best agreement for scattering angles larger than 140°. We note that the high value of the real part of the refractive index is

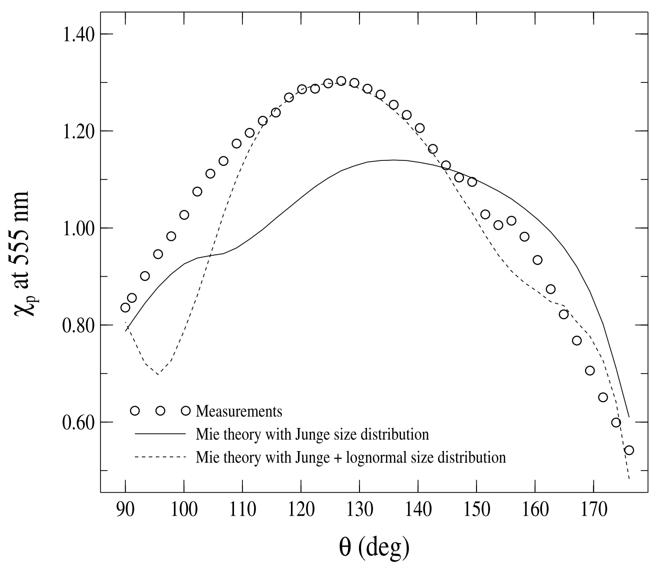

Figure 3. Retrieval of χ_p(555 nm) measured in the Black Sea based on Mie theory with a single Junge size distribution and with the sum of a Junge distribution and a lognormal size distribution. The single Junge size distribution was characterized by a refractive index of n_p = 1.16 and n'_p= 0 and a Junge exponent of ν = 4.2. The parameters of the mixed size distribution were as follows: for the Junge size distribution the retrieved refractive index was n_p = 1.20, n'_p= 0, and the Junge exponent was ν = 5.0; for the lognormal distribution the retrieved refractive index was n_p = 1.12 and n'_p= 0, r_{mean} = 1.0 μm, and σ = 0.4 μm.

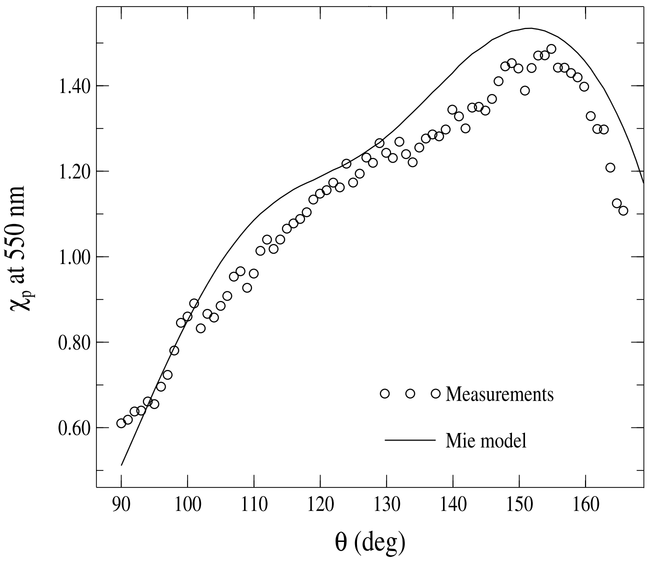

Figure 4. Retrieval of χ_p measured at 550 nm for *Karenia Mikomotoi* using Mie theory. The measured lognormal size distribution was used (see Table 3). The retrieved refractive index was n_p = 1.07 and n'_p = 0.

consistent with the high magnitude of the backscattering ratio $\tilde{b}_{bp}$ observed in the study area during the experiment (>2%), suggesting the presence of highly refractive particles (e.g., inorganic particles) in the water column [*Chami et al.*, 2005]. The relatively high value of the retrieved Junge exponent expresses the occurrence of small particles, which is also consistent with a significant value of the particulate backscattering ratio. Nevertheless, the modeled χ_p significantly underestimated the measurements in the angular range 110°–130°, where the RMS exceeded 20%. As an example, the modeled value of $\chi_p(120°)$ was 1.06, which was 21.6% smaller than the value obtained from the measurements. Therefore a Junge size distribution is not sufficient to explain the high values of χ_p observed at scattering angles smaller than 130°. Other size distributions were therefore tried.

[18] *Jonasz* [1983] studied the size distribution of particles in the Baltic Sea and showed that a model based on the sum of a Junge and a lognormal size distribution could be realistic. The lognormal size distribution typically characterizes the presence of monodispersed particles, while the Junge law is representative for a continuous background of particles. On this basis, we added a lognormal mode of particles to a Junge size distribution and adjusted the parameters of the lognormal distribution (refractive index, mean radius r_{mean}, and standard deviations σ). We varied the refractive index of the lognormal distribution from 1.02 to 1.20, varied the mean radius r_{mean} from 0.3 μm to 10 μm, and varied the standard deviation σ from 0.1 μm to 3 μm. The best agreement (Figure 3) was obtained for the following parameter values. The refractive index of the particles distributed according to the Junge law was n_p = 1.20 and n'_p = 0, the refractive index of the lognormal mode of the particles was n_p = 1.12 and n'_p = 0, the Junge exponent ν was 5.0, the mean radius was r_{mean} = 1.0 μm, and the standard deviation was σ = 0.4 μm. The relative RMS was 12.4%, which is slightly better than the RMS obtained by the use of a single Junge size distribution. However, the computed VSF was much closer to the measured VSF in the range 110°–177°, with a relative RMS of 5.3%. The order of magnitude of the retrieved refractive index for the particles distributed following the Junge distribution is still consistent with the high values of the backscattering ratio observed near the platform [*Chami et al.*, 2005].

[19] The high value for the retrieved refractive index of the lognormal mode (n_p > 1.09) suggests that the monodispersed particles were not dominated by phytoplankton, which is consistent with the fact that nonblooming conditions were observed near the oceanographic platform (the chlorophyll-*a* concentration was lower than 2.5 mg m^{-3} [*Chami et al.*, 2005]). *Morel and Bricaud* [1981] showed that monodispersed particles can be responsible for a significant spectral variation of the backscattering ratio $\tilde{b}_{bp}$, depending on their size and composition. During the experiment, *Chami et al.* [2005] observed that $\tilde{b}_{bp}$ was highly wavelength-dependent with spectral slopes reaching 30% between 443 nm and 555 nm. Therefore the presence of monodispersed particles in the study area, as inferred by Mie calculations, is also corroborated by the spectral observations of $\tilde{b}_{bp}$.

[20] Analyses of algal culture is of great interest to improve our understanding of the variation of χ_p during phytoplankton blooms since monospecific algae could dominate the optical properties of the water column under such conditions. The size distribution of living particles is often approximated by a lognormal function. Figure 4 shows the angular variation of χ_p at 550 nm, based on VSF measurements for *Karenia Mikomotoi*. The angular shape of χ_p regarding this specie highly differ from the average shape (Figure 2) for scattering angles larger than 150°. Here, χ_p decreases with increasing scattering angles, which is in agreement with the previous calculations of *Boss and Pegau* [2001]. When looking more closely at the data, one finds that $\chi_p(120°)$ = 1.15, which is in agreement with the value proposed by *Oishi* [1990] for phytoplankton blooms lognormally distributed ($\chi_p(120°)$ = 1.15 ± 0.10). However, one also finds that $\chi_p(140°)$ = 1.34, which is nearly 13 % higher than the values found for nonblooming phytoplankton by *Boss and Pegau* [2001] and in the Black Sea. Figure 4 shows a comparison of the results obtained for *Karenia mikomotoi* with those computed from Mie theory. Agreement is expected since the cells of *Karenia mikomotoi* are nearly spherical, and since the assumption of homogeneity is fairly well satisfied.

[21] The general trend of χ_p over the full angular range was well reproduced by the modeling results (with a relative RMS of 8.5%) when the central value of the refractive index was set equal to 1.07, which is in the range of experimental values for common algal cells [*Aas*, 1996]. Therefore the variability of the relationship between $\beta_p(\theta > 120°)$ and b_{bp} suggests that the assumption of a constant value of χ_p, as recommended by *Boss and Pegau* [2001], may be strongly violated when monospecific blooms of phytoplankton occur. However, attention should be paid to the fact that very narrow lognormal size distributions, such as those obtained in batch cultures, are rarely found in natural waters. The polydispersion that exists in the sea tends to smooth out the features observed when examining algal culture [*Bricaud*

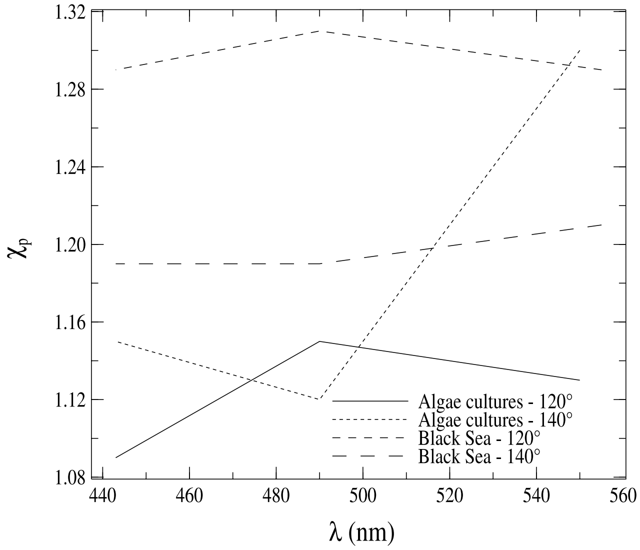

Figure 5. Mean spectra of χ_p measured at 120° and 140° for the Black Sea and algal culture experiments.

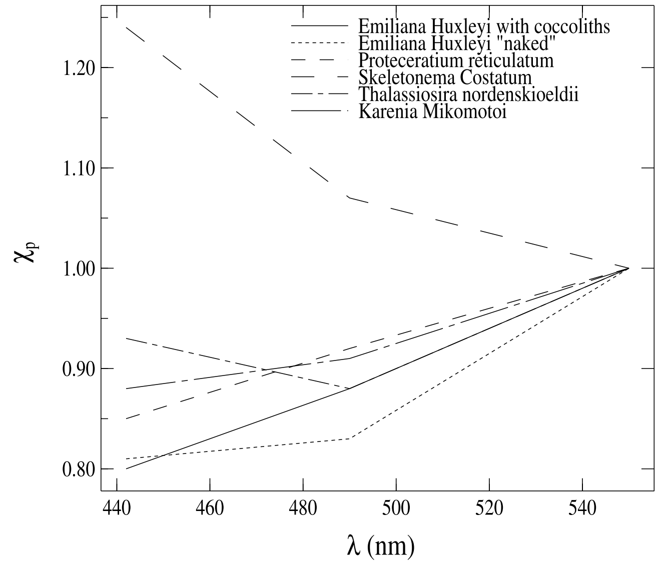

Figure 6. Examples of χ_p spectra at 140° as measured for different phytoplankton species. The spectra were normalized to 550 nm.

and Morel, 1986; *Quirantes and Bernard*, 2004]. Therefore the magnitude of the bias reported in this study with regard to χ_p(140°) will presumably be reduced in blooming natural waters.

4.2. Spectral Variation of χ_p

[22] In 1990, Oishi presented a theoretical study, based on Mie calculations, showing that χ_p(120°) is independent of the wavelength [*Oishi*, 1990]. Therefore χ_p is often considered to be spectrally neutral, not only in natural waters [*Boss and Pegau*, 2001; *Maffione and Dana*, 1997], but also for algal culture [*Vaillancourt et al.*, 2004]. Currently, χ_p is first derived by considering one single wavelength (typically in the green part of the spectrum) and then applied to estimate b_b at different wavelengths. As a result of this procedure, the spectral shape of b_b, which is of great importance in remote sensing applications, may be highly biased. The ability of the VSM and the LABVSM to measure at different wavelengths allows one for the first time to investigate the spectral variation of χ_p at different scattering angles using experimental data. Figure 5 shows the mean spectral shape of χ_p measured at 120° and 140° in the Black Sea and for the different cultures of phytoplankton species in the laboratory. The average spectral variation, which is expressed by the mean ratio χ_p(443 nm)/χ_p(555 nm) (note that 442 nm and 550 nm were used when examining algal culture), is shown in Table 5.

[23] The mean spectral shape of χ_p measured for the different phytoplankton species showed an increase with the wavelength (9% at 140° and 3% at 120°; Table 5 and Figure 5). Furthermore, the variability (i.e., see standard deviation in Table 5) was found to be greater than 10%, suggesting that the spectral shape is highly dependent on the species. Therefore we examined more closely the spectral variation of χ_p(140°) for different cultures of algae (Figure 6). We focused on a scattering angle of 140° because it is currently used to derive the backscattering coefficient from measurements of the VSF. To highlight the varying spectral shape of χ_p, the spectra were normalized with respect to the value at 555 nm. In Figure 6 it is interesting to note that χ_p may either increase or decrease with the wavelength, although most of the species show an increase. The magnitude of the slope between 443 nm and 555 nm varied within a wide range, typically from −20% (*Emiliania huxleyi*) to +20% (*Skeletonema costatum*).

Table 5. Mean Spectral Ratio Between χ_p in the Blue and in the Green Bands at 120° and 140° Obtained for the Black Sea and the Algal Culture Measurements

	120°	140°
χ_p(443 nm)/χ_p(555 nm): Black Sea, %	1.01 ± 7.8	0.99 ± 6.0
χ_p(442 nm)/χ_p(550 nm): algal culture, %	0.97 ± 11.7	0.91 ± 13.7

[24] The increase of χ_p with the wavelength may be explained by the influence of absorption on the scattering properties, due to anomalous dispersion [*van de Hulst*, 1957; *Bricaud and Morel*, 1986]. The real part of the refractive index exhibits small variations in the vicinity of absorption bands. As a result, the scattering and backscattering coefficients may decrease in the presence of absorption. To check whether the absorption may influence our spectral measurements of χ_p, we used a method described by *Bricaud and Morel* [1986] to estimate the imaginary part of the refractive index of nearly spherical algal cells. This method requires knowledge of the absorption, which was measured in this study using a Wetlabs AC9 instrument (Wetlabs Inc.). For *Karenia mikomotoi* the imaginary parts of the refractive index at 442 nm and 490 nm were determined to be 0.0041 and 0.0040, respectively. On the basis of these values, the retrieval of χ_p from Mie theory was in a good agreement with the measurements (the RMS was 8.1% at 442 nm and 8.7 % at 490 nm). In particular, Mie theory confirmed that the value of χ_p increased with the wavelength. Using Mie theory, we found the spectral ratios χ_p(442 nm)/χ_p(550 nm) and χ_p(490 nm)/χ_p(550 nm) to be 0.90 and 0.92, respectively, which is in good agreement with the measurements (0.88 and 0.91).

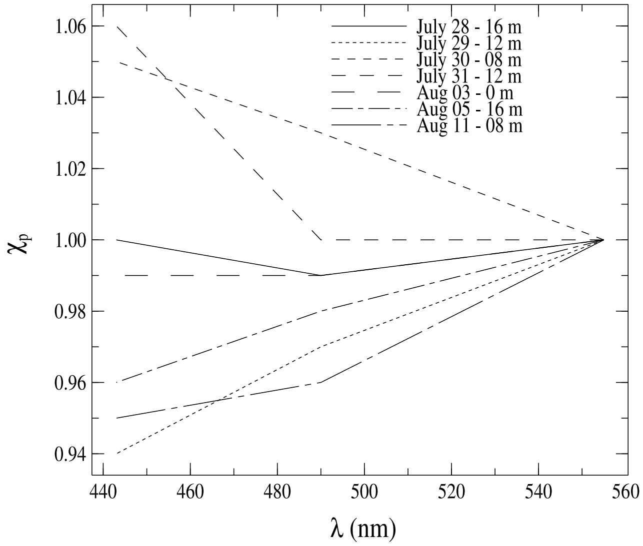

Figure 7. Examples of χ_p spectra at 140° as observed at different days during the Black Sea experiment. The spectra were normalized to 555 nm.

[25] In the Black Sea, the spectral shape of the mean χ_p at 120° was flat within ±1%, which is consistent with the computations reported by *Oishi* [1990]. But the variability in the spectral ratio χ_p(443 nm)/χ_p(555 nm) varied between 6% and 8%, depending on the scattering angle (Table 5). To illustrate this variability, different examples of spectra of χ_p(140°) are plotted in Figure 7. All types of spectral slopes occurred during the field measurements. Thus a decrease of χ_p with the wavelength occurred at the surface on 6 August 2002, an increase occurred at a depth of 12 m on 29 July 2002, and flat spectra were obtained at a depth of 16 m on 28 July 2002. For the overall data set, the spectral variation of χ_p(140°) may depart from the neutral shape by as much as ±6%. Only about one third of the data (36.1%) showed a deviation from the neutral spectrum that was smaller than ±3%, thus highlighting that most of the measurements exhibited a significant spectral variation. As suggested by the measurements on algal culture, the spectral variability of χ_p observed in the Black Sea was probably related to the occurrence of various types of algal particles near the platform. Because the effect of particulate absorption upon the backscattering coefficient b_{bp} was strong in the blue during the experiment (see discussion by *Chami et al.* [2005]), the spectral shape of χ_p was also likely influenced by absorption effects certain days. It should be emphasized that the magnitude of the spectral variability was smaller for the in situ measurements (±6%) than for the measurements on algal culture. A smoothing effect was expected in natural waters as a result of the polydispersion [*Bricaud and Morel*, 1986]. In any case, both laboratory and in situ measurements suggest that it is not possible to derive a systematic law for the spectral variation of χ_p.

4.3. Errors in the Estimated Particulate Backscattering Coefficient b_{bp}

[26] Since commercially available instruments, such as Hydroscat (Hobilabs Inc. [*Maffione and Dana*, 1997]), allow routine measurements of the VSF at 140°, the conversion factor χ_p(140°) is used to derive the particulate backscattering coefficient b_{bp} from equation (3). As previously mentioned, the estimation of b_{bp} currently relies on the following two assumptions: (1) a relatively constant value (independent of water type) for χ_p(140°) is used at 555 nm, e.g., χ_p(140°) = 1.18, which is the conversion factor proposed by *Boss and Pegau* [2001], and (2) χ_p(140°) is supposed to be wavelength-independent. A simple way to evaluate the errors induced on b_{bp} due to these two assumptions, consists of comparing the particulate backscattering coefficient estimated using the constant value of χ_p(140°) proposed by *Boss and Pegau* [2001] (hereafter referred to as $b_{bp\text{estimated}}$) with the b_{bp} value obtained by integrating the VSF over the backward hemisphere (hereafter referred to as $b_{bp\text{measured}}$) (Figure 8). The error in the retrieval of b_{bp} was calculated using the relative RMS (Table 6). The overall error in the b_{bp} (i.e., when all wavelengths were taken into account) was 7.1% and 25.8% for the Black Sea and algal culture data, respectively. *Maffione and Dana* [1997] showed, based on Mie calculations performed for nonblooming conditions, that the use of a constant value of χ_p results in a likely standard error in b_{bp} of about 10%, which is roughly the same as the error reported here for the Black Sea. A more important deviation of $b_{bp\text{estimated}}$ was expected from the laboratory data (Figure 8b) because the phytoplankton species exhibited a larger variation of χ_p. The error in b_{bp} was wavelength-dependent in both cases. In the Black Sea, the error decreased with the wavelength. At 555 nm, the error roughly reflects the variability in χ_p observed in the data. On the other hand, the error increased with the wavelength for the algal culture data. Since the measured values of χ_p (∼1.30) were much higher at 555 nm than the constant value adopted here (1.18), and since χ_p decreased from 555 nm to 443 nm for most of the species, the bias on the estimation of b_{bp} was smallest in the blue part of the spectrum. In any case, the spectral shape of b_{bp} may be significantly influenced by the wrong assumption that χ_p does not depend on the wavelength.

5. Conclusion

[27] The variability of the conversion factor χ_p, which relates the backscattering coefficient to the VSF measured at fixed angles, was studied under various conditions. The VSF data set consisted of in situ and algal culture measurements. The in situ data were acquired for nonblooming phytoplankton in a coastal environment of the Black Sea. The algal culture measurements pertained to phytoplankton species that are commonly found in the ocean. The latter data set is of interest because it may be representative for phytoplankton blooms in natural waters.

[28] The analyses of the Black Sea data showed that the mean value of χ_p(140°) at 555 nm was in agreement within ±2.5% with previous measurements and theoretical findings [*Boss and Pegau*, 2001]. Furthermore, the variability was small during the experiment. Our data thus support the assumption of using a constant value of χ_p at 140° to derive the backscattering coefficient in nonblooming oceanic waters. However, our laboratory measurements suggest that this assumption may be strongly inaccurate in the case of phytoplankton blooms. The in situ measurements also

revealed that the mean value of χ_p in the range 110°–130° is much higher than previously published results [*Oishi*, 1990; *Boss and Pegau*, 2001]. Therefore χ_p should not be considered as a constant in all types of waters. Such an assumption may lead to results for backscattering coefficient that deviate up to 15% from the correct value at 120° (Table 2), which is the fixed angle recommended by *Oishi* [1990]. The differences were related to the sensitivity of χ_p to the size distribution of the particles. In particular, a monodispersed mode of nonliving particles explained the measured values of χ_p. The occurrence of a modal distribution of particles in the study area was corroborated by the significant spectral variation of $\tilde{b}_{bp}$ observed during the experiment [*Chami et al.*, 2005]. Nevertheless, based on the agreement between the algal culture measurements and previous computations [*Oishi*, 1990], in the case of phytoplankton blooms conditions, the use of $\chi_p(120°)$ at 555 nm is recommended rather than $\chi_p(140°)$.

[29] The spectral variability of χ_p was small in the Black Sea (±6%) compared to that for the algal culture measurements (±20%). We tested the assumption that $\chi_p(140°)$ is wavelength-independent and found that the particulate backscattering coefficient b_{bp} would be estimated within ±10% error in nonblooming waters. Therefore a wavelength-independent value of χ_p may be assumed provided that careful attention is paid to the interpretation of the products derived from b_{bp}, such as the modeled sea surface reflectance, for remote sensing applications. However, χ_p should definitely be regarded as wavelength-dependent in the case of phytoplankton blooms.

Table 6. Relative Error in the Estimates of b_{bp} Assuming $\chi_p(140°)$ to Be Constant[a]

	443 nm	490 nm	555 nm	All Wavelengths
Black Sea	8.9	6.5	5.6	7.1
Algal culture	23.4	24.5	26.2	25.8

[a]Relative error is in %. The value proposed by *Boss and Pegau* [2001] was used, i.e., $\chi_p(140°) = 1.18$.

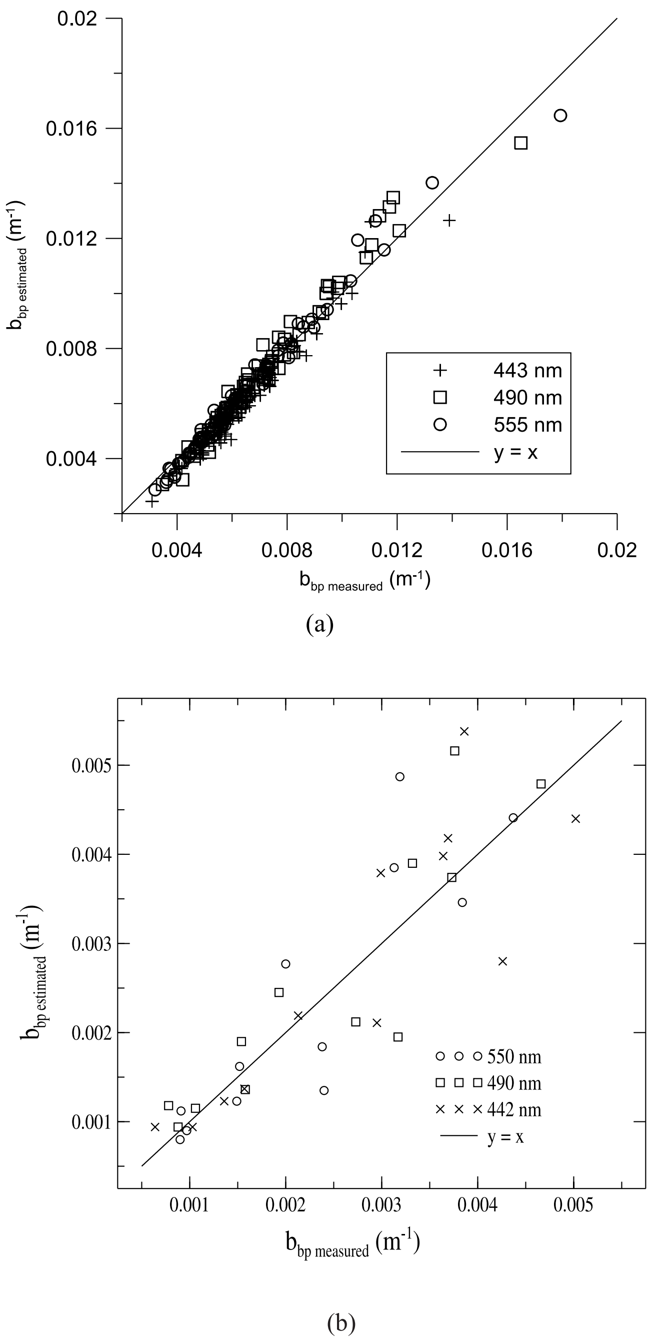

Figure 8. Comparison between b_{bp} estimated using a constant value of $\chi_p(140°)$ equal to 1.18 and b_{bp} measured (a) in the Black Sea and (b) in the laboratory.

Notation

b_b backscattering coefficient (m^{-1}).
b_{bp} particulate backscattering coefficient (m^{-1}).
$\tilde{b}_{bp}$ particulate backscattering ratio.
$\beta(\theta)$ volume scattering function at the scattering angle θ (m^{-1} sr^{-1}).
$\beta_p(\theta)$ particulate volume scattering function at the scattering angle θ (m^{-1} sr^{-1}).
$\beta_w(\theta)$ volume scattering function of pure seawater at the scattering angle θ (m^{-1} sr^{-1}).
χ_t conversion factor when the contribution to the volume scattering function from pure seawater is not removed.
χ_p conversion factor when the contribution to the volume scattering function from pure seawater is removed.
χ_w conversion factor related to pure seawater.
n_p real part of the refractive index.
n'_p imaginary part of the refractive index.
ν Junge exponent.
θ scattering angle (deg).
r_{mean} mean radius of the lognormal size distribution.
RMS relative root mean square error

$$\mathrm{RMS} = \sqrt{(1/n)\sum_{i=1}^{n}\left(\left(H_{i\mathrm{estimated}} - H_{i\mathrm{measured}}\right)/H_{i\mathrm{measured}}\right)^2},$$

where n is the number of measurements and H_i is the parameter being investigated (for example, H_i could be χ_p or b_{bp}).
σ standard deviation.
VSF volume scattering function.

VSM Volume Scattering Meter.
LABVSM Laboratory Volume Scattering Meter.

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