Optical properties of the particles in the Crimea coastal waters (Black Sea)


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[1] A field experiment was carried out in summer 2002 on an oceanographic platform near the coast of Crimea, in the Black Sea. For the first time, the spectral volume scattering function (VSF) was measured for a wide range of scattering angles (i.e., from 0.6 to 177.3 degrees) using a recently developed device. Our analysis revealed that the mineral particles are the primary component influencing the scattering and backscattering coefficient in the study area. The good correlation obtained between the backscattering coefficient bbp and the nonalgal particles absorption coefficient showed that the absorption efficiency of the mineral particles is high in the second half of the experiment. The ratio Chla/cp (where Chla is the chlorophyll a concentration and cp is the beam attenuation coefficient) did not correlate with the backscattering ratio and thus could not be used in this experiment as an alternative proxy to estimate the bulk composition of the particles. The spectral variation of bp (the scattering coefficient) and bbp (the backscattering coefficient) was less steep than what can be found in the open ocean waters. That was explained by the influence of the absorption on the scattering process, especially in the blue, as a consequence of the anomalous dispersion. The average backscattering ratio bbp varied spectrally within 4%. Nevertheless, a high spectral variability of bbp (around 30%) was observed suggesting that the use of a flat spectral variation is not accurate in coastal zones.


1. Introduction

[2] The Black Sea is subject to a considerable anthropogenic impact due to a large drainage basin accompanied by a high population density. The Black Sea is representative of a human-impacted enclosed area. Severe changes have been documented in the ecosystem of the Black Sea over the last decades [Murray, 1991; Aubrey et al., 1996; Besiktepe et al., 1999]. The primary ecological problem is the massive influx of nutrients and pollutants coupled with the poor ventilation of the deep water [Cociasu et al., 1997]. As a result, the natural balance of the ecosystem has been modified and the major part of the Black Sea, particularly its northwestern region, has become critically eutrophic and hypoxic [Zaitsev and Mamaev, 1997; Konovalov et al., 1999; Shiganova et al., 1998; Sur et al., 1994]. Eutrophication caused a substantial modification of the phytoplankton community structure as well as an increase in the intensity and frequency of microalgal blooms.

[3] Satellite observations of the Black Sea are often used to estimate the abundance of the water constituents (primarily the phytoplankton pigments) [Nezlin et al., 1999]. Previous studies showed that the atmospheric correction algorithms, applied for the processing of satellite sensor data like SeaWiFS, perform reasonably well [Burenkov et al., 1999]. Nevertheless, the standard pigment concentration products as delivered by CZCS and SeaWiFS sensors exhibit a significant disagreement with in situ data in the offshore part of the basin as well as in the coastal zones [Churilova et al., 2001; Barale et al., 2002]. To understand why standard algorithms do not work, the optical properties of the particles in the Black Sea water need to be carefully studied. Although several major international expeditions occurred between 1991 and 1995 (CoMsBlack and TuBlack projects), only a few measurements were devoted to marine optics in the Black Sea [Mankovsky, 1971; Mankovsky et al., 1998]. Exhaustive optical data sets that include the absorption together with the scattering and backscattering coefficients are required to develop local remote sensing algorithms.

[4] A field experiment was carried out in summer 2002 in the Crimea Peninsula, a coastal area of the Black Sea, to characterize the optical properties of the marine particles.
For the first time, the spectral volume scattering function (VSF) was measured over nearly the complete angular range of scattering angles. The Volume Scattering Meter (VSM) [Lee and Lewis, 2003] instrument was used. Contrary to other equipments that are commercially available, with the VSM instrument, the scattering and backscattering coefficients are derived from the integration of the VSF. Therefore this provided a good opportunity to improve our knowledge regarding the scattering and backscattering coefficients in coastal zones, especially their spectral shape, which, for the latter, remains insufficiently known. The backscattering properties are of particular interest since they contribute significantly to the upward signal measured by a satellite sensor. In the current paper, the variability of the scattering and backscattering coefficients are studied together with the absorption data. The scattering properties are analyzed in terms of the particulate composition of the water body. The spectral variation of the scattering coefficients is discussed in the last part of the paper.

2. Material and Methods

[5] Bio-optical measurements were collected in summer 2002 from 27 July until 15 August on an oceanographic platform of the Marine Hydrophysical Institute of the National Academy of Sciences of Ukraine (Figure 1). The platform is located at 44°23′N and 33°59′E which is 600 m offshore from the southern coast of Crimea, near the city of Katsiveli. The deck of the platform is 12 m above sea level and measures 20 m by 20 m. The bottom depth is 33 m. The platform is equipped with an ADCP (acoustic Doppler current profiler) instrument which routinely collects currents data. A meteorological station that provides the wind speed and direction is also available on the platform. The optical measurements were collected on the southern seaside part of the deck, which is always illuminated by the Sun.

2.1. Chlorophyll Concentration and Particulate Absorption

[6] The sampling and data processing was performed according to the ocean optics protocols recommended for the satellite ocean color sensor validation [Fargion and Mueller, 2000]. Water samples (132 in total) for the absorption measurements were collected once a day (at 8 h GMT) at fixed depths (0, 4, 8, 12, 16, 20 m) using a 5-L Niskin bottle. Duplicate 1000-mL subsamples were filtered onto 25-mm glass fiber filters (Whatman GF/F). The filters were then stored in liquid nitrogen for a few days before analysis in the laboratory.

[7] The particulate absorption measurements were achieved based on the methods described by Yentsch [1962] and Mitchell and Kiefer [1988]. The optical density of the filters was measured relatively to a blank filter saturated with filtered seawater using a dual beam spectrophotometer (SPECORD - M40, Carl Zeiss). The measured optical density at 750 nm was subtracted from the spectra and a correction for the path length amplification effects using the beta correction method of Mitchell [1990] was applied. The separation of the particulate absorption into phytoplankton and other components is based on the methanol extraction method [Kishino et al., 1985]. The measurement made before the extraction with methanol provides the total particulate absorption coefficient \( a_p(\lambda) \) while the de-pigmented particle absorption coefficient \( a_{NAP}(\lambda) \) is obtained after the extraction. The parameter \( a_{NAP} \) is consistent with the absorption by the detrital particulate matter and is thus referred as the nonalgal particle absorption coefficient. The phytoplankton absorption coefficient \( a_{ph}(\lambda) \), which represents the absorption by the living particles, is obtained by difference between \( a_p(\lambda) \) and \( a_{NAP}(\lambda) \).

[8] The chlorophyll \( a \) (Chla) concentrations were determined using the standard fluorometric method [Holm-Hansen et al., 1965]. Pigments were extracted in 90% acetone in the dark at 6–8°C for 18 hours.

2.2. Scattering Measurements

[9] The measurements of the volume scattering function were routinely carried out using the VSM instrument, recently developed at the Marine Hydrophysical Institute (Ukraine) in cooperation with the Satlantic Inc. Company (Canada) [Lee and Lewis, 2003]. The VSM provides measurements of the VSF between 0.6 and 177.3 degrees with

![Figure 1. Location of the oceanographic platform.](image)
an angular resolution of 0.3 degrees. A light source and a photodetector are fixed and the measurement angle is modified via the rotation of a special periscope prism with three reflecting facets. The shape of the prism together with precise design geometry allow the detection of the scattered radiance practically over the full angular range. When the measurement angle is equal to zero, the instrument allows also the measurement of the beam attenuation coefficient $c$. Despite their large differences in design and calibration, consistent intercomparisons of the backscattering ratio were found between the VSM instrument and two other devices, namely the ECO-VSF (Wetlabs Inc.) and Hydroscat (HOBI-Labs Inc.) [Boss et al., 2004]. The differences were within 10%, which is sufficiently small to avoid significant uncertainties of the derived geophysical products like the bulk refractive index of the particles. We used the same VSM instrument that was used by Lee and Lewis [2003] and Boss et al. [2004], with additional spectral measurements obtained by changing an optical filter [see Lee and Lewis, 2003]. The calibration of the VSM was carried out just before the experiment. A solution that consisted of latex polystyrene microspheres with precisely known geometry and refractive index was used. Since the beads are nearly spherical, the Mie theory allows to predict their VSF and thus, to calibrate the instrument. A set of beads size ranging from 0.6 μm to 160 μm was tested. The uncertainty in the VSF measurements based on the calibration was less than 10%. The uncertainty in the derived backscattering ratios was also within 10%. During the calibration experiment, a Wetlabs ac-9 instrument was used to measure the beam attenuation and scattering coefficients of the solution. The agreement with the VSM data was within ±1%. A post-deployment calibration confirmed that the instrument did not drift during the field experiment.

[10] The subsamples from the same Niskin bottle used for the Chla concentration and absorption measurements were introduced in the chamber of the VSM for analysis, providing us with 132 concurrent measurements of $a_p$, $a_{NAP}$, $a_{ph}$, Chla and the VSF. The measurements of the VSF were corrected for attenuation along the path length using the attenuation coefficient provided by the VSM.

[11] The scattering and the backscattering coefficients are computed by integrating the VSF, hereafter noted $\beta(\theta)$, over the whole and the half range of scattering angle, respectively (equations (1) and (2)).

\[
b = 2\pi \int_0^\pi \beta(\theta) \sin \theta d\theta \quad \text{(1)}
\]
\[
b_h = 2\pi \int_{\pi/2}^\pi \beta(\theta) \sin \theta d\theta. \quad \text{(2)}
\]

[12] To compute these coefficients, the VSF is extrapolated in the near-forward direction to $0^\circ$ through using a

Figure 2. Variation of the water temperature during the experiment.

Figure 3. Variation of the Chla concentration during the experiment.
power law dependency [Mobley et al., 2002]. In the full backward direction, the VSF is extended to 180 degrees by assuming constant values of the VSF between 177.3° and 180° according to Mobley et al. [2002]. The absorption coefficients derived from the VSM data when the scattering coefficient \( b \) is subtracted from the beam attenuation coefficient \( c \) were consistent within 5% with the absorption measurements using filters, which is an additional check of the VSM calibration procedure.

The backscattering ratio is defined as the ratio of the backscattering coefficient to the total scattering coefficient (equation (3)).

\[
\tilde{b}_b = \frac{b_b}{b}
\]

For the scattering spectra investigation, the VSM is equipped with a revolving wheel with three color filters, namely 443 nm, 490 nm and 555 nm.

In order to obtain the scattering properties of the particles, the VSF by the pure seawater was subtracted from the VSF measurements applying the coefficients provided by Morel [1974]. The correction for the salinity was carried out according to Boss and Pegau [2001]. In what follows, the particulate scattering and backscattering coefficients are denoted by \( b_p \) and \( b_{bp} \) and the particulate backscattering ratio is noted \( \tilde{b}_{bp} \).

3. Results

3.1. Environmental Conditions of the Field Experiment

The oceanographic platform was under the influence of an atmospheric anticyclone during the first days of measurements. A low pressure system passed over the Black Sea region during the first week (on 6–7 August) producing important changes in the weather conditions, especially an increase of the wind speed up to 12 m s\(^{-1}\). The thermal stratification then changed near the platform (Figure 2). The mixed layer was relatively shallow (\( \sim 15 \) m) until 6 August. After 8 August, the stratification vanished and the mixed layer depth increased up to 25 m. The wind gusting also modified the direction of the measured coastal currents. The eastern transport of the seawater along the coast observed before 6 August was replaced by a western transport in August. This sharp currents reversal led to an increased turbidity of the water and the daily average depth of the Secchi disk changed from 13 m to 8 m.

3.2. Chlorophyll \( a \) Concentration and Specific Absorption Spectra

The variation of the concentration of Chla is shown in Figure 3. At the beginning of the experiment and within the mixed layer, the Chla concentration varied within the range 0.45–0.7 mg m\(^{-3}\), which is typical of summer conditions [Berseneva and Churilova, 2001]. The concentration of Chla increased up to 0.9–1.2 mg m\(^{-3}\) below the thermocline around 15–20 m. After 6 August, the intensification of the wind and the reversal of the current changed both the thermal and biotic balances in the upper layer of the sea. After the wind gusting, the Chla concentration increased to 1.2–2.1 mg m\(^{-3}\) and was rather uniformly distributed between 0 m and 20 m. The sharp increase of Chla is consistent with the thermal front, which is noticeable on 8 August in Figure 2. After 11 August, the Chla at the surface decreased and the depth of Chla maximum in-
increased from 8 m (12 August) to 16 m (14 August) owing to increased thermal stratification.

The Chla specific absorption spectra, \( a_{\text{ph}}(\lambda) \), which is defined as the ratio of the chlorophyll absorption coefficient \( a_{\text{ph}} \) divided by the Chla concentration, contains information on the community structure of the phytoplankton [Bricaud et al., 1995]. The surface spectra of \( a_{\text{ph}} \), as shown in Figure 4, exhibit significant differences between the samples collected before and after 6 August when the meteorological changes occurred. In particular, the blue to red ratio (i.e., \( a_{\text{ph}}(443)/a_{\text{ph}}(676) \)) significantly decreases from 3.30 ± 0.57 to 2.44 ± 0.26 after 6 August. A higher packaging effect is thus observed from 8 to 14 August. The population of the phytoplankton changed with the occurrence of larger or low light acclimated cells that typically have a low blue to red ratio. However, it is not possible here to quantify the role of the accessory pigments in this study since HPLC data are not available.

3.3. Nonalgal Particles Absorption

The distribution of the nonalgal particles absorption coefficient \( a_{\text{NAP}} \) at 443 nm is plotted in Figure 5. During the experiment, \( a_{\text{NAP}} \) varied from 0.03 to 0.1 m\(^{-1}\). Before 6 August, the relatively high \( a_{\text{NAP}}(443) \) values occurred in the thermocline and in the deeper layers (16–20 m). The mixing induced by the wind after 6 August caused an increase of \( a_{\text{NAP}}(443) \). The uniform distribution, which is observed from 6 to 10 August, vanished at the end of the experiment. The maximum of \( a_{\text{NAP}}(443) \) is then observed near the thermocline (16 m), presumably reflecting the sinking and collection of the particles in the layer where the density gradient is maximum. Significant differences occur when comparing the distribution of \( a_{\text{NAP}}(443) \) with the Chla concentration (Figure 3). For instance, the patch of high absorption coefficients of the nonalgal particles that is observed near the bottom on 30 July is not seen in the Chla distribution. Quantitatively, the weak covariability between the phytoplankton and the nonalgal particles absorption is expressed through their low correlation coefficient of 0.24.

The variation of the ratio \( a_{\text{NAP}}(443)/a_{\text{p}}(443) \) is plotted in Figure 6. This ratio provides the contribution of the nonalgal particles to the total particulate absorption at 443 nm. Previous results obtained in 1996–1997 in the Black Sea showed that \( a_{\text{NAP}}(443)/a_{\text{p}}(443) \) can vary significantly from 20% for a quiet summer period up to 80% after intensive storms in the coastal waters [Berseneva and Churilova, 2001]. Here a mean value of 53% is observed. It is significantly higher than the values observed in the open ocean, where most of the data ranges within 25–40% [Bricaud et al., 1998; Cleveland, 1995]. High ratios as measured in near-coastal areas like the Crimea Peninsula.
could be partly explained either by the resuspended bottom particles or by the rivers runoff. During the experiment, the variation of $a_{\text{NAP}}(443)/a_{p}(443)$ ranged from 40% to 88%. On 30 July, the high value of the ratio $a_{\text{NAP}}(443)/a_{p}(443)$ at 16–20 m, is due to the resuspension of nonalgal particles from the bottom, which is consistent with the occurrence of an uniform temperature profile (see Figure 2). Except for 30 July, the highest values were observed when the low-pressure system arrived in the study area, especially just after the days when the gusts of wind were the strongest (6–7 August). A few days later, $a_{\text{NAP}}(443)/a_{p}(443)$ decreased from 60% to 44%, implying the influence of the living phytoplankton on the total particulate absorption is higher than what was observed in the beginning of the experiment. It occurred simultaneously with the change in the phytoplankton community structure previously highlighted (Figure 4) and due to the advection of another water mass in the study area.

### 3.4. Distribution of the Scattering Coefficients at 555 nm: $b_{p}$, $b_{bp}$, and $b_{bbp}$

[20] The daily measurements of the VSF for almost three weeks allow us to contour the vertical distribution of the scattering (Figure 7) and backscattering (Figure 8) coefficients of the particles with respect to time. In general, $b_{p}$ and $b_{bp}$ exhibit similar vertical and temporal features. Both coefficients are fairly homogeneous after 1 August, even if a weak heterogeneity can be observed, for example on 6 August at 4 m and on 14 August at 16 m. Most of the values of $b_{p}$ are within the range 0.2–0.5 m$^{-1}$. The $b_{bbp}$ coefficient is mostly within 0.003–0.010 m$^{-1}$. However, there is one sample at the surface on 30 July where both $b_{p}$ and $b_{bp}$ highly increased. This patch also corresponds with an increase of absorption by nonalgal particles (see Figure 5).

[21] The backscattering ratio $b_{bbp}$ contains information on the particle type and size distribution. It also provides one of the most relevant information since it plays a major role in the upward signal and in the satellite remote sensing. Indeed, as demonstrated in a previous study [Mobley et al., 2002], the use of a phase function having the correct $b_{bbp}$ drastically reduces (by 1 order of magnitude) the percentage error in the computed remote sensing reflectance ($R_{rs}$) when computing $R_{rs}$ from a measured $b_{p}$ and a modeled $b_{bbp}$. The variability of $b_{bp}$ at 555 nm for all days is plotted in Figure 9. The range of variation of $b_{bp}$ for
each wavelength and the averaged values are reported in Table 1. Figure 9 shows that $b_{bp}$ exhibits several patches of heterogeneity through the water column and with time. It is worth noting that the weak values of $b_{bp}$ observed at the surface on 30 July are inversely correlated to the patch of high values of $b_p$ and $b_{bbp}$ mentioned above. The general trend is an increase of $b_{bp}$ with the depth and the highest values are often observed near the bottom. Typically, the value of $b_{bp}$ near the bottom is roughly 10% higher than at the surface waters. For example, at 555 nm, the surface samples have a mean value of 1.86% and vary from 1.2% (the minimum is observed on 29 July) to 2.6% (the maximum is observed on 14 August). At the same wavelength, the bottom samples have a mean value of 2.06% with a range of variability from 1.64% (on 5 August) to 2.64% (on 30 July). As a comparison, the Petzold’s phase function [Petzold, 1972] provides a backscattering efficiency of 1.83%. Therefore the important variability as observed on a significant number of $b_{bp}$ measurements suggests that the use of a single phase function, like the Petzold one, is not appropriate to compute the apparent optical properties using radiative transfer modeling.

4. Discussion

4.1. Interpretation of the Scattering Measurements in Terms of Particulate Composition

[22] Previous works [Ulloa et al., 1994] demonstrated that $b_{bp}$ is a function of the shape of the particle size distribution: $b_{bp}$ usually increases with the occurrence of submicrometer particles because they have a pronounced scattering signature in the backward direction. The parameter $b_{bp}$ is also a function of the bulk refractive index of the particles [Twardowski et al., 2001; Boss et al., 2004]; $b_{bp}$ typically increases with the proportion of highly refractive particles. Therefore the backscattering ratio $b_{bp}$ is a key optical parameter for the characterization of the marine particles.

[23] In this study, the magnitude of $b_{bp}$ is relatively high exceeding 2% several times. In fact, such values of $b_{bp}$ are too high for biogenic particles that usually dominates in case I waters. Previous theoretical and experimental studies [Morel and Bricaud, 1981; Ahn et al., 1992; Ulloa et al., 1994] showed that the backscattering ratio of algal cells is very low (typically less than 1% and mostly around 0.5%). The magnitude obtained in our experiment is systematically greater than 1% and thus suggests the presence and significant contribution of the mineral particles to the optical properties near the oceanographic platform. To highlight these particles, the model developed by Twardowski et al. [2001] to estimate the bulk refractive index of the particles $n_p$ from $b_{bp}$ (equation (4)) is applied to our data at 555 nm,

$$n_p(b_{bp}) = 1 + 1.671 \frac{b_{bp}}{C_0/C_1} = 1 + 1.671 \frac{b_{bp}}{0.582}.$$ (4)

[24] The expected uncertainties in the retrieval of $n_p$ from the Twardowski model were evaluated at ±0.02 [Twardowski et al., 2001] and thus they should not limit our ability here to differentiate waters dominated by phytoplankton ($n_p \sim 1.05$) and minerals ($n_p \sim 1.16$). The estimations of $n_p$ using equation (4) are shown in Figure 10. The bulk refractive index varied from 1.12 to 1.20, which is consistent with a mineral composition of the particles commonly found in the ocean, such as quartz ($n_p = 1.15$) or mica ($n_p = 1.20$) [Lide, 1997]. The water body was then mineral dominated during the experiment. As a result, the mineral particles are the primary component influencing the scattering and backscattering coefficient in the study area. This is confirmed by the lack of correlations between Chla with $b_p$, $b_{bp}$ (not shown) and $b_{bbp}$ (Figure 11). Two bio-optical models previously developed to derive $b_{bp}$ from Chla, namely the Twardowski et al. [2001] model and the Morel and Maritorena [2001] model, were evaluated in this study. The results are presented in Figure 12 and show that the Twardowski model performs better than the Morel and Maritorena model.

<p>| $b_{bp}$ in Percent, for the Wavelengths 443 nm, 490 nm, and 555 nm |
|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>443 nm</th>
<th>490 nm</th>
<th>555 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average of $b_{bp}$</td>
<td>1.91</td>
<td>1.97</td>
</tr>
<tr>
<td>Range of variation of $b_{bp}$</td>
<td>1.2–3.2</td>
<td>1.2–2.6</td>
</tr>
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</table>
model, were expectedly unsuccessful when applied to our data (Figure 11). It is explained by the fact that these models were made on the basis of measurements obtained in phytoplankton dominated waters. To characterize the absorption properties of the mineral particles present near the platform, the relationship between \( b_{bp} \) at 555 nm and the absorption by the nonalgal particles \( a_{NAP} \) at 400 nm was studied (Figure 12). A correlation is found for the measurements collected after 7 August; almost 60% of the variability of the backscatter is explained by \( a_{NAP} \). It strongly suggests that some of the mineral particles present after the passage of the low pressure system have

\[
\begin{align*}
\text{Figure 10.} & \quad \text{Variation of the refractive index of the particles at 555 nm, estimated using Twardowski model (equation (4)).}
\end{align*}
\]

\[
\begin{align*}
\text{Figure 11.} & \quad \text{Scatterplot of} \quad b_{bp} \quad \text{at 555 nm as a function of the Chla concentration. The models developed by Morel and Maritorena [2001] \( (b_{bp} = 0.002 + 0.01 [0.50 - 0.25 \log_{10}(\text{Chla})]) \) and Twardowski et al. [2001] \( (b_{bp} = 0.0096 [\text{Chla}]^{-0.253}) \) are also shown.}
\end{align*}
\]
a significant absorption efficiency. Such particles probably explain the patterns observed in the Figures 5 and 10 on 14 August at the surface and at 16 m. Before 8 August, no correlation is found between \( bbp \) and \( a_{NAP} \), thus suggesting that the mineral particles absorb very weakly. The absorption efficiency of the mineral particles is then highly variable in the study area. As a result, the highly refractive materials near the platform are probably issued from different sources.

4.2. Analysis of the Particulate Volume Scattering Function

[25] Previous studies [Jerlov, 1953; Tyler, 1961; Deirmendjian, 1963; Beardsley et al., 1970] investigated the use of the VSF at 45° to derive the scattering coefficient and showed that a linear correlation exists between \( \beta_p(45°) \) and \( b_p \). This kind of relationship is of interest inasmuch as it could be used to estimate the refractive index of suspended matter in seawater [Zaneveld and Pak, 1973; Zaneveld et al., 1974]. Here the measured particulate VSF at 45° was found to be correlated with \( b_p \) (\( r^2 = 0.77 \)), as expected. The averaged value of the ratio \( \beta_p(45°)/b_p \) was 2.0 \( 10^{-2} \pm 0.3 \ 10^{-2} \ sr^{-1} \), which is 1.7 times lower than what was measured in the offshore part of the Black Sea by Mankovsky [1971] (3.4 \pm 0.2 \ sr^{-1} ). As the nature of the particles in coastal waters is often specific and variable (as previously observed in this study), a large deviation of the ratio from the values measured in offshore waters is expected [see also Morel, 1974]. The relationship between \( \beta_p(45°) \) and \( b_p \) obtained in this study also showed a high dispersion of the data, as inferred by the value of \( r^2 \). Our experiment provides new data on the VSF at small angles that allows us to examine the relationship between the VSF at different angles in the forward peak region (<10°) and \( b_p \) in order to determine the scattering angles which gives the best correlation. The highest correlation (\( r^2 = 0.96 \)) was found when the particulate VSF at 4° was used (Figure 13a). This is consistent with the observations made 3 decades ago by Kopelevich and Burenkov [1971] and Mankovsky [1971], who also found a highest correlation with the VSF at 4°. Kopelevich and Burenkov [1971] and Mankovsky [1971] also observed that the curves \( \beta_p/b_p \) of their data crossed each other at 4° meaning an apparent constancy of the ratio \( \beta_p(4°)/b_p \). This was supported theoretically by Morel [1974], who showed, based on Mie calculations, that \( \beta_p(4°)/b_p \) is weakly dependent on the refractive index and the size distribution. Nevertheless, the property of the invariance of \( \beta_p(4°)/b_p \) has never been verified empirically since Mankovsky’s [1971] study. The mean value of \( \beta_p(4°)/b_p \) calculated on the overall data set was 9.3 \pm 0.4 \ sr^{-1} , which is consistent within 12% with the measurements performed by Mankovsky [1971] (10.5 \pm 2.0 \ sr^{-1} ). Furthermore, the variability was very low (\pm 4.3%) despite the fact that the water mass and the nature of the particles significantly changed during the experiment. As a result, while the use of the VSF at 45° to derive \( b_p \) was shown to be highly dependent on the study area and thus, on the particulate composition of the water column, we verified here that the VSF at 4° appears to be the least sensitive parameter that could be apparently used in different waters to estimate \( b_p \) with a reasonable accuracy. The uncertainty in the derivation of \( b_p \) using \( \beta_p(4°) \) is 12% based on the comparison with previous studies and is much lower (\pm 4.3%) based on our single experiment. Therefore the ratio \( \beta_p(4°)/b_p \) is quite useful given the relative ease by which \( \beta_p(4°) \) can be measured (for example, using the LISST instrument, Sequoia Inc.) compared to the difficulty of measuring the full angular VSF.

[26] As demonstrated in several studies [Oishi, 1990; Maffione and Dana, 1997; Boss and Pegau, 2001], the backscattering coefficient \( bbp \) could be efficiently derived
from the VSF at $140^\circ$. In this study, $\beta_p(140^\circ)$ was highly correlated with $b_{bp}$ ($r^2 = 0.96$) (Figure 13b). The slope of the fitted relationship between $\beta_p(140^\circ)$ and $b_{bp}$ was 0.147 sr$^{-1}$. The coefficient $\beta_p(140^\circ)$ at 555 nm was also significantly correlated with $a_{NAP}$ at 400 nm ($r^2 = 0.60$), as expected from Figure 12. The full shape of the VSF allows us to investigate the use of angular ratios of the volume scattering coefficients to derive more information on the scattering properties of the particles. On the basis of Mie calculations, Morel [1974] showed that the angular ratio of the VSF at $10^\circ$ and $2^\circ$, $\beta_p(10^\circ)/\beta_p(2^\circ)$, is highly sensitive to the refractive index of the particles and thus, to their composition. Morel [1974] also highlighted the usefulness of this ratio.
because it expresses the degree of dissymmetry of the particulate VSF. Therefore, $b_p(10^6)/b_p(2^6)$ could be informative of the variability of the scattering properties of the particles during the experiment. The value of the ratio at 555 nm varied from $2.2 \times 10^{-2} \pm 0.3 \times 10^{-2}$ before 6 August to $2.7 \times 10^{-2} \pm 0.2 \times 10^{-2}$ after the wind gusting, which is significantly higher and corroborates the arrival of another water mass near the platform after 6 August as previously suggested by the variation of the Chla specific absorption coefficient (Figure 4) and by the correlation between $b_{bp}$ and $a_{NAP}$ (Figure 12).

Since $b_p(4^6)$ and $b_p(140^6)$ are well representative of the scattering and backscattering coefficients, respectively (Figure 13), the ratio $b_p(140^6)/b_p(4^6)$ was examined and related to the backscattering ratio. A linear significant correlation was found ($r^2 = 0.88$) (Figure 14a). Therefore it seems that the backscattering ratio could be efficiently derived from the ratio of the VSF at 140° and 4°. To evaluate the accuracy of the fixed angle method, we compared the backscattering ratio $\tilde{b}_{bp}$ estimated using the angular ratio of the VSF (hereinafter referred to as $\tilde{b}_{bp}$ estimated) with the backscattering ratio obtained by integrating the full VSF (hereinafter referred to as $\tilde{b}_{bp}$ measured) (see equation (3)). The estimation of the backscattering ratio was performed using the regressions mentioned above; clearly, the backscattering coefficient $b_{bp}$ was derived from $b_p(4^6)$ using the slope 0.147 and the scattering coefficient $b_p$ was derived from $b_p(4^6)$ using the regression coefficient of 9.3. The value of the slope of the linear fit between the $b_{bp}$ estimated and $b_{bp}$ measured was 0.98 (Figure 14b), which is satisfying. The accuracy of the retrieval of $\tilde{b}_{bp}$, which was calculated using the relative root mean square error, was 7.0%. Therefore the approach that consists of using the fixed angle VSF at 4° and 140° to derive the backscattering ratio is promising and useful since the full angular shape of the VSF is still rarely measured. Currently, this method could be applied with instruments that are commercially available like the LISST (Sequoia Inc.), with regard to the VSF at 4°, and Hydroscat (Hobilabs Inc. [Maffione and Dana, 1997]) or Eco-VSF (Wetlabs Inc.) with regard to the VSF at 140°.

4.3. Relationship Between the Backscattering Ratio and the Parameter $Chla/c_p$

Boss et al. [2004] recently used the relationship between the backscattering ratio and the parameter Chla/c_p (where c_p is the particulate beam attenuation coefficient) as an empirical support to the inversion of the backscattering ratio in terms of the particulate refractive index based on the Mie theory. The idea is based on the fact that Chla and c_p are not correlated in coastal zones. Because c_p is mostly due to inorganic suspended matter, a high contribution of the minerals will induce low values of the ratio Chla/c_p while a significant contribution of the phytoplankton will provide high values of Chla/c_p. Boss et al. [2004] showed that the backscattering ratio could be inversely correlated with the parameter Chla/c_p at 660 nm. In this study, since the backscattering ratio varied within the same range as that of Boss et al. [2004] (from 0.012 to 0.028) and because the mineral particles strongly dominates the signal, we wanted to verify their findings. Boss et al. [2004] proposed to use the wavelength 660 nm to reduce the influence of the phytoplankton on the c_p coefficient. Here we used the wavelength 555 nm instead of 660 nm which was not available. This is not a major problem because Chla was independent of $b_p$ at 555 nm in this experiment. Thus c_p(555 nm) is weakly affected by the phytoplankton and still remains a good indicator of the presence of inorganic materials. The measurements (Figure 15) show that the trend observed by Boss et al. [2004] does not hold in our study area. The parameter Chla/b_p(555 nm) was also tested (not shown) to remove the contribution of the absorption by the particles and to emphasize the influence of the mineral particles. Both variables ($b_{bp}$ and Chla/b_p(555 nm)) were observed to be uncorrelated as well.

![Figure 15](image-url)
Our data showed that the strategy of parameterizing the backscattering efficiency (Figure 11) and the scattering coefficients $b_p$ and $b_{bp}$ as a function of Chla fails here. This strategy was suggested by Gordon et al. [1988] relying on the basic idea that the scattering spectrum is roughly the inverse of the absorption spectrum. In this section, we show that the use of a combination of Chla with $c_p$ as an alternative proxy to estimate the bulk composition of the particles is no more useful. Apparently, the diversity of the particles found in coastal environments prevents building a reliable empirical algorithm to derive the Chla from optical data. Even if such a result was expected in coastal waters when the single Chla parameter is used, we believed that the ratio Chla/$c_p$ or Chla/$b_p$ would apply correctly in the Crimea Peninsula owing to the significant contribution of the mineral particles. Therefore the development of remote sensing and bio-optical algorithms in case II waters requires more sophisticated methodologies than the empirical approach. The algorithms, which are still currently being developed, based on the neural network method [Schiller and Doerffer, 1999; Gross et al., 2000] or more recently the genetic programming technique [Chami and Robilliard, 2002] should be robust enough to handle the inverse problem of the ocean color with a reasonable accuracy (less than 40%).

4.4. Spectral Variation of the Particulate Scattering and Backscattering Coefficients

4.4.1. Spectral Shape of $b_p$

To highlight the varying spectral shape of the scattering coefficient, the $b_p$ values are averaged over the whole data set and normalized with respect to their mean value at 555 nm (Figure 16). The spectral variation of $b_p$ presents non-linear features with a highest spectral dependency between 490 nm and 555 nm while it is fairly flat between 443 nm and 490 nm. Our mean spectrum is comparable with the average obtained in European coastal waters by Babin et al. [2003]. The standard deviation is significant (around 30%) and points out a high variability during the experiment. The spectral variation of the scattering coefficient $b_p(\lambda)$ was often parameterized as a $\lambda^{-1}$ power law for case I waters, which is realistic if the particles are non-absorbing and distributed according to a power law with a Junge parameter of 4 [Morel, 1988; Lee et al., 1994, Garver and Siegel, 1997]. A flat spectrum, especially between 443 nm and 490 nm, is typical of the presence of absorbing particles in the water column. It is explained by the theory of anomalous dispersion [Bricaud and Morel, 1986; Van de Hulst, 1957], which shows that the real part of the refractive index weakly decreases in the absorption bands of the particles. Thus, according to this theory, a high absorption will result in a lower scattering. In case I waters, the living algal cells together with the biogenic nonalgal particles are responsible for this effect since they increasingly absorb at short wavelengths. In case II waters, the effects of the living algal cells could be drastically reduced because of the higher contribution of the mineral particles. Previous studies demonstrated that the absorption by the mineral particles could vary by 1 order of magnitude in natural waters (typically from 0.001 to 0.01) [Bukata et al., 1995; Tassan and Ferrari, 1995; Bowers et al., 1996] or even more [Lide, 1997; Babin and Stramski, 2002]. Therefore the spectral shape of $b_p$ can have more complex features in the coastal zones [Babin et al., 2003] than in the open ocean waters because of the variability of the absorption efficiency of the mineral particles. In this study, the interpretation of the backscattering coefficients in terms of particulate composition showed the presence of colored mineral particles. The spectral shape of the particulate single scattering albedo $\omega_p$ (defined as the ratio $b_p/(a_p + b_p)$) (Figure 17) clearly demonstrates the significant influence of the absorption on the scattering process. The single scattering albedo exhibits an almost linear relationship with a significant drop at 443 nm (around 0.75). For the other wavelengths, a much smaller influence of the absorption on the scattering is expectedly observed ($\omega_p$ is greater
than 0.8). Therefore anomalous dispersion probably explains the fairly flat spectrum of \( \beta_p \).

### 4.4.2. Spectral Shape of \( \beta_{bp} \) and \( \beta_{bbp} \)

Currently, the backscattering properties of the oceanic particles remain poorly known even if some commercial instruments designed to measure \( \beta_{bp} \) are now available. So far, the lack of knowledge is even more important regarding the spectral behavior of \( \beta_{bp} \). For the open ocean waters, it was shown that the spectral variation of \( \beta_p \) and \( \beta_{bp} \) is not necessarily the same [Morel and Bricaud, 1981]. For this type of waters, Morel and Maritorena [2001] recently proposed to adjust the spectral dependency of \( \beta_{bp} \) depending on the Chla concentration. The basic idea relies on the fact that the living phytoplankton is not an efficient contributor to the backscattering processes and thus cannot be responsible for the spectral shape of \( \beta_{bp} \). Therefore a flat spectrum is assumed for the high levels of chlorophyll concentration (typically greater 2 mg m\(^{-3}\)) while a variation in \( \lambda^{-1} \) is adopted when small detritus particles dominate. The spectral shape of \( \beta_{bp} \) derived from our measurements is plotted in Figure 18. The convexity of the spectrum in the blue part is noticeable. The spectrum shows a maximum at 490 nm. A significant decrease of \( \beta_{bp} \) is observed from 490 nm and 555 nm (around 15%) as well as from 490 nm to 443 nm (around 6%). The depressive effect observed at 443 nm is due to the strong influence of the absorption on the scattering, as it was previously explained for \( \beta_p \). Here (i.e., for \( \beta_{bp} \)) the depressive effect is even more pronounced than what was showed for \( \beta_p \). A similar feature was observed for algal cells by Ahn et al. [1992]. The major difference between \( \beta_p \) and \( \beta_{bp} \) rests on the fact that \( \beta_p \) includes the forward scattering peak and thus, the diffraction process, which is independent of the absorption mechanisms. Therefore the absorption effects at 443 nm have a lower influence on the \( \beta_p \) coefficient when comparing with \( \beta_{bp} \), thus explaining the more pronounced depressive effect observed on the spectral shape of \( \beta_{bp} \). The variability of the spectral slope of \( \beta_{bp} \) calculated between 443 nm and 555 nm is around 20% during the experiment (the ratio \( \beta_{bp}(443)/\beta_{bp}(555) \) varied from 0.82 to 1.17), which is significant. As a result of this analysis, any single parameterization of the spectral shape of \( \beta_{bp}(\lambda) \) will be very difficult to describe in coastal zones.

[33] Because \( \beta_{bp} \) consists of the ratio of \( \beta_p \) with \( \beta_{pp} \), the effects of absorption at 443 nm on the scattering can be compensated and thus can be reduced with regard to the \( \beta_{bp} \) coefficient. A slight variation of 4% is observed on the mean \( \beta_{bp} \) coefficient from 490 nm to 555 nm while the spectrum is fairly flat between 443 nm and 555 nm (Figure 19). The spectral variation of \( \beta_{bp} \) then vary by less than 10% supporting the theoretical predictions [Ulloa et al., 1994; Twardowski et al., 2001] and some experimental observations [Twardowski et al., 2001]. Theoretically, a flat spectrum of \( \beta_{bp} \) is typical of the particles that are distributed according to a power law [Ulloa et al., 1994; Maffione and Dana, 1997]. Here it should be highlighted that an important spectral variability of \( \beta_{bp} \) was observed during the experiment. Figure 20 shows several significant examples of different \( \beta_{bp} \) spectra normalized at 555 nm. The samples selected in Figure 20 correspond to different types of events: 1 August at 20 m is characterized by a minimum of NAP absorption while 6, 8 and 14 August (at the surface) and 12 August at 16 m correspond to maxima of NAP absorption; 12 August at 12 m corresponds to a maximum of Chla. The spectral slopes are extremely variable. In the example of Figure 20, a flat spectrum is observed when the Chla is maximum and variable spectra are observed when NAP absorption is strong: flat (on 14 August), an increase with wavelength (during the windy days) or a decrease with wavelength (12 August at 16 m). When NAP absorption is minimum in Figure 20, \( \beta_{bp} \) decreases with wavelength. For the whole data set, the spectral slope of \( \beta_{bp} \) could depart from the flat shape by +30% when \( \beta_{bp} \) increases with wavelength (8 August at the surface) up to −20% (1 August at 20 m) when \( \beta_{bp} \) decreases with wavelength.
studies showed that monodispersed particles can have a strong wavelength dependency [Morel and Bricaud, 1981], depending on their size and composition. The significant spectral variation of $b_{bp}$ observed on certain days might suggest the occurrence of several modes of particles in the water column.

[33] We investigated the correlation between the spectral slope of $b_{bp}$ with other variables, typically the different absorption coefficients. For the whole data set, no correlation was found suggesting that it is not possible to derive a systematic law for the spectral variation of $b_{bp}$, as previously inferred by Figure 20. Nevertheless, since the optical properties of the particles were highly modified at the surface during the experiment, we focused on the spectral variation of $b_{bp}$ in the layer 0–4 m. The ratio of the backscattering efficiency between 443 nm and 555 nm (i.e., $b_{bp}(443)/b_{bp}(555)$), which tells us about the spectral slope of $b_{bp}$, was related to the parameter $a_{ph}/a_{nap}$ derived at 443 nm (Figure 21). The parameter $a_{ph}/a_{nap}$ is a good indicator of the importance of the absorption by phytoplankton relative to the absorption by non-chlorophyllous matter. The relationship plotted in Figure 21 allows to assess the role played by the phytoplankton and the NAP absorption in the spectral shape of $b_{bp}$. A significant positive correlation is observed ($r^2 = 0.76$); the spectral ratio of $b_{bp}$ increases from 0.70 to 1.20 with the parameter $a_{ph}/a_{nap}$. A depressive effect of $b_{bp}$ in the blue is often observed when the absorption by the nonalgal particles is dominant relatively to phytoplankton absorption ($a_{ph}/a_{nap} < 1$). The highest slopes (+30%) are observed when the absorption by nonalgal particles represents 88% and 66% of the total particulate absorption on 8 and 6 August, respectively. This is consistent with the fact the nonalgal particles are highly absorbing these days and thus they contribute to emphasize the convexity of the $b_{bp}$ spectrum. On the other hand, the spectra tend to be smoothed or linearly decreasing with wavelength when the relative importance of phytoplankton absorption is dominant.

Figure 20. Examples of the variability of the $b_{bp}$ spectra as observed for different days during the experiment; $b_{bp}$ is normalized at 555 nm.

Figure 21. Relationship between the ratio $b_{bp}(443) / b_{bp}(555)$ with the parameter $a_{ph}/a_{nap}$ at 443 nm for the surface layer 0–4 m during the experiment. The equation of the linear fit (solid line) is $b_{bp}(443) / b_{bp}(555) = 0.35 (a_{ph}/a_{nap}) + 0.58$ and $r^2 = 0.77$. 
absorption increases. Therefore the phytoplankton and NAP absorption have two opposite effects on the spectral shape of $b_{pp}$ in the surface layer. Because the phytoplankton cells usually have a larger size than the nonalgal particles, an increase of the ratio $q_{ph}/q_{np}$ is consistent with a nearly (i.e., within $\pm 10\%$) flat spectrum.

[35] Finally, as a result of our data analysis, we caution against the consideration of a spectrally neutral behavior of $b_{pp}$, which is often assumed [Mobley et al., 2002; Roessler and Boss, 2003], since it can be as far as 30% off. The implications for radiative transfer calculations which assume a constant spectrally invariant particulate phase function, like those based on Hydrolight [Mobley, 1994] or Monte Carlo simulations [Morel and Gentili, 1991], are important. Mobley et al. [2002] showed that a bias of 30% on the backscattering efficiency could induce an error on the marine reflectance up to 40%. Therefore our data suggest paying special attention to the interpretation of the modeled apparent optical properties (i.e., radiance or reflectance) when a neutral spectrum of $b_{pp}$ is assumed.

5. Conclusion

[35] A field experiment was conducted in summer 2002 in the Crimea coastal waters of the Black Sea. A set of optical and biological measurements were collected during 3 weeks on a platform located 600 m from the coast. The weather conditions during the experiment were marked by relatively strong gusts of wind, a few days after the beginning of the data acquisition. It is the first time that a significant amount of data on the spectral volume scattering function (angular range from 0.6 up to 177.3 degrees and three wavelengths) was collected in the Black Sea. On the basis of the analysis of the angular dependence of the VSF, the use of the volume scattering coefficient at 4° is recommended instead of the VSF at 45° to accurately estimate the particulate scattering coefficient in different types of waters. This study also showed that the backscattering ratio could be estimated using fixed angle measurements of the VSF, namely the ratio $\beta_p(140°)/\beta_p(4°)$, which is convenient since the full angular VSF is still difficult to measure. The interpretation of the scattering properties in terms of particulate composition was consistent with the occurrence of highly refractive material near the oceanographic platform meaning that the Crimea waters are optically mineral dominated. A fairly good correlation between the backscattering coefficient and the nonalgal particulate absorption showed that the mineral particles might have a significant absorption efficiency after the wind gusting. As expected, the parameterization of the scattering coefficients in terms of Chla failed. In the same way, the use of the parameter Chla/$c_p$, which was shown to be inversely related to the backscattering ratio in a previous study, was unsuccessful.

[36] Our data also allowed us to have a better understanding of the spectral shape and variability of the scattering properties in the coastal zones. This is important since the spectral behavior of the backscattering coefficient was not extensively measured during the last decades due to the lack of appropriate devices. Our results showed that the spectral properties of the scattering coefficients were significantly influenced by the absorption of the particulate matters, especially at 443 nm. That was consistent with the theory of anomalous dispersion. Regarding the spectra of the scattering coefficient, our data compared well with other measurements performed in coastal waters [Babin et al., 2003]. When all measurements were averaged, the backscattering ratio was found to vary spectrally within 4% which seems very weak. However, the high variability of the spectral slope observed ($\sim 30\%$) strongly caution against the use of a neutral spectral shape of $b_{pp}$, which is currently commonly assumed. Given the variability observed in this data set, empirical algorithms are unlikely to be successful and future efforts should be put on the development of more sophisticated regional scale algorithms to solve the inverse problem in coastal waters.

Notation

- $a_p$ total particulate absorption coefficient, m$^{-1}$.
- $q_{np}$ nonalgal particles absorption coefficient, m$^{-1}$.
- $q_{ph}$ Chla absorption coefficient, m$^{-1}$.
- $a_{ph}$ Chla specific absorption coefficient, m$^2$ mg$^{-1}$.
- $b_p$ particulate scattering coefficient, m$^{-1}$.
- $b_{pp}$ particulate backscattering coefficient, m$^{-1}$.
- $\beta_p(\theta)$ particulate backscattering ratio.
- $\beta_p(\theta)$ volume scattering function at the scattering angle $\theta$, m$^{-1}$ sr$^{-1}$.
- $c_p$ particulate attenuation coefficient ($c_p = a_p + b_p$), m$^{-1}$.
- $\lambda$ wavelength, nm.
- $n_p$ refractive index of the particles.
- $\omega_{sp}$ single scattering albedo of particles ($\omega_{sp} = b_p/c_p$).
- Chla chlorophyll $a$ concentration, mg m$^{-2}$.
- CZCS Coastal Zone Color Scanner.
- HPLC high performance liquid chromatograph.
- NAP nonalgal particles.
- Rs remote sensing reflectance.
- SeaWiFS Sea-viewing Wide Field-of-view Sensor.
- VSF volume scattering function.
- VSM volume scattering meter.

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References


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