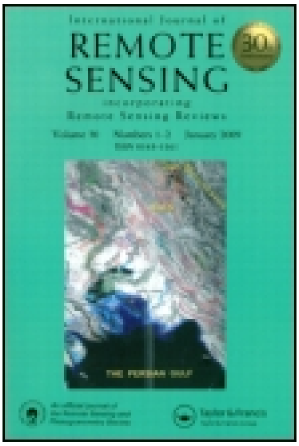

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Evaluation of SeaWiFS chlorophyll-a in the Black and Mediterranean Seas

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The performance of NASA's OC2 and OC4 algorithms to estimate chlorophyll-a concentrations from SeaWiFS radiometric measurements on the global scale was tested in two contrasted bio-optical environments, the Black Sea and the Mediterranean Sea. The in situ bio-optical measurements were made during October 1999 at 25 stations. Comparisons of the in situ measurements with the concurrent SeaWiFS retrievals indicate that the OC2 and OC4 algorithms are not working satisfactorily in both seas. Case 2 waters dominate the Black Sea and the failure of the algorithms is expected. On the other hand, failure of the algorithms in the case 1 waters of the Mediterranean Sea may be due to their specific optical properties. Modifying the OC4 algorithm to include SeaWiFS information at 412 nm yields a better performance in the Mediterranean Sea without degrading performance in the Black Sea. Combining a local algorithm adapted to oligotrophic waters of the Mediterranean Sea and OC4 provides the best results overall.

1. Introduction

Empirical models are currently used in bio-optical algorithms to estimate chlorophyll-a concentration (chl-a) from remote sensing reflectance measurements. The two standard algorithms for SeaWiFS-derived chl-a are OC2 and OC4, where 'OC' stands for 'ocean chl-a' and the number represents the number of bands used in the algorithm. Both algorithms are version 4, (OC2v4 and OC4v4); hence, they are simply referred to as OC2 and OC4 in this study. OC2 is an empirical equation relating remote sensing reflectances, R_{rs}, in the 490 and 555 nm bands to chl-a concentration (O'Reilly *et al.* 1998). OC4 is also an empirical equation, but is a bit more complicated than OC2 and uses the 443, 490, 510 and 555 nm bands (O'Reilly *et al.* 2000).

The cubic polynomial equation for OC2 is (O'Reilly *et al.* 1998):

$$\log_{10}(\text{chl-a}) = \left(0.319 - 2.336R_{2S} + 0.879R_{2S}^2 - 0.135R_{2S}^3\right) - 0.071 \tag{1}$$

where $R_{2S} = \log_{10}\left(R_{555}^{490}\right)$ and here $R_{\lambda_j}^{\lambda_i}$ is a compact notation for the $R_{rs}(\lambda_i)/R_{rs}(\lambda_j)$ band ratio.

The fourth order polynomial equation for OC4 is (O'Reilly *et al.* 2000):

$$\log_{10}(\text{chl-a}) = 0.366 - 3.067R_{4S} + 1.930R_{4S}^2 + 0.649R_{4S}^3 - 1.532R_{4S}^4 \tag{2}$$

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where $R_{4S} = \log_{10}(R^{443}_{555} > R^{490}_{555} > R^{510}_{555})$. The argument of the logarithm is a shorthand representation for the maximum of the three values. Subscript 'S' in R_{2S} and R_{4S} represents the code for specific satellite sensor, here SeaWiFS and the number part indicates the number of bands used.

These algorithms are developed for global ocean studies, and they may need to be adjusted for regional application (O'Reilly *et al.* 1998, Kahru and Mitchell 1999, O'Reilly *et al.* 2000). OC2 and OC4 are produced by the same group using a 57 separate datasets, which consists of 2853 in situ samples in total (O'Reilly *et al.* 2000). The previous version of OC2 fits the data generally well for case 1 waters with chl-a concentration between 0.003–1 mg m^{-3}, but tends to overestimate chl-a concentrations at higher levels. O'Reilly *et al.* tried to overcome this problem in version 4 but the results are not good as with OC4. The OC4 algorithm is observed to work well enough for clear case 1 waters. However, performance for turbid case 2 waters is not satisfactory.

Bricaud *et al.* (2002) compared in situ measurements of chl-a concentration (HPLC technique) with SeaWiFS estimates (OC4 algorithm) in various parts of the Mediterranean Sea. They found that the estimates are generally realistic except in oligotrophic areas (chl-a concentration $<$0.15 mg m^{-3}) where actual values are systematically overestimated by a factor of up to 5. Gitelson *et al.* (1996) had earlier reported lower than expected blue-to-green reflectance ratios in oligotrophic waters off the Israeli coast, in agreement with Bricaud *et al.*'s results.

Validations of various empirical algorithms for chl-a in the Mediterranean Sea were made by D'Ortenzio *et al.* (2002). They tested four former (including OC2 and OC4) and two new adapted algorithms. According to the results, OC2 and OC4 tended to overestimate the chl-a values while the new adapted formulas worked better than the other algorithms for the Mediterranean Sea. Gitelson *et al.* (1996) attributed the lower blue-to-green ratio they observed in clear waters of the Mediterranean Sea to the presence of small phytoplankton and coccolithophorids. Claustre *et al.* (2002), on the other hand, argued that the lower blue-to-green ratio could be explained by enhanced absorption in the blue and enhanced backscattering in the green due to submicron Saharan dust in suspension in the upper oceanic layer. Limited studies done in the Black Sea have indicated that the OC2 and OC4 algorithms are overestimating the chl-a values by an approximate factor of two (O.V. Kopelevich, personal communication).

The Black Sea and the Mediterranean Sea are two extreme examples in terms of their bio-optical characteristics. In the Black Sea, chl-a concentration measured in situ is in the range of 0.02–2.5 mg m^{-3} in the open waters and reaches to 0.02–34 mg m^{-3} in the shelf waters (Yilmaz *et al.* 1998b, Yunev *et al.* 2002). Light penetration is generally limited to the upper 15–40 m, with the downward attenuation coefficient varying between 0.125 and 0.350 m^{-1} (Yilmaz *et al.* 1998a, Bologa *et al.* 1999). Coastal waters of the region are fed by the riverine input whereas the cyclonically dominated open ecosystem is mainly controlled by influx from lower layers (Murray *et al.* 1995, Yilmaz *et al.* 1998a, Bologa *et al.* 1999). The photosynthetic carbon production rate range from 247–1925 and 405–687 mg C m^{-2} d^{-1} in the spring and summer-autumn periods, respectively (Yilmaz *et al.* 1998a, Bologa *et al.* 1999). There are major annual spring (diatoms) and autumn (coccolithophorids) blooms, followed in recent years by additional summer (dinoflagellates, coccolithophorids—*Emiliana huxleyi*) blooms (Sorokin 1983, Bologa 1985/1986, Hay and Honjo 1989, Hay *et al.* 1990, 1991, Sur *et al.* 1996, Yilmaz *et al.* 1998a, Bologa *et al.* 1999). The major primary producers are usually *Skeletonema costatum*, *Chaetoceros curvisetus*, *Nitzchia seriata*, *Peridinium trochoideum*, *Exuviaella cordata* and *Prorocentrum micans* (Bologa *et al.* 1999). Marmara Sea surface waters are originated from Black Sea waters and occupy upper 20 m of the basin. Hence, biochemical structure of Marmara surface waters is similar to Black Sea coastal waters (Besiktepe *et al.* 1994).

Surface chlorophyll in the North-Eastern Mediterranean water is low and varies between 0.01 and 1 mg m^{-3}, even in costal waters (Salihoglu *et al.* 1990, Yilmaz *et al.* 1994, Ediger and Yilmaz 1996a and the references cited there, Ediger *et al.* 1999). Light penetrates down to 50–120 m depending on the location and season (Ediger and Yilmaz 1996a, 1996b, Ediger *et al.* 1999, Coban-Yildiz *et al.* 2000). Taxonomic composition of phytoplankton shows high diversity, typical for oligotrophic subtropical waters (Yilmaz *et al.* 1994, Ediger and Yilmaz 1996a, Ediger *et al.* 1999, and the references cited in these papers). Phytoplankton in the late summer is small dinoflagellates, flagellates and coccolithophorids.

In the following, a validation of the SeaWiFS OC2 and OC4 algorithms for the seas surrounding Turkey is presented. The bio-optical data collected are used not only to test algorithms, but also to investigate ways to improve estimation of the chl-a concentration in these seas.

2. Material and methods

2.1 *Cruise plan*

The validation data were collected onboard R/V Bilim during 3–24 October 1999. Throughout the cruise, bio-optical measurements were made at 25 stations in the Black Sea, the Sea of Marmara, the Aegean Sea, and the Northern Levantine Basin in the Mediterranean Sea. The location of these stations overlapped onto the SeaWiFS chlorophyll map obtained on 29 September 1999 is given in figure 1. The measurements were carried out between 10:00 am and 5:00 pm where the ship was at least 8 km away from land. So the measurements were synchronized with the satellite overpass and the effect of land kept to a minimum (Tanre *et al.* 1979, Santer and Schmechtig 2000).

2.2 *The data*

The data used in this study include (i) in situ radiometric measurements (above and below water) and water sample analyses, and (ii) SeaWiFS remote sensing reflectance estimates corresponding to the time of the in situ measurements.

2.2.1 In situ measurements. The bio-optical data collected onboard R/V Bilim was upwelling and downwelling irradiances, reflectance (π times upwelled radiance over downwelled irradiance, $\pi L_u(0^+)/E_d(0^+)$, chl-a concentration, absorbance by particulate matter and soluble material.

Chlorophyll-a concentration was measured by the fluorometric method. Water samples were collected from the euphotic zone. 1 to 2 litres of seawater was filtered through Whatman GF/F filters (with a 0.7 μm pore size and 47mm diameter) using a vacuum of less than 0.5 atm. The filters were subsequently homogenized in 90% acetone, and the suspension was cleared by centrifugation. A standard fluorometric method was used for total chlorophyll-a determination (Holm-Hansen and Riemann 1978; JGOFS protocols 1994). Hitachi F-3000 Model fluorometer was

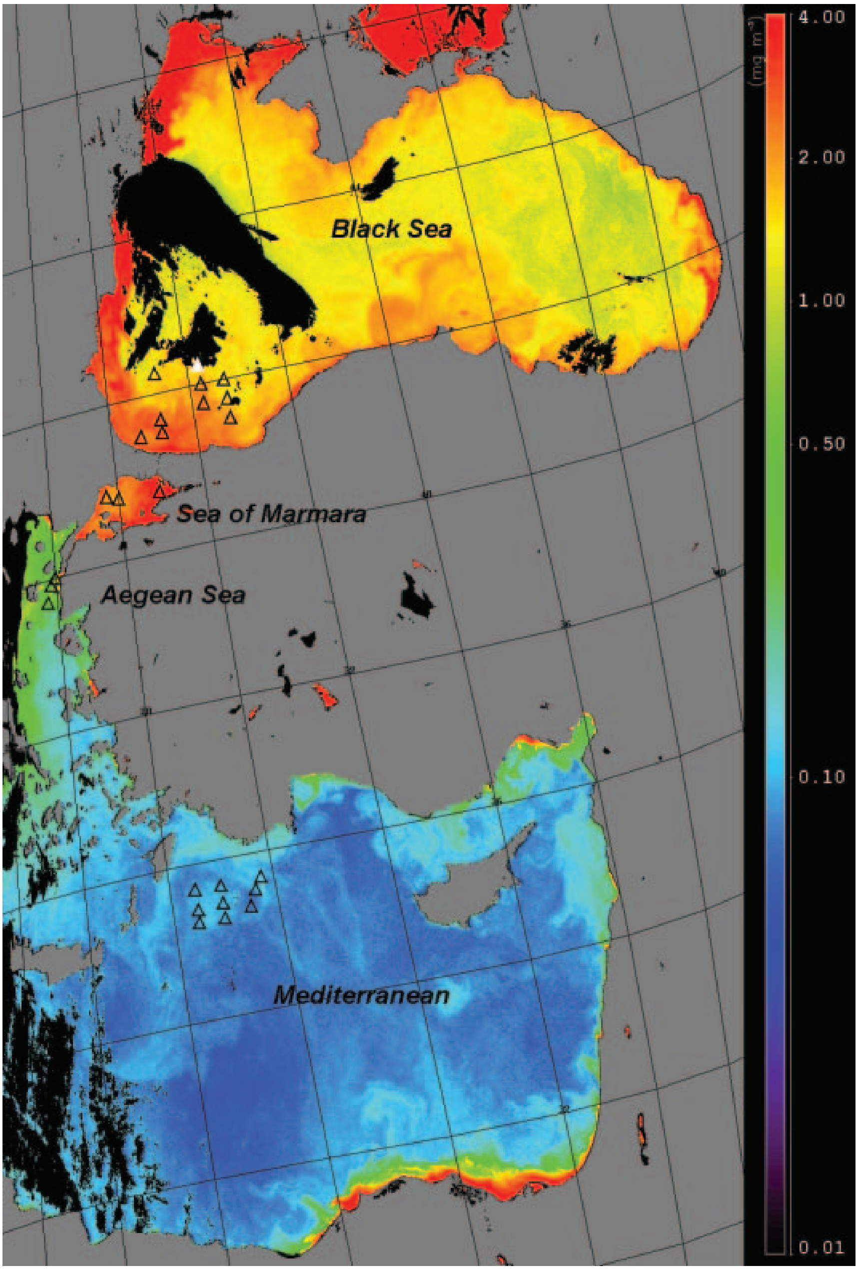

Figure 1. SeaWiFS chl-a imagery taken on 29 September 1999. Locations of the stations visited during the cruise are overlapped onto the SeaWiFS chl-a map.

used and calibration was performed using a commercially available chlorophyll-a standard from Sigma.

The irradiance measurements were made a using LI1800UW model spectro-radiometer of Licor Company. The data were collected between 300–800 nm with 1 nm intervals, along the water column with 2 metre intervals for both upward and downward irradiance.

The reflectance measurements were done using a floating spectroradiometer developed by the Marine Hydrophysical Institute (MHI) in Sevastopol, Ukraine. This instrument measures simultaneously upwelling radiance just beneath the sea surface and downwelling irradiance just above the sea surface at a distance from the ship to avoid shadowing effects. Spectral range is 340–750 nm, spectral resolution is 2 nm, scanning time is 15–30 seconds for a complete spectrum, aperture is 6 degrees, and relative error of measured ratio is 2–3%. Reflectance calibrations were performed under clear skies before and after the expedition, using test objects of well-known reflectance, including a Teflon-4 plaque. Marine reflectance was also measured from the side of the ship by a SIMBAD radiometer (Deschamps *et al.* 2004). This instrument operates in spectral bands centred at 443, 490, 560, 670, and 870 nm. It has been used to evaluate satellite-derived ocean colour (e.g. Fougnie *et al.* 1999, Frouin *et al.* 2001). The values obtained by the two instruments at seven stations in the Black Sea (SIMBAD data were only collected in the Black Sea) were in agreement (figure 2). The scatter about the 1/1 line gives an estimate of the inaccuracy of the radiometric measurements, which propagate into a 5% uncertainty in the 490/555 reflectance ratio. Using the OC2 algorithm, this incertainty yields a 7% error in chl-a concentration, well below the discrepancies discussed in section 3.

2.2.2 SeaWiFS data extraction. LAC SeaWiFS images corresponding to the cruise period were collected at IMS satellite observatory centre daily, during the satellite pass, and then analysed using SeaDAS (version 4.0). This version of the software implements procedures of SeaWiFS processing No. 3, also used in the work of Bricaud *et al.* (2002) discussed comparatively in the next section. The software was set to use all the default settings during the processing. The following methodology was adopted for matching the SeaWiFS data and the in situ measurements. First, the SeaWiFS pixel in the individual (i.e. instantaneous) SeaWiFS image that corresponded to the in situ station was taken as the nearest pixel to the exact

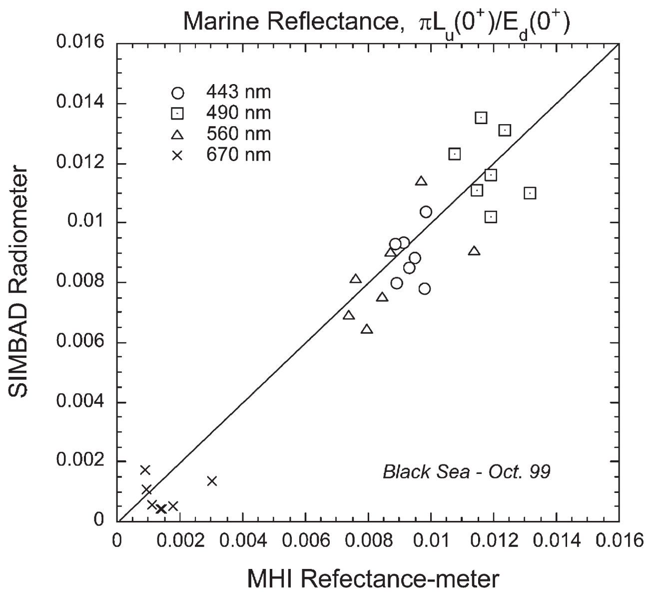

Figure 2. Comparison of marine reflectance measured by the MHI reflectance-meter and the SIMBAD radiometer at seven stations in the Black Sea.

location. To read the value of SeaWiFS derived parameters, a 3×3 pixel area (about $3 \times 3\,km^2$) centred on that nearest pixel was selected. Then the mean value over all 9 pixels was calculated. The shift between the location of pixel and the exact location of station was neglected. It is believed that the mean value represents better the value at the ship location than the centre pixel value.

Independently, the matchups of SeaWiFS and in situ chl-a data were obtained by the SIMBIOS Project at National Aeronautics and Space Administration (NASA)/ Goddard Space Flight Centre (GSFC) for cross-checking purposes and for eliminating subjectivity in the data extraction. Both results are compared and used in the analysis below.

3. Results and Discussion

In figure 3 typical irradiance reflectance spectra obtained just below the surface are displayed for the Black Sea and the Mediterranean Sea. It is obvious that the two

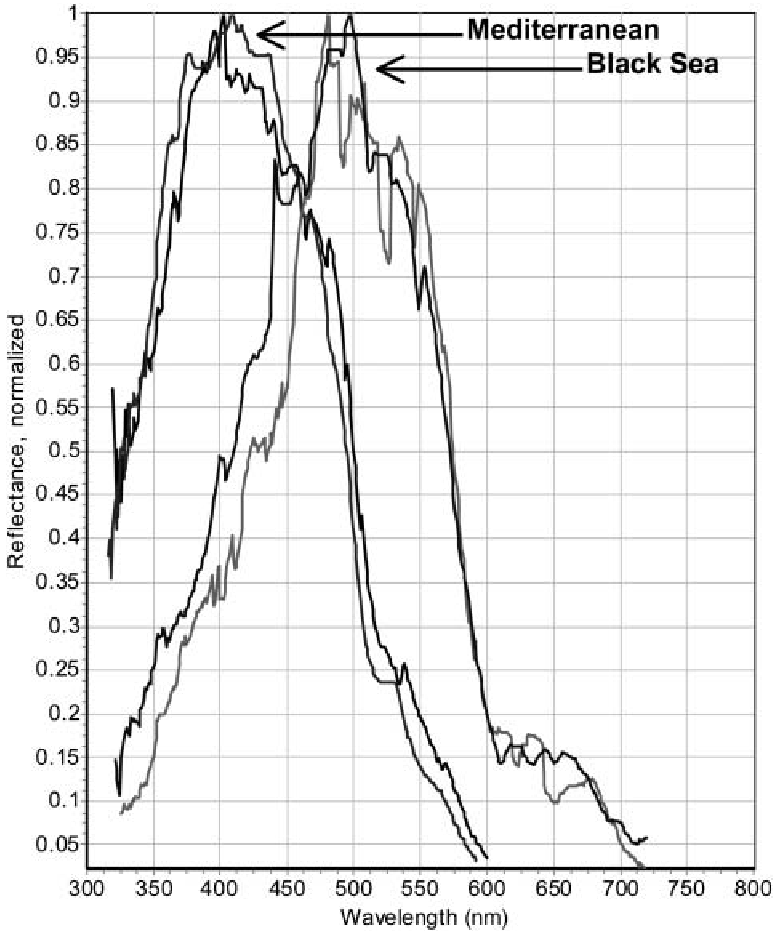

Figure 3. Normalized irradiance reflectance spectra from selected stations at the Black Sea and the Mediterranean Sea at surface. The maxima for Mediterranean Sea shifted towards shorter wavelengths. The OC4 formula is not using the SeaWiFS band, 412 nm, at these wavelengths.

seas have different optical properties. The reflectance maximum for Mediterranean Sea is around 410 nm while the maximum for Black Sea is around 490 nm. This difference in reflectance can be attributed to a higher chl-a concentration and yellow substance in the Black Sea.

Typical absorption spectra for suspended particles in the surface waters of the Black Sea, Marmara Sea, Aegean Sea, and Mediterranean Sea are given in Fig. 4. The spectral shape is characteristic of phytoplankton particles, with peaks at about 440 and 675 nm. The peaks are more pronounced in the Black Sea, Marmara Sea, and Aegean Sea, presumably because of higher chl-a concentration. In these seas, the higher absorption by suspended particles in the blue decreases reflectance, shifting the reflectance maximum to longer wavelengths compared with the oligotrophic Mediterranean Sea. Thus the difference between Black Sea and Mediterranean Sea in terms of absorption spectra seems to explain generally the difference in the irradiance reflectance spectra. The varied influences of particulate matter and dissolved constituents, by modifying the spectral shape of the absorbance and irradiance reflectance, are expected to effect the relationship between reflectance and chl-a concentration in the various seas.

In order to evaluate the performance of the OC2 and OC4 algorithms in situ and SeaWiFS derived reflectance data were used to derive chl-a concentrations and the results are presented in figure 5. Lines in the graphs show expected relations between in situ and remotely sensed chl-a ($y=x$). It can be seen that the chl-a estimates obtained using the reflectance measured in situ and derived from SeaWiFS are both overestimated. OC2 algorithm overestimated the in situ chl-a by 357% when SeaWiFS reflectance is used, and overestimated by 143% when in situ reflectance is used (table 1). This situation is slightly better in the case of OC4 is applied, but the percent error is still very high and out of the acceptable limits (235% and 120% for SeaWiFS reflectance and in situ reflectance, respectively).

The algorithms using in situ reflectance are in better agreement with in situ chl-a values as compared to chl-a estimations using remotely sensed reflectance. The overestimation is decreased to 143% for OC2 and 120% for OC2 (table 1). Since in situ reflectance is not affected by atmospheric correction, the difference between in

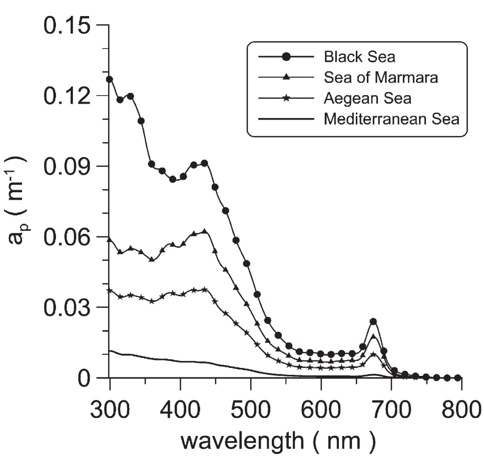

Figure 4. Absorbance by phytoplankton at the surface in the Black Sea, Marmara Sea, Aegean Sea and Mediterranean Sea.

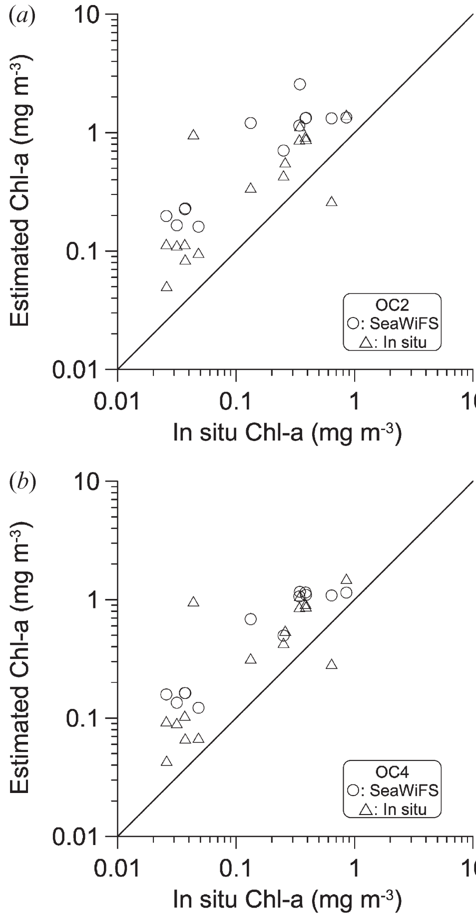

Figure 5. Comparison of in situ and remote sensed OC2, (*a*), and OC4, (*b*), chl-a values. Rrs(λ) and MHI's reflectance used in OC algorithms.

situ and remotely sensed chl-a values might be due to the atmospheric correction algorithm used in SeaDAS.

Although the estimation of the chl-a from reflectance measurements is improved when OC4 algorithm used, both OC2 and OC4 substantially overestimate in the four seas where sampling was made. This situation can be explained for the case 2 areas with high chl-a content (enhanced absorption in the blue due to yellow substance and possibly enhanced backscattering in the green due to sediment), but the failure of the algorithms in Mediterranean Sea cannot be explained easily. The overestimation in the Mediterranean Sea, however, is in agreement with the results reported in some studies (e.g. Bricaud *et al.* 2002, Claustre *et al.* 2002).

Bricaud *et al.* (2002) match weekly and monthly averaged SeaWiFS data with other sensors data and in situ data from Mediterranean, and find out that discrepancies appear particularly in oligotrophic areas. SeaWiFS overestimates lowest chl-a concentrations by up to a factor of 4 to 5; while the Ocean Colour and Temperature Scanner (OCTS) overestimates by a factor of 2. The interesting point is that the atmospheric correction algorithms of these two sensors are very similar (Bricaud *et al.* 2002). As a consequence they concluded that the systematic bias

Table 1. Percentage average errors and standard deviations of errors on chlorophyll-a concentration. Chl-a estimated by OC2, OC4, OC4*, Bricaud's algorithm and OC4 (Adj.) (see text for definitions). Statistics made for all data set and Mediterranean data set separately. Statistics for OC2 and OC4 algorithms repeated for these algorithms using remote sensed (RS) reflectance and in situ reflectance as comparision. For the other algorithms only in situ reflectance were used.

Algorithm	Data	AVG (error), %	STDEV (error)
OC2 RS	All	357	224
	Mediterranean	501	135
OC4 RS	All	235	157
	Mediterranean	371	112
OC2	All	143	93
	Mediterranean	189	99
OC4	All	120	78
	Mediterranean	138	87
OC4*	All	99	76
	Mediterranean	84	84
Bricaud	All	136	161
	Mediterranean	−2	42
OC4 (Adj.)	All	63	84
	Mediterranean	1	44

appearing between satellite and in situ chlorophyll concentrations appears to originate both from errors in atmospheric corrections and from inadequate bio-optical algorithms due to peculiar optical properties of Mediterranean waters. They proposed the following algorithm for the Mediterranean to reduce this bias.

$$\text{chl-a}\left(mg\,m^{-3}\right) = 2.094\left(R_{555}^{443}\right)^{-2.357} \tag{3}$$

The result of the application of this algorithm to our in situ reflectance dataset is given in figure 6 and table 1. This regional algorithm overestimated the in situ chl-a by 136% for the all dataset, and underestimated the Mediterranean chl-a by 2%. It is obvious that this regional algorithm works quite well in the Mediterranean (chl-a $<0.2\,\mathrm{mg\,m^{-3}}$) and it estimates the chl-a within the acceptable limits as expected while the performance is poor in the Black Sea.

To improve the chl-a estimates in the Mediterranean Sea, one may consider using OC4 SeaWiFS 412 nm band in addition to the other bands. Since the R_{555}^{412} reflectance ratio is generally higher than the R_{555}^{443} reflectance ratio usually selected by OC4 in oligotrophic waters, one expects lower chl-a values. Indeed, modifying OC4 in that way may not provide better results in other oligotrophic regions. Adding the 412 nm band to OC4 and keeping equation (2) the same, the R_{4S} part in the formula becomes: $R_{5S} = \log_{10}\left(R_{555}^{412} > R_{555}^{443} > R_{555}^{490} > R_{555}^{510}\right)$. This modified OC4 algorithm will be referred to as OC4* in the following.

It is important to note that the above procedure has no theoretical basis since equation (2) was not established using R_{5S}. It is attempted, however, because the higher R_{555}^{412} than R_{555}^{443} may compensate for the particular optical properties of the Mediterranean Sea not accounted for in OC4. To estimate the expected improvement, the relation between maximum reflectance ratio and chl-a concentration, obtained using 4 and 5 spectral bands (3 and 4 reflectance ratios), was simulated with the bio-optical model of Morel and Maritorena (2002). The modelled

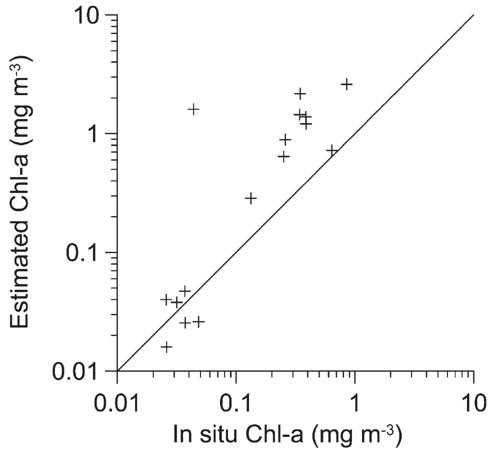

Figure 6. Comparison of in situ chl-a and chl-a derived from the new regional algorithm developed by Bricaud *et al.* (2002) using in situ reflectance data set.

relation is displayed in figure 7, curves labelled OC4 (Mod.) and OC5 (Mod.), respectively. Comparing these two curves for specified chl-a concentrations provides a measure of the differences expected in chl-a retrievals using OC4 with R_{5S}. The approach is justified since OC4 (Mod.) compares well with OC4, labelled OC4 (Exp.) in figure 7. Table 2 summarizes the resulting error with respect to the Bricaud

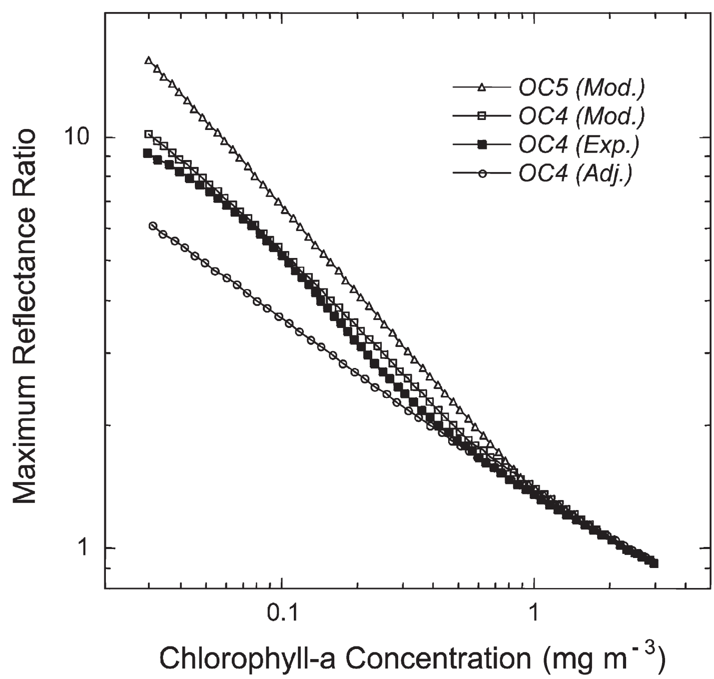

Figure 7. Relation between maximum reflectance ratio and chl-a concentration. Various algoritms are presented, OC4 (Mod.) and OC5 (Mod.) based on the bio-optical model of Morel and Maritorena (2002), OC4 (Exp.) (O'Reilly *et al.*, 2000), and OC4 (Adj.) combining the regional relation of Bricaud et al. (2002) and OC4 (Adj.). (See text for details.)

Table 2. Percentage error on chlorophyll-a concentration, chl-a, estimated by OC4, OC4*, and OC4(Adj.) (see text for definitions). Equation (3), from Bricaud *et al.* (2002), is assumed to represent actual conditions in oligotrophic waters of the Mediterranean Sea and, therefore, serves as the reference.

	Error, %		
chl-a, mgm^{-3}	OC4	OC4*	OC4(Adj.)
0.03	167	80	13
0.05	140	60	10
0.10	70	40	5
0.30	17	20	13

et al. (2002) empirical relation (equation 3), which serves as the reference. Using OC4*, overestimation by OC4 is substantially reduced, for example from 167% to 80% at $0.03\,mg\,m^{-3}$. Results become satisfactory and comparable for chl-a concentrations above $0.3\,mg\,m^{-3}$.

When OC4* is used with remotely sensed and in situ reflectance data and the derived chl-a concentrations are compared with in situ chl-a concentrations it will be seen that for Mediterranean Sea with low chl-a concentrations the modified algorithm works quite well while nothing changed for other waters with high chl-a concentrations. This is normal because the modified algorithm uses the same bands as OC4 for chl-a rich waters. Only for chl-a poor Mediterranean waters it selects the 412 nm band. In figure 8, in situ chl-a versus derived chl-a from OC4 and new derived OC4* algorithms are given. From the figure, OC4* can be seen to perform better, only for lower chl-a concentrations of the Mediterranean Sea. In the past, the SeaWiFS 412 nm band has not been used in bio-optical algorithms in large part because of atmospheric correction errors. Normalized water-leaving radiance is often underestimated at 412 nm, especially in the presence of absorbing aerosols

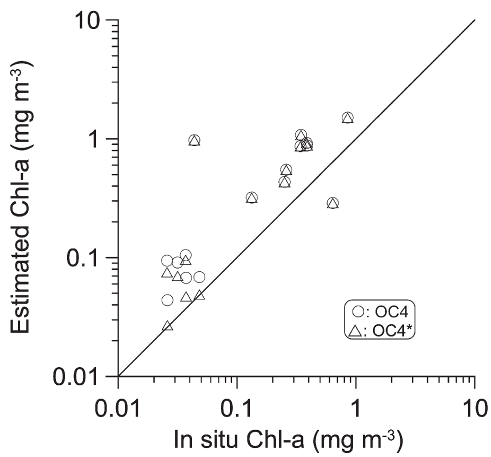

Figure 8. Algorithm derived chl-a values versus in situ chl-a. SeaWiFS remote sensing reflectances and in situ measured reflectances used in algorithms as input. OC4* is the new algorithm written with the knowledge that OC4 overlooks at around 410 nm wavelength for the Mediterranean. OC4* uses the SeaWiFS 412 nm band and in total 5 SeaWiFS band. The values for Mediterranean Sea are the grouped ones at lower values. The only difference from OC4 takes place at these values while at the others nothing changes. This is because the OC4* algorithm still chooses 443 nm band at these values like OC4.

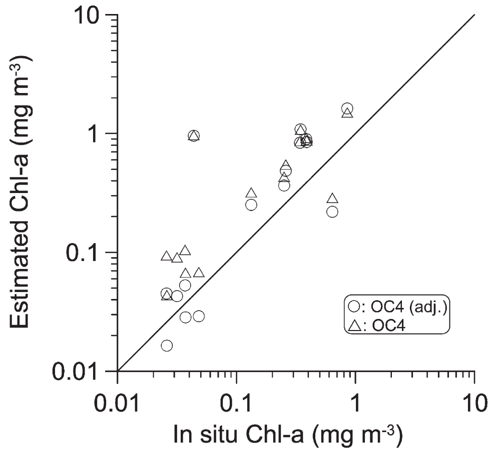

Figure 9. Estimated chl-a concentration using OC4 and OC4 (Adj.) versus measured chl-a concentration. Performance is much improved with OC4 (Adj.) at low pigment concentration (Mediterranean Sea stations), but values remain overestimated above 0.1 $\mathrm{mgm^{-3}}$ (Black Sea stations).

(Moulin *et al.* 2001). This may be the case in the Mediterranean Sea, subjected to Saharan dust event. Such underestimation would lower the R_{555}^{412} ratio artificially, reducing the expected improvement.

An alternative to OC4 and OC4* is a blended algorithm that combines OC4 with the bio-optical relation of Bricaud *et al.* (2002). This adjusted OC4 algorithm, labelled OC4 (Adj.), is displayed in figure 9. For a given R_{4S}, the chl-a concentration estimated with OC4 (Adj.) is lower than with OC4 in oligotrophic and mesotrophic waters. The OC4 (Adj.) chl-a concentration is obtained using the following cubic polynomial

$$\log_{10}(\text{chl-a}) = 0.379107 - 2.98124R_{4S} + 1.41615R_{4S}^2 - 0.876068R_{4S}^3 \tag{4}$$

Since the Bricaud *et al.* (2002) relation is adapted to the Mediterranean Sea, in table 2 the chl-a estimates using equation (4) are close to those using equation (3). The differences are only due to the accuracy of the fit between R_{4S} and chl-a concentration (using a cubic polynomial). Like with OC4*, performance will not be improved in case 2 waters, but not degraded. When applied to in situ measurements OC4 (Adj.), as expected, yields good chl-a estimates in the Mediterranean Sea and similar estimates to OC4 (i.e., too high values) in the Black Sea (figure 9). Overall, however, the overestimation for Mediterranean Sea is substantially reduced to 1%, a definite improvement compared with 84% using OC4*. Note that algorithms and calibration updates were implemented in the latest operational processing of SeaWiFS data, processing No. 4 (Patt *et al.* 2003), but they did not improve much the chl-a estimates in the Mediterranean Sea, which remained biased high by a similar factor of over 2 for the dataset considered (Casey and Gregg 2003).

It should be noted that, in the comparisons presented above, the in situ chl-a data was obtained using the fluorometric method. Comparisons with a few chl-a measurements in the Mediterranean Sea, obtained using the HPLC technique, indicate lower fluorometric readings by a factor of 2 for low chl-a. In addition, the specific absorption spectra for suspended particles may be too high at the red peak

(675 nm) for the low chl-a situations (i.e. 0.06–0.08 m^{-1}), and doubling the low chl-a values would make the specific absorption coefficient more realistic. However, if we re-calculate the OC4 and OC2 performance with fluorometric chl-a values higher by a factor of 2 in the Mediterranean Sea, we find that both algorithms still highly overestimate, even though there are some improvements, i.e. when remote sensing reflectance is used the 501% overestimation for OC2 decreased to 201% and the the 371% overestimation for OC4 decreased to 136%. On the other hand, when in situ reflectance is used, the OC2 overestimation of 189% is reduced to 45% and the OC4 overestimation of 138% to 19%. This suggests, errors due to atmospheric correction set aside, that OC4 is well adapted to the Mediterranean Sea, in contradiction with the findings of Bricaud *et al*. (2002) and d'Ortenzio *et al*. (2002) (see section 1). In fact, the Bricaud *et al*. (2002) algorithm would underestimate chl-a by −51% in the Mediterranean Sea if chl-a values are multiplied by 2. Unfortunately, it cannot be concluded from the analysed dataset whether the changes in percent error are due to the modified algorithms or uncertainties in the fluorometric chl-a readings. Nevertheless, the OC4* and OC4(Adj) algorithms offer alternatives to OC2 and OC4, with potential for improving performance.

4. Conclusion

OC algorithms are not working well in the four seas surrounding Turkey. Chlorophyll-a concentration is generally overestimated. This is expected for the Black Sea (case 2 waters) but not for the Mediterranean Sea (case 1 waters). To reduce the bias in the Mediterranean Sea, the OC4 algorithm was modified to include the SeaWiFS 412 nm band. Adding of the 412 nm band makes the OC4 formula work better for the Mediterranean while not affecting the results for other three seas. This is due to the higher R_{555}^{412} reflectance ratio in the Mediterranean Sea. In the three other seas, the bands centred at wavelengths greater than the 412 nm band are selected due to the optical properties of these seas. Thus the change only affects the chl-a values calculated for the Mediterranean Sea. Combining the bio-optical relation of Bricaud *et al.* (2002) with OC4 in a blended algorithm, OC4 (Adj.), provides the best results overall when fluorometric chl-a is used, but like with OC4 and OC4*, chl-a is overestimated in the Black Sea. Uncertainties in the fluorometric chl-a readings at low concentration, however, prevent a definite conclusion about performance.

Even though the OC4* and OC4 (Adj.) algorithms appear to improve chl-a estimates in the Mediterranean Sea in comparisons with fluorometric chl-a measurements, they should be further evaluated with more accurate and with a much larger amount of in situ chl-a data, especially at chl-a values between 0.05 and 0.2 mg m^{-3} and greater than 1 mg m^{-3}. On the other hand, these modified algorithms still overestimate chl-a concentration in the Black Sea and the existing dataset is insufficient to develop a regional algorithm for the Black Sea yet. Hence, there is a need to collect more in situ data to understand the living and non-living biological content of the water column affecting the reflected light from the Black Sea.

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References

Besiktepe, S.T., Sur, H.I., Ozsoy, E., Latif, M.A., Oguz, T. and Unluata, U., 1994, The circulation and hydrography of the Marmara Sea. *Progress in Oceanography*, **34**, pp. 285–334.

Bologa, A.S., 1985/1986, Planktonic primary productivity of the Black Sea: a review. *Thalassia Jugoslavica*, **21/22**, pp. 1–22.

Bologa, A.S., Frangopol, P.T., Vedernikov, V.I., Stelmakh, L.V., Yunev, O.A., Yilmaz, A. and Oguz, T., 1999, Distribution of planktonic primary production in the Black Sea. In *NATO TU-Black Sea Project: Environmental Degradation of the Black Sea: Challenges and Remedies*, S.T. Besiktepe, U. Unluata and A.S. Bologa (Eds) (Dordrecht: Kluwer Academic Publishers), pp. 131–145.

Bricaud, A., Bosc, E. and Antoine, D., 2002, Algal biomass and sea surface temperature in the Mediterranean Basin. Intercomparison of data from various satellite sensors, and implications for primary production estimates. *Remote Sensing of Environment*, **81**, pp. 163–178.

Casey, N.W. and Gregg, W.W., 2003, Comparing SeaWiFS reprocessing versions (R3 vs. R4). SeaWiFS postlaunch technical report series, S.B. Hooker and E.R. Firestone (Eds), NASA/TM-32003-212235, pp. 20.

Claustre, H., Morel, A., Hooker, S.B., Babin, M., Antoine, D., Oubelkheir, K., Bricaud, A., Leblanc, K., Queguiner, B. and Maritorena, S., 2002, Is desert dust making oligotrophic waters greener? *Geophysical Research Letters*, **29**, 10.1029/2001GL014056.

Coban-Yildiz, Y., Fabbri, D., Tartari, D., Tugrul, S. and Gaines, A.F., 2000, Application of pyrolysis-GC/MS for the characterisation of suspended particulate organic matter in the Mediterranean Sea: a comparison with the Black Sea. *Organic Geochemistry*, **31**, pp. 1627–1639.

Deschamps, P.-Y., Fougnie, B., Frouin, R., Lecomte, P. and Verwaerde, C., 2004, SIMBAD: An advanced field radiometer to measure aerosol optical thickness and marine reflectance. *Applied Optics*, **43**, pp. 4055–4069.

D'Ortenzio F., Marullo, S., Ragni, M., D'Alcala M.R. and Santoleri, R., 2002, Validation of empirical SeaWiFS algorithms for chlorophyll-a retrieval in the Mediterranean Sea A case study for oligotrophic seas. *Remote Sensing of the Environment*, **82**, pp. 79–94.

Ediger, D. and Yilmaz, A., 1996a, Characteristics of deep chlorophyll maximum in the North-Eastern Mediterranean with respect to environmental conditions. *Journal of Marine Systems*, **9**, pp. 291–303.

Ediger, D. and Yilmaz, A., 1996b, Variability of light transparency in physically and biochemically different water masses: Turkish Seas. *Fresenius Environmental Bulletin*, **5**, pp. 133–140.

Ediger, D., Tugrul, S., Polat, C.S., Yilmaz, A. and Salihoglu, I., 1999, Abundance and elemental composition of particulate matter in the upper layer of North-Eastern Mediterranean. In *The Eastern Mediterranean as a Laboratory Basin for the Assessment of Contrasting Ecosystems*, P. Malanotte-Rizzoli and V.N. Eremeev (Eds) (Netherlands: Kluwer Academic Publishers), pp. 241–266.

FOUGNIE, B., DESCHAMPS, P.-Y. and FROUIN, R., 1999, Vicarious calibration of the POLDER ocean colour spectral bands using in situ measurements. *IEEE Transactions on Geoscience and Remote Sensing*, **37**, pp. 1567–1574.

FROUIN, R., CUTCHIN, D.L. and DESCHAMPS, P.-Y., 2001, Satellite ocean colour validation using merchant ships. In *SIMBIOS Project 2000 Annual Report*, G.S. Fargion and C.R. McClain (Eds), NASA/TM–2001–209976, pp. 71–79.

GITELSON, A., KARNIELI, A., GOLDMAN, N., YACOBI, Y.Z. and MAYO, M., 1996, Chlorophyll estimation in the South-Eastern Mediterranean using CZCS images: adaptation of an algorithm and its validation. *Journal of Marine Systems*, **9**, pp. 283–290.

HAY, B.J. and HONJO, S., 1989, Particle deposition in the present and Holocene Black Sea. *Oceanography*, **2**, pp. 26–31.

HAY, B.J., HONJO, S., KEMPE, S., ITEKKOT, V.A., DEGENS, E.T., KONUK, T. and IZDAR, E., 1990, Interannual variability in particle flux in the South-Western Black Sea. *Deep-Sea Research*, **37**, pp. 911–928.

HAY, B.J., ARTHUR, M.A., DEAN, W.E. and NEFF, E.D., 1991, Sediment deposition in the Late Halocene abyssal Black Sea: Terrigeneous and biogenic matter. *Deep-Sea Research*, **38(Suppl.)**, pp. S711–S723.

HOLM-HANSEN, O. and RIEMANN, B., 1978, Chlorophyll a determination: improvements in methodology. Oikos, **30**, pp. 438–447.

JGOFS, 1994, Protocols for the Joint Global Ocean Flux Study (JGOFS) Core Measurements. Manual and Guides 29, UNESCO, pp. 170.

KAHRU, M. and MITCHELL, B.G., 1999, Empirical chlorophyll algorithm and preliminary SeaWiFS validation for the California Current. *International Journal of Remote Sensing*, **20**, pp. 3423–3429.

MOREL, A. and MARITORENA, S., 2002, Bio-optical properties of oceanic waters: a Reappraisal. *Journal of Geophysical Research*, **106**, pp. 7163–7180.

MOULIN, C., GORDON, H.R., CHOMKO, R.M., BANZON, V.F. and EVANS, R.H., 2001, Atmospheric correction of ocean colour imagery through thick layers of Saharan dust. *Geophysical Research Letters*, **28**, pp. 5–8.

MURRAY, J.M., CODISPOTI, L.A. and FREIDERICH, G.E., 1995, Oxidation-reduction environments: The suboxic zone in the Black Sea. In *Aquatic Chemistry*, C.P. Huang, C.R. O'Melia and J.J. Morgan (Eds), *ACS Advances in Chemistry Series*, **244**, pp. 157–176.

O'REILLY, J.E., MARITORENA, S., MITCHELL, B.G., SIEGEL, D.A., CARDER, K.L., GARVER, S.A., KAHRU, M. and MCCLAIN, C., 1998, Ocean colour chlorophyll algorithms for SeaWiFS. *Journal of Geophysical Research*, **103**, pp. 24937–24953.

O'REILLY, J.E., MARITORENA, S., O'BRIEN, M.C., SIEGAL, D.A., TOOLE, D., MENZIES, D., SMITH, R.C., MUELLER, J.L., MITCHELL, B.G., KAHRU, M., CHAVEZ, F.P., STRUTTON, P., COTA, G.F., HOOKER, S.B., MCCLAIN, C.R., CARDER, K.L., MULLER-KARGER, F., HARDING, L., MAGNUSON, A., PHINNEY, D., MOORE, G.F., AIKEN, J., ARRIGO, K.R., LETELIER, R. and CULVER, M., 2000, *SeaWiFS Postlaunch Calibration and Validation Analyses*, part 3, S.B. Hooker and E.R. Firestone (Eds), NASA Technical Memorandum 2000–206892, Vol. 11, NASA Goddard Space Flight Centre, Greenbelt, Maryland.

PATT, F.S., BARNES, R.A., EPLEE JR, R.E., FRANZ, B.A., ROBINSON, W.D., FELDMAN, G.C., BAILEY, S.W., GALES, J., WERDELL, P.J., WANG, M., FROUIN, R., STUMPF, R.P., ARNONE, R.A., GOULD JR, R.W., MARTINOLICH, P.M., RANSIBRAHMANAKUL, V., O'REILLY, J.E. and YODER, J.A., 2003, Algorithm updates for the fourth SeaWiFS data reprocessing. In *SeaWiFS Postlaunch Technical Report Series*, S.B. Hooker and E.R. Firestone (Eds), NASA/TM-32003-206892, Vol. 22, pp. 74.

SOROKIN, Yu.I., 1983, The Black Sea. In Ecosystems of the World Estuaries and Enclosed Seas, B.H. Ketchum (Ed.) (Amsterdam: Elsevier), pp. 253–291.

SALIHOGLU, I., SAYDAM, C., BASTURK, O., YILMAZ, K., GOCMEN, D., HATIPOGLU, E. and YILMAZ, A., 1990, Transport and distribution of nutrients and chlorophyll-a by mesoscale eddies in the North-Eeastern Mediterranean. *Marine Chemistry*, **29**, pp. 375–390.

SANTER, R. and SCHMECHTIG, C., 2000, Adjacency effects on water surfaces: Primary scattering approximation and sensitivity study. *Applied Optics*, **39**, pp. 361–375.

SUR, H.I., OZSOY, E., ILYIN, Y.P. and UNLUATA, U., 1996, Coastal/deep ocean interactions in the Black Sea and their ecological/environmental impacts. *Journal of Marine Systems*, **7**, pp. 293–320.

TANRE, D., HERMAN, M., DESCHAMPS, P.-Y. and DELEFFE, A., 1979, Atmospheric modelling for measurements of ground reflectances: Including bi-directional properties. *Applied Optics*, **18**, pp. 3587–3596.

YILMAZ, A., EDIGER, D., BASTURK, O. and TUGRUL, S., 1994, Phytoplankton fluorescence and deep chlorophyll maxima in the North-Eastern Mediterranean. *Oceanologica Acta*, **17**, pp. 69–77.

YILMAZ, A., TUGRUL, S., POLAT, C., EDIGER, D., COBAN, Y. and MORKOC, E., 1998a, On the production, elemental composition (C,N,P) and distribution of photosynthetic organic matter in the Southern Black Sea. *Hydrobiologia*, **363**, pp. 141–156.

YILMAZ, A., YUNEV, O., VEDERNIKOV, V., MONCHEVA, S., BOLOGA, A.S., COCIASU, A. and EDIGER, D., 1998b, Unusual temporal variations in the spatial distribution of chlorophyll a in the Black Sea during 1990–1996. In *NATO TU-Black Sea Project: Ecosystem Modeling as a Management Tool for the Black Sea*, Vol. I, L. Ivanov and T. Oguz (Eds) (Dordrecht: Kluwer Academic Publishers), pp. 105–120.

YUNEV, O.A., VEDERNIKOV, V.I., BASTURK, O., YILMAZ, A., KIDEYS, A., MONCHEVA, S. and KONOVALOV, S.K., 2002, Long-term variations of surface chlorophyll-a and primary production in the open Black Sea. *Marine Ecology Progress Series*, **230**, pp. 11–28.