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The colour of the Mediterranean Sea: Global versus regional bio-optical algorithms evaluation and implication for satellite chlorophyll estimates

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Abstract

In this paper, uncertainties in the retrieval of satellite surface chlorophyll concentrations in the Mediterranean Sea have been evaluated using both regional and global ocean colour algorithms. The rationale for this effort was to define the most suitable ocean colour algorithm for the reprocessing of the entire SeaWiFS archive over the Mediterranean region where standard algorithms were demonstrated to be inappropriate. Using a large dataset of coincident *in situ* chlorophyll and optical measurements, covering most of the trophic regimes of the basin, we validated two existing regional algorithms [Bricaud, A., E. Bosc, and D. Antoine, 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(2–3), 163–178.; D'Ortenzio, F., S. Marullo, M. Ragni, M. R. d'Alcala and R. Santoleri, 2002. Validation of empirical SeaWiFS algorithms for chlorophyll-alpha retrieval in the Mediterranean Sea — A case study for oligotrophic seas. Remote Sensing of Environment, 82(1), 79–94.] and the global algorithm OC4v4 used for standard NASA SeaWiFS products. The results of our analysis confirmed that the OC4v4 performs worse than the two existing regional algorithms. Nonetheless, these two regional algorithms do show uncertainties dependent on chlorophyll values. Then, we introduced a better tuned algorithm, the MedOC4. Using an independent set of *in situ* chlorophyll data, we quantified the uncertainties in SeaWiFS chlorophyll estimates using the existing and new regional algorithms. The results confirmed that MedOC4 is the best algorithm matching the requirement of unbiased satellite chlorophyll estimates and improving the percentage of the satellite uncertainty, and that the NASA standard chlorophyll products are affected by an uncertainty of the order of 100%. Moreover, the analysis suggests that the poor quality of the SeaWiFS chlorophyll in the Mediterranean is not due to the atmospheric correction term but to peculiarities in the optical properties of the water column. Finally the observed discrepancy between the global and the regional bio-optical algorithms has been discussed analysing the differences between the two *in situ* datasets used for tuning the algorithms (SeaBASS versus ours). The main results are that methodological differences in the two datasets cannot play a major role and the inherent bio-optical properties of the basin can explain the observed discrepancy. In particular the oligotrophic water of the Mediterranean Sea is less blue (30%) and greener (15%) than the global ocean.

Keywords: Ocean colour; Mediterranean Sea; Algorithm; Chlorophyll; SeaWiFS

1. Introduction

Satellite ocean colour data has been successfully used to provide unique and important information on surface phytoplankton distribution (e.g. chlorophyll), representing an essential element to address marine environmental issues and sustainable management of marine resources. They can provide near real-time, long-term, synoptic, global estimates of key parameters to validate high resolution models and to be assimilated by ecosystem models. Nonetheless, their efficient exploitation requires the production of quality controlled dataset accompanied by robust statistical analyses of the errors

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associated with the retrieval procedures, e.g. atmospheric correction, bio-optical algorithms.

For this reason, the space agencies involved in ocean colour missions have established important projects to collect vast databases of *in situ* data for calibration and validation of satellite products (Gregg & Casey, 2004; McClain & Fargion, 1999; O'Reilly et al., 2000). These *in situ* data have been then used to develop the empirical algorithms used in the satellite data processing chains (OC4v4 for SeaWiFS, OC3 for MODIS and Algal1 for MERIS). These standard algorithms proposed by space agencies to process data from their sensors have a nominal accuracy of ~35% in the retrieval of surface chlorophyll in case 1 waters.

Among ocean colour sensors, an extensive calibration and validation activity has been performed on SeaWiFS data by SeaWiFS and SIMBIOS Projects. At global scale, the SeaWiFS algorithms showed errors in the range proposed by the space agencies (<5% for radiances; <35% for chlorophyll) (Gregg & Casey, 2004; O'Reilly et al., 2000). However in the Baltic Sea (Darecki & Stramski, 2004), Southwestern Atlantic Ocean, Southern Ocean (Garcia et al., 2005), and Mediterranean Sea standard empirical algorithms perform generally and sensibly worse.

More specifically in the Mediterranean Sea, Bricaud et al. (2002), Claustre et al. (2002), and D'Ortenzio et al. (2002) demonstrated that the standard NASA algorithms (OC2v4 and OC4v4) lead to a significant overestimation of the SeaWiFS derived chlorophyll concentration (>70% for chlorophyll <0.2 mg m^{-3}). The failure of the SeaWiFS estimates in the Mediterranean Sea was confirmed also by other authors (e.g. Gregg & Casey, 2004). Claustre et al. (2002) suggested that the observed bias could be attributed to the presence of Saharan dust in the water column, while D'Ortenzio et al. (2002), along with Gitelson et al. (1996), proposed as an alternative explanation that the presence of coccoliths, due to the relative abundance of coccolithophores, could account, at least partially, for the observed discrepancy.

This observed bias in chlorophyll retrieval can have a strong impact in the use of SeaWiFS global products in primary production models, in validation and tuning of ecosystem modelling and especially in data assimilation systems.

Regional algorithms provide a suitable solution to overcome the above problems (Garcia et al., 2005; Gitelson et al., 1996, among the others). Bricaud et al. (2002) and D'Ortenzio et al. (2002) provided the first attempts for SeaWiFS regional algorithms over the Mediterranean basin. D'Ortenzio et al. (2002), using a preliminary Mediterranean bio-optical dataset (45 in- and above-water bio-optical stations), proposed a two band algorithm based on the OC2 NASA functional form (hereafter DORMA). The algorithm was built with *in situ* chlorophyll concentration ranging between 0.06 and 1.92 mg m^{-3}. Contemporaneously, Bricaud et al. (2002) proposed a new regional algorithm for the retrieval of the SeaWiFS chlorophyll concentration in oligotrophic conditions (<0.4 mg m^{-3}) switching to OC4v4 for values grater than this threshold (hereafter BRIC). Both algorithms improved the performance of the SeaWiFS pigment retrieval in the Mediterranean Sea. Nonetheless, the statistical robustness of these algorithms is rather weak mainly because *in situ* data used to retrieve the proposed algorithms did not cover the whole range of Mediterranean trophic conditions. Moreover, these bio-optical regional algorithms, a part of a local validation exercise limited to the Gulf of Lions (Ouillon & Petrenko, 2005), have never been validated against an independent *in situ* dataset at basin scale. Finally, their impact on the chlorophyll retrieval with SeaWiFS sensor has never been fully evaluated.

Using a much larger bio-optical dataset we aim at quantifying the uncertainties of the existing regional and global ocean colour algorithms in the Mediterranean waters and at identifying and developing an optimal algorithm for the production of high quality ocean colour datasets for this basin. This work is part of the EU project Marine EnviRonment and Security for the European Area (MERSEA), which aims, besides other objectives, to provide high quality satellite products for data assimilation and validation of global and regional models. The identification of the best suited Mediterranean algorithm for chlorophyll retrieval and its associated uncertainty is an essential step to proceed to the re-processing of the entire SeaWiFS mission. In more details, this work will produce a new chlorophyll dataset suitable for the assessment of and assimilation into the coupled biochemical and physical model, as required by the modelling community of the MERSEA Project (http://www.mersea.eu.org/Research/Assimilation-Modelling.html). Moreover, this dataset can be used as input parameter into primary production model studies for the Mediterranean basin (e.g. Bosc et al., 2004).

The paper is organized as follows. In Section 2 we present the *in situ* and satellite data and describe the procedure used to build up the matchup datasets. In Section 3, the quantification of the uncertainties, introduced by regional (DORMA, BRIC) and global (OC4v4) bio-optical algorithms, is analyzed using *in situ* bio-optical measurements. A new regional algorithm is proposed in Section 4 while the validation of SeaWiFS chlorophyll estimates obtained using the selected algorithms is presented in Section 5. Discussion and conclusions are drawn in Section 6.

2. Data and methods

2.1. In situ chlorophyll

In situ pigment measurements used in this work consist of 1144 chlorophyll profiles acquired during several cruises performed in the Mediterranean Sea between 1997 and 2004 (Table 1). Most of these data were acquired on board R/V Urania of the Italian National Research Council (CNR). During these cruises, standard oceanographic parameters, such as temperature, salinity and fluorescence were measured using a SBE 911 CTD profiler and a SeaTech fluorometer. Water samples were collected by means of a G.O. Rosette equipped with 24 Niskin Bottles and filtered on board on GF/F filters (low vacuum) and immediately deep-frozen, then chlorophyll concentrations were determined on 90% acetone extracts within few weeks of the sampling using a SPEX Fluorolog

Table 1
List of oceanographic cruises in the Mediterranean Sea from 1997 to 2005

Cruise	Period	Zone	# of Chl Profiles			Chl range [mg m^{-3}]		# of in-water meas. (SPMR)	# of above-water meas. (SIMBADA)		
			A	B	C	MIN	MAX		D	E	F
MATER 3	Oct 97	Sardinia Channel	76		6	0.034	0.061				
MATER 4	Apr–May 98	Sardinia–Sicily	57		38	0.025	0.073				
MATER 5	Oct-98	Sicily Channel	57		7	0.047	0.085				
EMTEC 99	Apr-May 99	Ionian Sea	126	18	43	0.039	0.095	18			
MATER 6	May 99	Sardinia–Sicily	100		58	0.003	0.094				
PROSOPE	Sep–Oct 99	Western Basin Ionian Sea	16	16		0.020	0.078	16			
SYMPLEX	Oct–Nov 99	Sicily Channel Ionian Sea	221	12	75	0.039	0.122	12			
NORBAL 1	Mar–Apr 00	Gulf of Lions	81		35	0.078	2.289				
MASSFLUX	Oct 01	Tyrrhenian Sea Sicily Channel							64	28	
NORBAL 2	Dec 01	Gulf of Lions Tyrrhenian Sea	65	27	27	0.088	0.268	12	44	16	15
MIPOT	Mar 02	Ionian Sea							23	2	
MEDGOOS 1	May 02	Sardinia(Coastal)							61	24	
M5ODAS	Jun–Jul 02	Ligurian Sea							50	33	
NAPOLI	Jul 02	Ligurian Sea							12	12	
NORBAL 3	Sep–Oct 02	Gulf of Lions	39	7	18	0.115	0.481	7			
LIGURE 1	Oct 02	Corsica(Coastal)							2		
MEDGOOS 5	Nov 02	Sardinia(Coastal)							6		
NORBAL 4	Mar 03	Gulf of Lions	115	43	51	0.297	7.061	16	82	65	27
MEDGOOS 6	Apr 03	Sardinia(Coastal)							25	14	
NORBAL 5	Apr 03	Gulf of Lions	40	11	13	0.420	2.096	4	18	17	7
LIPRO 1	Apr–May 03	Ligurian Sea							37	26	
LIGURE 2	Sep 03	Ligurian Sea							76	51	
MEDGOOS 7	Jan 04	Sicily Channel Sardinia(Coastal)							21	4	
MEDGOOS 8	May 04	Tyrrhenian Sea							96	51	
ALT 1	Aug 04	Tyrrhenian Sea	85	11	43	0.030	0.090	11	95	54	
MFSTEP 1	Sep 04	Ligurian Sea							69	26	
MEDGOOS 9	Oct 04	Western Basin							132	43	
MFSTEP 2	Apr 05	Ligurian Sea Tyrrhenian Sea							22		
DAPHNEII	May 05	North Adriatic							3		
DINA*	Mar–Aug 01	Tyrrhenian Sea	11	10	1	0.079	0.316	10			
DYFAMED*	Feb–98 Nov–02	Liguro–Provencal	55		25	0.042	2.366				
All cruises	1997–2005	Mediterranean	1144	155	440	0.003	7.061	106	938	466	49

Total Number of Chlorophyll profiles acquired in each cruise is reported in column A. Column B indicates the number of chlorophyll profiles constituting the *in situ* bio-optical dataset. Column C indicates the number of *in situ*-SeaWiFS chlorophyll matchups. Chlorophyll ranges (C_M), measured during each cruise, are given in the 7th and 8th columns. The 9th column provides the number of stations in which corresponding in-water optical profiles (Satlantic SPMR) and chlorophyll samples were carried out. In column D the total number of above-water measurements (SIMBADA) acquired in each cruise is listed. The number of *in situ* Rrs-SeaWiFS matchups is displayed in column E, while the number of SIMBADA station in which also *in situ* chlorophyll measurements were acquired is shown in column F. Symbol * indicates permanent stations. DYFAMED row give information about the number of stations acquired from the DYFAMED web site. DINA is a permanent station located 18 nautical miles offshore the Gulf of Naples (Southern Italy) where "Stazione Zoologica di Napoli *A. Dohrn*" collect data regularly.

spectrofluorometer with an estimated coefficient of variation for chlorophyll *a* concentration of 10% (Neveux & Panouse, 1987). To increase the depth resolution of pigment data, fluorescence profiles were converted to chlorophyll values after fitting them with bottle data. Conversion factors were obtained with linear regression analysis on log-transformed data (Campbell, 1995). The fluorescence-chlorophyll calibration was performed for each cruise to take account of the intercruise variability of fluorometer sensor response. The uncertainty of the fluorescence-derived chlorophyll, in terms of absolute percentage difference (APD, see Appendix for the definition of the statistical parameters), was estimated to be on average 20%.

Additional data were extracted from DYFAMED station time series dataset (Marty et al., 1995) and from SeaWiFS Bio-optical Archive and Storage System (SeaBASS) bio-optical archive (PROSOPE cruise in the Mediterranean Sea; Hooker et al., 1994). These additional data are available on the web (http://www.obs-vlfr.fr/jgofs2/sodyf/home.htm for DYFAMED and http://www.obs-vlfr.fr/cd_rom_dmtt/pr_main.htm for PROSOPE).

To minimize the effect due to non-uniform chlorophyll profiles (Stramska & Stramski, 2005), the mean chlorophyll concentration within the penetration depth and weighted for the attenuation coefficient of light, C_M (see Appendix for formula), was used as a proxy for the Optical Weighted Pigment Concentration (Clark, 1997; D'Ortenzio et al., 2002). It is important to underline that, chlorophyll values range from 0.003 to 7.06 mg m^{-3}, covering almost the whole range of possible values typical of the Mediterranean Sea.

2.2. In situ optical measurements

The optical dataset used in this work includes both in-water (106 stations) and above-water measurements (938 data points)

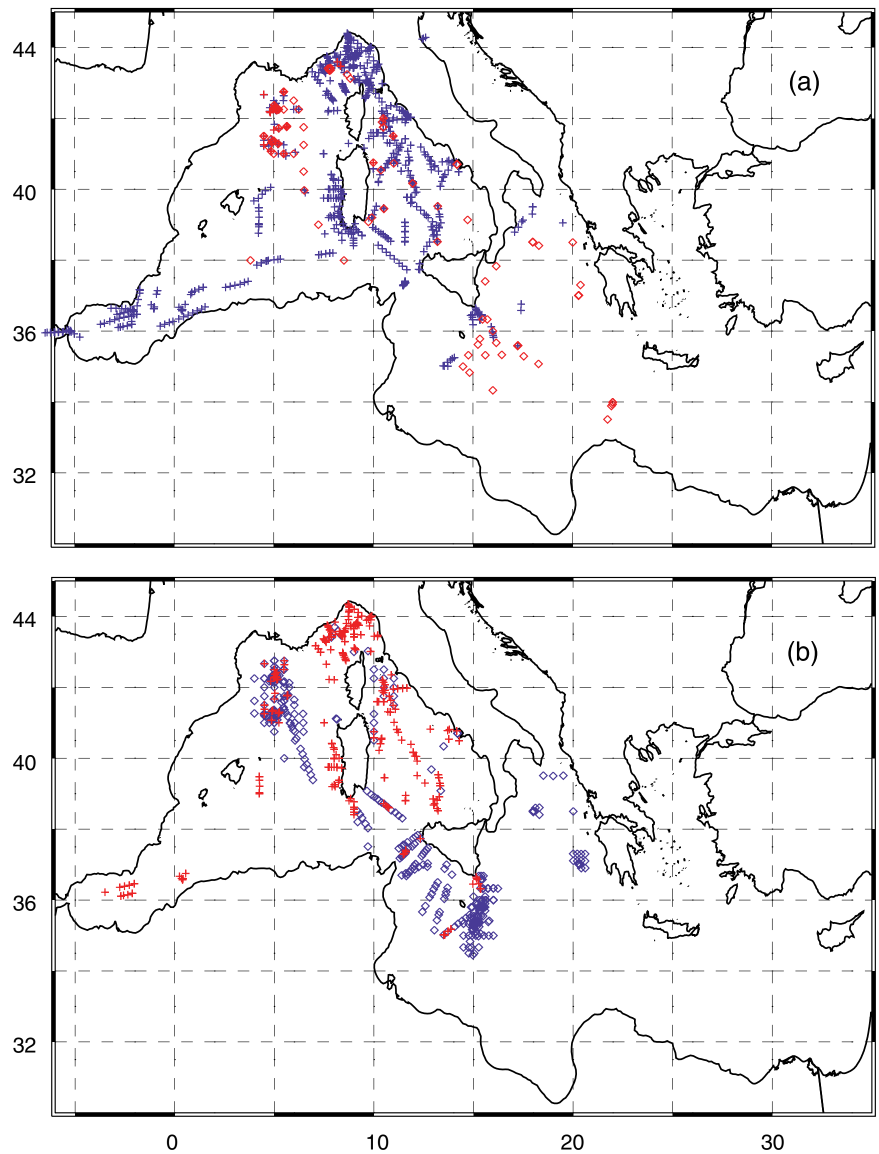

Fig. 1. (a) Map of *in situ* optical stations. Crosses indicate above-water measurements and diamonds indicate in-water measurements. Points corresponding to co-located chlorophyll *a* measurements are coloured in red. (b) Map of satellite matchup data points. Blue diamonds indicate SeaWiFS-chlorophyll matchups, red crosses indicate SeaWiFS Rrs and *in situ* SIMBADA measurements matchups.

(Table 1, Fig. 1a). In water downwelling irradiance (E_d) and upwelling radiance (L_u) profiles were acquired using a Satlantic SPMR (SeaWiFS Profiling Multi-channel Radiometer), following the standard SeaWiFS protocols (Mueller, 2000; Mueller & Austin, 1995; Mueller & Fargion, 2002).

Out of the 106 SPMR measurements, 16 bio-optical stations were obtained by the SeaBASS archive (Hooker et al., 1994). These data were collected in the Mediterranean Sea during the PROSOPE cruise (Claustre et al., 2002) (see Fig. 1a for stations location).

Above-water measurements were acquired with a SIMBADA radiometer during 20 cruises covering all Mediterranean seasonal conditions (Table 1). These data were then processed at LOA (Laboratoire d'Optique Atmospherique) of the University of Lille (Fougnie et al., 1998). Chlorophyll profiles were acquired concurrently with all in-water optical casts, and with 49 SIMBADA stations. As for the latter, Hooker and Morel (2003) describe the difficulty of achieving a reliable above-water measurement of the water leaving radiance with a ±5% uncertainty, required for ocean colour algorithm calibration and validation activity, and conclude that the space agencies requirements are unlikely to be achievable by means of this approach. This is an important issue since our above-water dataset is much lager then the in-water one. Therefore we compared the above-water dataset with the available in-water measurements in order to assess the consistency between the two measurements within our dataset. As long as input parameters for the above-mentioned bio-optical algorithms are Rrs ratios, we will hereafter concern with band ratios:

$$R_{555}^{\lambda} = \frac{\mathrm{Rrs}(\lambda)}{\mathrm{Rrs}(555)} \quad (1)$$

with λ equal to 443, 490 and 510 nm, and MBR (Maximum Band Ratio):

$$\mathrm{MBR} = \mathrm{MAX}(R_{555}^{443}, R_{555}^{490}, R_{555}^{510}) \quad (2)$$

The maximum band ratio (MBR) has the potential advantage of maintaining the highest possible satellite sensor signal-to-noise ratio over a 3-orders-of-magnitude range in chlorophyll concentration (O'Reilly et al., 1998).

Fig. 2 shows the scatterplot of R_{555}^{λ} and MBR as measured by Satlantic SPMR and SIMBADA instruments in the space-time co-located available stations. Measurements from the two radiometers show a sensibly high agreement with RMS of 0.2, BIAS of 0.02, a relative bias (RPD) of 1.67% and an APD of 7.38% (see Appendix for the definition of the statistical parameters). Therefore our SIMBADA and SPMR measurements can be mutually interchanged and constitute the bio-optical dataset analyzed in this paper for the purpose of algorithms' evaluation.

The remaining above-water optical data were used to evaluate the efficiency of the atmospheric correction procedure to retrieve remote sensing reflectances. The chlorophyll profiles collected without optical measurements were used instead to build up a match-up data set for the validation of SeaWiFS derived chlorophyll.

2.3. Satellite data

High-Resolution Picture Transmission (HRPT) SeaWiFS Level-1A data, acquired by the receiving station HROM at ISAC in correspondence of all *in situ* measurement stations (chlorophyll *a* and/or Rrs, Table 1), have been used for satellite data validation. SeaWiFS Level-1A passes were processed up to Level-2 with the SeaWiFS Data Analysis System (SeaDAS) software package version 4.8 available from NASA website (www.seadas.gsfc.nasa.gov). Each Level-2 product includes:

- Chlorophyll *a*
- Rrs at 412, 443, 490, 510, 555, 670, 765 and 865 nm
- SeaDAS Level-2 flags (l2_flags)

Siegel's atmospheric correction algorithm was applied to Level-1A raw data (Siegel et al., 2000), which is based on a first guess of chlorophyll concentration to compute water-leaving radiances. Since we selected three bio-optical algorithms (BRIC, DORMA and OC4v4) for our analysis, each Level-1A SeaWiFS pass was processed up to Level-2 two times. In fact, DORMA Level-2 products were obtained directly from SeaDAS after a modification of the code that includes the DORMA regional algorithm as a further option of the SeaDAS code. On the contrary, following Bricaud et al. (2002) the BRIC chlorophyll maps were obtained applying the BRIC algorithm to Rrs produced by the OC4v4 processing.

Finally all Level-2 products and chlorophyll maps were remapped at 1 km spatial resolution at Nadir on an equirectangular grid covering the Mediterranean Basin and the Black Sea.

Two matchup files have been generated (Fig. 1b): one between SeaWiFS-derived chlorophyll and C_{M}, the other between SeaWiFS-derived Rrs's and SIMBADA measurements. Satellite data were averaged on a 3×3 full resolution pixel box centred on the location of the *in situ* measurements, and only boxes with all pixels passing all the l2_flags tests were retained for the analysis. Temporal Criteria for coincidence was within the same day for chlorophyll (Gregg & Casey, 2004) and within 4 h for Rrs's (McClain et al., 1995). The rationale for discriminating the two parameter matchup time windows is that the chlorophyll field temporal variability is believed to be slower than the Rrs one which depends, beside other factor, also by the cloudiness of the area whose variability is quite fast. It is important to underline that the matchup dataset between SeaWiFS-derived chlorophyll and C_{M} was built not using the chlorophyll profiles of the bio-optical dataset described in the previous section. In other words, columns B and C (Table 1) are two subsets of the entire chlorophyll archive (column A, Table 1). The criteria employed reduced the matching observations to 440 (chlorophyll) and to 466 (Rrs).

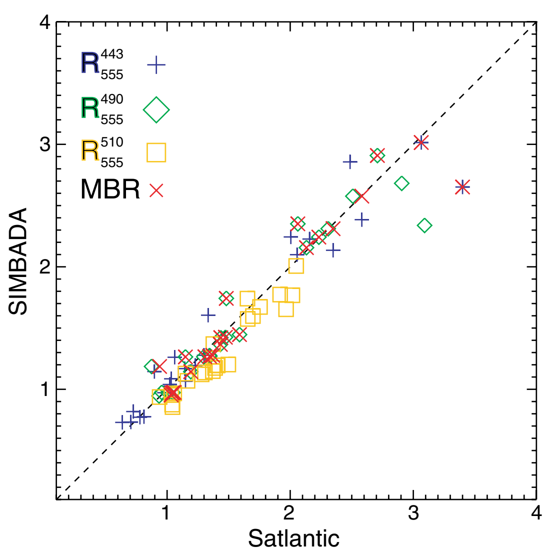

Fig. 2. Scatter plot of SIMBADA versus Satlantic Rrs ratios. R_{555}^{443} in blue, R_{555}^{490} in green, R_{555}^{510} in orange and MBR red.

3. Algorithms validation: *in situ* analysis

We applied the three selected algorithms to our *in situ* optical dataset to estimate chlorophyll concentrations, which were then compared with corresponding *in situ* chlorophylls (C_{M}). The derived scatter plot (Fig. 3a) confirms that the global NASA algorithm overestimates *in situ* concentrations at low chlorophyll values (<0.4 mg m^{-3}) while regional algorithms are more efficient in reproducing C_{M} concentrations for this chlorophyll range (Fig. 3b–c). In particular, BRIC behaves well for chlorophyll values <0.1 mg m^{-3} but overestimates C_{M} in the 0.1–0.4 mg m^{-3} range. On the other hand, DORMA reproduces well low chlorophyll concentrations even if it is less efficient for chlorophyll values >1 mg m^{-3}.

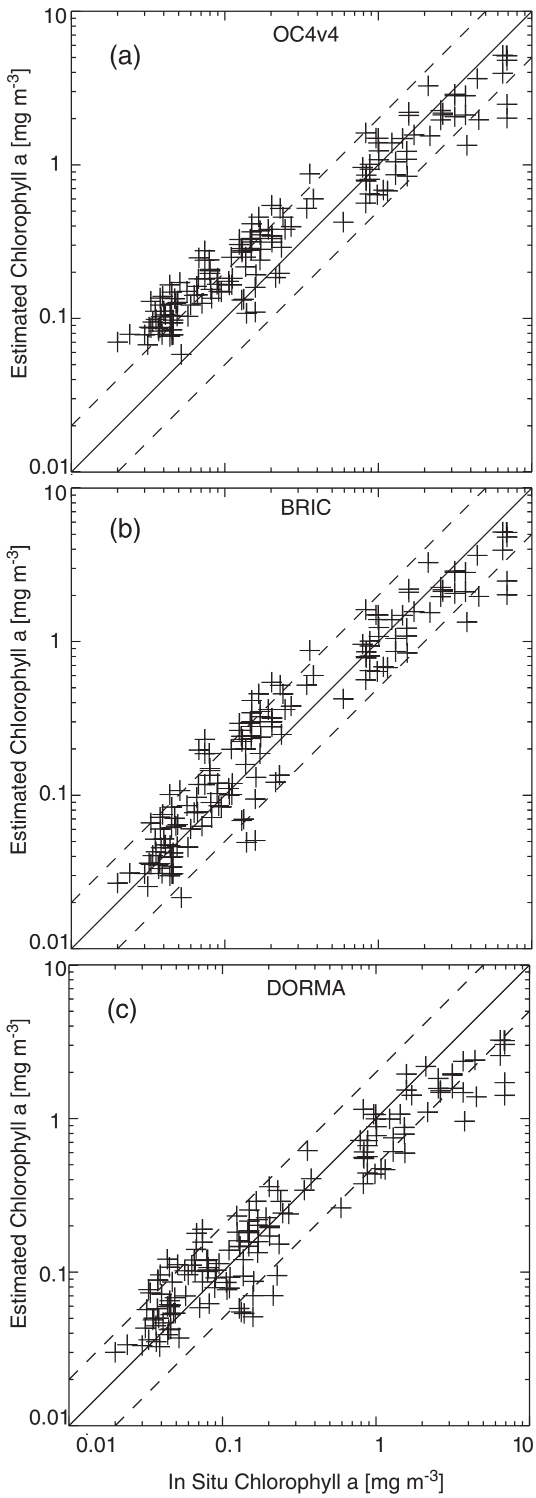

Fig. 3. Scatter plot of algorithm derived chlorophyll concentration from *in situ* optical data versus *in situ* chlorophyll (C_M). (a) The estimated chlorophyll is obtained using OC4v4 algorithm. (b) The estimated chlorophyll is obtained using BRIC algorithm. (c) The estimated chlorophyll is obtained using DORMA algorithm. The 1:1 (continuous line) 1:2 (bottom dashed line) and the 2:1 (top dashed line) lines are also plotted.

Along with the major patterns displayed in Fig. 3, we divided the dataset into two clusters with the C_M threshold value of 0.4 mg m^{-3}. The two subsets reflect the main trophic regimes of the Mediterranean open waters: oligotrophic and meso-eutrophic (Antoine et al., 1995).

The statistical parameters (see Appendix for definitions) are reported in Table 2 which includes also results for the whole dataset.

For the whole dataset (Table 2a) all algorithms display a similar r^2. RMS ranges from 0.75 mg m^{-3} (BRIC and OC4v4) to 1.04 mg m^{-3} (DORMA), whereas BIAS indicates that all the algorithms underestimate *in situ* values by an amount ranging from −0.12 and −0.16 mg m^{-3} (OC4v4 and BRIC) to −0.36 mg m^{-3} (DORMA). On the other hand, the analyses of the RPD and APD (i.e. statistical parameters accounting for the absolute value of the variable) indicate an opposite trend. APD values range from 43% and 47% (DORMA and BRIC) to 92% (OC4v4) and RPD from 8% to 25% (DORMA and BRIC) to 78% (OC4v4). Note that the evaluation of statistical parameters, such as RMS and BIAS, provide results in complete discordance with those evaluated accounting for the absolute values of the variable (i.e. RPD and APD), which reflects the non normal distribution of chlorophyll around its mean value, spanning over three order of magnitude. In this case the mentioned discordance is due to the fact that differences between measured and estimated chlorophylls at low values are negligible as compared to that at high values.

For C_M<0.40 mg m^{-3} (Table 2b), r^2 coefficients do not significantly vary for OC4v4 and BRIC (0.73 and 0.74), while DORMA presents an r^2 coefficient of 0.64. RMS ranges from 0.06 mg m^{-3}, for DORMA, to 0.13 mg m^{-3}, for OC4v4. The comparison between *in situ* measurements and DORMA-derived chlorophyll reveals a BIAS of 0.02 mg m^{-3}, while

Table 2
Validation of the selected bio-optical chlorophyll algorithms in the Mediterranean Sea

(a)

$0.01<C_M<10.0$ mg m^{-3} N=155

Algorithms	r^2	RMS	BIAS	APD	RPD
OC4v4	0.85	0.75	−0.12	92	78
BRIC	0.85	0.75	−0.16	47	25
DORMA	0.83	1.04	−0.36	43	8

(b)

$0.01<C_M<0.40$ mg m^{-3} N=105

Algorithms	r^2	RMS	BIAS	APD	RPD
OC4v4	0.74	0.13	0.10	122	120
BRIC	0.73	0.11	0.06	56	42
DORMA	0.64	0.06	0.02	45	29

(c)

$0.40<C_M<10.0$ mg m^{-3} N=50

Algorithms	r^2	RMS	BIAS	APD	RPD
OC4v4	0.71	1.31	−0.60	29	−11
BRIC	0.71	1.31	−0.60	29	−11
DORMA	0.68	1.83	−1.16	40	−36

Correlation coefficient (r^2), Root Mean Square (RMS), Mean Bias Error (BIAS), Relative Percentage Difference (RPD) and Absolute Percentage Different (APD) between *in situ* Chlorophyll (C_M) and the algorithms-derived chlorophyll *a* using *in situ* Rrs. The statistical parameters are shown for different C_M ranges.

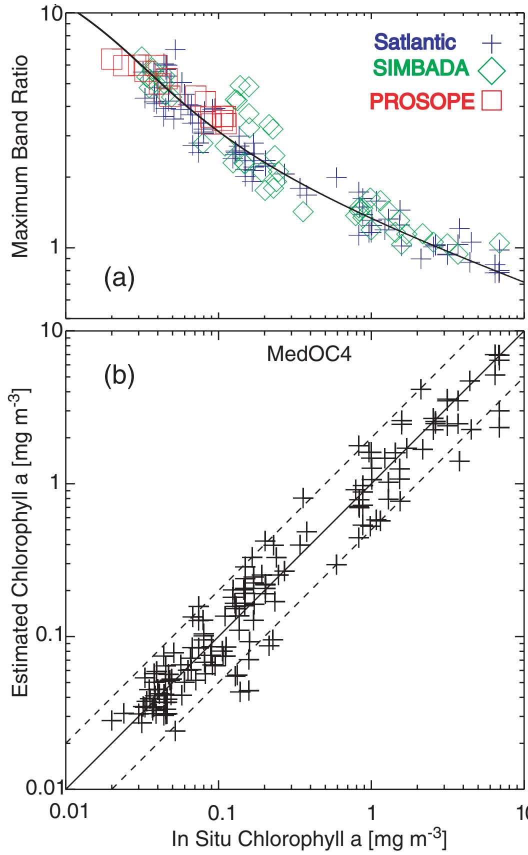

Fig. 4. (a) Relation between *in situ* MBR and C_M used to derive the new coefficients for the MedOC4 algorithm. Different optical data sources are highlighted with different colours and symbols. MedOC4 functional form is superimposed. (b) MedOC4-derived chlorophyll versus C_M. The 1:1 (continuous line) 1:2 (bottom dashed line) and the 2:1 (top dashed line) lines are also plotted.

the comparison with BRIC- and OC4v4-derived observations yields 0.06 and 0.1 mg m^{-3}, respectively. Since chlorophyll range in this case is narrower than previous scenario's, APD and RPD values are consistent with the RMS and the BIAS statistical parameters. In more details, APD decreases from OC4v4 (122%) to BRIC (56%) and DORMA (45%). Similarly,

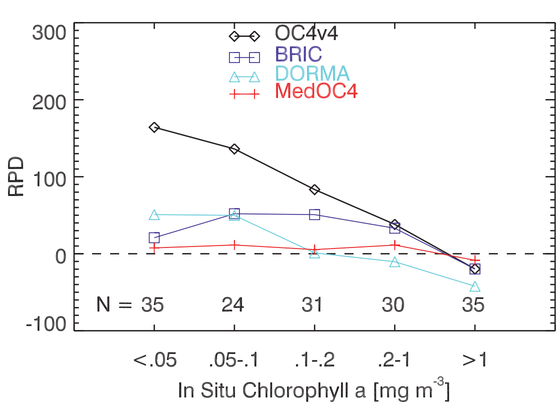

Fig. 5. Relative Percentage Difference (RPD) for all the four examined algorithms as a function of *in situ* chlorophyll in five different ranges. Numbers within the plot indicate the number of data points used to retrieve RPD in each range.

RPD improves from OC4v4 (120%) to BRIC (42%) and to DORMA (29%) indicating that the regional algorithms are more effective in reproducing *in situ* chlorophyll for this range of concentrations.

For $C_M > 0.40$ mg m^{-3} (Table 2c), the OC4v4 and BRIC statistics obviously coincide. OC4v4 performs better than DORMA for all the statistical parameters.

DORMA is then the most suitable algorithm for C_M values < 0.4 mg m^{-3}, whereas it is worse than OC4v4 for $C_M >$ 0.4 mg m^{-3}. It is worth reminding that DORMA was built with only few points exceeding 0.4 mg m^{-3} (only 3 > 1 mg m^{-3}), and this could explain the weak performances of DORMA in the third scenario, where most of the dataset is composed with values > 1 mg m^{-3}. Similarly, BRIC does behave well in oligotrophic condition and might probably improve by varying the band ratio instead of using only the R_{555}^{443}.

4. Bio-optical algorithm tuning: the MedOC4

In the previous section, we confirmed that the global algorithm, OC4v4, exhibits uncertainty levels in the chlorophyll estimation, which are incompatible with the expected requirements of the ocean colour mission (chlorophyll uncertainty < 35%) when applied to the Mediterranean Sea. On the other hand, regional algorithms have been demonstrated to perform better in retrieving chlorophyll concentrations in oligotrophic condition. However, BRIC requires the a priori knowledge of the chlorophyll field as obtained from the OC4v4 and then it is implicitly affected by the intrinsic uncertainty on OC4v4. Moreover the systematic use of R_{555}^{443} instead of MBR leads to another unidentified source of error. Similarly, DORMA algorithm gives good performance for low chlorophyll concentrations but underestimates it at high values.

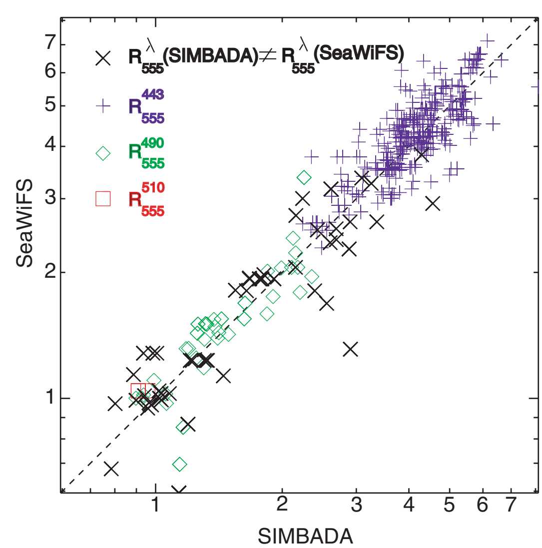

Fig. 6. Scatter plot of space-time co-located MBRs from SIMBADA and SeaWiFS. Different symbols represent different band ratio selections: blue crosses refer to R_{555}^{443}, green diamonds refer to R_{555}^{490} and red squares refer to R_{555}^{510}. Black "x's" refer to points where MBRs selected by SIMBADA are different from those selected by SeaWiFS.

Table 3
Correlation coefficient (r^2), Root Mean Square (RMS), Mean Bias Error (BIAS), Relative Percentage Difference (RPD), Absolute Percentage Different (APD) for 466 co-located measurements between SIMBADA and SeaWiFS radiometers

R_{555}^{λ}	r^2	RMS	BIAS	APD	RPD
λ=443	0.85	0.59	0.06	14	3
λ=490	0.76	0.48	0.12	12	4
λ=510	0.70	0.28	0.17	14	10
MBR	0.85	0.58	0.06	12	2

Statistics refer to $R_{555}^{\lambda} = \frac{\mathrm{Rrs}(\lambda)}{\mathrm{Rrs}(555)}$ ratio (with λ=443, 490 and 510 respectively) and to the Maximum of Band Ratio (MBR, see Eq. (2)). MBR coincides with the single band ratios as 79% (R_{555}^{443}), 20% (R_{555}^{490}) and 1% (R_{555}^{510}) of the 466 matchup points.

The analysis of the largest *in situ* bio-optical dataset ever used for the Mediterranean area, indicates then the need and implicitly suggests the means for developing a new regional algorithm of the Mediterranean Sea. Although no data are available from the Levantine basin, the present dataset covers the main Mediterranean trophic regimes (0.02 to ~7 mg m^{-3}), whereas DORMA and BRIC were developed using datasets covering limited range of bio-optical conditions. Therefore, our bio-optical dataset (Fig. 4a) has been used to derive a set of coefficients for a new regional algorithm based on the OC4 functional form, namely MedOC4. The coefficients were estimated through a fourth power polynomial regression fit between log-transformed *in situ* MBR and C_M:

$$\mathrm{Chl}_{\mathrm{MedOC4}} = 10^{(0.4424-3.686\ R+1.076\ R^2+1.684\ R^3-1.437\ R^4)} \quad (3)$$

where

$$R = \log_{10}(\mathrm{MBR})$$

In Fig. 4b, the comparison between the new MedOC4 algorithm and C_M shows that the functional form fits well the observed values. The data points are uniformly distributed around the line of best agreement, with a percent difference that rarely exceeds the 1:2 and 2:1 lines. The RMS is obviously zero and APD is 30%.

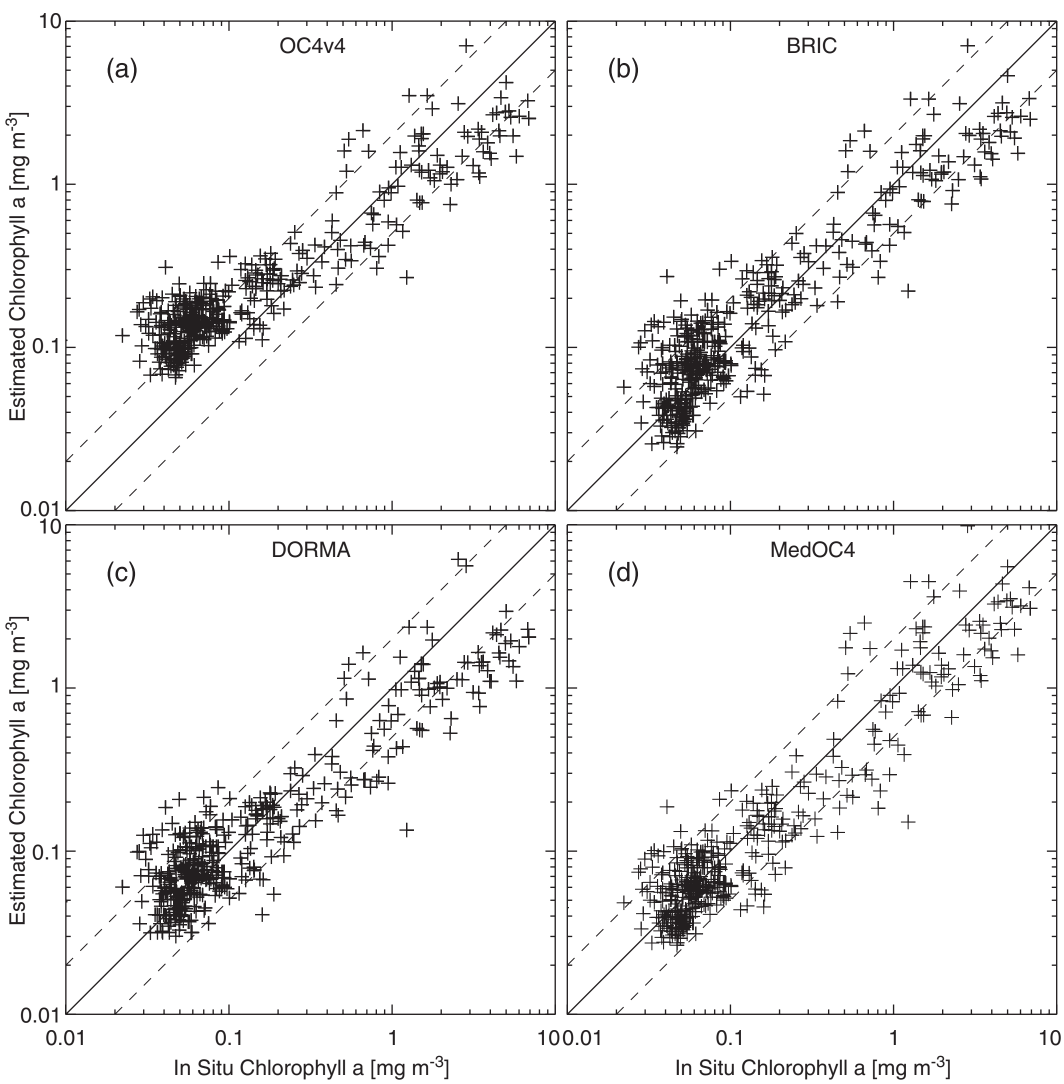

Fig. 7. Validation of SeaWiFS chlorophyll *a* estimates against concurrent *in situ* chlorophyll *a* data (C_M). (a) SeaWiFS estimates are obtained applying the OC4v4 algorithm. (b) SeaWiFS estimates are obtained applying the BRIC algorithm. (c) SeaWiFS estimates are obtained applying the DORMA algorithm. (d) SeaWiFS estimated are obtained applying the MedOC4 algorithm. The 1:1 (continuous line) 1:2 (bottom dashed line) and the 2:1 (top dashed line) lines are also plotted.

A final comparison of all algorithms has been carried out by analysing the RPD values in five different chlorophyll ranges (Fig. 5). They have been chosen to maintain a roughly constant number of points in all intervals. The graph displays RPD trends versus chlorophyll concentration. In particular, OC4v4's RPD improves as chlorophyll increases, whereas BRIC's RPD exhibits a bell shaped curve, with the maximum in correspondence of 0.05–1 mg m^{-3} chlorophyll range. For these ranges, the use of R_{555}^{443} instead of the maximum band ratio is likely to cause the observed peak in the RPD. Similarly, DORMA performs better when the maximum band ratio coincides with R_{555}^{490} (0.1–1 mg m^{-3}), diverting from the zero RPD line for values lower than 0.1 mg m^{-3} and larger than 1 mg m^{-3}. Compared to the two previous regional algorithms, the MedOC4 is definitively closer to zero RPD for all the considered chlorophyll ranges (RPD ranges between 5 and 11%).

5. Validation of SeaWiFS chlorophyll

To quantify the uncertainties on the satellite oceanic products, we compared SeaWiFS remotely sensed Rrs ratio (i.e., input for the ocean colour algorithms) and chlorophyll (output) with corresponding *in situ* measurements.

The scatterplot of SIMBADA versus SeaWiFS MBRs for 466 co-located measurements (Fig. 6) shows a good agreement between the two independent datasets, which is also confirmed by the statistics in Table 3. Moreover, in Fig. 6, different colours have been used to highlight the different band ratios used to compute MBR from which no evident bias is appreciable as a function of the different band ratios. From Table 3, the correlation coefficients decrease as wavelength in the blue spectrum increases. Conversely, RMS values improve with wavelength. This is due to the increasing distance between the extrapolated blue bands and the NIR region during the atmospheric correction procedure. APD values appear independent of the wavelength and stable around ~10%. However, MBR, by maximizing the signal-to-noise ratio, yields the highest r^2 (0.85) and the lowest BIAS (0.06) and RPD (2%) values. This result agrees with previous comparison of satellite radiometric products and *in situ* measurements in the Mediterranean Sea (Zibordi et al., 2006). It is worth noting that the derivative of the chlorophyll concentration with respect to MBR is higher for low values of MBR. Therefore the observed uncertainty on MBR could eventually affect the chlorophyll estimates only at high chlorophyll concentrations.

To verify the impact of the regional algorithms in the production of Level-3 data with respect to the standard global products, the three selected algorithms and the new MedOC4 were used to retrieve chlorophyll concentrations from SeaWiFS data and subsequently compared with the *in situ* co-located chlorophyll measurements. It is important to underline that the *in situ* chlorophyll dataset used in this section to build up the matchup dataset is independent from the one used in § 3 and § 4 (Table 1).

Scatterplots between C_M and SeaWiFS matchups (Fig. 7) show that all the regional algorithms improve the SeaWiFS chlorophyll estimates and confirm the results obtained in the previous algorithms validation section: the global OC4v4 algorithm significantly overestimates the chlorophyll in oligotrophic conditions whereas the regional ones do not display significant bias. For higher chlorophyll concentrations, satellite-derived values appear more scattered around the line of best agreement than the corresponding ones derived from *in situ* radiances (Figs. 3 and 4b) and less correlated to *in situ* measurements (Table 4c).

The analysis of the statistical parameters shows that the overall algorithms' performance is slightly decreased, as compared to results from purely *in situ* data (Rrs and C_M). For consistency with Section 3, the statistical analysis has been performed for the whole dataset and the two subsets defined in Section 3 (Table 4).

For the whole dataset r^2, RMS and BIAS are of the same order of magnitude for all algorithms, and show a general C_M underestimation (negative BIAS); on the other hand APD and RPD decrease from OC4v4 (117% and 103%) to MedOC4 (40% and 3%).

For C_M<0.40 mg m^{-3}, the correlation coefficient significantly decreases for all algorithms (ranging between 0.49 and 0.56); RMS and BIAS significantly decrease from OC4v4 (0.09 and 0.08 mg m^{-3}) to MedOC4 (0.04 and zero mg m^{-3}). Similarly, APD and RPD indicate an increase in algorithms' performance from OC4v4 (134% and 133%) to MedOC4 (35% and 6%).

Table 4
Validation of the SeaWiFS Level 3 products produced using the selected regional/global bio-optical chlorophyll algorithms in the satellite data processing chain

(a)

$0.01 < C_M < 10.0$ mg m^{-3} $N=440$

Algorithms	r^2	RMS	BIAS	APD	RPD
OC4v4	0.66	0.72	−0.08	117	103
BRIC	0.66	0.72	−0.13	54	27
DORMA	0.57	0.84	−0.21	48	15
MedOC4	0.62	0.73	−0.11	40	3

(b)

$0.01 < C_M < 0.40$ mg m^{-3} $N=348$

Algorithms	r^2	RMS	BIAS	APD	RPD
OC4v4	0.54	0.09	0.08	134	133
BRIC	0.56	0.06	0.02	55	38
DORMA	0.49	0.05	0.01	46	28
MedOC4	0.55	0.04	0.00	35	6

(c)

$0.40 < C_M < 10.0$ mg m^{-3} $N=92$

Algorithms	r^2	RMS	BIAS	APD	RPD
OC4v4	0.33	1.56	−0.68	50	−10
BRIC	0.33	1.57	−0.71	50	−12
DORMA	0.24	1.83	−1.04	55	−33
MedOC4	0.31	1.59	−0.49	58	−6

Correlation coefficient (r^2), Root Mean Square (RMS), Mean Bias Error (BIAS), Relative Percentage Difference (RPD), Absolute Percentage Different (APD) for the 440 co-located *in situ* Chlorophyll (C_M) and SeaWiFS matchups. The statistical parameters are shown for different C_M ranges.

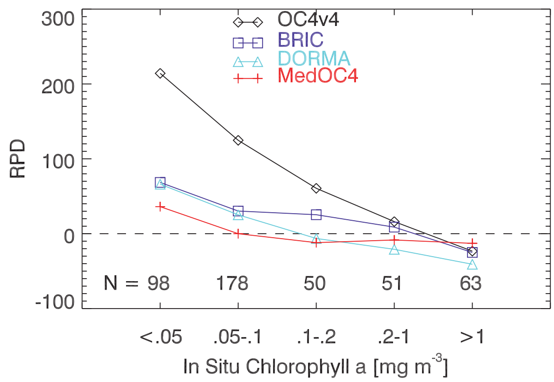

Fig. 8. Relative Percentage Difference (RPD) between SeaWiFS-derived chlorophyll and co-located *in situ* C_M for all the four algorithms and for five chlorophyll ranges. Numbers within the plot indicate the number of data points used to retrieve RPD in each range.

For $C_M > 0.40$ mg m^{-3} the correlation coefficient drops to 0.2–0.3; RMS is sensibly high (1.6–1.8 mg m^{-3}) for all algorithms while BIAS ranges from −0.49 (MedOC4) to −1.04 mg m^{-3} (DORMA). APD and RPD show that there is no significant difference among all algorithms.

The plot of the RPD as a function of chlorophyll range concentrations (Fig. 8) shows that for $C_M < 0.05$ mg m^{-3} there is a general decrease in algorithms' performance. Moreover, the OC4v4 exhibits an increasing performance towards higher chlorophyll values. BRIC and DORMA performances are similar to that in Fig. 5. On the other hand, MedOC4 significantly improves the SeaWiFS chlorophyll retrieval in the Mediterranean Sea being very close to zero bias conditions in almost all ranges of C_M.

6. Discussion and conclusions

In this paper, uncertainties in the retrieval of satellite surface chlorophyll concentrations have been evaluated using both regional and global ocean colour algorithms. The rationale for this effort was to define the most suitable ocean colour algorithm for the reprocessing of the entire SeaWiFS archive over the Mediterranean region where standard algorithms were demonstrated to be inappropriate. Using a large dataset of coincident *in situ* chlorophyll and optical measurements, covering most of the trophic regimes of the basin, we validated two existing regional algorithms and tuned a new algorithm for the basin.

The results of our analysis confirmed that the OC4v4 standard algorithm performs worse than the two existing regional algorithms (BRIC and DORMA), at least during the time interval of our dataset (1997–2004). Nonetheless, these two regional algorithms do show errors dependent to chlorophyll values. In fact, these algorithms were based on possibly under-representative *in situ* datasets. In particular the high chlorophyll values used to calibrate BRIC were all from the Alboran Sea, whose dynamics is quite peculiar and strongly connected with the inflowing Atlantic Ocean (Astraldi et al., 1999), while DORMA did not include values beyond 1.9 mg m^{-3} in its *in situ* dataset. Due to the more extensive integrated dataset in our hands we introduced a better tuned algorithm, the MedOC4, having the same functional form than OC4v4 but an overall performance significantly better than all the tested ones.

We then analyzed the performance of all the algorithms when used to retrieve chlorophyll concentration from SeaWiFS using an independent set of *in situ* data. The results of this analysis confirmed that MedOC4 is the best algorithm matching the requirement of unbiased satellite chlorophyll estimates and improving the percentage of the satellite estimate errors. Moreover, we found that the difference between the chlorophyll concentrations based on bio-optical *in situ* measurements and those derived from satellite display, on average, a very small difference (Figs. 5 and 8). This suggests that the poor performance of the standard algorithm is not due to the atmospheric

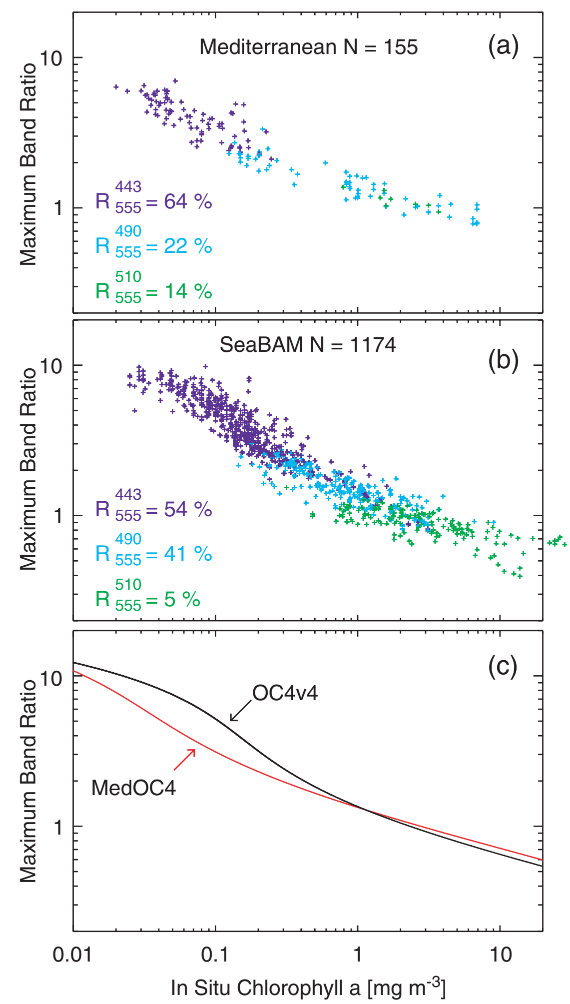

Fig. 9. Intercomparison between Mediterranean and global (SeaBAM) *in situ* bio-optical measurements. (a) Relationship between *in situ* MBR and C_M for the Mediterranean dataset (this work, Table 1) (b) Relationship between *in situ* MBR and C_M for the global SeaBAM dataset. Blue crosses indicate that MBR corresponds to R_{555}^{443}; light blue crosses indicate that MBR corresponds to R_{555}^{490}; green crosses indicate that MBR corresponds to R_{555}^{510}. The percent number of times in which the three R_{555}^{λ} correspond to MBR are also superimposed. (c) The two best lines fitting the Mediterranean and SeaBAM datasets are plotted: MedOC4 (red) and OC4v4 (black). SeaBAM dataset archive is available on the Internet at http://seabass.gsfc.nasa.gov/seabam/pub/maritorena_oreilly_schieber/seabam919.txt web page.

correction term, as one might have been hypothesized due to the peculiar aerosol of the region (Claustre et al., 2002; D'Ortenzio et al., 2002). This conclusion is also supported by the analysis we conducted on the SIMBADA–SeaWiFS matchup dataset to test the accuracy of the satellite band ratios over the Mediterranean Sea.

The observed discrepancy between the global and the regional bio-optical algorithms might depend on methodological differences between the datasets used to derive the algorithms coefficients, or on differences among the inherent bio-optical properties of the two domains. The OC4v4 algorithm was built on a later version of the SeaBAM bio-optical archive which is prevalently composed of above-water radiance measurements (88%, Fig. 9). On the other hand, the bio-optical dataset used to develop the MedOC4 is mainly based on in-water radiance measurements (67%). A recent study by Hooker and Morel (2003) showed that above-water measurements could account up to 4–8% RPD for the blue-to-green ratios. The comparison of the two MBRs do show a difference (~65% in the chlorophyll range 0.01–0.05 mg m^{-3} and ~37% for chlorophyll at 0.2 mg m^{-3}) which is an order of magnitude grater than what found by Hooker and Morel (2003).

A second methodological difference between the datasets is the utilization of mostly surface chlorophyll concentration (SeaBAM) instead of the optically weighted chlorophyll concentration (MedOC4).

Recently, Stramska and Stramski (2005) demonstrated that a deep chlorophyll maximum (DCM) close to the surface can

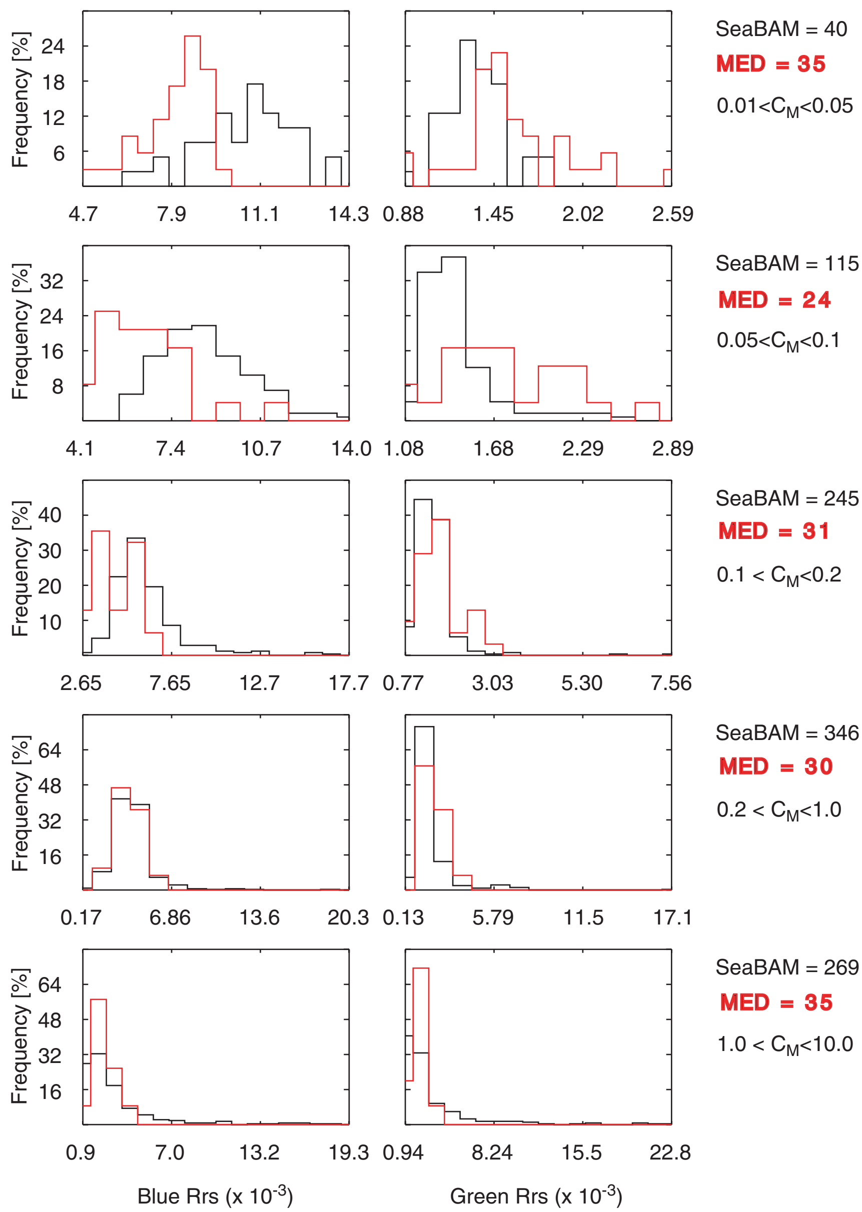

Fig. 10. Normalized frequency histograms of the Rrs for the Mediterranean (red) and SeaBAM global datasets (black) for five different chlorophyll ranges. Left panels indicate the maximum value among Rrs(443), Rrs(490) and Rrs(510) (i.e., the numerator of MBR). Right panels indicate Rrs(555) (i.e., the denominator). Chlorophyll *a* ranges are indicated on the right hand side of each row along with the number of points used for each of the two datasets.

affect the radiant field by a non-negligible amount. This can quantitatively explain the failure of standard algorithms (OC4v4) on a regional basis, as long as the use of the surface chlorophyll value, as in the OC4v4, assumes a homogeneous distribution of the pigment for the first optical depth. The extent of the uncertainty depends mostly on the depth of the DCM, but also on its amplitude. Therefore we selected among our profiles those with a DCM within the first optical depth. Only 10% of the profiles fell within this category. Afterwards we modelled our profiles with the Stramska and Stramski (2005) approach, defining a series of coupled values (chlorophyll at surface — DCM depth), and concluded that only 1 to 2% of them had a chlorophyll value at surface and a DCM depth such to significantly affect the Rrs(λ). This implies that the influence of the DCM on the surface radiant field is negligible in the Mediterranean Sea.

So far it appears that the observed differences are attributable to environmental bio-optical characteristics of the Mediterranean, which ask for further investigations.

We attempted to characterize the spectral pattern of Rrs, for the two datasets (SeaBAM and ours) at different chlorophyll ranges to highlight the differences in the spectral signatures of the basin versus the global ocean.

To this aim, we analyzed the statistical distribution of Rrs's values in the blue (numerator of MBR) and green bands (denominator of MBR), in the two datasets in different chlorophyll ranges (Fig. 10). Statistical tests (*t*-Student, 99% significance) were performed on sample data to verify whether the two datasets are significantly different. In fact, the Mediterranean Sea looks relatively “greener” for low chlorophyll values than the global ocean (Fig. 9) and this can be either due to the fact that the Mediterranean Sea is less blue and/or effectively greener. The opposite is true for higher chlorophyll values in which the global ocean appears slightly greener than the Mediterranean Sea. Histograms in Fig. 10 show that in the 0.01–0.05 mg m^{-3} chlorophyll range the Mediterranean Sea is both less blue and greener than the global ocean. The amount of such a shift has been quantified in $\sim$30% RPD for the blue bands and $\sim$15% RPD for the green bands. In the second range, this shift is even more evident: the Rrs in the blue bands measured in the Mediterranean is $\sim$35% lower than that of the global ocean and the Rrs in the green is $\sim$18% higher than that measured in the global ocean. In the 0.1–0.2 mg m^{-3} chlorophyll range the different Rrs ratio is due to a blue shift of approximately 32% while the green bands are not significantly different. The blue and the green in the 0.2–1 mg m^{-3} range are not significantly different. In the last of the considered ranges, even if the two fitting lines appear to be very close to each other (Fig. 9c), the datasets are significantly different. The Mediterranean is 23% bluer and 35% RPD less green than the global ocean.

It is important to underline that the upgraded version of former SeaBAM dataset has been used also to develop the ocean colour algorithms for MODIS Aqua and Terra as well as for MERIS. So it is likely that chlorophyll estimates in the Mediterranean Sea with remote sensors other than SeaWiFS, will be biased as well. The presence of a bias in the chlorophyll estimates is quite problematic when satellite products are used in primary production models, in validation and tuning of ecosystem modelling and especially in data assimilation systems where an error in satellite estimate can worsening rather than improving the model performance. Therefore, the re-analysis of SeaWiFS dataset using the MedOC4 regional algorithm planned in MERSEA is mandatory before the possible use of satellite data in Mediterranean assimilation system.

The impact of the new MedOC4 algorithm on primary production estimates of the Mediterranean Sea was quantified to be approximately 10% less than the same estimate using BRIC (Colella, personal communication). Note that the use of BRIC already reduced the Mediterranean primary production estimate of approximately 30% with respect to the same calculation made using OC4v4 (Bosc et al., 2004; Bricaud et al., 2002). Since primary production models exhibit high sensitivity to the surface chlorophyll concentration then the selection of an adequate bio-optical algorithm becomes critical.

Why then the Mediterranean Sea displays a different colour than the global ocean? Our dataset cannot basically answer this question. Though, some insight can come from two recent studies by Alvain et al. (2005, 2006). They, using the GeP and CO (Dandonneau et al., 2004) dataset which is an upgraded version of the SeaBAM, generated two independent sets of classes for HPLC pigment spectra and normalized water leaving radiances (nL_w^*) and found a one to one correspondence among the two sets. Since each HPLC class corresponded to a phytoplankton association with the dominance of one of the main group, e.g., diatoms, haptophytes, *Synechococcus* Like Cyanobacteria (SLC) and *Prochlorococcus*, the corresponding class of nL_w^* should then result from the presence of the same association *in situ*. In other words a specific colour signature, within the reduced number of classes they were able to discriminate, should result from the dominance of a phytoplankton group, i.e., from the ecological dynamics of the area. Their approach allowed for the derivation of four community specific bio-optical algorithms which are embedded in the NOMAD global bio-optical dataset. Therefore their curves fall outside the peculiar Mediterranean dataset. Nevertheless, we think that their approach is very enlightening and suggests that Mediterranean peculiarity can likely be related to ecological reasons, rather than abiotic environmental components. Among those, the already stressed presence of coccolitophores (Malinverno et al., 2003), the dominance of prokaryots or a high ratio among eterotrophs and autotrophs (Casotti et al., 2003 and references therein) could play a role.

The extent to which a different phytoplankton community structure and distribution could alter the spectral signature of the water column can be assessed with more refined bio-optical measurements, which will be likely acquired in future campaign. This target should be at hand with the new generation of bio-optical sensors.

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Appendix A

For the purpose of algorithms' validation, five statistical parameters were chosen. These parameters are:

1. correlation coefficient (r^2)
2. root mean square (RMS)
3. mean relative percentage difference (RPD)
4. bias
5. mean absolute percentage difference (APD)

The r^2 coefficient from the correlation analysis indicates the covariance between the *in situ* observations (C_M) and algorithms-derived chlorophyll (Alg). C_M is the mean chlorophyll concentration within the penetration depth (z_{pd}) weighted for the attenuation coefficient of light (k). It is here used as a proxy for the optically weighted pigment (Eq. (6) in Clark, 1997) and has been computed as:

$$C_M = \frac{\int_0^{z_{pd}} \mathrm{Chl}(z)\exp(-2Kz)\mathrm{d}z}{\int_0^{z_{pd}} \exp(-2Kz)\mathrm{d}z}$$

RMS indicates the spread of data as compared to the best agreement and was computed as:

$$\mathrm{RMS} = \sqrt{\frac{\sum_{i=1}^{N} (\mathrm{Alg}_i - C_{Mi})^2}{N}}$$

The mean bias error was computed as:

$$\mathrm{BIAS} = \frac{1}{N}\sum_{i=1}^{N} (\mathrm{Alg}_i - C_{Mi})$$

RPD is the mean percentage difference between Alg and C_M weighted on C_M values; RPD gives an estimate of the uncertainty as a function of the chlorophyll value and can be thought as a relative BIAS; it was computed as:

$$\mathrm{RPD} = \frac{1}{N}\sum_{i=1}^{N} \left(\frac{\mathrm{Alg}_i - C_{Mi}}{C_{Mi}}\right) \times 100$$

APD, as RPD, is the difference between the algorithm estimate and the measurement, weighted on the measured chlorophyll value but, differently, it does not give any information about the direction of discrepancy; that is the difference can be either positive or negative and it represents a sort of relative RMS. APD was computed as:

$$\mathrm{APD} = \frac{1}{N}\sum_{i=1}^{N} \left|\frac{\mathrm{Alg}_i - C_{Mi}}{C_{Mi}}\right| \times 100$$

These statistical parameters provide information on the performance and uncertainty about the algorithms.

References

Alvain, S., Moulin, C., Dandonneau, Y., & Breon, F. M. (2005). Remote sensing of phytoplankton groups in case 1 waters from global SeaWiFS imagery. *Deep-Sea Research. Part 1. Oceanographic Research Papers, 52*(11), 1989−2004.

Alvain, S., Moulin, C., Dandonneau, Y., Loisel, H., & Breon, F. M. (2006). A species-dependent bio-optical model of case I waters for global ocean color processing. *Deep-Sea Research. Part 1. Oceanographic Research Papers*, *53*(5), 917−925.

Antoine, D., Morel, A., & Andre, J. M. (1995). Algal pigment distribution and primary production in the Eastern Mediterranean as derived from coastal zone color scanner observations. *Journal of Geophysical Research-Oceans*, *100*(C8), 16193−16209.

Astraldi, M., Balopoulos, S., Candela, J., Font, J., Gacic, M., Gasparini, G., et al. (1999). The role of Straits and channels in understanding the characteristics of Mediterranean circulation. *Progress in Oceanography*, *44*, 65−108.

Bosc, E., Bricaud, A., & Antoine, D. (2004). Seasonal and interannual variability in algal biomass and primary production in the Mediterranean Sea, as derived from 4 years of SeaWiFS observations. *Global Biogeochemical Cycles*, *18*(GB1005).

Bricaud, A., Bosc, E., & 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*(2–3), 163−178.

Campbell, J. W. (1995). The lognormal-distribution as a model for bio-optical variability in the Sea. *Journal of Geophysical Research-Oceans*, *100*(C7), 13237−13254.

Casotti, R., Landolfi, A., Brunet, C., D'Ortenzio, F., Mangoni, O., Ribera d'Alcala, M., et al. (2003). Composition and dynamics of the phytoplankton of the Ionian Sea (eastern Mediterranean). *Journal of Geophysical Research*, *108*(C9), 8116.

Clark, D. K. (1997). *Bio-optical algorithms — Case 1 waters.* MODIS algorithm theoretical basis document 19.

Claustre, H., Morel, A., Hooker, S. B., Babin, M., Antoine, D., Oubelkheir, K., et al. (2002). Is desert dust making oligotrophic waters greener? *Geophysical Research Letters*, *29*(10) (art. no.-1469).

D'Ortenzio, F., Marullo, S., Ragni, M., d'Alcala, M. R., & Santoleri, R. (2002). Validation of empirical SeaWiFS algorithms for chlorophyll-alpha retrieval in the Mediterranean Sea — a case study for oligotrophic seas. *Remote Sensing of Environment*, *82*(1), 79−94.

Dandonneau, Y., Deschamps, P. -Y., Nicolas, J. -M., Loisel, H., Blanchot, J., Montel, Y., et al. (2004). Seasonal and interannual variability of ocean color and composition of phytoplankton communities in the North Atlantic, Equatorial Pacific and South Pacific. *Deep-Sea Research II*, *51*, 303−318.

Darecki, M., & Stramski, D. (2004). An evaluation of MODIS and SeaWiFS bio-optical algorithms in the Baltic Sea. *Remote Sensing of Environment*, *89*(3), 326−350.

Fougnie, B., Deschamps, P. Y., Frouin, R., & Mitchell, B. G. (1998). Measuring water-leaving radiance with a polarization radiometer: theory and experimental verification. *EOS Transactions*, *79*(1), 99.

Garcia, C. A. E., Garcia, V. M. T., & McClain, C. R. (2005). Evaluation of SeaWiFS chlorophyll algorithms in the Southwestern Atlantic and Southern Oceans. *Remote Sensing of Environment*, *95*, 125−137.

Gitelson, A., Karnieli, A., Goldman, N., Yacobi, Y. Z., & Mayo, M. (1996). Chlorophyll estimation in the Southeastern Mediterranean using CZCS images: adaptation of an algorithm and its validation. *Journal of Marine Systems*, *9*(3–4), 283−290.

Gregg, W. W., & Casey, N. W. (2004). Global and regional evaluation of the SeaWiFS chlorophyll data set. *Remote Sensing of Environment*, *93*(4), 463−479.

Hooker, S. B., McClain, C. R., Firestone, J. K., Westphal, T. L., Yeh, E. -n., & Ge, Y. (1994). *The SeaWiFS Bio-optical Archive and Storage System. N.T.M. 104566.* Greenbelt, Maryland: NASA Goddard Space Flight Center.

Hooker, S. B., & Morel, A. (2003). Platform and environmental effects on above-water determinations of water-leaving radiances. *Journal Of Atmospheric And Oceanic Technology*, *20*(1), 187−205.

Malinverno, E., Ziveri, P., & Corselli, C. (2003). Coccolithophorid distribution in the Ionian Sea and its relationship to eastern Mediterranean circulation during late fall to early winter 1997. *Journal of Geophysical Research-Oceans*, *108*(C9).

Marty, J. C., Chiaverini, J., La Rosa, J., & Miquel, J. C. (1995). Dyfamed, une station d'observation de l'environnement marin en Méditerranée. *Met. Mar.*, *Vol. 167* (pp. 33−36).

McClain, C. R., Arrigo, K. R., Esaias, W., Darzi, M., Patt, F. S., Evans, R. H., et al. (1995). SeaWiFS Algorithms, Part 1. *NASA Tech. Memo. 104566*, *Vol. 28* Greenbelt, Maryland: NASA Goddard Space Flight Center.

McClain, M. E., & Fargion, G. S. (1999). *Simbios project annual report. N.T. M. 1999-208645.* Greenbelt, MD: NASA Goddard Space Flight Center.

Mueller, J. L. (2000). In-water radiometric profile measurements and data analysis protocols. In G. S. Fargion & J. L. Mueller (Eds.), *NASA Tech. Memo. 2000-209966, Ocean Optics Protocols for Satellite Ocean Color Sensor Validation, Revision 2.* Greenbelt, Maryland: NASA Goddard Space Flight Center.

Mueller, J. L., & Austin, R. W. (1995). *Ocean Optics Protocols for SeaWiFS Validation, Revision 1. S.B.H.a. E.R.Firestone.* Greenbelt, Maryland: NASA Goddard Space Flight Center.

Mueller, J. L., & Fargion, G. S. (2002). *Ocean Optics Protocols for SeaWiFS Validation, Revision 3. NASA Tech. Memo. 2002-210004.* Greenbelt, Maryland: NASA Goddard Space Flight Center.

Neveux, J., & Panouse, M. (1987). Spectrofluorometric determination of chlorophylls and pheophytins. *Archive of Hydrobiology*, *109*, 561−567.

O'Reilly, J. E., Maritorena, S., Mitchell, B. G., Siegel, D. A., Carder, K. L., Garver, S. A., et al. (1998). Ocean color chlorophyll algorithms for SeaWiFS. *Journal of Geophysical Research-Oceans*, *103*(C11), 24937−24953.

O'Reilly, J. E., Maritorena, S., Siegel, D., O'Brien, M. C., Toole, D., Mitchell, B. G., et al. (2000). Ocean color chlorophyll a algorithms for SeaWiFS, OC2, and OC4: Version 4. *SeaWiFS Postlaunch Technical Report Series, Vol.11*. SeaWiFS postlaunch calibration and validation analyses: part 3.

Ouillon, S., & Petrenko, A. A. (2005). Above-water measurements of reflectance and chlorophyll-a algorithms in the Gulf of Lions, NW Mediterranean Sea. *Optics Express*, *13*(7), 2531−2548.

Siegel, D. A., Wang, M., Maritorena, S., & Robinson, W. (2000). Atmospheric correction of satellite ocean color imagery: the black pixel assumption. *Applied Optics*, *39*(21), 3582−3591.

Stramska, M., & Stramski, D. (2005). Effects of a nonuniform vertical profile of chlorophyll concentration on remote-sensing reflectance of the ocean. *Applied Optics*, *44*(9), 1735−1747.

Zibordi, G., Melin, F., & Berthon, J. F. (2006). Comparison of SeaWiFS, MODIS and MERIS radiometric products at a coastal site. *Geophysical Research Letters*, *33*(6).