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**Yellow absorbing
substances in the
Mediterranean Sea**

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Yellow substance and the shades of blue in the Mediterranean Sea

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Abstract

When the nominal algorithms commonly in use in Space Agencies are applied to satellite Ocean Color data, the retrieved chlorophyll concentrations in the Mediterranean Sea are recurrently notable overestimates of the field values. Accordingly, several re-
5   gionally tuned algorithms have been proposed in the past to correct for this deviation; actually, the blueness of the Mediterranean waters is not as deep as expected from the actual (low) chlorophyll content, and the modified algorithm account for this peculiarity. Among the possible causes for such a deviation, an excessive amount of yellow substance, or of colored detrital matter (CDM), has been frequently cited. This conjecture
10   is presently tested, by using a new technique simply based on the simultaneous consideration of marine reflectance determined at four spectral bands (namely 412, 443, 490, and 555 nm, available on the NASA-SeaWiFS satellite). It results from this test that the concentration in yellow colored material (quantified as a_y, the absorption coefficient at 443 nm) is about twice that one observed in the nearby Atlantic Ocean at the same lat-
15   itude. There is a strong seasonal signal, with maximal a_y values in late fall and winter, an abrupt decrease beginning in spring, and then a deep minimum during the summer months, which plausibly results from the intense photo-bleaching process favored by the high level of sunshine in these areas. Systematically, the a_y values, reproducible from year to year, are higher in the western basin compared with those in the eastern
20   basin (by about 50%). The relative importance of the river discharges into this semi-enclosed sea, as well as the winter deep vertical mixing occurring in the northern parts of the basins may explain the high yellow substance background. The regionally tuned [Chl] algorithms, actually reflect the presence of an excess of CDM with respect to its standard (Chl- related) values. When corrected for the presence of the actual CDM
25   content, the [Chl] values as derived via the nominal algorithms are restored to more realistic values, i.e., approximately divided by about two; the strong autumnal increase is smoothed whereas the spring bloom remains as an isolated feature.

1 Introduction

The blue color of the Mediterranean Sea is legendary and rightly regarded as a sign of oligotrophic conditions. Sporadically and intermittently, however, this trophic status is modified. Indeed, in the northern parts of the Western and Eastern basins, vernal blooms develop leading to moderate to high chlorophyll concentrations and to a color shift toward blue-green shades typical of meso- to eutrophic regimes. Satellite remote radiometry of Ocean Color is a technique which is intended to detect and map such color changes and interpret them in terms of optically influential constituents, in particular of phytoplankton abundance, quantified as chlorophyll concentration, [Chl] $(\mathrm{mg\,m}^{-3})$.

Yet, the first applications of this remote sensing technique to Mediterranean waters (using the data from the CZCS, the Coastal Zone Color Sensor from NASA, operating during the years 1979–1984) showed that [Chl] retrieved from space was a notable overestimate of the true concentration as determined in situ (Gitelson et al., 1996; Antoine et al., 1995). Bricaud et al. (2002) and Antoine et al. (2008, their Fig. 14) arrived at the same conclusion when using the SeaWiFS data (Sea-viewing Wide Field-of-view Sensor). More accurately stated, the empirical algorithms, based on the ratio of ocean radiance (reflectance) in the blue and green domains, and routinely used to quantify [Chl], failed in the case of these waters. Not only remote radiometric determinations, but also in situ spectral measurements of water-leaving radiances, demonstrated that Mediterranean waters are "greener" than it would normally result from their (generally low) phytoplankton content (Claustre et al., 2002).

This often observed color "anomaly" motivated the development of specifically tuned algorithms able to reconcile the remotely sensed [Chl] (using various sensors) with the field determinations, especially when [Chl] is low (D'Ortenzio et al., 2002; Bricaud et al., 2002; Volpe et al., 2007). As also noted by Gregg and Casey (2004), anomalous optical properties of the Mediterranean Sea (and Black Sea) entail a substantial and systematic positive bias of the nominal SeaWiFS returns with respect to in situ [Chl]

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data. By applying a rather tight criterion to the SeaWiFS data, Lee and Hu (2006, their Fig. 3) also showed that if Case-1 waters prevail in Mediterranean during summer, what they called "non-Case-1" waters would be present in the Western basin in Spring and Autumn, and in both (Western and Eastern) basins at wintertime. According to these authors, such departures from the Case-1 status would essentially be due to an increase in absorption by the "colored- or chromophoric-dissolved organic matter", or equivalently, "yellow substance". Beside this possible enhanced contribution of yellow absorbing material (e.g., Siegel et al., 2002; Claustre and Maritorena, 2003), the presence of abundant coccoliths, or the episodic injection of aeolian dust, or even imperfect atmospheric corrections, were also suggested as possible causes for the persistent anomaly (Gregg and Casey, 2004; Claustre et al., 2002).

Another study (Morel et al., 2007a), however, strongly supported the hypothesis of an unusually high yellow substance content. This study was based on the consideration of the spectral diffuse attenuation coefficient, $K_d(\lambda)$. Indeed, an anomaly was detected which consisted of $K_d(\lambda)$ values in the blue part of the spectrum systematically exceeding the average values, that were expected from the [Chl] levels. Moreover, this anomaly was found to steadily increase when progressing into the UV domain, which is a typical trait of yellow substance absorption. Correlatively, the irradiance ratio in the blue-violet and near UV parts of the spectrum are distinctly depressed. The same study also showed that in similar trophic conditions (i.e., with similar [Chl] values), the yellow substance absorption coefficient at 370 nm in the Mediterranean Sea, turns out to be at least twice its value in Pacific (Fig. 9, ibid.). Along the same line, the depth of the euphotic layer is considerably reduced in the Mediterranean Sea with respect to its integrated [Chl] content (Morel and Gentili, 2004). Such a reduction can be explained if another absorbing agent is present in notable concentration and competes with algae in the bulk absorption process (Morel et al., 2007a, their Fig. 4).

A recently developed tool (Morel and Gentili, 2009), based on the simultaneous consideration of spectral marine reflectance at four wavelengths, $R(\lambda)$, allows the signatures of yellow absorbing substances (or colored detrital materials, CDM), and [Chl] to

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be disentangled. This technique can be applied to the Mediterranean Sea to determine if the CDM content is above the expected average level, and, as a consequence of such a positive deviation, if [Chl] could have been overestimated when using classical algorithms (see e.g., Hu et al., 2006). By systematically applying this discriminating tool to remotely sensed color data over the Mediterranean Sea, it will be possible to examine how, and when the CDM-related anomaly, if any, is geographically and seasonally distributed within the Western and Eastern basins of this Sea.

2 Methodology

The technique developed to separately assess the yellow substance absorption coefficient at a given wavelength λ, $a_y(\lambda)$, and the chlorophyll concentration, [Chl], was described in detail elsewhere (Morel and Gentili, 2009). For completeness, the main features are summarized below. In Case-1 waters, the above quantities were indirectly related through a non-linear mean relationship (Morel, 2009; Morel and Gentili, 2009) of the form

$$a_y(\lambda, [\text{Chl}]) = Y(\lambda)[\text{Chl}]^{0.63} \tag{1}$$

The term a_y was obtained by subtracting the water absorption and the particle absorption from the total absorption. Equation (1) represents an "average" relationship in the sense that it statistically derives from a considerable number of optical data (total absorption and particle absorption) obtained at differing seasons, in various trophic situations, and in several zones of the world ocean. When assembling these various data, however, the restriction was to exclusively consider well identified Case-1 waters. It must be noted that according to the way it is derived, the a_y term actually refers to the absorption by the truly dissolved yellow substance, but, at least partially, a_y also includes the influence of some colored detrital particles or non-algal particles (discussion in Morel, 2009). In spite of the possible slight difference in their meaning, the terms yellow substance and CDM will be interchangeably used hereafter.

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In Eq. (1), $a_y(\lambda, [\text{Chl}])$, expressed as m^{-1}, represents the "standard" values of yellow substance absorption at the wavelength λ, and for a given [Chl] value. A rather high variability around this loose relationship occurs in natural environment, and the deviations observed in the Mediterranean Sea with respect to the CDM standard value will
5 be at the basis, and also the aim, of the present study. In Eq. (1), $Y(\lambda)$ is a coefficient which decreases exponentially with λ, according to

$$Y(\lambda) = Y(\lambda_0) \exp\left[-S(\lambda - \lambda_0)\right] \tag{2}$$

where λ_0 is a reference wavelength, and S is the slope of the exponential decay for the spectral domain considered (412–560 nm). The empirical Eq. (1) was initially es-
10 tablished (Morel, 2009) for λ=400 nm. By using Eq. (2) and letting S=0.018 nm^{-1}, the following expressions

$$a_y(400, [\text{Chl}]) = 0.0650[\text{Chl}]^{0.63} \tag{3a}$$

$$a_y(412, [\text{Chl}]) = 0.0524[\text{Chl}]^{0.63} \tag{3b}$$

$$a_y(443, [\text{Chl}]) = 0.0316[\text{Chl}]^{0.63} \tag{3c}$$

15 $$a_y(490, [\text{Chl}]) = 0.0129[\text{Chl}]^{0.63} \tag{3d}$$

$$a_y(555, [\text{Chl}]) = 0.0040[\text{Chl}]^{0.63} \tag{3e}$$

can be derived for the wavelengths thereafter involved in the computations. The discriminating tool referenced above is purposely designed to detect geographical and temporal departures from the [Chl]-dependent standard CDM value. Departures are
20 simulated by introducing a factor Φ which modifies Eq. (1) (and the derived Eq. 3) according to

$$a_y(\lambda, [\text{Chl}]) = \Phi Y(\lambda)[\text{Chl}]^{0.63} \tag{4}$$

This factor Φ may be below or above unity, so that the simulated departure may be either a deficit or an excess with respect to the reference CDM values corresponding to the coefficients in Eq. (3). It is important to emphasize that the adopted reference value does not influence the result of Eq. (4), which is determined by the product $\Phi Y(\lambda)$; accordingly, the scale for Φ, in particular its neutral point ($\Phi=1$) depends on the initial choice made for $Y(\lambda)$.

The rationale behind the tool can be summarized as follows. It relies on the consideration of the reflectances, R, at 412, 443, 490, and 555 nm; they are combined to form two ratios, namely R(412)/R(443) and R(490)/R(555), thereafter simply written R_{443}^{412} and R_{555}^{490}. Within the frame of the bio-optical model for Case-1 waters denoted MM-01 (Morel and Maritorena, 2001; slightly revised in Morel et al., 2007), a unique relationship between R_{443}^{412} and R_{555}^{490} exists and can be numerically established. This relationship, which is graphically represented by the curve denoted $\Phi=1$ in Fig. 1a and b, implicitly includes the average [CDM]-[Chl] relationship (i.e., Eqs. 3 for the four wavelengths in question). When Φ is given various discrete values, a family of R_{443}^{412}–R_{555}^{490} relationships is generated, and a family of curves can be drawn (for instance, the curves for $\Phi=2$ and 5 which are displayed in Fig. 1a and b).

When R_{443}^{412} and R_{555}^{490} have been simultaneously derived from measurements at sea, or as well from space, this couple of actual values can be compared to those forming the family of curves, as theoretically generated for various Φ values. From this comparison, a factor Φ can be univocally determined. Practically, a lookup table (available at ftp://oceane.obs-vlfr./pub/gentili:CDOM-index-Table.interpol) allows such a determination through an appropriate numerical interpolation. Once Φ has been obtained, and [Chl] retrieved via a specific algorithm (e.g., OC4v4, O'Reilly et al., 1998, 2000), Eq. (3b), for instance, can provide the corresponding $a_y(443)$ value.

SeaWiFS data (from NASA) will be used in the present study, mainly as monthly composites. Normalized water-leaving radiances at 412, 443, 490 and 555 nm are converted into irradiance reflectances, and then the ratios R_{443}^{412} and R_{555}^{490} are computed and introduced into the lookup table to derive the Φ value. The turbid coastal waters

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are identified through their high reflectance at 555 nm, based on a threshold which depends on [Chl] (Morel and Bélanger, 2006), in such a way that they are no longer considered in further analyses.

3   Results

When introduced into the R_{443}^{412}–R_{555}^{490} plane, the ratios obtained from recent radiometric measurements in the Mediterranean Sea confirm the anomalously high yellow substance content, since from these field data, Φ always exceeds 1 (Fig. 1a). Ratios of SeaWiFS reflectance also lead to the same conclusion (Fig. 1b). Therefore the CDM concentration in this Sea would systematically exceed what is expected from the [Chl] values by, at least, a factor 2 in most cases.

3.1   Geographical distribution and temporal evolution of the yellow substance "excess"

To ascertain the reality of a particular behavior of the Mediterranean Sea, it seems appropriate to compare this Sea to other geographical zones, submitted to a similar climate, yet with differing circulation patterns and hydrography. An instructive comparison can thus be made by considering the contiguous zone in the North East Atlantic, West of the Gibraltar Strait, at the same latitudes (30 and 45° N), and of similar size (5°–35° W). To the extent that this Atlantic zone, off the Iberian peninsula and Moroccan coast (where coastal upwellings occur) might also be special, the entire zonal stripe extending from 30° to 45° N and encompassing the whole ocean (Atlantic and Pacific) is also considered for reference.

In a first step, the comparison is based on the maps of the Φ factor within the Mediterranean and Atlantic zones, as derived from the SeaWiFS monthly composites. Instances of these maps are shown (Fig. 2) for the months of March and August, selected because they correspond to contrasted situations in terms of biological activity

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(vernal blooms versus oligotrophic summer conditions). In the Mediterranean Sea, the lowest Φ values ($\sim$1.5–2) are found in March south of the island of Rhodes (between the islands of Crete and Cyprus), and off the Gulf of Lions, actually in those locations where the main algal blooms are known to take place (a weak bloom also occurs south of Sardinia) . These minima in Φ do not indicate a lower CDM content, but a lower relative content, in as much as [Chl] has increased up to $\sim$0.5–1.5 mg m^{-3} within these localized blooms, while the yellow substance absorption has remained rather unchanged. Except in these restricted zones, high Φ values (>3) dominate everywhere in the entire Mediterranean Sea. In contrast, low Φ values prevail in the near Atlantic; there is even a zonal belt (roughly centered on 38° N) where Φ is slightly below 1, also in coincidence with the vernal bloom. This bloom, and the concomitant low Φ values, migrate northward during the following months (not shown).

In August, the Φ values reach their minimal level ($\sim$1–2) in both the Atlantic and Mediterranean zones. Higher values, however, are present along the coast of Portugal (the seat of a coastal upwelling), and within the Gulf of Lions (probably related to the Rhone river discharge). The Aegean Sea, especially its northernmost part under the influence of the water exiting the Black Sea through the Bosporus, is permanently a zone with very high Φ values (no longer discussed). In the Black Sea, when not flagged as a turbid Case-2 zone, the radiances at 412 nm are extremely low, and Φ values always extremely high. The importance of the river discharges (Danube, Don, Dniepr) into this Sea can explain such a situation, which is no longer examined in what follows.

The temporal evolutions of the various quantities associated with the CDM content and the algal biomass are computed from the SeaWiFS monthly composites, and assembled in Fig. 3. Mean monthly values for Φ, for [Chl] (before and after correction, see later), and for a_y (443) are shown; they are also averaged within each of five geographical zones, which are delimited as follows. The western and eastern Mediterranean basins are separately considered. Actually (see Fig. 2), the eastern basin has been limited northward by the 38° N parallel, which excludes the Aegean and Adriatic Seas

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and part of the Ionian Sea; the influence of the Black Sea and Marmora Sea (mentioned above), as well as that of the often turbid Adriatic Sea are thus discarded. With such borders, the two basins distinctly differ regarding their mean latitude; the Eastern and Western basins are located southward and northward of the 38° parallel, respec-
5 tively. For consistency, in particular with respect to solar illumination conditions and thus seasonal variations, the same 38° N parallel is also used to distinguish a northern sector and a southern sector within the near-Atlantic region. The zonal belt around the globe from 30° to 45° N is not subdivided.

Globally, the Mediterranean Φ values are systematically above (by about 50 to
10 100%) those in the neighboring Atlantic, or those of the whole ocean between the same latitudes (Fig. 3, upper row). The annual cycle in the Mediterranean Sea is more featured than elsewhere. In particular, after a minimum extending from June to September, the increase from October to December, especially in the western basin, is steeper in the Mediterranean Sea than in adjacent Atlantic. It must be noted that
15 extended cloudiness and low solar illumination (which means difficult atmospheric correction) prevent from getting fully reliable data in the northern part of the western basin around the winter solstice; the same statement could be repeated for the Adriatic Sea (not discussed).

The second row shows the temporal change in the monthly and spatially averaged
20 algal [Chl] biomass, as retrieved in each zone using the OC4v4 algorithm (O'Reilly et al., 2000). Compared to the global Ocean, or to the near-Atlantic zone, there are some important particularities in the Mediterranean Sea. First of all, the [Chl] values in fall, and then the [Chl] maximum during the bloom in the Western basin (peaking in March) are higher than everywhere else. In the Eastern basin, after an early bloom in
25 February, an oligotrophic situation prevails for an extended summer period, like in the corresponding Southern Atlantic sector.

3.2 Yellow substance absorption and chlorophyll assessment

The $a_y(443)$ coefficient can be derived by inserting the Φ and [Chl] values into Eq. (3b). The absolute a_y values must be regarded with some caution, as they might be affected by an inaccurate atmospheric correction, particularly at 412 nm (discussed later); rela-
5   tive comparisons of a_y regional values, however, are safer. The monthly mean $a_y(443)$ values are displayed for each region in the third row of Fig. 3. The seasonal a_y varia- tions are considerably more accentuated in both the Mediterranean basins than in their Atlantic counterparts, and year-round, the a_y values in this eastern basin are signifi- cantly lower than those in the western basin The prominent feature is the broad winter
10 maximum which occurs in the western Mediterranean basin, starting in November and extending up to May; the a_y values are almost twice those in the corresponding At- lantic sectors, except in summertime. In the eastern basin, the winter a_y maximum is sharper and coincides with the Levantine algal bloom, occurring in February. The sum- mer (July-August-September) mean values in the Eastern basin ($a_y(443) \sim 0.013\,\mathrm{m}^{-1}$,
15 Fig. 3) are hardly above those ($0.010\,\mathrm{m}^{-1}$) in the southern Atlantic zone, which them- selves are not far from those observed in the Sargasso Sea by Nelson et al. (2007). Indeed, these authors observed at 325 nm yellow substance absorption coefficients amounting to about $0.06\,\mathrm{m}^{-1}$, approximately equivalent to $a_y(443) \sim 0.01\,\mathrm{m}^{-1}$. So, the eastern Mediterranean would be almost as "blue" as the Sargasso Sea, at least in
20 summer.

The seasonal Φ cycle as detected in 2006, actually is repeated each year without notable modification (Fig. 4a). In terms of absolute values, the absorption coefficients, $a_y(443)$, permanently differ in the western and eastern basins, since in all seasons the values in the former are above those in the latter by at least 50% (Fig. 4b). The
25 absorption coefficients at 443 nm of the dissolved and detrital (particulate) organic matter, a_{CDM}, as retrieved via the "GSM" method (Siegel et al., 2002) exhibit the same regional differences and follow the same seasonal patterns with, however, slightly lower values particularly during the blooms (not shown, but easily visualized via the Giovanni

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tool – http://reason.gsfc.nasa.gov/Giovanni/).

As explained elsewhere (Morel and Gentili, 2009), the variations in Φ lead to biased estimates of [Chl] when [Chl] is retrieved by applying standard algorithms, which implicitly includes the hypothesis $\Phi=1$. With Φ generally well above 1 in the Mediterranean Sea, and thus with an excess of CDM compared to the standard value as prescribed by Eq. (1), the corrections result in diminishing the initial OC4v4 [Chl] estimates. The correction can reach −50% when $\Phi\sim4$ (Fig. 9 in Morel and Gentili, 2009). In both the Mediterranean basins, such a halving happens in winter and early spring (last row in Fig. 3), while the correction is less ($\sim$ −20/30%) in summertime. After correction, the spatially averaged [Chl] values in the Eastern basin would not exceed $0.10\,\mathrm{mg\,m}^{-3}$ in February–March, and are almost constant (around $0.065\,\mathrm{mg\,m}^{-3}$) for the rest of the year, confirming the oligotrophic status of this province. In the Western basin, the bloom peaking in March is considerably reduced when corrected (0.25 versus $0.47\,\mathrm{mg\,m}^{-3}$), and thereafter [Chl] remains roughly constant amounting on average to $\sim0.1\,\mathrm{mg\,m}^{-3}$. Importantly, the strong progressive increase in [Chl] from September to January, that appears in both basins through the use of standard algorithms, is largely smoothed out after correction, in such a way that the bloom in March (Western basin) emerges as a more isolated feature. Actually, field data in the northern part of the western basin (Marty et al., 2002; Antoine et al., 2008) do not indicate a regular and so strong algal biomass increase during autumn, and instead tend to support the corrected values. It is also worth noting that the northern Atlantic sector, where the Φ and a_y values are notably below those of Mediterranean, exhibits the most prominent [Chl] peak during the spring bloom (in April), almost unaffected by the CDM correction.

3.3 Yellow substance excess and regionally tuned algorithms

To reconcile the field and satellite determinations of [Chl] in the Mediterranean Sea, "regional" algorithms were empirically proposed; they were simply based on regression analyses of blue-to-green reflectance ratios, such as R_{555}^{443} (in Gitelson et al., 1996; or Bricaud et al., 2002), or R_{555}^{490} (in D'Ortenzio et al., 2002) or MBR (Maximum band

ratio, in Volpe et al., 2007) versus field determinations of [Chl]. These empirical relationships were used by these authors instead of the algorithms regularly operated at global scale by Space Agencies. They provided more realistic [Chl] values when compared to the overestimated concentrations returned by the routine algorithms. It is thus logical to examine to what extent the CDM excess detected in the Mediterranean is able to perturb the returns of the standard algorithms, and correlatively, whether the empirically algorithms actually reflect in their tuned version the influence of an excess in CDM.

For that purpose, the bio-optical model for Case-1 waters (MM-01) is operated to get the spectral reflectance as a function of [Chl], and produce the ratios of reflectances which are successively considered in the MBR algorithm (O'Reilly et al., 2000). The result is the semi-analytical OC4Me555 algorithm (already presented in Morel et al., 2007b), which differs only slightly from the purely empirical algorithm OC4v4 employed with SeaWiFS data. The obvious advantage of using the semi-analytical approach (compared to empirical approach) is the possibility of simulating "perturbations" and examining their effects. The first perturbation here considered consists of increasing the partial absorption due to CDM (by letting $\Phi > 1$); the results are graphically shown in Fig. 5a. Besides the unperturbed nominal algorithm (i.e., when $\Phi = 1$), the curves corresponding to $\Phi = 2$ and 4 are also drawn. They can be compared with the regionally tuned algorithms, which roughly agree with the modeled algorithm when a doubling in CDM ($\Phi = 2$) has been introduced. This agreement tends to demonstrate that the proposed algorithms have indeed been influenced by the excess of yellow substance, and "bent" or distorted accordingly.

Another scenario, however, must be envisaged, by which CDM would stay at its standard level, while the particle backscattering coefficient, b_{bp}, would be modified. This hypothesis was already examined in Morel and Gentili (2009): for that they introduced a perturbation, represented by Ψ (either <1 or >1), which is the ratio of the modified b_{bp} coefficient to its standard, [Chl]-dependent, value. By operating the MM-01 model, the modified MBR $\leftrightarrow$ [Chl] relationships can be produced for various Ψ values, as it was

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made for Φ. Increasing Ψ above 1 produces an effect in the same direction as that observed when increasing Φ, but the amplitude of this effect is much lesser (Fig. 5b). For instance, the position (in Fig. 5a) of the empirical algorithm proposed by Bricaud et al. (2002) can be explained if the CDM content is doubled (as said above), but if the change in particle backscattering is presumed to be the cause of the shifted algorithm, a more considerable increase of b_{bp} must be considered (approximately by a factor Ψ=5).

Nevertheless, it cannot be dismissed that the difference between the regionally derived relationships and the regular algorithm does not reflect exclusively a change inyellow substance concentration. Indeed, an enhanced backscattering, b_{bp}, was hypothesized by Gitelson et al. (1996), whereas the effect of calcite was also examined by D'Ortenzio et al. (2002). Actually, the couples of wavelengths involved in the maximum band ratio, or in the above empirical regional algorithms (namely 443–555 or 490–555 nm), cannot provide an efficient mean to discriminate the cause of the anomaly (either CDM, or backscattering). To be efficient a tool must involve the 412 nm band, which is particularly sensitive to the CDM amount. This is demonstrated by Fig. 6a and b, where the modeled R_{443}^{412} reflectance ratio is plotted as a function of [Chl]. Beside the nominal relationship (when Φ and Ψ=1), are shown the modified relationships, namely when Φ=2 and 4 (while Ψ=1), or when Ψ=2 and 4 (while Φ=1). Changes in the backscattering coefficient result in reduced modifications compared to those induced by changes in CDM. The SeaWiFS data (R_{443}^{412} and [Chl]) for the year 2006, taken as examples, are also displayed. Two features are particularly significant: i) the actual R_{443}^{412} ratios seldom reach the ceiling curve which would correspond to a standard situation with Φ=1, and ii) their distance from this curve is such that a (moderate) excess of yellow substance is the most plausible explanation to the observed departures, rather than a huge b_{bp} increase needed to generate departures of similar amplitude. Anyway, if existing, such large excesses in backscattering would have inevitably been detected (and the corresponding pixels flagged) when the turbidity criterion was applied.

An additional confirmation of the crucial role of yellow absorbing substance(s) can

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be found by comparing the distribution of the same (SeaWiFS, 2006) data in Fig. 1b with the theoretical curves of Fig. 2c in Morel and Gentili (2009). In the latter, it can be seen that when [Chl] is $<0.25\,\text{mg m}^{-3}$ approximately (i.e., when $R_{555}^{490}>2.5$), the impact of changes in Ψ becomes extremely weak. This is a logical consequence of the pre-dominance of the backscattering by water molecules over the particle backscattering in this low-[Chl] range. Most of the pixels in the Mediterranean Sea fall in this range, and thus are rather insensitive to changes in Ψ (if any).

4   Discussion and conclusion

The major initial motivation of the present study was to understand why the ocean color radiometry applied to the Mediterranean Sea has recurrently provided data contradict-ing the historically acknowledged low Chlorophyll concentration. This contradiction was maintained when contemporaneous [Chl] measurements performed at sea during sev-eral cruises were compared to satellite returns (e.g., Claustre et al., 2002). Among the potential causes invoked to account for such a discrepancy, an "anomalously" high yellow substance content compared to oceanic average values was a plausible can-didate. This hypothesis has been tested by operating and applying to SeaWiFS data a recently proposed method capable of detecting such an excess. As a first conclu-sion, it appears that a notable yellow substance excess does exist in both basins of the Mediterranean Sea when they are compared with the neighboring Atlantic sectors. This excess explains why the current algorithms have generally overestimated [Chl], and also how the regionally tuned algorithms have been able to return more realistic values.

A first discussion necessarily deals with the accuracy of the present results and their numerical significance. As already underlined when describing the method here em-ployed (Morel and Gentili, 2009), the quality of the retrieved marine signal at 412 nm is crucial, via the R_{443}^{412} ratio. Unfortunately, beside the sensor calibration problem, achieving an accurate atmospheric correction at this wavelength is a difficult task so

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that the assessment of the marine signal may be affected. The difficulty increases when the air mass increases, i.e., when the sun-zenith angle and the viewing angle increases (Wang, 2009). A recent match-up analysis of satellite derived reflectances compared with in situ radiometric observations (Antoine et al., 2008) showed that the poorest performances are precisely observed for this 412 nm channel. For the three major sensors (SeaWiFS, MODIS-A, and MERIS), the scatter of the satellite values compared with field values (Fig. 9, and Tables 2, 3, and 4, ibid.) is larger at 412 nm than at any other wavelength, and in addition, the three sensors behave differently. For instance, the MERIS reflectances at 412 nm are considerably overestimated with an average MERIS-to-in situ data ratio amounting to about 1.60 (and 1.32 and 443 nm). In contrast, this ratio is closer to unity (0.92 for SeaWiFS, and 0.90 for MODIS-A), likely because these sensors have been vicariously calibrated on orbit, which is not yet the case for MERIS. As an overestimate of the marine reflectance at 412, and hence of the R_{443}^{412} ratio, leads to a reduction of the Φ factor, and subsequently of the $a_y(443)$ values, it is not surprising that the $a_y(443)$ values derived from MERIS data (not shown) are systematically below those derived from SeaWiFS; the divergence increases in winter when the sun-zenith angle reaches its highest values ($\sim70°$) in the northern part of the Mediterranean basins. The examination of the atmospheric correction performance at the bluest wavebands is a topic in itself, and a difficult topic, out of the scope of the present study. It is worth noting that the results here presented actually rest on the use of a single sensor and a single atmospheric scheme, developed for SeaWiFS, which at least allows an internal consistency of the results to be preserved. This caution regarding the quality of the violet signal, however, has to be kept in mind and justifies the previous recommendation of considering the relative variations from zones to zones, rather than the absolute $a_y(443)$ values. Field measurements of the yellow substance content in the Mediterranean Sea and neighboring Atlantic are not yet available to consolidate the satellite derived a_y values. As said before, however, indirect estimates via field values of the diffuse attenuation coefficient and spectral reflectance in the near UV domain (Morel et al., 2007a) qualitatively support the existence of high

yellow substance content in the Mediterranean Sea.

Even if the enigmatic failure in the remote assessment of [Chl] in the Mediterranean Sea, and the presumably peculiar optical properties in this area have formed the main motivations of the present paper, it is difficult to dodge the issue of the origin of such a singularity. A second discussion will briefly deal with this geochemical aspect. The main specific traits can be summarized as follows; i) the CDM level in the Mediterranean Sea is about twice that of nearby oceanic waters with similar trophic conditions, ii) the level is higher in the western basin than in the eastern basin, and inside the western basin the level is higher in the northern zone compared to the southern zone, iii) there is everywhere a pronounced seasonal signal, mainly shaped by the strong depression during summer, superimposed upon a background of high values.

First of all, the sources and sinks of CDM in the open ocean, as well as the (physical, chemical, biological) interactions regulating its concentration and distribution remain largely elusive (e.g., discussion in Nelson and Siegel, 2002). This general statement obviously continues to hold true as far as the Mediterranean Sea is concerned. A clue, perhaps, to get some insight into the question of a higher CDM content could be to examine what are the specificities of this semi-enclosed sea.

The possibility that such a CDM background (and particularly its dissolved fraction) may have a significant terrestrial component is to be considered (Nelson and Siegel, 2002). As suggested by Siegel et al. (2002), for instance, the difference in the bulk CDM concentration in the North Atlantic Ocean and in the North Pacific Ocean could plausibly originate from differences in riverine inputs, 3 times greater in the former zone than in the latter. Is such a similar explanation applicable to the Mediterranean Sea, and to the contrast between this sea and the neighboring Atlantic?

To examine this question, the water discharge of the major world rivers are considered; they are taken in Cauwet (2002), and the oceanic areas in Sverdrup et al. (1963). From these data it can be inferred that the annual mean river discharges is equivalent to a layer of about 180 mm yr^{-1} for the ocean within the Northern Hemisphere (including its Arctic and Baltic regions), and 27 mm yr^{-1} for the ocean within the Southern

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Hemisphere; note that such computations assume that the two oceanic hemispheres are hypothetically disconnected. The dissymmetry in the oceanic distribution of CDM, with higher mean concentration in the Northern Hemisphere, compared to that in the Southern Hemisphere (e.g. Fig. 4 in Siegel et al., 2002, and Figs. 5 and 6c in Morel and Gentili, 2009) could thus originate from the dissymmetry in the river impact. The same kind of computation for the ensemble Mediterranean Sea plus Black Sea leads to an annual river discharge equivalent to approximately $135\,\mathrm{mm\,yr^{-1}}$ ($100\,\mathrm{mm\,yr^{-1}}$ in Mariotti et al., 2002). This value is thus below the average for the entire Northern hemisphere, that admittedly is geographically biased, by its arctic water budget. Such a value, however, is probably above the typical values for the same (30–45° N) band in the near-Atlantic, but this assumption cannot be easily verified. Therefore, the riverine contribution in the formation of a high level in yellow absorbing substances is a possible explanation, but not a decisive one.

An exceptional trait of the Mediterranean hydrology is the formation of specific deep waters and bottom waters which occur in winter within the coldest northernmost parts of the basins. The most active convection occurs in the gulf of Lions and results in the formation of the deep water for the western basin. In north Aegean and Adriatic seas similar processes lead to the formation of the deep water of the eastern basin, whereas the Levantine intermediate water is formed in the vicinity of the island of Rhodes (see e.g., Lacombe and Tchernia, 1972). These zones are the seat of deep vertical convections in winter, followed thereafter by vernal algal blooms supported by the upward flux of nutrients. During the convection episodes, a vertical transport of deep (not bleached) yellow substance occurs (Nelson and Siegel, 2002) and may account for its enhancement within the upper layers, more accentuated in the western basin where the vertical mixing process is more active than in the eastern basin. Actually, the maxima in a_y are progressively built during the autumnal period, and apparently are associated with the erosion and deepening of the pycnocline, rather than with the vernal algal blooms which occur more abruptly and later.

According to its latitude, the Mediterranean region experiences a contrasted seasonal cycle, with high sunshine and cloudless skies in summer, particularly in its southern parts engaged into the semiarid climate belt. Combined with the stratification of the water column, the strong solar flux in summer is able to explain, via the photochemical bleaching process, the precipitous decrease in both basins of Φ and a_y from their maxima in winter to a flat minimum extended from July to September. A similar process comes into play everywhere at the same latitude, in Atlantic for instance. It appears to be more marked in the Mediterranean Sea, but this appearance is perhaps due to the fact that the initial (i.e., winter) background in Atlantic is lower than in Mediterranean, so that the winter-summer contrast lessens.

There are not presently adequate biochemical information nor in situ determinations, including at depth, to consolidate the above attempts to explain the yellow substance levels and their cycles in the Mediterranean Sea and in the near Atlantic. Nevertheless, their comparative detection, which was the aim of the present work, is clearly established. The resulting inaccuracy in the assessment of [Chl] is also demonstrated, and, if not accounted for, leads to a non negligible readjustment of the algal biomass estimate, and thus of the productivity in this sea.

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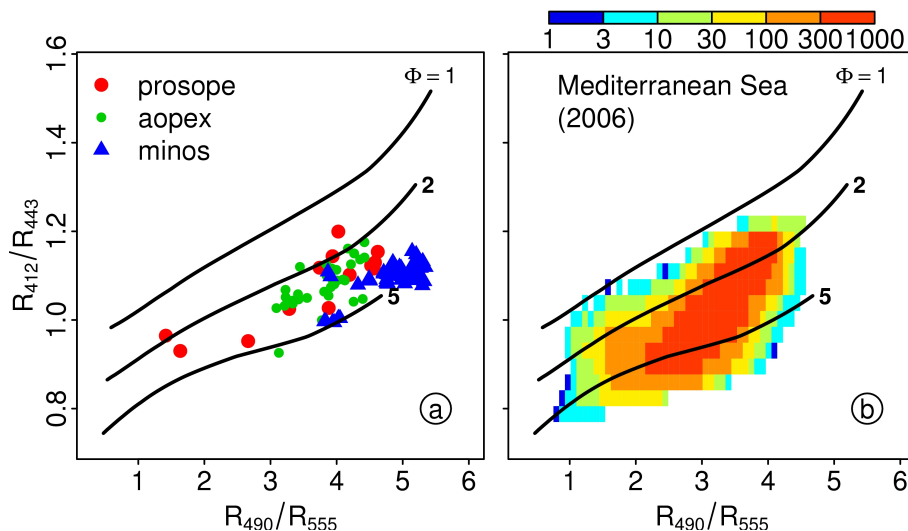
Fig. 1. Ratio of reflectance at 412 and 443 nm, R^{412}_{443}, plotted as a function of the ratio R^{490}_{555}. The theoretical (black) curves are computed for the standard situation (Φ=1), or when the yellow substance concentration is multiplied by 2 or 5, with respect to its Chl-dependent standard value. **(a)** actual ratios determined at sea during the Prosope, Minos, and Aopex cruises (data and information available on www.obs-vlfr/proof/index-vt.htm for Prosope, and on www.Ifremer.fr/sismer for Minos and Aopex); **(b)** same ratios derived from the SeaWifs data, during the whole 2006 year, taken as an example; for the 12 monthly composites, the total number of pixels is 364 000; the number of occurrences is visualized through the frequency color scale.
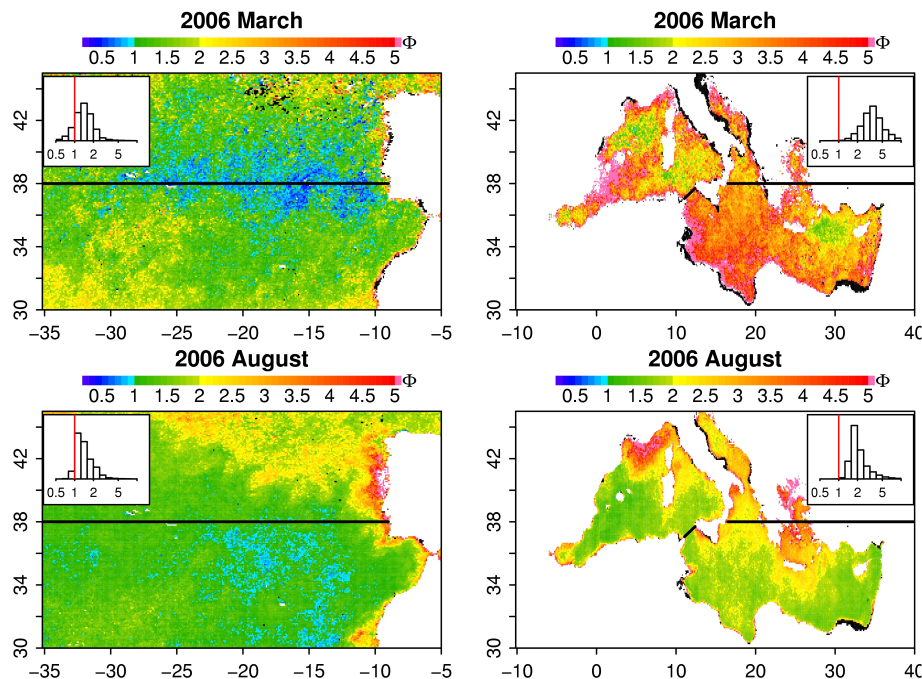
Fig. 2. Derived from SeaWiFS data for March and August 2006, and according to the color scale as displayed, distribution of the Φ parameter within the Mediterranean Sea and the Near-Atlantic, between the latitudes 30° and 45° N. The black lines (the line between Tunisia and Sicily, and the 38th parallel) are the limits adopted for the Eastern and Western Mediterranean basins; the northern and southern sector in the Near Atlantic are also delimited by the 38th parallel. The black pixels correspond to waters identified as turbid. The frequency distributions of the pixels according to their Φ values are shown in insert.
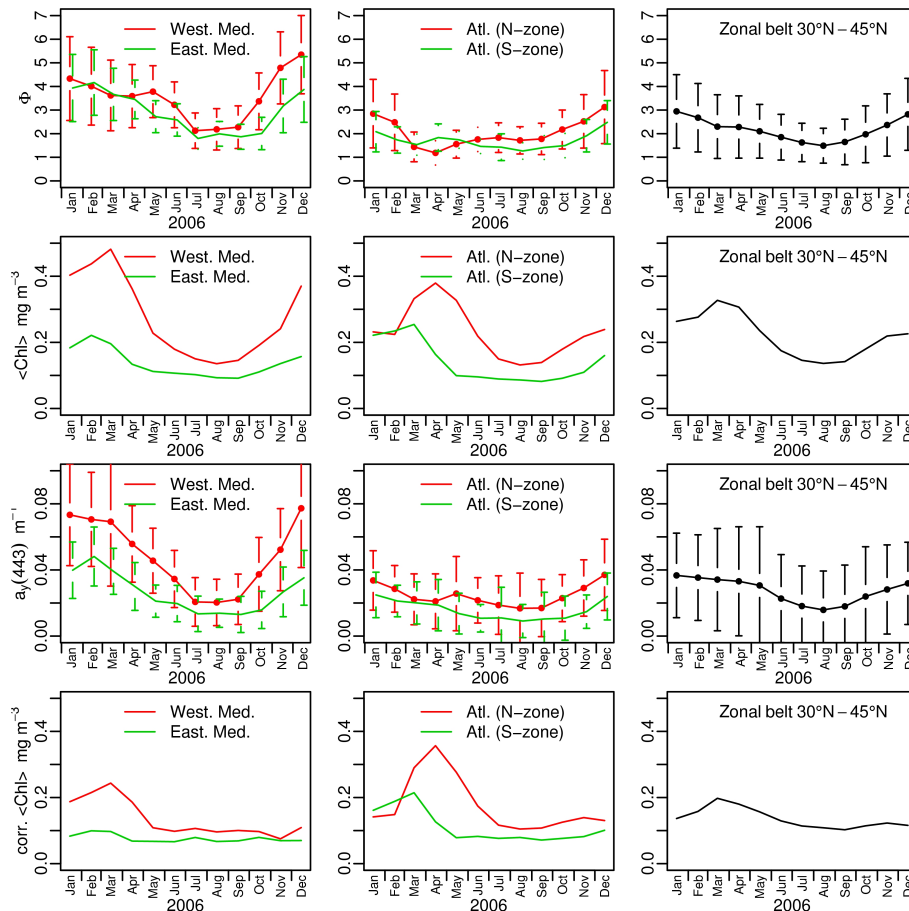
Fig. 3. From SeaWiFS data, seasonal course during the year 2006 of the monthly mean Φ values (first row) for each of the five regions as indicated in inserts; second row, for the same regions, monthly mean [Chl] values ($\mathrm{mg\,m^{-3}}$), as derived via the OC4v4 algorithm; third row, monthly mean $a_y(443)$ values ($\mathrm{m^{-1}}$); last row, corrected [Chl] values (see text) for the same zones.

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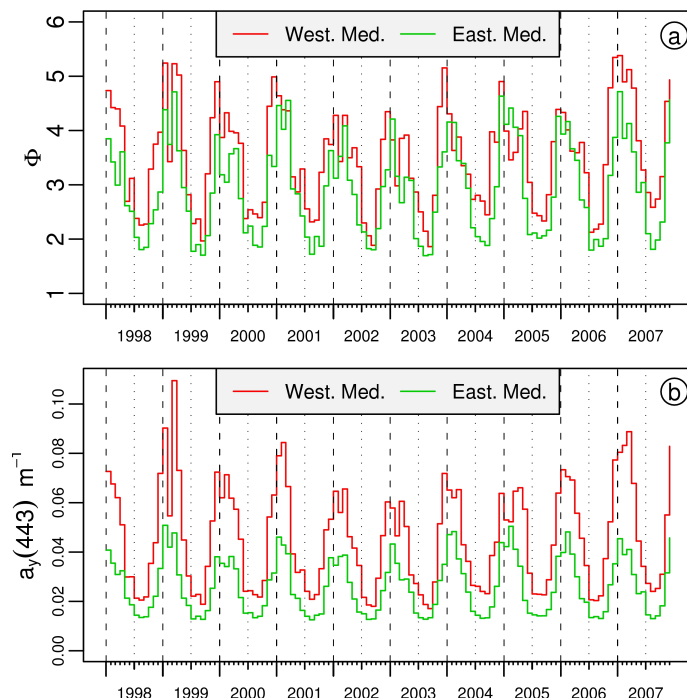
Fig. 4. Time series over a 10-year period of **(a)** the Φ factor, and **(b)** of the absorption coefficient by yellow substance, $a_y(443)$. Monthly averaged SeaWiFS data were used and separately averaged for the western and eastern basins, as indicated.
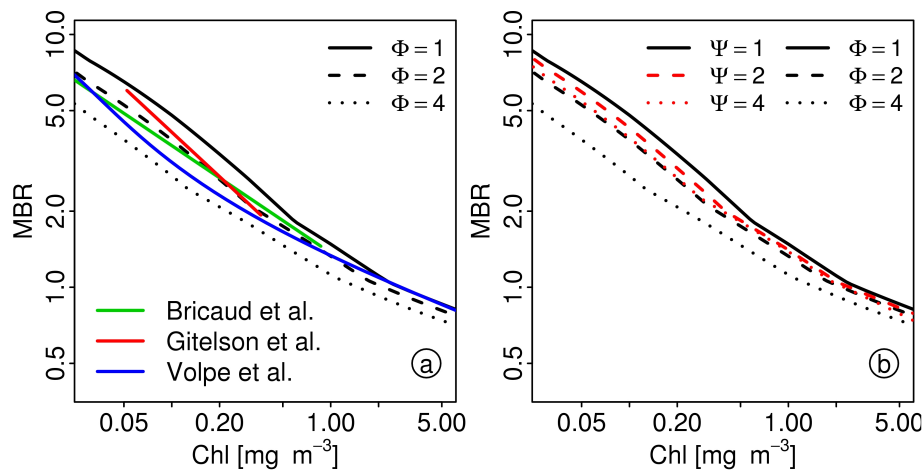
Fig. 5. Maximum band ratio algorithm (OC4Me555, Morel et al., 2007b) for the retrieval of [Chl]; the nominal algorithm (black solid curve) is for the average standard situation in terms of CDM content (i.e., when $\Phi=1$); this content is doubled, or multiplied by 4, for the dashed curve and the dotted black curve, respectively.

In **(a)**, the green straight line represents the regionally tuned algorithm, proposed and used by Bricaud et al. (2002), namely $[Chl]=2.094\,(R_{555}^{443})^{-2.357}$ the red straight line represents the regionally tuned algorithm, proposed and used by Gitelson et al. (1996), namely $[Chl]=0.914\,(R_{550}^{440})^{-1.86}$. The MBR algorithm ("MedOC4") proposed by Volpe et al. (2007) is represented by the blue curve.

In **(b)**, the dashed and dotted red curves are derived from the nominal algorithm (black curve) when the particle backscattering is doubled ($\Psi=2$) or multiplied by 4 ($\Psi=4$). the dashed and dotted black curves are as in (a).
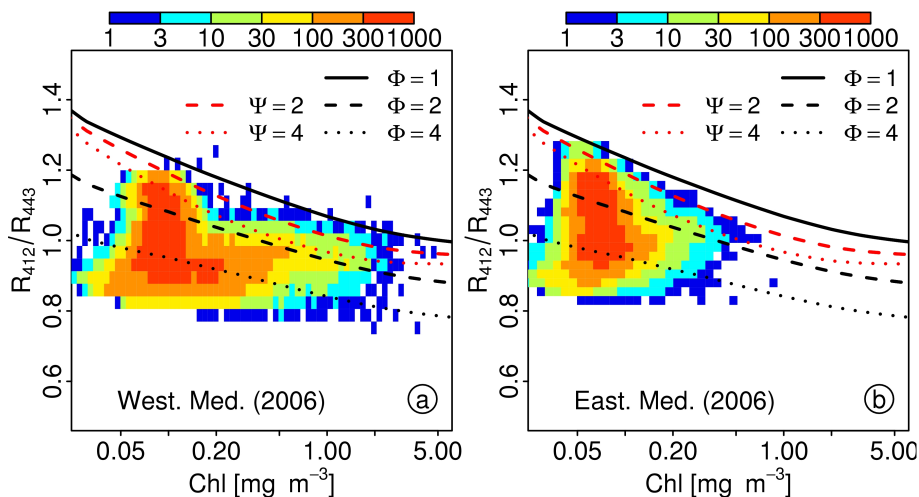
Fig. 6. Computed relationships between R_{443}^{412} and [Chl], for the standard situation (solid black curve, with Φ and Ψ=1), and for the situations modified by increasing the CDM content (dashed and dotted black curves, with Φ=2 and 4, respectively), or modified by increasing the particle backscattering (dashed and dotted red curves, with Ψ=2 and 4, respectively). Superimposed are the R_{443}^{412} and [Chl] values extracted from the pixels in the western **(a)** and the eastern Mediterranean **(b)** basins during the 12 months of the year 2006. The number of occurrences is visualized through the frequency color scale; the total number of pixels represented in each basin is about $1.4\,10^5$).

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