Variability of the underwater light field and chlorophyll *a* in the Blanes Canyon (NW Mediterranean Sea) during the MERIS-ENVISAT calibration exercise

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Abstract

Time variation of spectral downwelling irradiance (E_d), upwelling radiance (L_u), chlorophyll *a* (Chla) and density was monitored above 200 m depth from June through September 2002 at the head of the Blanes Canyon located in a narrow shelf section of the NW Mediterranean Sea. The water column showed typical stratified oligotrophic conditions with no signals of freshwater intrusions. The thermocline strength was found to partially control the depth and magnitude of the Chl *a* maximum that was positioned below the thermocline during late spring and summer. At the end of the summer and early autumn the thermocline tends to be shallower while the Chla maximum spread across the thermocline. Subthermocline oscillations contribute to control the Chla at its maximum, often spreading it toward deeper waters below 100 m depth. The 10% PAR depth around 21 – 27 m was used as the lower limit to integrate the surface Chla that remained relatively constant. The mean surface Chla was 0.18 mg m^{-3} in spring and 0.13 mg m^{-3} in summer and early autumn. The surface to total Chla ratio showed relatively high variability around 0.13 ± 0.06 SD explained by the upward dispersion of the Chl *a* maximum in the late summer and early autumn. E_d and L_u were used to estimate surface remote sensing reflectance (R_{rs}) and normalised water-leaving radiance (L_{wn}) that showed a relatively small variation in shape and magnitude with time. R_{rs} and L_{wn} at the 560, 620 and 510 wavebands showed the maximum correlation with surface chlorophyll with determination coefficients over 0.72. Comparisons of weighted surface Chl *a* with bio-optical estimates of Chl *a* from different equations based on R_{rs} *(a)* [O'Reilly, J.E. *et al*., 1998. Journal of Geophysical Research, 103:24937-24953], *(b)* [D'Ortenzio, F. *et al*., 2002. Remote Sensing of Environment 82: 79-94], and L_{wn} *(c)* [Gordon, H.R., *et al*., 1988. Journal of Geophysical Research, 93:10909-10924] were carried out. Equation *(b)* adapted from *(a)* to retrieve surface Chl *a* in Western Mediterranean yielded best estimates with mean errors below 35% in most of the observations. The equations *(a)* and *(c)*, of more general application, showed a bias exceeding *in situ* values by 35%. This reaffirms the need of independent treatment for bio-optical characteristics of Mediterranean waters in order to obtain reliable estimates of remotely sensed phytoplankton chlorophylls.

1. Introduction

In thermally stratified waters, most of the phytoplankton chlorophyll is typically found around or below the thermocline with a small fraction of chlorophyll near the surface. Since satellite observation of the surface ocean is the most promising method to quantify chlorophyll at regional and global scales, the study of hydrodynamic processes around the thermocline, out of the satellite viewing, is of great importance to understand the spatial and temporal changes of chlorophyll concentrations. Isopycnal oscillations around the thermocline often displace pigments up and down the lower limit of the euphotic zone, defined as the water layer illuminated with more than 1% the surface photosynthetically available radiation (PAR). A direct implication of the isopycnal oscillations is that the chlorophyll placed below the euphotic zone can eventually reach the illuminated zone and even the surface by upward displacements of water due to vertical advection or upwelling processes. This potentially changes the surface chlorophyll and bio-optical properties of water thus modifying the response of satellite observations.

The radiant energy penetrating the water is of great importance for photochemical processes in which chlorophylls are involved, since it controls the growth and cellular physiology of phytoplankton. The photosynthetic pigments are influenced not only by the amount but also by the manner in which radiative energy is received, depending on factors like sea surface waves, clouds and dissolved and particulate materials (Geider *et al*., 1998). Particles in water affecting the underwater light penetration modify the physiological response of phytoplankton. The phytoplanktonic cells, part of those particles, contribute to the reduction of underwater light penetration altering the vertical light attenuation. Particulate material and coloured dissolved organic matter affect the course of light by scattering and absorption. The oligotrophic waters with a blue appearance become darker and greener with the increasing of phytoplankton concentrations (Morel, 1988). The wavelength dependent water-leaving radiance is proportional to the backscatter coefficient and the absorption coefficient (Joint and Groom, 2000).

Chlorophyll *a* absorbs its energy from the violet-blue and reddish orange-red wavelengths, and little from the intermediate (green, yellow, orange) wavelengths (Campbell, 1995). At 676 nm, the absorption due to colored dissolved organic matter can be considered as negligible in oceanic waters, thus making possible to estimate the absorption by phytoplankton and therefore can be used to estimate chlorophyll concentration (Claustre *et al*., 2000; Joint and Groom, 2000). Moreover the colored substances and phytoplankton, the non-algal particles including detritus and non-pigmented cells contribute to alter the absorption coefficient in oceanic areas, whose contributions are additive (Joint and Groom, 2000). The 412 wavelength is appropriate and sensitive to study the dynamics of the colored dissolved materials because of the well-known absorption at 412 increasing with decreasing wavelengths. However, in order to estimate absorption at 412 nm, the contribution of phytoplankton to this absorption has to be subtracted (Hoepffener and

Sathyendranath, 1991). An average absorption budget performed at 412 nm shows that phytoplankton, non-algal particles and CDOM contribute to 33%, 11% and 56% of the absorption at 412 nm (Claustre *et al*., 2000).

The facility to observe phytoplankton from space is based on the spectral variation in phytoplankton pigment absorption that varies depending on the pigment composition (Hoepffner and Sathyendranath, 1991). The magnitude of absorption varies between species due to the cell size of phytoplankton and other factors related to packaging effects (Bisset *et a*l., 1997; Geider *et al*., 1998). Empirical and semi-analytic approaches have been used to retrieve phytoplankton pigment concentration from the water signal. Bio-optical equations are empirical approaches often using blue to green ratios in order to retrieve chlorophyll from radiance. The radiance in the blue decreases with increasing pigment concentration while the green may slightly increase due to scattering (Ciotti *et al*., 1999). Furthermore, by taking a ratio, the magnitude differences in absorption and scattering, opposed to spectral variation, are partly cancelled (Carder *et al*., 1999).

The chlorophyll estimates from satellite sensors are limited to the surface detecting pigments in an optical depth (*Zpd*) which definition varies according to diverse assumptions of the attenuation of the surface radiance. Morel and Berthon (1989) consider *Zdp* as the 1%PAR depth / 4.6 ratio. Clark (1997) simply assumes *Zdp* to be the inverse of the attenuation coefficient of the downwelling radiance. Other authors (Garver and Siegel, 1994; Gordon and Morel, 1983) use the 10% PAR depth as the optical depth. Joint and Groom (2000) assume *Zdp* as the depth at which surface irradiance is attenuated to 37% of the surface PAR. The information obtained about phytoplankton at the surface is due to the light penetrating through the water column and back to the sea surface. Open sea Case I waters with low concentrations of suspended particles and coloured dissolved organic matter (CDOM) provide more precise estimates of chlorophyll concentration than Case II coastal waters, with high concentration of suspended particulate matter and CDOM.

The understanding of underwater phytoplankton variability and its dependence and influence on light, nutrients as well as hydrodynamics is important to obtain reliable satellite observations (Claustre *et al*., 2000; Garcia-Gorriz *et al*., 2003; Stramska and Dickey, 1998) and the design of *in situ* experiments based on optical techniques. The present study aimed at assessing the variability of the surface chlorophyll *a* observed by the satellite and the subsurface chlorophyll *a*, as well as the underwater spectral irradiance during thermally stratified conditions in an oligotrophic area of North-Western Mediterranean Sea. Emphasis is made on the hydrographical conditions altering the chlorophyll distribution and the assessment of bio-optical equations to retrieve surface chlorophyll. The study was carried out at the time of the MERIS-ENVISAT overpasses for further comparison and validation of the estimates of surface chlorophyll *a* in oligotrophic Case I waters.

2. The study area

The Blanes Canyon head is located off the Catalan coast at 41° 39' 10"N, 2° 52' 41"E. The Canyon is one of the most prominent on the NW Mediterranean shelf (Fig. 1). The continental shelf off Blanes is about 20 nm wide while the Canyon intersects the shelf bringing the 1000 m isobath to a distance of less than 10 nm from shore. The Canyon potentially affects the path of the Catalan current, which is a continuation of the Liguro-Provençal current flowing SW along the coast of Catalonia after meandering in the Gulf of Lions. This current, a major feature in this region, may have relevant effects on the marine ecosystem due to the interaction with the bottom topography.

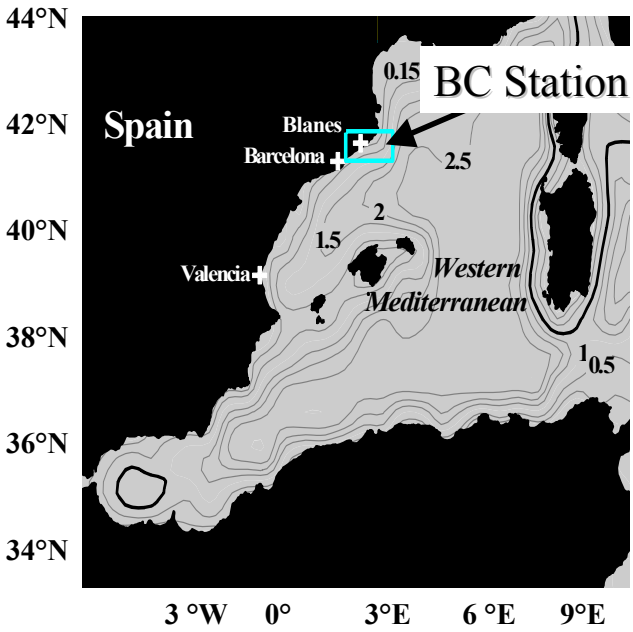

Fig. 1. The Blanes Canyon (BC) station location. Contours represent the bottom topography (km).

The site is relatively cloud-free and ecological conditions are appropriate for Case I waters studies. The typical range of chlorophyll concentration at the site throughout the year is less than 1 $\mu g\ l^{-1}$, and the spatial distribution is believed to be relatively homogeneous. Yet although the water depth is up to 1000 m, and conditions are more like the open ocean, the site is close enough to the shore to make it logistically convenient for frequent *in situ* data gathering. Thus it was considered reasonable to aim at making measurements and sampling seawater at every MERIS overpass, weather permitting, throughout the six-month calibration and validation phase of the ENVISAT mission.

3. Methods

General

Time series of biological and hydrographical variables at the Blanes Canyon station were made visiting the place on board the *R/V Itxasbide*, approximately twice a week once the MERIS was operational from 20th May to 30th October 2002. Visits to the

place were subject to suitable weather for safe data collection and instrument overhauling during working days. This strategy yielded 21 successful, cloud free surveys. Profiles of irradiance, fluorescence, temperature and salinity were obtained and discrete water samples were collected for later chlorophyll and nutrient analysis in the laboratory.

Irradiance

An OCP-100 s/n023 Satlantic optical sensor package was used to measure spectral downwelling irradiance (*Ed*) and upwelling radiance (*Lu*) up to 60 m depth. The instrument measured at seven spectral bands with 10 nm bandwidths centred at 412, 446, 489, 510, 560, 620, and 665 nm. An OCR-507 optical sensor system was used to measure air reference (*Es*) at the same optical bands at 2.1 meters above the sea level. The *Es* data were used as a clear sky reference for underwater profiles. Spectral *Ed* and *Lu* were measured at a rate of 3 Hz over 10-15 minute long intervals when possible twice a week at the time of the ENVISAT overpasses. The post-processing of data was carried out using *Prosoft*, software provided by Satlantic in order to standardize and produce results comparable with other experiments. Using a trapezoidal integration, PAR (quanta/cm^{2}s) was estimated as $PAR = \int_{400}^{700} (\lambda / hc) Ed(\lambda) d\lambda$, where λ is the wavelength, h is the Planck's constant 6.625 x 10^{-34} Js, c is the speed of light 3x10^8 m/s, $Ed(\lambda)$ is the downwelling spectral irradiance (μW/cm^2/nm). The diffuse attenuation coefficients for downwelling PAR (k) was estimated in order to extrapolate the irradiance below the nominal 60 m depth of the Satlantic cable.

Nearly simultaneously to the irradiance measurements, 200 m profiles of oceanographic magnitudes using a Seabird 19plus CTD were carried out to measure the vertical structure of temperature and salinity. A WETStar miniature fluorometer coupled to the CTD allowed measuring relative chlorophyll concentrations by directly measuring the amount of fluorescence emission from a given sample of water. As for irradiance profiles, CTD and fluorometer data were averaged in 1m depth bins. The post-processing of CTD data was done using Seabird's software *Satview*.

Chlorophylls and nutrients

Discrete water samples at 1, 5, 25, 50, 75, 100, 125, 160 and 185 m depth were taken using 5 l Niskin bottles for chlorophyll and nutrient analysis. Chlorophylls were determined on non-fractionated particulate matter from 3.3 liter water samples, filtered through 4.7 cm Whatman GF/F filters and kept in a deep-freezer for more than 24 hours. The pigments were determined after extraction for more than 24 hours in the dark with 5 ml acetone (90 %). The resulting suspension was centrifuged at 3000 rpm for 30 min. and the absorbance read in the supernatant at 750, 664, 647 and 630 nm. The concentrations were estimated with the equations described in Jeffrey and Humphrey (1975). The spectrophotometric chlorophyll was calibrated against standard chlorophyll extract dilutions. The regression equation of the standard versus nominal concentrations of chlorophyll *a* yielded a determination coefficient (r^2) of 0.9995. A subset of 30 samples from the maximum and minimum chlorophyll concentration depths was selected from a total of 42 in order to calibrate the

fluorescence to chlorophyll conversion factor. The spectrophotometric chlorophyll *a* explained 72% of the variation of the fluorometer voltage.

The chlorophyll *a* spectrophotometric method was subject to two intercomparison exercises carried out among all the participants in the MERIS cal/val project with very coherent and accurate results (Sorensen, this issue).

Unfiltered nutrient samples were collected and analysed for nitrate+nitrite, nitrite, orthophosphate, and orthosilicic acid on a BRAN-LUEBBE TRAACS 2000 continuous segmented-flow autoanalyzer (CFA). In the present study we will refer only to the nitrate data. The frozen water samples were kept in ~100 cm^3 high-density polyethylene, narrow mouth, screw-capped bottles and introduced into the CFA sampler by pouring the sample water into ~8.5 cm^3 polystyrene cups which fit the sampler tray. Both the 100 cm^3 bottles and 8.5 cm^3 sample cups were rinsed three times with the seawater prior to sample collection and sample analysis respectively. Between analyses from each station run, the sampler cups and sample bottles were rinsed with a diluted solution (~10% v/v) of hydrochloric acid and distilled water (DIW). Running replicate samples from Niskin bottles tripped at a single depth monitored short-term precision.

Bio-optical assumptions and estimates

The fluorometric surface chlorophyll *a* ($\overline{C}$) was computed following the formulation: $\overline{C} = \int_0^{Zdp} C(z)\exp(-2kz)dz \Big/ \int_0^{Zdp} \exp(-2kz)dz$, where *Zdp* is 10% PAR depth (Garver and Siegel, 1994; Gordon and Morel, 1983), and *k* is the diffuse attenuation coefficient for downwelling PAR. Moreover, in order to compute surface chlorophyll from upwelling radiance and downwelling irradiance, the remote sensing reflectance (*Rrs*) just above the surface and normalised water-leaving radiance (*Lwn*) were calculated using *Prosoft* following the equations:

$Rrs(0^+,\lambda) = Lw(0^+,\lambda)/Ed(0^+,\lambda)$, where *Lw* is the upwelling spectral radiance propagated through the surface using: $Lw(0^+,\lambda) = L_u(0^-\lambda)\ \left(1-\rho(\lambda,\theta)/\eta_w^2(\lambda)\right)$, with $\rho(\lambda,\theta) = 0.021$, the Fresnel reflectance index of seawater, and $\eta_w(\lambda) = 1.345$, the Fresnel refractive index of seawater. *Ed* is also extrapolated through the surface using: $Ed(0^+,\lambda) = Ed(0^-,\lambda)(1+\alpha)$ with $\alpha = 0.043$ representing the Fresnel reflection albedo for irradiance from sun and sky.

$Lwn = Lw(\lambda)F_0(\lambda)/Ed(\lambda)$, where $F_0(\lambda)$ is the mean extraterrestrial solar irradiance.

Three bio-optical equations from literature (used in previous SeaWiFS observations and validations) were selected in order to retrieve chlorophyll *a* (Chl *a*) from spectral irradiance. The equations by O'Reilly *et al*. (1998) (OR98) and D'Ortenzio *et al*. (2002) (DO02) use *Rrs* on the base of the following equations:

$Chl = 10^{(0.217-2.728R+0.704R^2+0.297R^3)} - 0.035$ for DO, and

$Chl = 10^{(0.2974-2.429R+0.8358R^2-0.0077R^3)} - 0.0929$ for OR. In both cases

$R = \log_{10}(Rrs490nm/Rrs555nm)$. A third equation by Gordon *et al*. (1988) (GO) uses *Lwn* as follows: $Chl = 1.15(Lwn443/Lwn560)^{-1.42}\ Chl \leq 1 \mu g\ l^{-1}$.

4. Results

Thermal stratification with typically oligotrophic conditions was observed in the Blanes Canyon site along the whole sampling period, even thought it spanned from mid spring to early autumn (Fig. 2). The thermal stratification, the nutrient-depleted surface water and the presence of a subsurface chlorophyll *a* maximum are ecological conditions expected for oligotrophic Case I waters ecosystems.

The thermocline layer was thicker from September (day 241), except in day 261 when deepening and a strong reduction in thermocline layer thickness were observed. The nitracline layer, here assumed to be from 0.5 to 1.0 µM nitrate isolines, closely linked to the chlorophyll maximum layer, was found around 17 m deeper than the thermocline. Day 261 was also atypical for the chlorophyll maximum that spread out from the very thin thermocline at 60 m depth to near the surface.

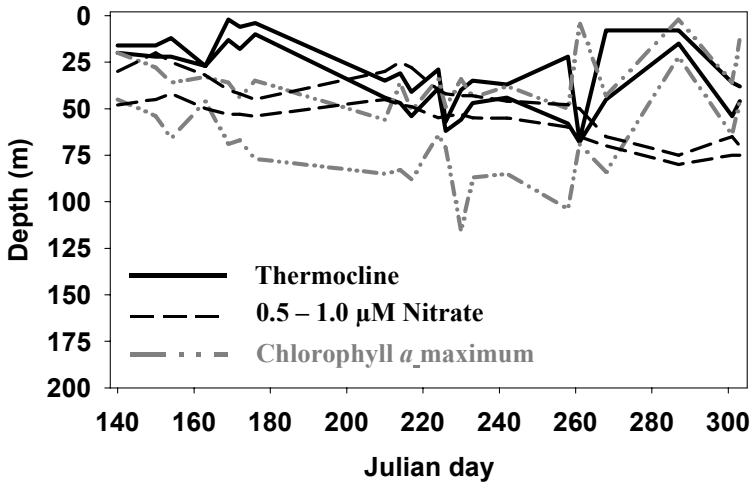

Fig. 2. The upper and lower boundaries for the thermocline, nitracline assumed to be from 0.5 to 1.0 µM nitrate isolines, and chlorophyll *a* maximum layers. The average depths (±SD) for the layers are: 33±17 m for the thermocline, 50±12 m for nitracline, and 53±17 m for the chlorophyll *a* maximum.

The density in the above thermocline surface water layer was relatively homogeneous, as expected for the mixed layer (Fig.3). Density anomaly was higher at the end of May (days 140 to 155) over 27.5 kg m^{-3} due to the mixing with deeper waters in winter and early spring, when a complete vertical convection takes place (Bahamon and Cruzado, 2003). The lowest density anomaly was observed at the end of August and early September (days 230 – 255) when density reached values lower than 26.0 kg m^{-3} coincident with surface temperature rising above 24°C.

The chlorophyll maximum was close to the lower limit of the euphotic zone (the depth of 1.0 % surface PAR) coincident with the nitracline between ~45 – 65 m depth (Fig.3). Subthermocline isopycnal oscillations often dispersed the chlorophyll maximum toward deeper waters, making the chlorophyll values in deep waters higher than in surface, i.e. over 0.1 µg l^{-1} Chl *a* below 100 m depth during most of August and September (days 210 to 270; Fig 3). The deep Chl *a* maximum layer was relatively far below the euphotic zone, receiving less than 0.1% the surface PAR.

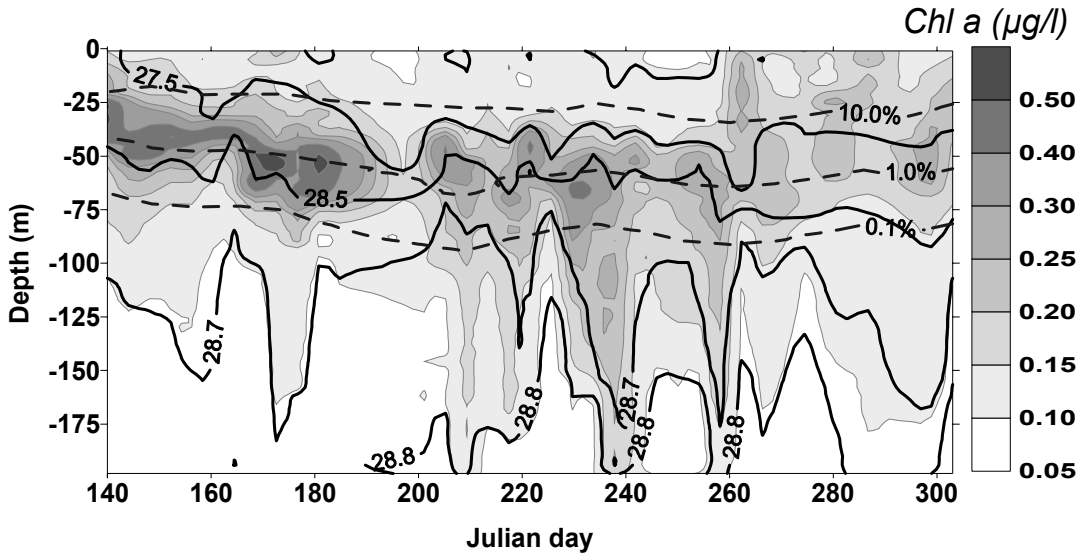

Fig 3. Time series contours of chlorophyll *a* (shading contours, µg l^{-1}), density anomaly (Φ_t, solid dark lines, kg m^{-3}), and PAR (dashed lines, %).

The surface chlorophyll was not significantly higher in spring than in summer with a median of 0.18 µg l^{-1} in spring and 0.13 µg l^{-1} in summer and early autumn (Fig. 4). Day 261, in summer, showed atypically high chlorophyll concentrations (0.25 µg l^{-1}). However, eliminating the temporal component and integrating all the data, the day 261 is within the range of the observations. Instead, the first day of measurements, the day 140 was found with atypically high Chl *a* (around 0.29 µg l^{-1}). Fifty percent of total observations were between 0.12 and 0.18 µg l^{-1} Chl *a*.

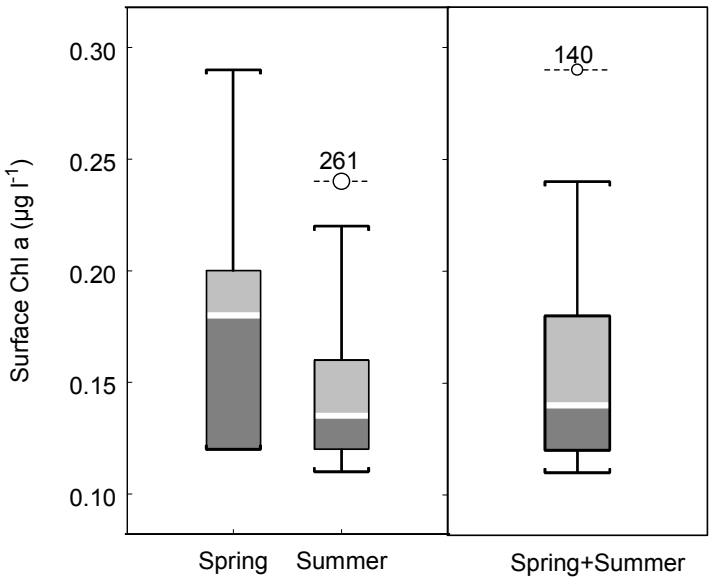

Fig.4. Variability of surface chlorophyll around the median during spring and summer (including early autumn) and including all the observations. The white line in the boxes indicates the median. The 25% of the observations above and below the median make the boxes. The sampling (Julian) days with atypical data are indicated above the whiskers.

The remote sensing reflectance showed a left-sided Gaussian distribution with maximum reflectance in the blue band at 446 nm and minimum, in the red band, at 620 and 665 nm (Fig 5). This distribution is typical for oligotrophic Case I waters with low concentrations of suspended particles and coloured dissolved organic matter that modify the distribution of the reflectance in the visible spectrum. Three sampling days showed values atypically greater than the rest of the observations at specific wavelengths as shown in Fig. 5.

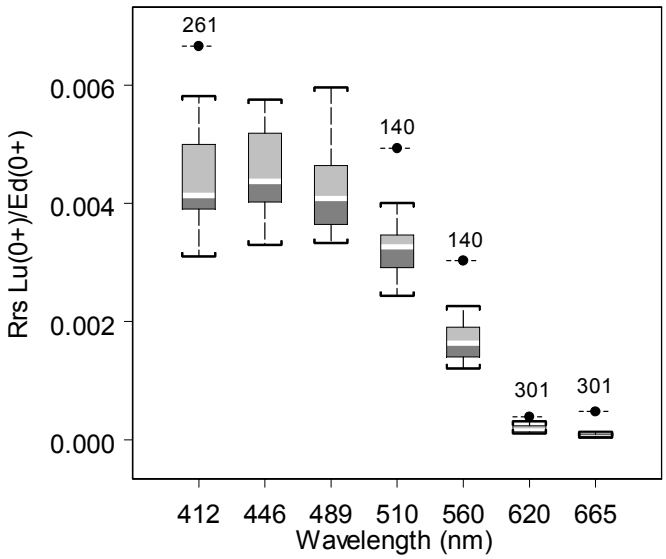

Fig. 5. Box and whisker plots indicating the variability around the median for remote sensing reflectance (*Rrs*) in the visible spectrum. The sampling (Julian) days with atypical data are indicated above the whiskers.

The three bio-optical equations selected to retrieve surface chlorophyll from *in situ* irradiance, yielded chlorophyll values in general higher than *in situ* (Fig. 6). The equations by Gordon *et al* (1988) and O'Reilly *et al.* (1998) produced values with higher error in comparison with *in situ* chlorophyll, overestimating (about twofold) the chlorophyll *a* values. The best fitting equation for the present study was the equation by D'Ortenzio *et al.* (2002) yielding the most realistic chlorophyll values.

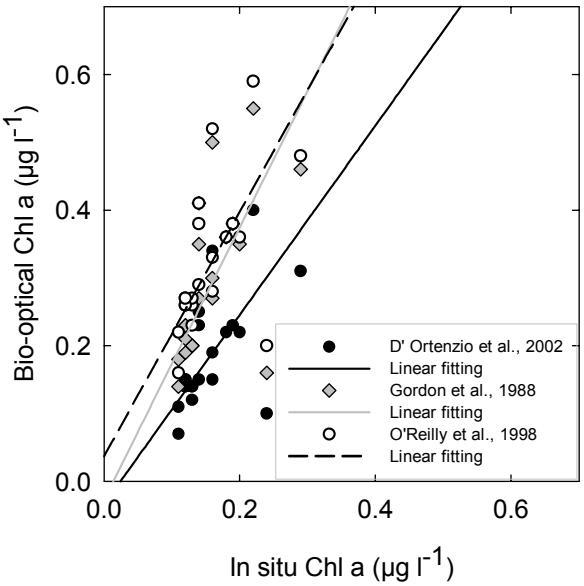

Fig. 6. Retrieval of surface chlorophyll using three bio-optical equations based on the remote sensing reflectance (D'Ortenzio et al., 2002; O'Reilly et al., 1998) and normalised water-leaving radiance (Gordon et al., 1988).

5. Discussion

The dispersion of the chlorophyll maximum toward deeper waters was a consequence of the subthermocline oscillations taking place in a few days period as shown in Fig. 3. These displacements of water and particles brought the chlorophyll-bearing particles far below the euphotic zone (more than 50 m below) in an area with a strict growth limitation by light deficit. It is therefore deduced that density, more than light, is controlling the lower limit for the phytoplankton growth. This is in agreement with preliminary observations made in the tropical Atlantic (Herbland and Voituriez, 1979). In a transatlantic section in the tropical Atlantic Ocean along 24.5° N (Bahamon *et al*., 2003) isopycnals appear to control the distribution of subsurface chlorophylls, particularly in the mid and eastern Atlantic. The study in the North Atlantic also pointed out that subthermocline oscillations in the Western Sargasso

Sea are apparently not controlling the phytoplankton chlorophyll in depth, what is done by light. This can be attributed to the persistency along the year of the isopycnal oscillations in Western Sargasso allowing the phytoplankton to be adapted to the local conditions. This contrasts with the relatively short time scale of days in which subthermocline oscillations in the NW Mediterranean site bring the chlorophyll down and up the euphotic zone and even to the 0.1% PAR depth. In Western Sargasso, the isopycnals crossing down the 0.1% PAR depth are less dense around 26.0 kg m^{-3} (sigma-t) in comparison with the Mediterranean (28.6 kg m^{-3}) and are much deeper (around twice) than in the Mediterranean (roughly ~ 75 m in the Mediterranean and ~150 m in the Atlantic).

The inventory of chlorophyll *a* (depth-integrated) in surface and the whole water column allowed an approximation as to the representativeness of the surface chlorophyll as observed by the satellite with regard to the total chlorophyll inventory. The mean integrated (±SD) chlorophyll in the whole water column was 31.9 ± 4.4 mg m^{-2} and the surface chlorophyll was 4.0 ± 1.5 mg m^{-2}. Hence, surface chlorophyll (above 10% PAR depth) represents between 7 and 29% of the total chlorophyll inventory (above 200 m depth) (Fig 7). This relatively high variability of the surface to total chlorophyll ratio is mainly explained by changes of the ratio in atypical days with percentages over 15% at the end of summer and early autumn (days 233, 287, 301 and 303). The increase in the surface to total chlorophyll ratio does not increase necessarily the fluorometric chlorophyll that remains relatively constant around 0.13 µg l^{-1} as shown if Fig. 4. In general, the depth-integrated chlorophyll *a* was in the range of other oligotrophic environments in the Mediterranean and the Atlantic (Bahamon *et al*., 2003). The fact that the surface chlorophyll does not reflect rigorously changes of the chlorophyll distribution and concentration in the water column, as observed in the present time series, is an important limitation for models attempting to reconstruct the chlorophyll and primary production (Campbell and Aarup, 1992; Garcia-Gorriz *et al*., 2003; Geider *et al*., 1998) on the base of satellite observed chlorophyll. Nevertheless, a more regular and longer time series is required in order to reaffirm the present observations.

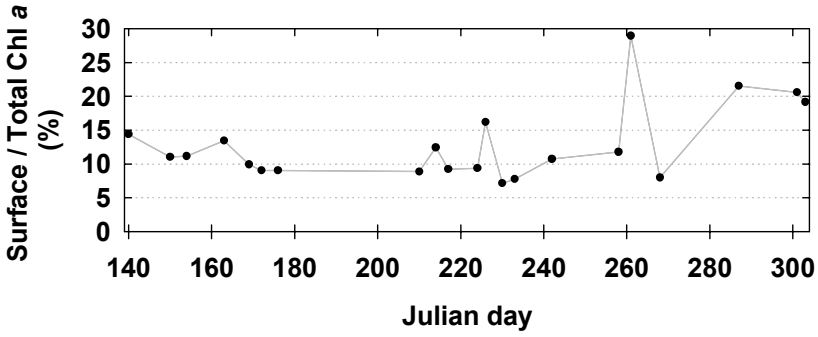

Fig. 7. The surface chlorophyll *a* represents a fraction between 7 and 29% of the chlorophyll inventory in the upper 200 m depth.

In the present study, reflectance computed by using upwelling/downwelling radiance in surface, better fitting the surface chlorophyll, were 560 nm (n=21; r^2=0.58), 620

(n=21; r^2=0.56) and 510 nm (n=21; r^2=0.55). After excluding the outlayers of days 261, 287 and 301, being the former and the latter days previously indicated as atypical days, the regressions yielded better determination coefficients >0.65 as shown in Fig. 8. The other reflectance values didn't show significant regressions.

Results similar to those shown in the Fig. 8 were found for the regressions of surface chlorophyll against *Lwn* at the same wavelengths: 560 nm (n=18; r^2=0.85), 620 nm (n=18; r^2=0.75) and 510 nm (n=18; r^2=0.72). These results reaffirm *Rrs* and *Lwn* 560 nm as the most adequate to be used in the empirical bio-optical equations to estimate surface chlorophyll in the area.

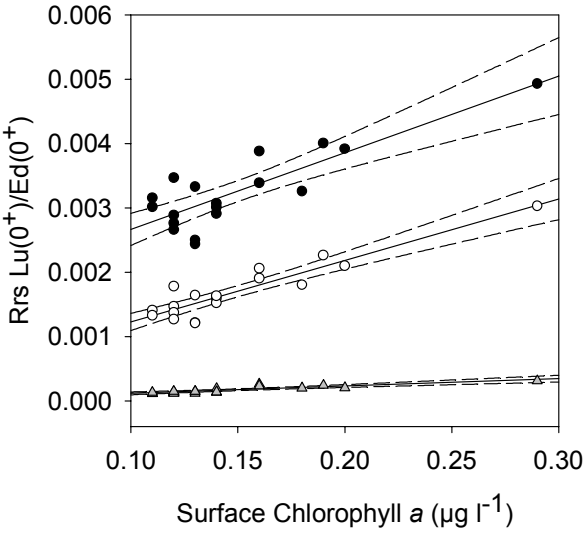

Fig 8. Remote sensing reflectance better fitting the surface chlorophyll *a*: *Rrs* 510 nm (black circles; n=18; r^2=0.72); *Rrs* 560 nm (white circles; n=18; r^2=0.85), *Rrs* 620 nm (grey triangles; n=18; r^2=0.75). Solid lines represent linear regressions and dashed lines indicate 95% confidence intervals.

The empirical bio-optical approaches to retrieve the surface chlorophyll tested in the present study use the *Rrs* and *Lwn* at different wavelengths allowing further comparison with satellite retrieval of chlorophyll in wider areas. The Gordon *et al*. (1988) (GO) equation uses a ratio of *Lwn* 443nm/*Lwn*560 and O'Reilly *et al*. (1998) (OR) use an equation with a *Rrs* 443nm/*Rrs*555nm ratio. An adaptation for NW Mediterranean conditions of the OR equation mainly used for SeaWiFS estimates of surface chlorophyll, was made by D'Ortenzio *et al.* (2002) (DO). The equation uses a non linear polynomial function with similar reflectance than OR equation but different constant values. Authors of DO found that previous bio-optical equations are not applicable to Mediterranean conditions since they nearly double the values of surface chlorophyll. The fitted equation for Western Mediterranean conditions was also suitable for our study facilitating the way for further development of algorithms for the MERIS observations.

The error of the bio-optical equations with regard to in-situ chlorophyll *vs.* surface chlorophyll data was estimated as $\%E = 100(C_{situ} - C_{\mathrm{mod}}/C_{situ})$. The equations by GO and OR yielded similar results, both of them showing a good precision but an undesirable accuracy, with most of data error over 35% (Fig. 9). Instead, the DO function reproduced satisfactorily the *in situ* data with most of the estimates showing less than 35% of error. Data out of this range were from days 217 and 261, which underestimated the *in situ* chlorophyll, and the days 233 and 268 that overestimated the chlorophyll. The discrepancy with in-situ surface chlorophyll can be linked to the presence of dissolved and suspended materials altering the reflectance ratios not accounted in the present study. The presence of coccolitophores contribute to overestimate the surface chlorophyll retrieval from optical measurements, due to the decrease in reflectance ratio as calcite concentration increases (D'Ortenzio *et al*., 2002). Preliminary observations of phytoplankton populations under inverted microscope for the atypical days, not shown here, could give support to the latter assumption.

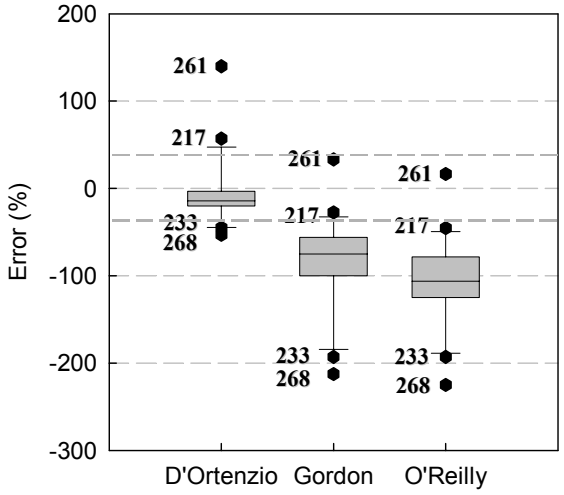

Fig. 9. Estimated error by bio-optical equations used to retrieve surface chlorophyll in comparison with *in situ* chlorophyll *a* data. The horizontal black line in the boxes indicates the median and boxes involve 50% of the estimated errors. Black points show atypical days with errors above or below the median.

From the 21 successful observations in the time series, six match-ups were selected with existing and appropriate MERIS images allowing estimating surface chlorophyll (Fig. 10). Detail of the processing images are described in Weeks *et al*. (*in prep*). Here, a comparison of the chlorophyll measured by calibrated fluorescence chlorophyll with chlorophyll estimated using the best fitting bio-optical equation (DO equation) with chlorophyll by MERIS is shown. Even though the small amount of data prevents application of statistics, it is shown first, that in general, MERIS overestimates by a factor of two the *in situ* chlorophyll. Second, MERIS better fits the chlorophyll estimates using DO equation (based on *in situ* upwelling and downwelling irradiance) than using *in situ* fluorescence, what is deduced from an

apparent linear trend in the grey points. This is not decisive since more match-ups are required to validate the MERIS estimates, but preliminarily a trend by MERIS to overestimate the surface *in situ* chlorophyll is suggested.

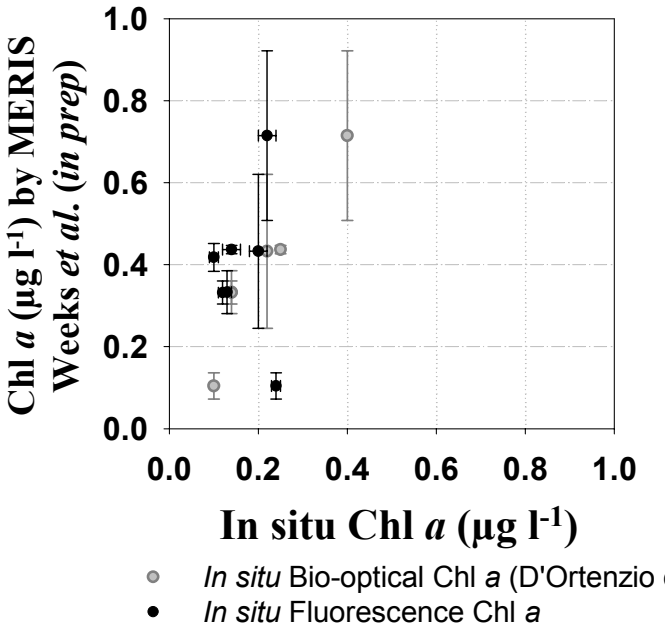

Fig. 10. Comparison of *in situ* bio-optical and fluorescence chlorophyll *a* against MERIS (bio-optical) derived chlorophyll *a*.

6. Conclusions

Under clear sky conditions, the chlorophyll in the surface water layer observed by the satellite is homogenous because of relatively small variations of the Chl *a* inventory. Even though the chlorophyll remains relatively constant in surface, the proportion of the surface chlorophyll with respect to the total chlorophyll inventory can experience significant changes. This provides evidence that processes affecting surface chlorophyll, even in a relatively homogeneous stratified environment, are not rigorously inferred from surface satellite chlorophyll images.

The best fitting algorithm (based on SeaWiFS algorithms) for chlorophyll *a* retrieval was that calibrated against irradiance data for Western Mediterranean by D'Ortenzio *et al*., (2002) showing most of estimates lower than 35% of error.

Subthermocline isopycnal oscillations explain the greater chlorophyll concentrations below the thermocline rather than above, because of downwelling or convection processes downward dispersion of the chlorophyll maximum layer.

In situ bio-optical Chl *a* values agree better with MERIS estimates of Chl *a* than fluorometric Chl *a*, suggesting factors other than Chl *a* to be altering the local underwater irradiance conditions and therefore the outgoing – incoming irradiance ratios.

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