Is desert dust making oligotrophic waters greener?

H. Claustre,[1] A. Morel,[1] S. B. Hooker,[2] M. Babin,[1] D. Antoine,[1] K. Oubelkheir,[1] A. Bricaud,[1] K. Leblanc,[3] B. Quéguiner,[3] and S. Maritorena[4]

Received 8 September 2001; accepted 28 January 2002; published 28 May 2002.

[1] In situ optical measurements provide evidence that oligotrophic waters of the Mediterranean Sea have a greener color than would result from their phytoplankton content alone. This anomaly, detectable in low chlorophyll waters, remains unnoticed in the chlorophyll-rich waters of the nearby waters of the Moroccan upwelling zone. It is due to enhanced absorption in the blue and enhanced backscattering in the green parts of the visible spectrum likely resulting from the presence of submicron Saharan dust in suspension within the upper layer. This result implies that regional estimations of carbon fixation from ocean color images might be significantly overestimated, not only in the Mediterranean Sea, but also in other oligotrophic areas of the Northern hemisphere, subjected to desert dust deposition. *INDEX TERMS:* 4552 Oceanography: Physical: Ocean optics; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 1640 Global Change: Remote sensing

1. Introduction

[2] Brick-red or pink dust massively exported from the Sahara is at the origin of the so-called "red-rains", sporadically falling over Europe. Besides this spectacular effect, Saharan dust influences several atmospheric and marine processes, such as regional radiative budgets [*Legrand et al.*, 1992], the formation of clouds and rain [*Levin and Ganor*, 1996], the acidity of rainfall [*Loÿe-Pilot et al.*, 1986]. Dust deposition also affects sedimentary processes and the biogeochemistry of the Mediterranean Sea, including, perhaps, its productivity through iron enrichment of surface waters [*Guerzoni et al.*, 1997]. Desert dust also impacts optical properties of the atmosphere, leading to some biases in the retrieval of the chlorophyll *a* concentration ($\langle$Chl*a*$\rangle$) from color images of the upper ocean [*Moulin et al.*, 2001].

[3] The possible effect of desert dust on optical properties of oceanic waters remains however unknown. Therefore, one of the objectives of the PROSOPE (French acronym for Productivity of Pelagic Oceanic Systems) cruise (Figure 1) was to examine if any peculiar optical characteristic caused by Saharan dust deposition could be detected in oligotrophic Mediterranean waters, that would bias the optical assessment (in situ or remotely) of $\langle$Chl*a*$\rangle$.

2. Methods-Background

[4] The cruise took place from 4 September to 4 October, 1999. The upwelling waters off Morocco (UPW station) were sampled over 3 days, and the MIO (Ionian Sea, eastern basin) and DYF (Ligurian Sea, western basin) stations were occupied for 5 days each. Short intermediate stations (St 1 to St 9) were sampled over 4-h periods. Optical measurements and pigment sampling were always performed around noon, within 1 h of overflight by the SeaWiFS satellite.

[5] $\langle$Chl*a*$\rangle$ was analysed according to a slightly modified version of the HPLC method described by *Vidussi et al.* [1996]. The accuracy of $\langle$Chl*a*$\rangle$ measurements (8%) was checked as part of an international intercomparison exercise (four laboratories were involved) performed on samples taken during the cruise [*Hooker et al.*, 2001].

[6] In situ spectral measurements of upwelling irradiance or radiance and downwelling irradiance were performed using three instruments: LI-1800 LICOR, Satlantic LoCNESS and Satlantic SeaFALLS.

[7] The reflectance of a water body, $R(\lambda)$, is defined as the ratio of upwelling irradiance (or radiance) to downwelling irradiance, and the spectral shape of $R(\lambda)$ define the so-called "water color". This color is indexed by the blue-to-green reflectance ratio (B/G), R(443)/R(555), which, in open-ocean (Case-1) water is essentially governed by the phytoplankton content (actually B/G decreases with increasing phytoplankton content). Therefore, algorithms have been developed that relate surface $\langle$Chl*a*$\rangle$ to B/G [*O'Reilly et al.*, 1998; *Morel and Maritorena*, 2001]. $R(\lambda)$ is approximately proportional to the ratio of the backscattering and absorption coefficients, $b_b(\lambda)/a(\lambda)$.

3. Results

[8] The PROSOPE data set spans two orders of magnitude in surface $\langle$Chl*a*$\rangle$ (0.03 to 3.75 mg m^{-3}) and about one order of magnitude in B/G (0.5 to 6.7) (Figure 2). Data collected in the upwelling (station UPW) off Morocco, are in close agreement with global algorithms (Figure 2). This is no longer the case for Mediterranean waters which look systematically greener (lower B/G) than typical oceanic waters with the same $\langle$Chl*a*$\rangle$, as already observed by *Gitelson et al.* [1996] for the eastern Mediterranean sea. As a consequence, derivation of $\langle$Chl*a*$\rangle$ from B/G measurements through conventional algorithms overestimates actual $\langle$Chl*a*$\rangle$ in Mediterranean waters by a factor exceeding 2 (Table 1).

[9] For a given $\langle$Chl*a*$\rangle$, a lower than expected B/G (Figure 2) is due to a lower than expected $b_b(440)/b_b(555)$ and/or a lower than expected a(555)/a(440). When compared to optical properties modeled for a standard ocean with similar $\langle$Chl*a*$\rangle$, PROSOPE data show two important features (Table 1): (i) the color shift is caused by both anomalous absorption and backscattering ratios (Mediterranean waters absorb more blue light and backscatter more green light than anticipated); and (ii) the particle scattering coefficients, $b_p(555)$, are anomalously high compared to those modeled for a standard ocean.

[10] Additional absorption measurements performed during the cruise permitted an inquiry into the substance(s) potentially responsible for the B/G changes. An absorption budget can be written as :

$$a(\lambda) = a_W(\lambda) + a_P(\lambda) + a_{OS}(\lambda) \quad (1)$$

[1]Laboratoire d'Océanographie de Villefranche, Villefranche-sur-mer, France.
[2]Laboratory for Hydrospheric Processes, NASA Goddard Space Flight Center, Greenbelt, MD, USA.
[3]Laboratoire d'Océanographie et de Biogéochimie, Marseille, France.
[4]Institute for Computational Earth System Science, University of California, Santa Barbara, CA, USA.

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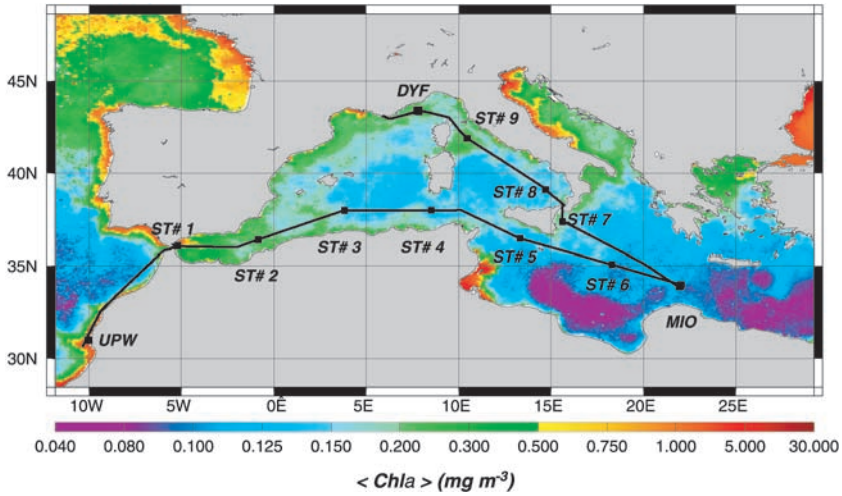

Figure 1. PROSOPE cruise track superimposed on the composite SeaWiFS image of surface ⟨Chl*a*⟩ for September 1999. This composite was derived from SeaWiFS reflectances using the OC4v4 algorithm [*O'Reilly et al.*, 1998].

where a(λ) is the total absorption, $a_W(\lambda)$ and $a_P(\lambda)$ are the absorption by water and particles (phytoplankton, heterotrophs, and associated biogenic detritus), respectively and $a_{OS}(\lambda)$ is a residual term accounting for "other substances". The latter can be estimated by subtraction, because $a_W(\lambda)$ is known and a(λ) and $a_P(\lambda)$ were measured.

[11] The high $a_P(440)$ values (Table 1) result primarily from the presence of non-photosynthetic carotenoids, typical of algae in oligotrophic surface waters, and, to a lesser extent, from non-algal particles. Such a pigmentation slightly decreases the ratio a(555)/a(440). In open-ocean Case-1 waters, a_{OS} is generally believed to result from the presence of colored dissolved organic matter (CDOM). However, the PROSOPE $a_{OS}(440)$ values are inappropriately high when compared to modeled $a_{CDOM}(440)$ values for standard oceanic waters. Moreover, high CDOM content is unlikely for two reasons: (i) CDOM is a by-product of biological activity, which is rather low in the Mediterranean; and (ii) CDOM is exposed to intense photo-bleaching [*Vodacek et al.*, 1997], favored by the summer vertical stratification combined with high surface irradiance. In addition, CDOM has no scattering capability able to account for the high $b_p(555)$ value as well as for the unexpectedly low $b_b(440)/b_b(555)$ ratio, also observed. The presence of bubbles could be put forward to account for the enhanced scattering coefficient [*Zhang et al.*, 1998]. It is unlikely, however, as the conditions during the cruise were exceptionally good in term of sea state and ambient wind.

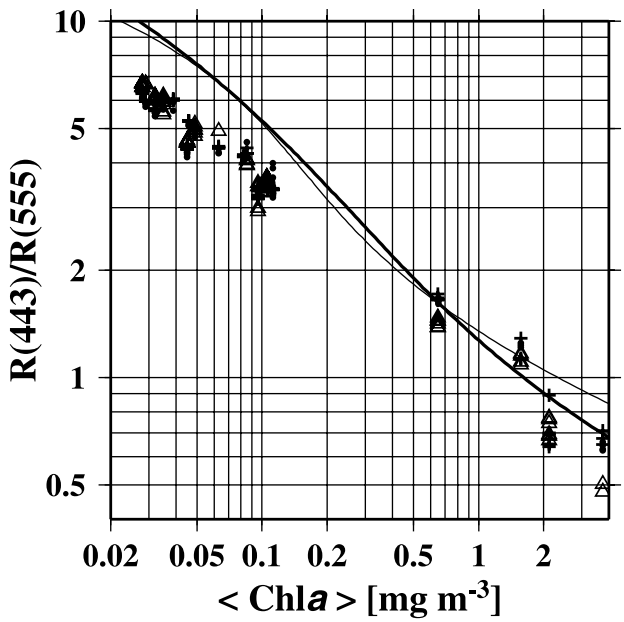

Figure 2. Relationship between surface ⟨Chl*a*⟩ and the blue-to-green reflectance ratio derived from in situ data (determined just below the surface). The ⟨Chl*a*⟩ values below 0.15 mg m^{-3} are from the Mediterranean, and values >0.6 mg m^{-3} are from the upwelling area off Morocco. The blue-to-green reflectance ratios were derived from spectral irradiance or radiance measurements performed by a LI-1800 LICOR (△), aSatlantic LoCNESS (▲) and aSatlantic SeaFALLS (+). The field data are compared to an empirical model [*O'Reilly et al.*, 1998] (algorithm OC4v4, thin line) and to a semi-analytical model [*Morel and Maritorena*, 2001] (thick line).

[12] Given that algal, non-algal particles, CDOM and bubbles are not plausible causes for concomitant decreases in both a(555)/a(440) and $b_b(440)/b_b(555)$, and for enhanced $b_p(555)$ values, "other substances" have to be found to explain the conspicuous green color shift. We suggest that submicron Saharan dust, probably smaller than 0.7 μm [*D'Almeda, and Schütz*, 1983; *Gomes et al.*, 1990], is responsible for this unexpected observation. This hypothesis is supported by several observations: (i) Surface waters were enriched in lithogenic silica (Figure 3), a desert dust tracer [*Betzer et al.*, 1998] (ii) The absorbing aerosol index derived from TOMS observation (http://toms.gsfc.nasa.gov/aerosols/aerosols.html) show massive dust events over the Mediterranean before our campaign. They started in May (17–18), intensified in the first half of June. Then, between August 18 and September 19, 1999, eight Saharan dust events, leading to a total deposition of about 1 g m^{-2}, were recorded at a monitoring station near the DYF site (Guieu, pers. comm.). (iii) The sinking velocity of such minute desert dust particles is negligible, so they accumulate in the upper mixed layer (about 20 m thick in the present case, Figure 3), as long as deep convective processes do not occur.

[13] A red-rain event of 0.9 g m^{-2} was sampled on July 23, 2000, in Saint-Jean Cap Ferrat (52 km from the DYF site). The absorption spectrum of this rainwater was typical of clay particles, with a blue-to-green absorption ratio of about 2, while the scattering coefficient was essentially wavelength independent. We calculated that the increases in a(440) and $b_p(555)$ that this "red rain" would have generated in a 20 m water column are 0.005 m^{-1} and 0.015 m^{-1}, respectively. Therefore, the conclusion is that 2 to 3 dust events of about 1 g m^{-2} are sufficient to explain the changes in the optical properties recorded here in the Mediterranean Sea

(Table 1). By comparison, the average annual fluxes recorded in the areas of DYF and MIO sites are 12 (range 4–25) and 21 (range 6–46) g m^{-2}, respectively [*Guerzoni et al.*, 1997].

[14] At the upwelling site, the dust was very likely present; nevertheless, its effect on water optical properties is masked by high ⟨Chl*a*⟩, so that the color of these rich waters remains essentially unaffected (Figure 2).

4. Biogeochemical Implications

[15] A prerequisite for assessing the role of the ocean in the carbon cycle is to accurately estimate ⟨Chl*a*⟩ fields. Indeed, carbon fixation by a water column is proportional to its integrated ⟨Chl*a*⟩ content, which varies approximately as the square root of surface ⟨Chl*a*⟩ [*Antoine and Morel*, 1996]. In other words, an overestimation by a factor of ∼2 of surface ⟨Chl*a*⟩ (as it is the case for Mediterranean waters, Figure 2), converts into a ∼40% overestimation of carbon fixation. Applying generic algorithms to remotely-sensed B/G for dust-contaminated surface waters would result in an overestimation of ⟨Chl*a*⟩ and thus of carbon fixation.

Table 1. Optical Properties, Measured in Two Locations of the Mediterranean Sea, Compared to Properties Modeled for Standard Oceanic Waters (see Figure 1 for station location)

		MIO	DYF
⟨Chl*a*⟩ (mg m^{-3})	in situ measured	0.035	0.109
	SeaWiFS[a]	0.106	0.223
R440/R550	measured	5.9	3.4
	modeled[b]	9.1	5.1
a(555)/a(440)	measured[c]	3.3	2
	modeled[d]	4.1	2.6
$b_b(440)/b_b(555)$	derived[e]	1.8	1.7
	modeled[f]	2.4	2.1
$b_p(555)$ (m^{-1})	measured[g]	0.067	0.102
	modeled[h]	0.028	0.077
$a(440)-a_w(440)$ (m^{-1})	measured[c]	0.013	0.031
	modeled[d]	0.009	0.019
$a_p(440)$ (m^{-1})	measured[i]	0.008	0.017
	modeled[j]	0.006	0.013
$a_{OS}(440)$ (m^{-1})	derived[k]	0.005	0.014
$a_{CDOM}(440)$ (m^{-1})	modeled[l]	0.003	0.005
$a_{rr}(440)$ (m^{-1})	measured[m]	0.005	0.005
$b_{OS}(440)$ (m^{-1})	derived[n]	0.039	0.025
$b_{rr}(440)$ (m^{-1})	measured[m]	0.015	0.015

[a] ⟨Chl*a*⟩ retrieved from values averaged over 15 km × 15 km around the station and for September 1999.

[b] see *Morel and Maritorena* [2001].

[c] $a(\lambda)$ is derived from the measurement of the diffuse attenuation coefficient $K_d(\lambda)$ according to $a(\lambda) \approx K_d(\lambda)\,\mu_d(\lambda)$, where μ_d, the average cosine for downwelling irradiance, is computed through the radiative transfer equation for a sun zenith angle equal to 30° (μ_d = 0.800 and 0.797 for MIO and DYF conditions, respectively).

[d] $a(\lambda)$ is derived as above, but from modeled $K_d(\lambda)$ [*Morel and Maritorena*, 2001].

[e] measured R440/R555 divided by measured a(555)/a(440).

[f] modeled [*Morel and Maritorena*, 2001].

[g] $b_p(555)$, the particle scattering coefficient, is estimated as $c(555) - a(555) - b_w(555)$, where c(555) is the attenuation coefficient at 555 nm; vertical profiles of c(555) were acquired using a Wet Labs AC9 and averaged over the upper 20 m.

[h] modeled according to *Loisel and Morel* [1998].

[i] $a_P(440)$ was measured as described by *Claustre et al.* [2000] after water filtration onto a GF/F filter (nominal porosity of 0.7 μm).

[j] see *Bricaud et al.* [1998].

[k] $a_{OS}(440)$, the absorption by other substances, was computed using equation (1) and corresponds to absorption by substances (dissolved and/or particulate) <0.7 μm.

[l] $a_{CDOM}(440)$ modeled according to *Morel and Maritorena* [2001].

[m] Subscript rr stands for red rain. The reported values corresponds to the effect of 1 g m^{-2} flux in a 20 m thick water column.

[n] $b_{OS}(555)$ is the difference between measured and modeled $b_p(555)$.

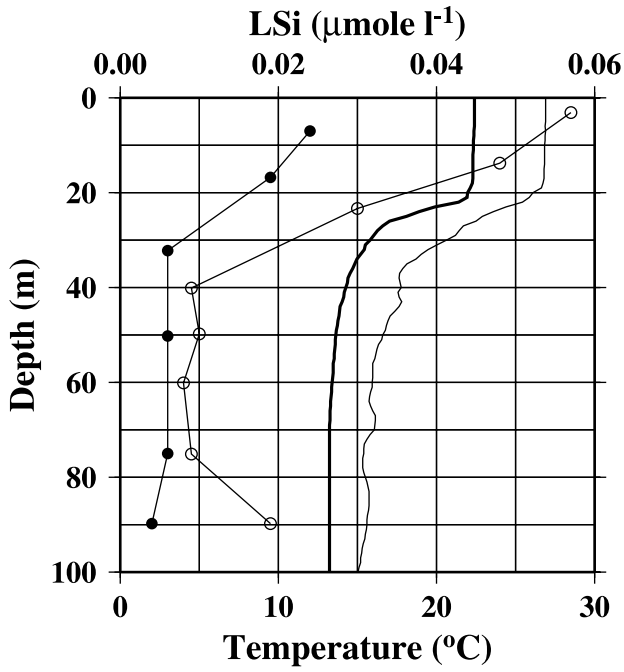

Figure 3. Vertical profiles of lithogenic silica in Mediterranean waters in September 1999. Profiles in the western (DYF, ●) and eastern (MIO, ○) basins are displayed together with corresponding temperature profiles (DYF: thick line; MIO, thin line). Lithogenic silica was measured according to *Brzezinski and Nelson* [1989] after concentrating particles on a 0.6 μm polycarbonate filter. Water samples were taken at the MIO and DYF stations on 24 and 30 September 1999, respectively.

[16] Improving the estimation of carbon fixation by marine biota at global scale would require that oceanic areas potentially contaminated by desert dust have been identified. Those areas have to be sought in oligotrophic areas (i.e. ⟨Chl*a*⟩ is ≤0.1 mg m^{-3}) to the extent that only optical properties of such clear waters are sensitive to dust presence. Indeed, assuming a Chla-specific absorption coefficient at 440 nm of 0.10 m^2 mg $Chla^{-1}$ [*Bricaud et al.*, 1998], the a(440) increase (see above) resulting from a ∼ 1 g m^{-2} dust flux is equivalent to 0.05 mg Chl*a* m^{-3}, which is very significant for oligotrophic waters. The sub-tropical gyres [about 40% of the world ocean] meet the criterion of oligotrophy. As the gyres of the southern hemisphere receive low dust fluxes [*Duce and Tindale*, 1991], their optical properties should be not affected by dust presence. In contrast, the north Pacific and north Atlantic gyres experience large dust deposition from the Asian (Gobi) and Saharan deserts [*Young et al.*, 1991; *Prospero and Ness*, 1986], respectively. Therefore, the optical properties of these gyres are expected of being, temporarily or permanently, affected by dust presence.

5. Concluding Remarks

[17] It has been shown that the presence of non-phytoplankton constituents — namely of dust — in open ocean waters with low ⟨Chl*a*⟩ can depress the in situ B/G compared to its expected value. Moreover, the remotely-sensed B/G can be even more lowered because the atmospheric correction of the blue bands is less accurate when absorbing aerosols are present in the atmosphere [*Moulin et al.*, 2001], which leads to an underevaluation of the actual B/G. This appears to be the case in oligotrophic Mediterranean waters where the ⟨Chl*a*⟩ retrieved from SeaWiFS (Figure 1) are distinctly higher than the sea truth data (Table 1). These observations suggest that regional algorithms are needed and that

the dependence of ⟨Chl*a*⟩ retrieval on the proximity of desert dust sources must be systematically investigated. Given the large spatial extension of sub-tropical gyres, a proper estimation of their contribution to oceanic carbon fixation requires very accurate estimate of their surface ⟨Chl*a*⟩. A careful re-examination of their optical properties is, therefore, a prerequisite to address (and quantify) potential dust-induced bias in ⟨Chl*a*⟩ retrieval.

[18] **Acknowledgments.** The pigment analyses could not have been accomplished without the unselfish contributions of J.-C. Marty and J. Ras. B. Gentili is thanked for drafting the figures. We also thank the DYFAMED atmospheric time-series service of Cap Ferrat which gave us the opportunity for sampling a "red rain" event. Fruitful discussions with H. Loisel and suggestions by L. Legendre and C. Moulin were greatly appreciated. This is a contribution of the PROSOPE group (PROOF-JGOFS-France). Information and data concerning the PROSOPE cruise can be found at : http://www.obs-vlfr.fr/jgofs/html/prosope/home.htm

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H. Claustre, A. Morel, M. Babin, D. Antoine, K. Oubelkheir, and A. Bricaud, Observatoire Océanologique, Laboratoire d'Océanographie de Villefranche, CNRS-INSU, and UPMC, B.P. 08, Villefranche-sur-mer, 06238 France. (claustre@obs-vlfr.fr; Morel@obs-vlfr.fr; babin@obs-vlfr.fr; antoine@obs-vlfr.fr; kadija@obs-vlfr.fr; bricaud@obs-vlfr.fr)

S. B. Hooker, NASA Goddard Space Flight Center, Greenbelt, MD, USA. (stan@ardbeg.gsfc.nasa.gov)

K. Leblanc and B. Quéguiner, Centre Océanologique de Marseille, Laboratoire d'Océanographie et de Biogéochimie, Campus de Luminy, Case 901, Marseille, F-13288, France. (karine.leblanc@com.univ-mrs.fr; bernard.queguiner@com.univ-mrs.fr)

S. Maritorena, Institute for computational Earth System Science, University of California at Santa Barbara, 6841 Ellison Hall, Santa Barbara, CA 93106-3060, USA. (stephane@icess.ucsb.edu)