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Seasonal dynamics in colored dissolved organic matter in the Mediterranean Sea: Patterns and drivers

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ABSTRACT

Two autonomous profiling "Bio-Argo" floats were deployed in the northwestern and eastern sub-basins of the Mediterranean Sea in 2008. They recorded at high vertical (1 m) and temporal (5 day) resolution, the vertical distribution and seasonal variation of colored dissolved organic matter (CDOM), as well as of chlorophyll-a concentration and hydrological variables. The CDOM standing stock presented a clear seasonal dynamics with the progressive summer formation and winter destruction of subsurface CDOM maxima (YSM, for Yellow Substance Maximum). It was argued that subsurface CDOM is a by-product of phytoplankton, based on two main characteristics, (1) the YSM was located at the same depth than the deep chlorophyll maximum (DCM) and (2) the CDOM increased in summer parallels the decline in chlorophyll-a. These observations suggested an indirect but tight coupling between subsurface CDOM and phytoplankton via microbial activity or planktonic foodweb interactions. Moreover, the surface CDOM variations observed both by floats and MODIS displayed different seasonal dynamics from what recorded at subsurface one. This implies that CDOM standing stock can be hardly detected by satellite. It is worthnoting that surface CDOM was found to be more related to the sea surface temperature (SST) than chlorophyll-a concentration, suggesting its physical origin, in contrast to the biological origin of YSM and subsurface standing stocks.

1. Introduction

Colored (or Chromophoric) Dissolved Organic Matter (abbreviated as "CDOM"), also known as "gelbstoff" (Kalle, 1938), "yellow substance" (Shifrin, 1988), or "gilvin" (Kirk, 1994), is an important component of the dissolved organic carbon (DOC) pool in natural waters where it plays a major role in determining underwater light availability (Siegel et al., 1995, 2002; Siegel and Michaels, 1996; Nelson et al., 1998; Nelson and Siegel, 2002; Coble, 2007; Morel and Gentili, 2009a).

The main optical behavior of CDOM resides in its light absorption over a broad range of visible and UV wavelengths. Especially in the UV and blue light region, the non-water absorption is dominated by CDOM (Nelson and Siegel, 2002). Statistical analysis using global satellite data shows that nearly 50% of non-water absorption is due to CDOM at 440 nm, which also corresponds to the main phytoplankton absorption peak (Swan et al., 2009). Thus, CDOM can affect on the accuracy of the retrieval of ocean chlorophyll-a concentration and subsequently primary productivity by satellite ocean color radiometry.

However, due to severe under-sampling through the use of ship-based observation, in situ measurements have remained scarce and hence our understanding of CDOM dynamics in various open ocean regions. In this context, the CDOM time series (based on monthly cruises) at BATS and analyzed by Nelson et al. (1998) can be considered as a reference study for open ocean waters. More recently, the availability of new sensors (such as in situ CDOM fluorometers, Belzile et al., 2006; Kowalczuk et al., 2010) associated with the progressive maturation of autonomous platforms that can carry them (e.g. Johnson et al., 2009), might be of considerable importance in view of improving our understanding of CDOM dynamics by increasing temporal as well spatial resolution of measurements.

The fluorescent properties of CDOM have been reported as early as 1949 by Kalle (1949) who found that the same material was able to emit blue fluorescence when excited by UV radiations. Although relationships between CDOM absorption and fluorescence do not seem to be ubiquitous, nevertheless, linear relationships between both measurements were observed

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in open oceans and coastal waters (e.g., Ferrari and Tassan, 1991; Hoge et al., 1993; Vodacek et al., 1997; Ferrari and Dowell, 1998; Ferrari, 2000; Belzile et al., 2006; Yamashita and Tanoue, 2009; Kowalczuk et al., 2010).

The recent development of the so-called Bio-Argo floats (profiling floats equipped with bio-optical and biogeochemical sensors) now offers the possibility to develop innovative strategies for the observation of oceanic biogeochemistry and ecosystem (Claustre et al., 2010). Bio-Argo floats not only allow for long-term (annual/multiyear), quasi-continuous (at least once per 10 days), and highly resolved vertical (1 m resolution) oceanic properties observations, but also provides unique, synchronous and multi-parameter datasets. Such datasets are especially required for physical and biological/biogeochemical/bio-optical coupling research (IOCCG, 2011).

In 2008, a fleet of 8 Bio-Argo floats were deployed in various oceanic areas representative of the diversity of the trophic conditions prevailing in the open ocean, equipped with CDOM fluorometer, chlorophyll-a fluorometer, as well as other bio-optical and biogeochemical sensors. The acquired dataset by this fleet supported methodological development allowing the accurate retrieval of key biogeochemical variables like chlorophyll-a concentration (Xing et al., 2011) and CDOM absorption at 412 nm (Xing et al., 2012). Two of these 8 floats were deployed in the northwestern and eastern sub-basins of the Mediterranean Sea and continuously recorded, over more than 1 year, the vertical distributions (from surface to 400 m) of CDOM as well as hydrological parameters and chlorophyll-a concentration. Here these high-resolution measurements are used as the basis for an assessment of the regional and seasonal CDOM dynamics.

The present study highlights the seasonal cycle of CDOM in both sub-basins, the decoupling between its surface and subsurface dynamics, and the tight link between its subsurface maximum and deep chlorophyll-a maximum (DCM). A specific attention is dedicated to the yellow substance subsurface maximum (hereafter denoted as YSM), a feature already investigated in Case I waters (e.g. Nelson et al., 1998, 2004; Coble et al., 1998; Chen, 1999; Lund-Hansen et al., 2006; Kitidis et al., 2006; Chekalyuk et al., 2012), and also reported in the Mediterranean Sea (Oubelkheir et al., 2005, 2007). Here in the Mediterranean Sea and thanks to the first complete high-resolution time series, the temporal CDOM dynamics and associated drivers can be addressed for the first time. In particular, the possible biogeochemical and/or the hydrological origins of the observed variations are presented and discussed.

2. Materials and methods

2.1. Bio-Argo data

The two Bio-Argo floats were deployed in May 2008, in the Northwestern Mediterranean Sea (NWM), and in June 2008, in the Levantine Sea (LS) (Fig. 1). They are named "MED_NW_B02" and "MED_LV_B06", respectively. Both floats are based on the PROVOR CTS3 free-drifting profilers (NKE instrumentation, France), equipped with a OC4 radiometer (Satlantic, Halifax, Canada), a transmissometer and an ECO Puck instrument (WET Labs, Inc., Philomath, OR, USA). In addition to the standard hydrological observation by PROVOR, the OC4 radiometer measures the downward planar irradiance, E_d, at three wavelengths (412, 490, and 550 nm); the transmissometer measures the beam attenuation coefficient at 660 nm; and the ECO Puck integrates three independent sensors, for backscattering at 532 nm, Chla fluorescence, and CDOM fluorescence (excitation at 370 nm, emission at 460 nm) measurements, respectively. The observation frequency was generally programmed as a profile every 5 days, with few exception of a profile every 1 day just after the deployment (to check float performances). For each profile, the observation mission included acquisition of a CTD profile from 1000 m up to surface, whereas the bio-optical sensors started acquisition from 400 m (this was done to save energy and hence increase the life-time of float).

In previous studies (Xing et al., 2011, 2012), two successive processing procedures were presented respectively for retrieval of chlorophyll-a concentration (units mg m^{-3}, thereafter denoted [Chla]) and CDOM absorption coefficient at 412 nm (units m^{-1}, thereafter denoted $a_y(412)$), combining the radiometry ($E_d(412)$ and $E_d(490)$) and fluorometry (chlorophyll and CDOM fluorescence). For the sake of completion, the retrieval methods are briefly introduced here.

First of all, two linear relationships were assumed as the basis of procedures, as shown below:

$$[\text{Chla}] = \text{Slope}_C(\text{Fluo}_C - \text{Offset}_C) \quad (1)$$

$$a_y(412) = \text{Slope}_Y(\text{Fluo}_Y - \text{Offset}_Y) \quad (2)$$

where [Chla] and $a_y(412)$ are the finally retrieved variables; Fluo_C and Fluo_Y represent the chlorophyll and CDOM fluorescence signals acquired by two fluorometers; and all the remaining terms (Slope_C, Slope_Y, Offset_C and Offset_Y) are regarded as the coefficients to be retrieved.

The Offset_C is determined profile by profile firstly based on a common assumption that the [Chla] at depths larger than 300 m is zero, so that the Fluo_C profiles are simply reset to zero beyond this level and the Offset_C are obtained as the deep Fluo_C signal. In light of the classical bio-optical relationship prevailing for open ocean Case I waters (Morel et al., 2007), the diffuse attenuation coefficient at 490 nm (thereafter denoted $K_d(490)$) can be calculated as a function of [Chla]:

$$K_d(490) = 0.01660 + 0.0825[\text{Chla}]^{0.6529} \quad (3)$$

By introducing Eq. (1) into Eq. (3), the Slope_C will be figured out while $K_d(490)$ is determined through the vertical derivation

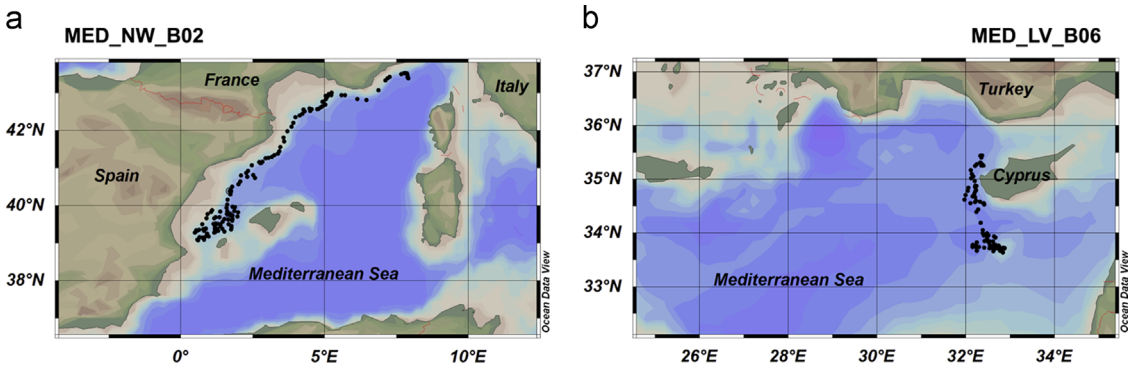

Fig. 1. The trajectories and observation positions of the "MED_NW_B02" float (a) in the northwestern sub-basin of Mediterranean Sea and the "MED_LV_B06" float (b) in the eastern sub-basin.