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Key Points:

- Nitrate profiling floats observed deep convection and bloom in the Mediterranean
- Cyclonic basin circulation appears critical for bloom onset

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Observing mixed layer depth, nitrate and chlorophyll concentrations in the northwestern Mediterranean: A combined satellite and NO₃ profiling floats experiment

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Abstract Two profiling floats, equipped with nitrate concentration sensors were deployed in the northwestern Mediterranean from summer 2012 to summer 2013. Satellite ocean color data were extracted to evaluate surface chlorophyll concentration at float locations. Time series of mixed layer depths and nitrate and chlorophyll concentrations were analyzed to characterize the interplay between the physical-chemical and biological dynamics in the area. Deep convection (mixed layer depth > 1000 m) was observed in January–February, although high-nitrate surface concentrations could be already observed in December. Chlorophyll increase is observed since December, although high values were observed only in March. The early nitrate availability in subsurface layers, which is likely due to the permanent cyclonic circulation of the area, appears to drive the bloom onset. The additional nitrate supply associated to the deep convection events, although strengthening the overall nitrate uptake, seems decoupled of the December increase of chlorophyll.

1. Introduction

In temperate seas, the seasonal dynamics of the mixed layer depth (MLD) are considered to be the primary mechanism injecting nutrients in the illuminated surface layers [*Williams and Follows*, 2003]. Phytoplankton reacts to nutrient availability by its growth, and when the resulting increase of biomass exceeds losses (due to export, sinking, grazing, or respiration), phytoplankton cells begin to accumulate, and a bloom is observed [*Sverdrup*, 1953]. The intensity and duration of a bloom are influenced by many factors, both biotic and abiotic [*Henson et al.*, 2006; *Levy et al.*, 1999; *Siegel et al.*, 2002]. Among all these factors, however, the MLD is generally recognized as a key one, since it directly controls the quantity of nutrients available for the phytoplankton, the time of residence of phytoplankton in the enlightened layers, and the encounter rate between phytoplankton and grazers.

In the northwestern (NW) Mediterranean basin, a strong seasonality of the MLD has been observed [*D'Ortenzio and Prieur*, 2012]. During summer, the MLD is very shallow, as a consequence of the strong warming of the Mediterranean region [*Lionello*, 2006]. In winter, deep MLDs are recurrently observed, due to orographic constraints and to the specific meteorological and hydrological conditions of the area [*Mertens and Schott*, 1998]. Winter MLDs reach regularly 800–1000 m, although a complete homogenization of the water column (down to bottom, ~2300 m) can be observed in a restricted area (about 2500 km², around 42°N 5°E) and under specific conditions [*de Madron et al.*, 2013]. Bottom water is hence formed, and this contributes to drive the thermohaline circulation characterizing the whole western Mediterranean basin [*Robinson and Golnaraghi*, 1995]. In the same region, although across a larger area (more than thousands of km²), an intense phytoplankton bloom is recurrently observed in spring, from both satellite [*Bosc et al.*, 2004] and in situ [*Marty and Chiaverini*, 2002] measurements. The NW Mediterranean bloom is somewhat anomalous in the Mediterranean Sea, which is generally considered as an oligotrophic ocean

[D'Ortenzio and d'Alcala, 2009]. The variability of the MLD and, in particular, the extreme events of deep convection are generally evoked as the main cause for the trophic specificity of the area [Lazzari et al., 2012; Marty and Chiavérini, 2010]. However, recent findings [Lavigne et al., 2013] indicate that preconditioning factors (i.e., the cyclonic circulation of the area) should be more critical to set up favorable conditions for a bloom, as they should control the nutricline depth at the end of winter. Apart from modeling approaches [Lazzari et al., 2012; Levy et al., 1999], a definitive answer is, however, still lacking. Scarcity of data, in particular for chemical and biological observations, prevent any high-resolution description of a complete annual cycle of the NW Mediterranean area, puzzling the comprehension of the mechanisms linking the MLD evolution, the nutrient uptake, and the spring bloom (see discussion on the subject in *de Madron et al.* [2011]).

During the past years, automated platforms like gliders [*Ruiz et al.*, 2012], buoys [*de Madron et al.*, 2013], or profiling floats [*Smith et al.*, 2008] have strongly enhanced our comprehension of the physical functioning of the NW Mediterranean. Similarly, Bio-Argo floats [*Xing et al.*, 2011] and Bio-gliders [*Niewiadomska et al.*, 2008] demonstrated that these platforms have critical potentialities to assess the NW Mediterranean physical-biological functioning. However, until present, the chemical compartment is still missing.

In summer 2011, two profiling floats equipped with nitrate concentration (hereafter NO₃) sensors were deployed in the NW Mediterranean. The two floats (hereafter named PRONUTS) were based on the PROVOR CTSO3 platform, which contributes to about 10% of the temperature and salinity floats of the global Argo network [*Freeland and Cummins*, 2005]. On the PRONUTS floats, in addition to the standard temperature and salinity sensors, two optical-based instruments for NO₃ estimation were installed. The two sensors, an In Situ Ultraviolet Spectrophotometer (ISUS) and a Submersible Ultraviolet Nitrate Analyzer (SUNA) (commercialized by Satlantic Inc.), are based on the same principle (i.e., UV absorption), although they have different specificities, demanding different implementations on the PROVOR platforms (see *D'Ortenzio et al.* [2012] for more details).

The potentiality of UV NO₃ sensors on profiling floats has already been successfully demonstrated [*Johnson et al.*, 2010], although several issues require a careful analysis of the data. The nominal limit of detection (0.5 μ M) and accuracy (2 μ M) are high compared to classical analysis based on water samples. Moreover, the stability of the sensor over long deployments and in the absence of any maintenance could induce some bias in the NO₃ estimation [*Johnson and Coletti*, 2002a]. However, if an accurate and robust data quality control is provided, NO₃ profiling float-based observations represent a significant improvement for oceanic biogeochemical monitoring [*Johnson et al.*, 2013]. Additionally, NO₃ data from profiling floats have a promising application in the assimilation techniques for operational numerical systems [*Brasseur et al.*, 2009].

The two PRONUTS floats sampled the NW Mediterranean region over more than a year. The first was recovered 393 days after the deployment, while the second was recovered in July 2013, more than 2 years after deployment. Both floats observed deep-mixing preconditions, a huge deep convection event, and an intense uptake of nutrients in the surface layers. Moreover, they stayed in the area during a large phytoplankton bloom, which occurred later in spring.

In this paper, we present 1 year (June 2011 to June 2012) of observations of the PRONUTS floats in the NW Mediterranean area. A specific calibration procedure was applied, as we used old versions of the SUNA and ISUS processing software, which did not include the recently developed algorithms (see further). Float data were also analyzed with concurrent satellite ocean color observations.

The main objective of the paper is to improve the comprehension of the biogeochemical functioning of the NW Mediterranean Sea, by exploiting the potentiality of the coupled PRONUTS and ocean color remote sensing observations.

2. Data and Methods

2.1. The PRONUTS Platform

The PRONUTS characteristics were based on the PROVOR CTSO3 profiling float, additionally equipped with an Iridium antenna, allowing for double-way communication and offering the capability to modify the sampling strategy during the mission. Similar to Argo floats, PRONUTS spent most of the time at depth (i.e., 1000 m), starting a profile at a given temporal frequency, and transmitting data at the end of the profiling phase (i.e., at surface). On one PRONUTS, an ISUS sensor was fully integrated into the float (PRONUTS-ISUS),

while, on the other PRONUTS, a SUNA sensor was externally clamped to the float hull (PRONUTS-SUNA). NO₃ estimations were performed at 60 fixed depths, from 0 to 1000 m (about 10 m resolution in the 0–100 m layer, and 15 m resolution in the remaining range). Temperature and salinity profiles were also collected, though at higher vertical resolution (about 2 m in the 0–100 m layer, and 10 m at depth).

2.2. NO₃ Sensors Calibration

The SUNA and the ISUS sensors share the same measurement principle and algorithms, based on a fitting of the measured absorption UV spectra (from 217 to 242 nm), with a bromide correction and seawater absorption [Johnson and Coletti, 2002b]. In the PRONUTS, NO₃ computations were carried out on board, and only the processed data were transmitted to land (the raw data, i.e., sampled UV spectrum, were not transmitted). Recent algorithms for temperature and salinity correction, which have proved to strongly improve NO₃ estimations [Sakamoto et al., 2009], were not implemented on the versions of SUNA and ISUS that were used. The lack of absorption spectrum data (i.e., not transmitted) prevented the application of a postprocessing procedure using the Sakamoto et al. [2009] correction, as strongly recommended by Johnson et al. [2013]. A specific calibration of the sensors was developed (fully explained in the supporting information), which accounted for the pressure, temperature, and salinity influence, and which is based on the general principles of the existing methods (see supporting information in Johnson et al. [2010] and Johnson et al. [2013]). Additionally, a temporal drift was observed and corrected profile by profile. Comparisons with in situ NO₃ colorimetric data (obtained from discrete sampling during the deployment and the recovery) provided an assessment of the algorithm performances (root-mean-square errors for the ISUS and SUNA calibrated NO₃ are 0.36 and 0.19 μ M, respectively, see the supporting information).

3. Mission

The two PRONUTS were simultaneously deployed on 29 June 2011, 60 km offshore from the French coast, in the Gulf of Lion (see Figure S1 in the supporting information). They were programmed to have parking and profiling depths of 1000 m. The profiling period was initially set to 10 days and then modified to 2 days in February 2012. The PRONUTS-ISUS experienced a system breakdown, interrupting communication from 17 September to 4 November 2011. After this date, the float recovered a regular functioning. It was then recovered on 27 July 2012. The PRONUTS-SUNA was recovered 1 year later (July 2013). In the following, we will analyze only the period from June 2011 to June 2012. During this period, both floats remained in the region indicated by *D'Ortenzio and d'Alcala* [2009] as having a blooming regime (Figure S1 in the supporting information, dotted lines). Moreover, they sampled the area where a deep convection mixed patch was observed (grey regions in Figure S1 in the supporting information, representing pixels with surface chlorophyll concentration < 0.1 mg/m³ in the Moderate Resolution Imaging Spectroradiometer (MODIS) image of the 22 February 2012 [*de Madron et al.*, 2013]).

3.1. Satellite Ocean Color

Images of surface chlorophyll concentrations (CHL) from level 2 MODIS product (daily and at 1 km resolution) were extracted on the NW Mediterranean area for the period of interest. From the images, and after application of all the MODIS L2 flags, CHL values are extracted from a box of 5 × 5 km around the last available float position and then averaged. Only boxes having more than 50% valid pixels were retained. From the CHL values, the euphotic depth (Ze) was estimated, by calculating the diffuse attenuation coefficient at 490 nm [*Morel and Maritorena*, 2001], then the total attenuation coefficient for photosynthetically available radiation [*Rochford et al.*, 2001], and finally the Ze, i.e., the depth where the light level represents 1% of its surface value, was assessed.

3.2. Results and Discussion

The time series of MLD, estimated from PRONUTS temperature and salinity profiles (using a 0.03 threshold density criteria [*D'Ortenzio et al.*, 2005]), the time series of the averaged NO₃ in the MLD (NO_{3mld}) and the time series of the surface CHL and Ze obtained from satellite describe the evolution of the NW Mediterranean area during the June 2011 to June 2012 annual cycle (Figures 1a and 1c). A selection of CHL images, with the concurrent float positions, illustrates the large-scale situation of the area sampled by the PRONUTS during the studied period (Figure 2).



Figure 1. Time series and metrics of the PRONUTS and satellite observations for the (a and b) ISUS and for the (c and d) SUNA. In Figures 1a and 1c, grey diamonds represent MLD, red diamonds NO_{3mld} , yellow points Ze, and green diamonds CHL. The blue marks on the upper *x* axis of Figures 1a and 1c indicate the date of the satellite images drawn in Figure 2. In Figures 1b and 1d, vertical short colored lines indicate the dates of parameter increasing (red for NO₃, dark green for CHL × MLD, light green for CHL, and grey for MLD); circles indicate date of absolute maximum (same color code); and black lines indicate the dates of the first and the last occurrences of the MLD = Ze condition. Triangles indicate the date of negative-to-positive Qtot inversion. See Table S2 in the supporting information for the list of the metric values and of the method to compute them.

From June 2011 to February 2012, MLD time series have similar shapes for both floats, with shallow values during summer and early autumn, and a slow deepening phase starting in December. The PRONUTS-SUNA sampled a short MLD deepening event in December, likely related to local conditions. Then, from February 2012, the two MLD time series diverge, as a result of the different positions of the floats (see Figure 2, images of 8 December and 21 January). Closer to the center of the isopycnal doming induced by the cyclonic circulation of the area [*Robinson et al.*, 2001], the PRONUTS-ISUS observed deeper MLDs than the PRONUTS-SUNA. In late February, PRONUTS-ISUS detected very deep MLDs, indicating the intense convection episode of the 2011–2012 winter period (also described by *de Madron et al.* [2013]). The deep convection mixed patch, as well as the position of the two floats, is clearly evident in the MODIS image of 22 February (Figure 2, i.e., the violet region in the image, indicating very low CHL, resulting from deep mixing [see *de Madron et al.*, 2013]). While the PRONUTS-ISUS sampled the deep convection mixed patch, the PRONUTS-SUNA position was drifting rather at the

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Figure 2. Chlorophyll concentration maps of the NW Mediterranean, as derived by MODIS satellite. Red circles and white diamonds indicate the position of the SUNA and ISUS PRONUTS, respectively, at the date of the image. In the first image, white and black continuous lines indicate the trajectories of the SUNA and ISUS PRONUTS, respectively.

periphery of the mixed patch, and the observed MLD did not exceed 400 m depth. For both time series, MLDs became shallow in late March. A deep MLD was still observed by PRONUTS-SUNA in March (see Figure 2, image of 12 March) when the SUNA float sampled residuals of the deep convection mixed patch. For the rest of the year (from April to June), MLDs remained shallow.

Similar to the MLD, the NO_{3mld} time series of the two PRONUTS have analogous patterns. NO_{3mld} increases since December and reaches maxima values in February–March. Winter NO_{3mld} concentrations are, however, different for the two floats. The complete homogenization of the water column occurring in the deep convection mixed patch led to a match between the PRONUTS-ISUS NO_{3mld} and the NO₃ at depth (about 8–9 μ M) since February. The PRONUTS-SUNA observed lower NO_{3mld} during January and February. In late February a first short peak was observed. It decreased until March then was followed by a second, longer peak (when the float sampled the mixed patch at the mixing phase, see Figure 2, image of 12 March). The NO_{3mld} values from the two floats decreased in late March, when the shallowing of the MLD favored the onset of the bloom (see Figure 2, image of the 29 March), which strongly consumed the surface NO₃. The NO₃mld series then decreased slightly from March to May, although PRONUTS-ISUS values were

higher than those of the PRONUTS-SUNA, in particular during late April. During this period, the float was entrapped in a mesoscale feature (partially visible in Figure 2, image of 20 April and by the *T* and *S* profiles of the float, not shown), which induced a local increase of NO_{3mld} . In late May, the NO_{3mld} for both floats fell to autumn levels.

From November to January, the biomass response to the observed widespread NO₃ availability was indicated by an increase of satellite CHLs, which are generally stable around 0.2 to 0.3 mg/m^3 for both time series (i.e., 2 to 3 times greater than the summer values of about 0.1 mg/m^3). Deep MLD events were always concomitant to local decreases of CHL, as expected during intense mixing episodes. In late March, high CHL values (i.e., greater than 1.0 mg/m^3) could be observed in both time series in late March. The CHL values then rapidly decreased, with concentrations around $0.15/0.2 \text{ mg/m}^3$ during April–May. Finally, in June, CHL concentrations decreased below 0.1 mg/m^3 .

The simultaneous availability of MLD, NO₃, and CHL observations allows a unique reconstruction of the physical, chemical, and biological interactions in the NW Mediterranean area. This interplay will be further discussed in the framework of the existing models of the bloom onset and development in the temperate seas [*Behrenfeld and Boss*, 2014; *Dutkiewicz et al.*, 2001; *Sverdrup*, 1953; *Taylor and Ferrari*, 2011]. Metrics indicating the first increasing and the seasonal maximum for the different parameters (NO_{3mld}, MLD, CHL, and CHL × MLD) have been then computed and plotted (Figures 1b and 1d and Table S2 in the supporting information for methodological details and a report of computed values). To calculate the date of the heat fluxes negative-to-positive transition ("Qtot inversion" [*Taylor and Ferrari*, 2011]), heat budget estimations (Qtot) for the period June 2011 to June 2012 are obtained from European Centre for Medium-Range Weather Forecasts website (www.ecmwf.int). Considering the coarse spatial resolution of the available data (2.5°) only a single grid point is used for both PRONUTS time series. Qtot inversion is the date where the Qtot values pass from negative to positive. At least three values are required to fix the data.

For both the time series, the timing of the first increases in CHL and in CHL × MLD matches. It coincides with the date when MLD = Ze for the first time. This condition, proposed as a proxy of the phytoplankton changing regime [*Dutkiewicz et al.*, 2001; *Marra et al.*, 2014], appears to be respected in the NW Mediterranean area. Two hypotheses could explain the concomitant increase in CHL and CHL × MLD: the injection of nutrients in surface with the deepening of the MLD [*Cullen et al.*, 2002] or a decrease in the encounter rate between phytoplankton and zooplankton (dilution-recoupling hypothesis [*Behrenfeld*, 2010]). Although it is difficult to make a definitive answer to the question with the PRONUTS data only, we observe that only when high values of nutrients are present, a phytoplankton increase is observed in the NW Med and in late autumn. This information, somewhat logical, is, however, often lacking in the previous analyses.

The timing where MLD = Ze for the last time (again coincident in both PRONUTS) marks another important date (note that, for the ISUS time series, we did not considered the April time period for the computation of the last occurrence of MLD = Ze, because the float was entrapped in a mesoscale structure), as it coincides with the dates of the maximum values of CHL for both the floats. However, for the ISUS series, this date of the second MLD = Ze occurrence is delayed of about 1 month respect to the dates of CHL × MLD, NO₃, and MLD maximum values, suggesting that surface and integrated phytoplankton biomasses have different dynamics. A more clear pattern is the coincidence of the dates of maximum of CHL × MLD with the dates of maximum of MLD, which suggests the consistency of our data with the dilution-recoupling hypothesis proposed by *Behrenfeld* [2010]. This date coincides also with the date of Qtot negative-to-positive inversion [*Taylor and Ferrari*, 2011], which, however, seems indicating more the maximum of the bloom rather than its onset.

Despite of the general problematic of the bloom onset and evolution, however, the PRONUTS data provided a new assessment of the impact of deep convection on the phytoplankton winter-to-spring transition in the specific case of the NW Mediterranean area.

In this zone, the deep MLD associated to deep convection are often believed to trigger the spring bloom. All PRONUTS data showed, however, that CHL and CHL × MLD increasing occurred two months before the strong mixing event. Moreover, even relatively shallow MLDs (400 m) induced high NO₃mld concentrations (6–7 μ M, as observed by the PRONUTS-SUNA). More generally, both time series showed high surface nutrients from January to March, although MLD magnitudes differed. This common pattern of the NO₃ fields suggests that the whole NW Mediterranean region (and not the deep convection area only) is favorably preconditioned for phytoplankton growth. This large-scale availability of NO₃ has already been observed in the past [*Manca et al.*, 2004] and is likely related to the cyclonic circulation of the NW Mediterranean. The latter, inducing a doming of the isopycnals, leads to an approaching of the NO₃ deep reservoir to the surface [*Crise et al.*, 1999]. The main consequence is that significant NO₃ concentrations are observed in surface layers since the month of December, even though the MLD depths are not exceptionally deep (i.e., PRONUTS-SUNA time series during winter).

The deep convection event of the February–March 2012 period (as observed by the PRONUTS-ISUS float, and, less clearly, by the PRONUTS-SUNA) does not seem to significantly modify this pattern of NO₃. However, the deep convection event seems more relevant for the evolution of CHL. CHLs are minimal in the convection patch (as observed by the PRONUTS-ISUS, see Figure 2, image of 22 February), although NO₃ is at its maximum.

The deep convection, which is characterized by very deep MLDs, does not appear to be the primary cause for the onset of the bloom. More likely, the maintenance of subsurface layers rich in nutrients close to the surface is ascribed to the permanent large-scale cyclonic circulation of the NW Mediterranean, which, in turn, induces favorable blooming conditions from December onward. In this NO₃-rich context (which appears to involve the whole NW Mediterranean area), the interplay between light availability and mixing appears to be a key factor controlling the variation of CHL. The Ze/MLD ratio is lower than 1 over the whole December to March period, suggesting that the deep convection event (observed in February) occurred when favorable blooming conditions were already established. More interestingly, the dates at which Ze equaled MLD marked specific breaking points. In December, the date coincides with the first annual increase of CHL and CHL × MLD. Later, in March, it marks the date of the surface phytoplankton burst and the exhausting of surface nutrients.

As already shown by *Levy et al.* [1999], however, the redistribution of nutrients following the deep convection events, and related to mesoscale activity, contributes to maintain high-nutrient concentrations in the surface layers for a longer period, and, consequently, to increase the longevity of the bloom. During the month of April, when a small feature entrapped the PRONUTS-SUNA float, elevated NO_{3mld} and CHL values were observed, thus suggesting a positive feedback of mesoscale activity after deep convection.

4. Conclusions

One year of NO₃ and MLD profiles from two profiling floats equipped with a NO₃ sensor (PRONUTS) was analyzed in combination with satellite ocean color observations in the NW Mediterranean. The very high temporal resolution of the data, as well as the capability of the floats to monitor a complete annual cycle, provided an exceptional picture of the interplay between the physical and chemical forcings and the phytoplankton response. The PRONUTS sampled a complete annual cycle, which was characterized by a sequence of events typical of temperate seas: strong oligotrophy, onset of favorable conditions for phytoplankton growth, a huge event of deep MLD, and a relevant, large-scale bloom. The presented analysis suggests that the blooming conditions of the area are mainly dependent upon the large-scale cyclonic circulation of the region (as already proposed by D'Ortenzio and d'Alcala [2009] and D'Ortenzio and Prieur [2012]). The latter maintains high-NO₃ concentrations close to the surface and induces a phytoplankton increase from the month of December onward. In this context, the large MLDs associated to the deep water formation, occurring in a reduced area of the analyzed region, appear as secondary factors (in terms of timing) that influence the bloom development. The interplay between Ze and MLD and the high availability of NO₃ induced by the large-scale circulation appear to be all the more important for the bloom onset, in agreement with the "classical" temperate sea bloom theories [Dutkiewicz et al., 2001; Sverdrup, 1953]. In the NW Mediterranean area, however, this theory does not seem to be in opposition with the alternative hypothesis of Behrenfeld and Boss' [2014], which better apply on the MLD-integrated chlorophyll content. Deep MLDs, however, remain responsible for the temporal delay between the establishment of favorable blooming conditions (December) and the CHL peaks (March), as already proposed by Lavigne et al. [2013]. Moreover, deep MLDs have also been shown to play a key role in the longevity of the bloom, by generating intense mesoscale activity, which then redistributes nutrients to surface layers and promotes phytoplankton growth when stratification conditions appear [Levy et al., 1999].

Further investigations are required, in particular, to obtain in situ estimations of the CHL evolution. Most of these issues will be likely resolved in the near future. In 2013, three new generation biogeochemical profiling floats were deployed in the NW Mediterranean area, in the framework of the Novel Argo Ocean observing System (NAOS) French project (http://en.naos-equipex.fr/). These new floats [*Leymarie et al.*, 2013] share the same characteristics as the PRONUTS prototypes, and they are additionally equipped with a fluorometer for CHL profiling and with an up-to-date version of the NO₃ sensors (which includes *Sakamoto et al.* [2009] correction). The analysis of these new observations should be able to confirm or not the hypothesis that have been proposed in this paper for the NW Mediterranean physical-biogeochemical functioning, based on the PRONUTS data only.

Overall, the PRONUTS floats provided relevant observations on the biogeochemical functioning of the NW Mediterranean. They also left several questions open, to which a network of floats, systematically equipped with biogeochemical sensors (Bio-Argo), should help answer.

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