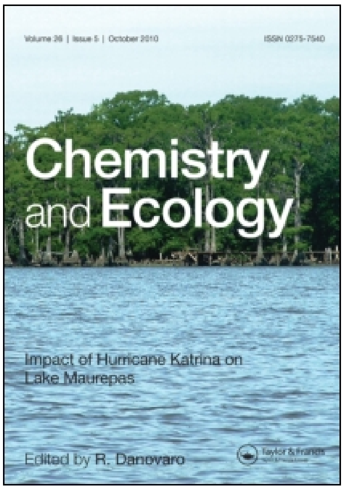

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Variability and sustenance of the deep-chlorophyll maximum over a narrow shelf, Augusta Gulf (Sicily)

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VARIABILITY AND SUSTENANCE OF THE DEEP-CHLOROPHYLL MAXIMUM OVER A NARROW SHELF, AUGUSTA GULF (SICILY)

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This work reports on the temporal variability of the deep-chlorophyll *a* maximum (DCM) in a Mediterranean coastal environment. In contrast to a supply through vertical diffusion normally found offshelf, in the study area the nutrients were supplied laterally through intermittent, pycnoclinal intrusions over the shelf by the enriched Messina Mixed Water mass. A 48 h time series revealed a strong variability in the nutrient concentrations and size-fractioned chlorophyll *a* distributions. This variability appeared to be less correlated with the diurnal biological cycle and more correlated with the availability of newly advected nutrients. The observations also demonstrated that the planktonic community of DCM remains vertically non-homogenous when exposed to strong vertical shears caused by deformations in the depth of the pycnocline. For this shelf situation, assumptions regarding the distribution of the DCM, *e.g.*, steady state, vertical or horizontal coherence, were all counterindicated.

Keywords: Ionian Sea; Deep-chlorophyll maximum; Shelf processes; Chl*a* time dependency

1 INTRODUCTION

This study results from an oceanographic cruise conducted in the Gulf of Augusta during 28 September to 5 October 2001, which has been described in the technical reports of Budillon (2003) and Decembrini (2003). The intent of the cruise was to conduct a preliminary survey of the Gulf with a focus on the shelf circulation, the extent of eutrophic production, and the geology of the benthos. During the initial hydrographic survey, no evidence was found of eutrophication, in the form of freshwater input, elevated nutrients, or bottom-water hypoxia. Consequently, the biological effort was directed toward an investigation of the variability of the DCM at its intersection with the shelf bathymetry. Specifically, this paper reports on: (1) the temporal variability of the DCM over a 48 h period; (2) the source of new nutrients; and (3) the physical control of its variability. The other objectives are reported in separate papers: the circulation by Raffa and Hopkins (2004), the micro-biology by Zaccone *et al.* (2004) and the sediments and geomorphology by Budillon *et al.* (2003).

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1.1 Background

The Gulf of Augusta is located on the Eastern coast of Sicily and is formed by the concave coastline between the two Capes of S. Croce and Syracuse, both prominent along the eastern Sicilian Coast (Fig. 1). The Sicilian continental shelf is very narrow and the slope very steep. The Gulf has a shelf break at ~100 m depth and a width of ~4 km off the Capes and ~8 km in the center. It has two notable bathymetric irregularities: a ridge off of Cape Syracuse and an escarpment at the depth range of 25–50 m, both of which have a significant impact on the circulation Raffa and Hopkins (2004). The natural harbor opens to the southeast, but has been enclosed by rock jetties, except for two dredged channels.

In oligotrophic, temperate seas, the vertical distribution of phytoplankton biomass is typically characterized by a prominent deep-chlorophyll maximum (DCM; cf. Hobson and Lorenzen, 1972; Cullen, 1982; Fasham *et al.*, 1985; Varela *et al.*, 1992; Estrada *et al.*, 1993; Li, 1994; Yacobi *et al.*, 1995). Its depth is associated with the seasonal pycnocline (cf. Cullen, 1982; Estrada, 1985), where a balance is achieved between the phytoplankton growth, due to the availability of light and nutrients (cf. Kiefer and Kremer, 1981; Gieskes and Kraay, 1986; Krom *et al.*, 1991; Raimbault *et al.*, 1993; Herut *et al.*, 2000), and loss, due to grazing and dispersion (cf. Mountin and Raimbault, 2002). The supply of nutrients is generally controlled by a diffusive flux from below, which is controlled by the nutrient

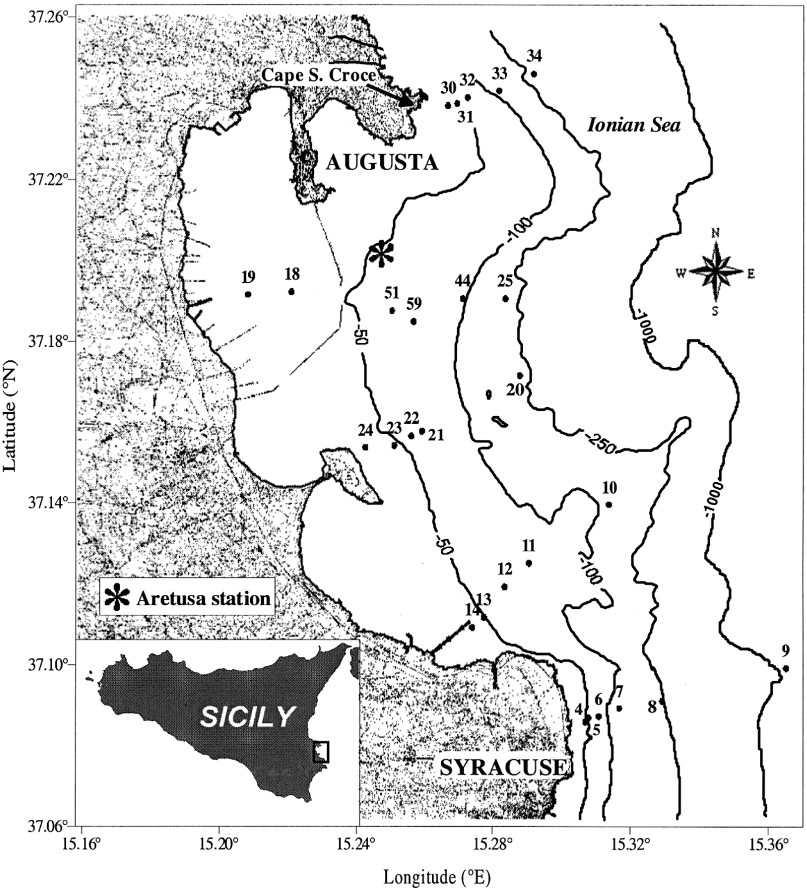

FIGURE 1 Station locations in the Gulf of Augusta (*Aretusa station time series).

gradient and strength of the pycnocline. Reductions in new-nutrient fluxes from below are mitigated by the regeneration of nutrients by the *in situ* microbial community (cf. Azam *et al.*, 1983). In the coastal environment, two other possible sources of nutrients are onshore advection and regeneration by the benthic community. The importance of these latter two sources has not been investigated in detail within the environment of the eastern coast of Sicily.

The oceanography of the eastern Sicilian shelf has not been extensively studied, but historically it has been known anecdotally for its relatively rich biological production (Magazzù, 1980), and this richness is known to be related to the vertical mixing in the Strait of Messina. The existence of this mixed water mass has been noted scientifically for some time (cf. Grancini and Magazzù, 1973; Hopkins *et al.*, 1984; Adragna and Salusti, 1990), and its presence in the form of a southward current along the coast of Sicily has been reported in satellite thermal imagery by Böhm *et al.* (1987).

2 MATERIAL AND METHODS

This work is based on data taken during 7–11 October on the R/V *Thetis.* In the first two days, a preliminary hydrographic survey was conducted using a SeaBird Electronics SBE-911 + CTOD/Rosette profiler down-casts equipped with a Turner Scufa fluorometer (for Chl*a*). The array of stations consisted of five transects with several intervening stations (Fig. 1). Based on an onboard assessment, one of these stations was selected for a 48 h experiment, referred to as 'Aretusa'. The location required that the Aretusa St. be close to the Port for the purpose of transporting samples to the laboratory in the town of Augusta and that it would be at depth where the lower limit of the DCM would intersect the bottom. The sampling interval (<4 h) allowed time for additional CTD casts at stations centered around Aretusa for later analysis of parameter gradients and their advective fluxes (Raffa and Hopkins, 2004). With these constraints, we were able to conduct 14 casts at Aretusa within the 48 h. Water samples were collected at five depths from each station, above, within and below the DCM. For the purpose of this paper, the DCM layer has been calculated as the depth range in which the concentration of the chlorophyll *a* remained >40% of its maximum value.

The CTD salinities and oxygens were controlled by comparisons with water samples analyzed by an AUTOSAL salinometer and by Winkler methods, respectively. The conversion from CTD fluorescence (Chl*a*-Fl) to chlorophyll *a* was done through statistical comparisons with the Chl*a* water samples analyzed in the laboratory using a spectrofluorometric method as reported above. Samples for nutrient analyses were immediately frozen (−20 °C) and subsequently analyzed in the Institute's laboratory for nitrate + nitrite, orthophosphate (Strickland and Parsons, 1973), and ammonium (Aminot and Chaussepied, 1983) using US/Vis spectrophotometer (Varian, mod. cary 50). A more complete description of the methods and sampling can be found in Decembrini (2003), while the methods specific to this work are given below.

Water samples for the size-fractionated pigment analysis (0.8–1.0 l) were sequentially filtered through Nuclepore polycarbonate filters, of 10.0 μm and 2.0 μm porosity, and with Whatman GF/F glass-fiber filters. After filtration, filters were immediately stored at −20 °C. Photosynthetic pigments were extracted in 90% acetone and read before and after acidification. Determinations were carried out with a Varian mod. Eclipse spectrofluorometer. The maximum excitation and emission (431 nm and 667 nm, respectively) were selected on a prescan with a solution of chlorophyll *a* from *Anacystis nidulans* (by Sigma Co.). The concentrations of Chl*a* and phaeopigments (FEO) were calculated according to Lorenzen (1967).

Photosynthetically active radiation (PAR) from 400 to 700 nm was measured with a Biospherical PNF-300 profiler equipped with a spherical scalar sensor. The euphotic depth was defined as the depth of 1% surface light penetration (Z 1% E_0).

For water-column comparisons of Chl*a* and nutrients, vertical integrations from 0 to 75 m were calculated using the trapezoid rule of (Chl*a*-Fl) and nutrient values (at rosette depths).

3 RESULTS

3.1 Vertical Structure

The surface layer of the Gulf was occupied by the Ionian Surface Water (ISW) with a summer-water-type high temperature and salinity (25.0 °C, 38.7 ppt) due to seasonal exposure to heating and evaporation processes. The Messina Mixed Water (MMW) mass is sandwiched between the ISW and the remnants of the local winter water mass, Ionian Intermediate Water (IIW). As described by Raffa and Hopkins (2004), the MMW occupied the pycnocline through the ~20–60 m depth range with a thermo-haline water type of 18–20 °C, 38.4–38.5 ppt. This structure is anomalous relative to similar depths in the open Ionian, i.e. the MMW is cooler and less saline than waters at similar depths offshore. The mixing that generates the MMW combines a source of lower-salinity water from the Tyrrhenian Surface Water (TSW) and a source of higher nutrients from the IIW. Consequently, the coastal waters influenced by the MMW are richer in nutrients than waters offshore of the same depth.

Over the shelf, our observations revealed relative vertical maxima within the MMW for both nutrient (3.1 μM NO_3) and chlorophyll *a* concentrations (0.63 $\mu g\,l^{-1}$). The surface waters above the MMW contained lower nutrient and Chl*a* concentrations (<0.7 μM NO_3; <0.2 μM PO_4; <0.2 μg Chl*a* l^{-1}). The waters underneath the MMW on the shelf (55–75 m) also contained fewer nutrients and Chl*a* (<1.0 μM NO_3; <0.2 μM PO_4; <0.3–0.2 μg Chl*a* l^{-1}). For this analysis, the MMW mass is defined by the depth range where the salinities are less than 38.5 ppt, the DCM yet defined, and the pycnocline by the range ~27.2–28.2 sigma-t units.

Representative vertical profiles of Aretusa St. (11.25 h, first sampling) are shown in Figure 2, where the nitrate concentration is 0.51 μM in the surface layer, reaching a maximum 1.9 μM in the pycnocline, and decreasing near the bottom to <1.0 μM. The other nutrients showed similar variations with respect to nitrate. The orthophosphate at the same station had a low concentration (0.22 μM) in the surface and decreased further at the fluorescence maximum to ~0.1 μM. The ammonium generally varied around the values of 0.3 μM in the surface and doubled below the Chl*a* maximum (0.6 μM). The vertical distribution of Chl*a*-Fl was clearly associated with the upper pycnocline and exhibited a bimodal structure in the DCM, separated at about 43 m.

The percentage of the active Chl*a* with respect to its degraded pigments (FEO) had a maximum of 60% at the same depth of the Chl*a* maximum and thereafter decreased with depth to 47% downward.

The (underwater) PAR profile ranged between 1600 and 0.05 $\mu E\,m^{-2}\,s^{-1}$ in the euphotic zone, whereas to 50 $\mu E\,m^{-2}\,s^{-1}$ at the Chl*a* maximum at 40 m and corresponding to 2% of the surface PAR. For example, at the Aretusa St. (11.25 h), the DCM layer extended between the irradiance extinction of 5% and that of 1% at corresponding PAR values of 120 and 12 $\mu E\,m^{-2}\,s^{-1}$.

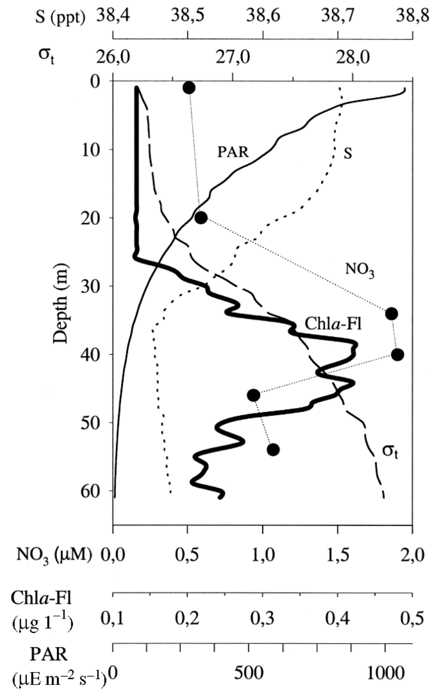

FIGURE 2 Aretusa station first sampling (11.25 h): vertical profile of salinity (S, ppt), density (σ_t), chlorophyll *a* fluorescence (Chl*a*-Fl, $\mu g\, l^{-1}$), nitrate concentrations (NO_3, μM) and photosynthetically active radiation (PAR, $\mu E\, m^{-2}\, s^{-1}$).

3.2 Horizontal Structure

Phytoplankton biomass, expressed as Chl*a*, showed a mean concentration of $0.34 \pm 0.17\ \mu g\, l^{-1}$ ($n = 54$) over the sampling area (27 stations on five transects). The depth of Chl*a* maximum ranged between 25 and 55 m. Phosphorus and nitrogen concentrations ($n = 91$) showed mean values of 0.22 ± 0.17 μM PO_4, 0.49 ± 1.0 μM NH_4, and 0.61 ± 0.80 μM NO_3, respectively. These high standard deviations relative to the mean value are indicative of horizontal patchiness.

A comparison of the vertically integrated Chl*a* values for the entire euphotic layer (EL) and for only the DCM layer is shown in Figure 3. The euphotic layer had a mean value of 14.4 ± 6.8 mg Chl*a* m^{-2}, a maximum of 24.3 mg Chl*a* m^{-2}, and a minimum of 2.3 mg Chl*a* m^{-2}. Generally, the highest values of phytoplanktonic biomass were located near the shelf break with values decreasing shoreward, with a mean over the shelf of 6.9 mg Chl*a* m^{-2} and a mean offshelf of 16.3 mg Chl*a* m^{-2}. Higher values were also observed (>20 mg Chl*a* m^{-2}) in the transect south of Syracuse, where a fresher, surface water mass was present. Overall, the integrated values from the DCM layer represented ~70% of values from the euphotic layer, except for the stations close to the shelf break where the percentage exceeded 90%.

The horizontal distribution of nutrients integrated through the eutrophic layer had mean concentrations of $25.5 \pm 17.6\ \mu M\, m^{-2}$ for nitrate, $10.1 \pm 5.7\ \mu M\, m^{-2}$ for orthophosphate, and $20.8 \pm 24.4\ \mu M\, m^{-2}$ for ammonium ($n = 91$). Only the distribution of nitrate was similar to that described for Chl*a*; it had higher values near the shelf break and in the southern portion. The other nutrients had a less consistent distribution pattern with some indication of lower values in the southern section.

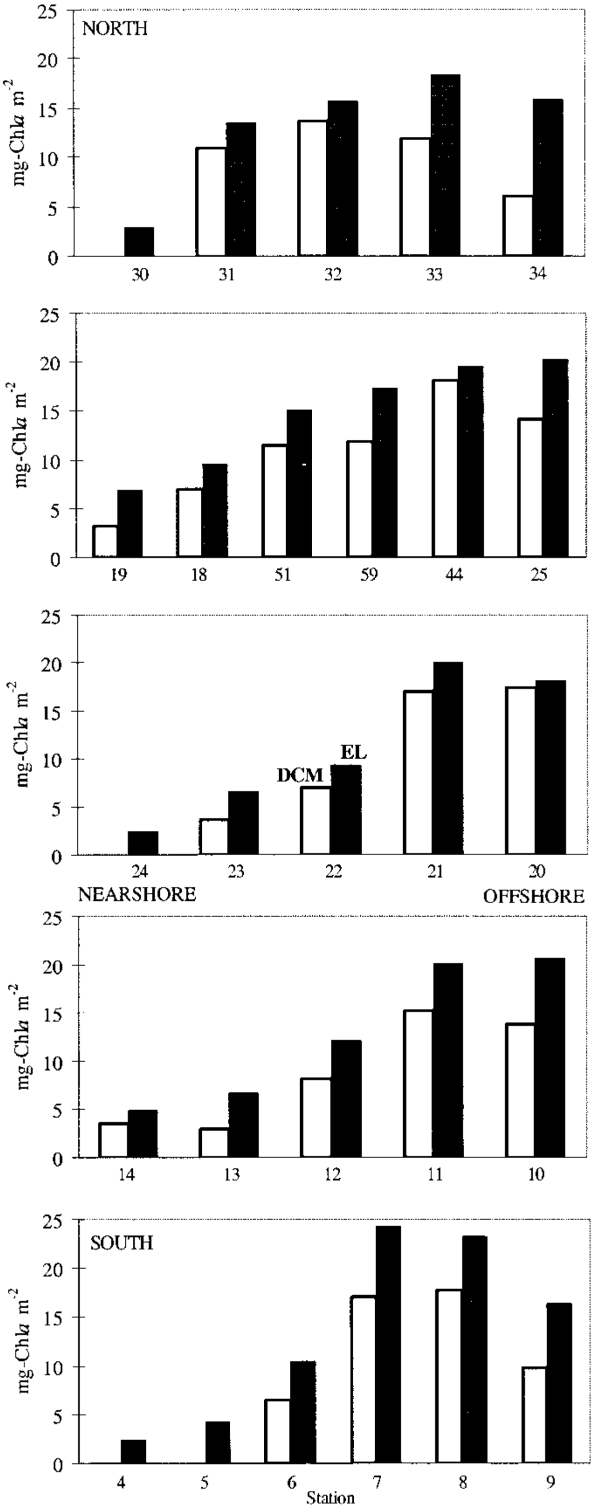

FIGURE 3 Horizontal distribution of the vertical integrated chlorophyll *a* (Chl*a*-Fl, mg m^{-2}) in the DCM layer and in the euphotic layer (EL) along the five transects in the Augusta Gulf.

3.3 Temporal Variability

The vertical structure of the fluorescence at the Aretusa St. varied considerably over the 48 h period (Fig. 4) with changes in the vertical Chl*a* maximum from 0.37 to 0.53 $\mu g\, l^{-1}$ and changes in the depth of the pycnocline from 20 to 44 m.

In order to refer to the dominant variability in Chl*a*, we have divided the series into approximately equal quadrants of 12 h, as shown in Figure 4, in which the first quadrant includes the series maximum, the second includes the series minimum, the third exhibits a secondary maximum, and the final quadrant displays a more steady distribution.

As expected, the higher Chl*a* values were found at shallower depths, but they were also correlated with thicker pycnolcine conditions. The thickness of the DCM layer, as defined above, varied between 14 m (9.30 h, second day) and 33 m (22.35 h, first day).

The temporal variability of the integrated phytoplankton biomass was only weakly correlated with the diurnal variation in light. Figure 5a shows the time series of integrated Chl*a* values of euphotic and DCM layers. The integrated Chl*a* showed an increase from 13.5 and 19.8 mg m^{-2} during the first quadrant. During the second quadrant, the Chl*a* values decreased to a minimum of 14.0 mg m^{-2} at 09.30 h on the second day. A smaller vertical maximum occurred at 14.00 h on the second day resulting in a second maximum in the integrated values at 17.00 h (15.8 mg Chl*a* m^{-2}). During the remainder of the third quadrant, the previous maximum decreased, but the DCM layer thickened, resulting in a gradual increase in the integrated values to 17.5 mg Chl*a* m^{-2} through the fourth quadrant to the end of the series at 9.00 h on the third day. The DCM contribution to entire euphotic layer varied from 69% to 89%, with the smaller contributions associated with sharp narrow chlorophyll *a* maxima and the larger with broad (or multiple) peaks in the Chl*a*.

The corresponding values of the integrated-nutrient concentrations (Fig. 5b) exhibit a greater amplitude in variability and a higher frequency of change (hours) than the slower, smoother variability of the integrated Chl*a* values. The series mean values for the nutrients were 5.7 ± 2.8 $\mu M\, m^{-2}$ for orthophosphate, 28.2 ± 15.0 $\mu M\, m^{-2}$ for nitrate, and 10.6 ± 7.4 $\mu M\, m^{-2}$ for ammonium. During the first quadrant, the nitrate values reached peaks ($\sim$57 $\mu M\, m^{-2}$), nearly double those of the remainder of the series ($<$30 $\mu M\, m^{-2}$). A somewhat similar pattern was evident for the other nutrients, with both having a maximum concentration in the first quadrant but with decreasing concentrations during the second quadrant of 21.9 $\mu M\, m^{-2}$ for ammonium and 10.1 $\mu M\, m^{-2}$ for orthophosphate.

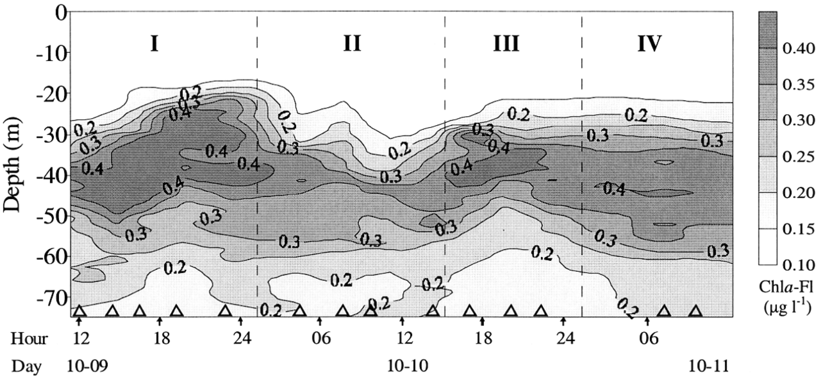

FIGURE 4 Aretusa station time series: chlorophyll *a* vertical distribution (Chl*a*-Fl, $\mu g\, l^{-1}$).

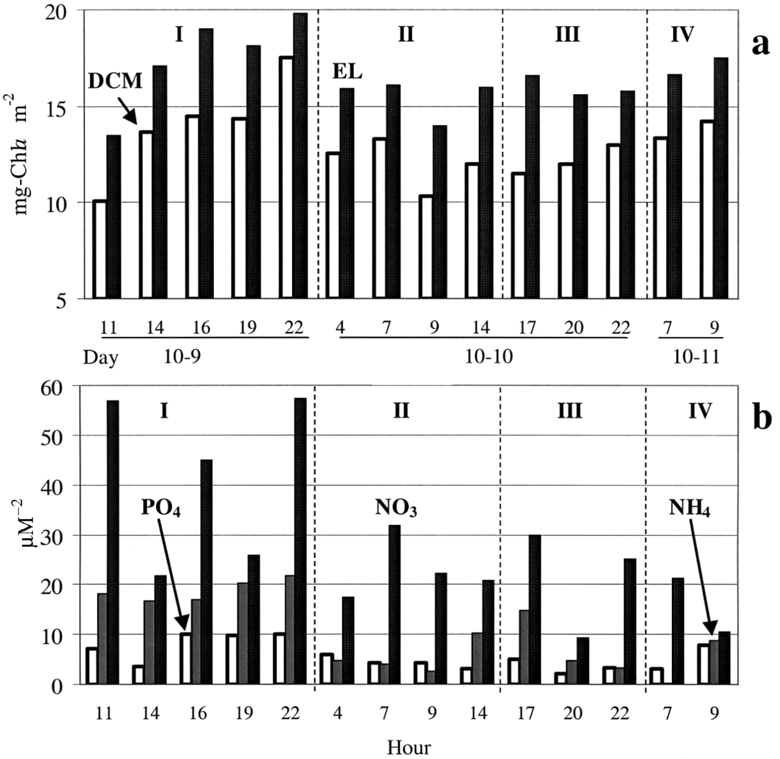

FIGURE 5 Aretusa station time series: (a) integrated chlorophyll *a* (Chl*a*-Fl, mg m^{-2}) in the DCM and in the euphotic layer (EL); (b) integrated N and P nutrients (μM m^{-2}) in the DCM layer.

The impact of the DCM primary production can be clearly seen by the oxygen saturation levels (Fig. 6a) with a vertical maximum (>108%) being sustained during the entire period. However, during the daylight hours, the maxima exceeded 110%. Generally, the oxygen maximum during the first quadrant was coincident with that of the Chl*a*, whereas during the third quadrant, the oxygen maximum occurred above that of the maximum of the Chl*a*, presumably due to the different planktonic structure.

Changes in the size-fractionated phytoplankton were associated differently with changes in the nutrient environment. This was evident by the different size contributions to the total biomass occurring between the first quadrant and the rest of the series (Fig. 7). During the first quadrant, the micro-phytoplankton fraction (>10 μm, Fig. 7a) dominated and consisted mainly of diatoms (Zaccone *et al.*, 2004). In contrast, the picoplankton fraction (<2 μm, Fig. 7b) was more abundant during the remainder of the series. The pico-fraction biomass and its cell density correlated well with the direct count of pico-cell density ($r = 0.41$, $P < 0.01$, $n = 57$). The nanophytoplankton fraction (<10 and >2 μm) comprised phytoflagellates and remained fairly constant over the time series. In sum, the micro-fraction represented approximately half and the pico-fraction about a third of the Chl*a* concentration during the first quadrant when both nutrient concentrations and biomass values were shallower in the water column, and vice versa during the other three quadrants. The nano-fraction remained about a fourth to a third of the total biomass.

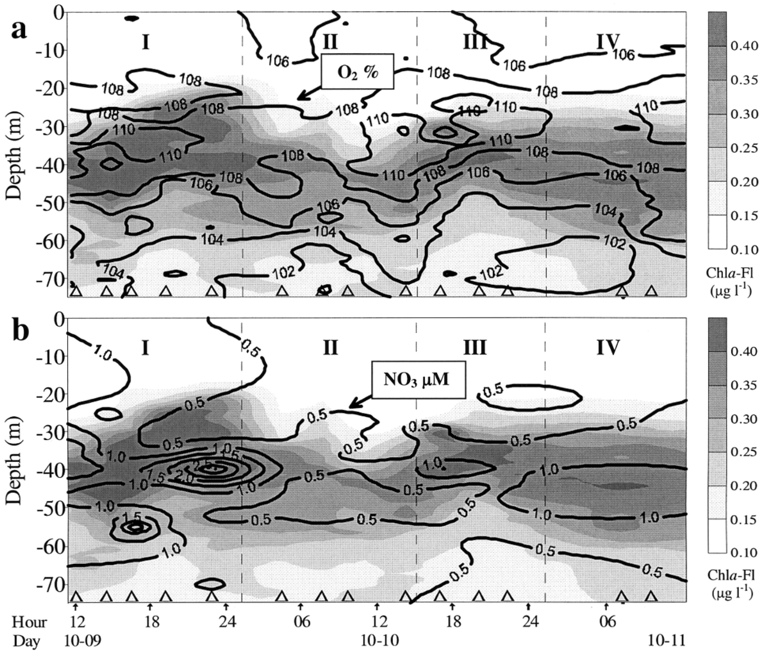

FIGURE 6 Aretusa station time series: vertical chlorophyll *a* distribution (Chl*a*-Fl, μg l^{-1}, background); contour lines of (a) oxygen saturation (O_2 %) and (b) nitrate concentration (μM).

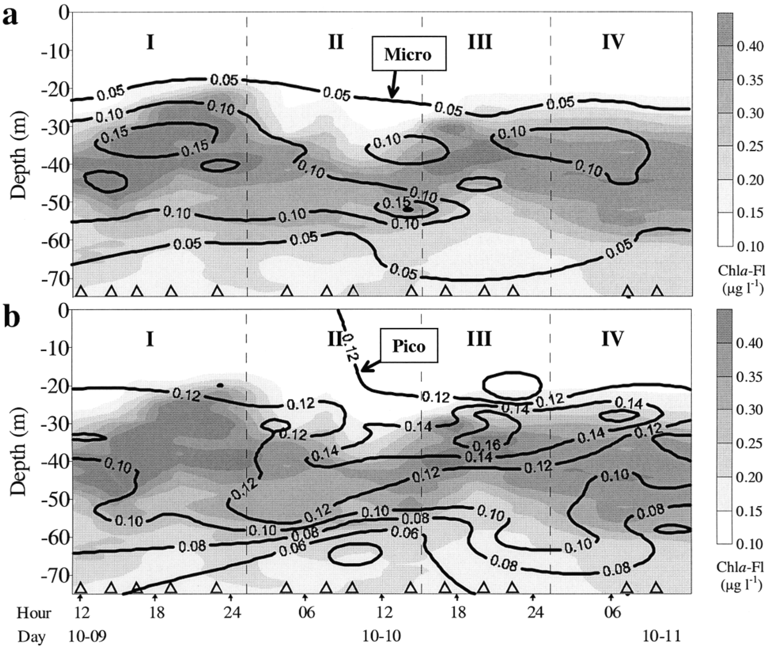

FIGURE 7 Aretusa station time series: total chlorophyll *a* (Chl*a*-Fl, μg l^{-1}, background); contour lines of (a) micro-phytoplanktonic Chl*a* (>10 μm) and (b) pico-phytoplanktonic Chl*a* (<2.0 μm).

4 DISCUSSION

With this fairly limited data set, we would like to focus on possible relationships between the most obvious changes in the DCM relative to other characteristics, e.g., in its thickness, intensity, nutrient content, and biological composition. The main observed characteristics are listed in Table I and are discussed in the subsequent sections.

4.1 Nutrients

The observed nutrient variability does not suggest a steady source. If so, the nutrients and Chl*a* would tend to be inversely correlated. The overlay of Chl*a* and nitrate (Fig. 6b) suggests more of a positive correlation between the two parameters, suggesting that the biomass growth was forced by an increased supply of nutrients. Also, in Figure 5, the first quadrant series maximum in integrated Chl*a* was associated with an integrated nitrate maximum and the subsequent Chl*a* minimum in the second quadrant ($10.3\ \mathrm{mg\ m^{-2}}$) with lower values of nitrate. Temporal distributions of ammonia and orthophosphate showed similar but weaker correlations with Chl*a*.

Chl*a*–nitrate correlations conducted on a per-sample basis did not reveal the above relationships ($r = -0.16$, $n = 57$), because the parameter peaks occurred at different depths. During the first quadrant, the Chl*a* maximum was more closely correlated in depth with the orthophosphate maximum than with the nitrate maximum, which was situated several meters underneath the Chl*a* maximum. During the second quadrant, the same pattern was repeated but with less dislocation in the vertical. In all cases, the ammonia peaks were located at depths between those of orthophosphate and nitrate. A possible reason for these vertical distributions could be that the increased regeneration rates of orthophosphate and ammonia relative to nitrate on slowly sinking particulate matter would have resulted in a displacement of the respective peaks in the vertical. We note that the per-sample Chl*a*–orthophosphate correlations were significantly higher ($r = 0.28$, $P < 0.005$, $n = 29$) than those for nitrate. These displaced accumulations of phosphate and nitrate, with respect to each other and to Chl*a*, may suggest some *in situ* nitrogen limitation, which is also confirmed by the lower N/P ratios (mean value of 8.3 for all Aretusa bottle samples). This value is significantly lower than that from Redfield's ratio (16) and lower with respect to the mean value of deep Mediterranean waters (20–25). However, the literature reports a broad range for this ratio (2–25) in the upper 100 m in the Eastern Mediterranean Sea (Krom *et al.*, 1991; Herut *et al.*, 2000) and a more variable range (1–60) in surface waters of Western Mediterranean (Marty *et al.*, 2002). However, our data at depths >200 m off the Gulf of Augusta give an N/P ratio of ~ 20, too.

4.2 Nutrient Sources

Our results provide no evidence that nutrient enrichment from terrestrial sources were stimulating phytoplankton growth in the Gulf of Augusta that might have provided subsurface enrichment through regeneration at the pycnocline. The possibility of nutrient enrichment due to an interaction between the DCM layer and the benthos was excluded due to the observed lifeless state of the local benthos (Budillon, 2003). In addition, the possibility of a diffusive flux of nutrients from waters underneath the DCM is counterindicated by the observed negative gradient (decreasing nitrate under the DCM).

A more plausible nutrient source is an advective supply of new nutrients from the MMW flowing southward along the shelf break, as explained by Raffa and Hopkins (2004). In fact,

TABLE I Characteristics of the DCM within the four quadrants (time lag, depth, Chl*a* concentration, Chl*a* size fraction, phytoplankton main groups, N and P nutrient concentration, pycnocline thickness, current velocity and direction, depth of the 1% light level = Z 1% E_0) at Aretusa station (peak values).

Quadrants	*Time lag (local time)*	*DCM (m)*	*Chla ($\mu g\ s^{-1}$)*	*Size-fraction (phyto-groups)*	*NO_3*	*NH_4 (μM)*	*PO_4*	*Pycnocline thickness (m)*	*Current velocity peak and direction*	*Z 1% E_0 (m)*
I	11.00 01.00	42.0	0.528	Micro (diatoms)	0.90	0.40	0.34	16.0	10 cm s^{-1} N → S	48.0
II	01.00 15.00	44.0	0.373	Micro–pico	0.42	0.12	0.19	20.0	11 cm s^{-1} S → N	50.0
III	15.00 01.00	40.0	0.494	Nano (phytoflagellates)	1.57	0.45	0.33	15.0	08 cm s^{-1} N → S	46.0
IV	01.00 11.00	42.0	0.399	Pico	0.23	0.07	0.26	10.0	15 cm s^{-1} S → N	47.0

our observations indicated that the MMW was ubiquitous over the shelf, which coincided with both the pycnocline and DCM, but with slightly water properties with the respect to the water in the core of the current. Raffa and Hopkins (2004) explain that the pool of MMW over the shelf is maintained, against mixing loss, by onshore intrusions of the MMW from its core oriented over the shelf break. Consequently, the supply of 'new' nutrients at any location on the shelf was subject to the physical processes governing mesoscale circulations and the biological history of the arriving water parcel. Thus, the shelf acts as a sink for the MMW, as it passes southward along the upper slope, where onshore intrusions result in changes in its water properties due to mixing and biological uptake.

Our observations were not sufficient to completely describe the regeneration processes that help to sustain the production in the DCM. However, Zaccone *et al.* (2004) have reported on the phosphatase esoenzymatic activity (AP) by the microplankton community, which showed significant variability in the DCM layer. This variability appeared to be less directly associated with the diel cycle than with the changing biological community. During the first quadrant, an AP maximum was observed coincident with the Chl*a* maximum that was also colocated with the orthophosphate maximum and which was located above that of the nitrate maximum (Fig. 6b). This contrasts with the poor coherence between these distributions observed during the remainder of the series. For example, an orthophosphate maximum was colocated with the Chl*a* maximum of the third quadrant and with a minimum of AP. In addition, an AP maximum occurred, in the fourth quadrant (~12 h later) after the orthophosphate maximum of the third quadrant. These differences may be partially explained by the different planktonic community assemblages together with advective changes. It is possible that during the first quadrant, strong bacterial recycling of orthophosphate was occurring, in direct association with diatom assemblage (cf. Azam *et al.*, 1994). For the remaining three quadrants, when the phytoplankton was dominated by picoplankton, the regeneration of orthophosphate was more a function of particulate organic carbon (POC) than of Chl*a*.

4.3 Phytoplankton Variability

One might assume that the Chl*a* events are mostly driven by light and that the maxima are the result of an accumulative net growth in biomass during the day with significant decreases during the dark periods. However, this interpretation is counterindicated by the absolute minimum of biomass during the second quadrant and the continuation of the second biomass peak during the night and into the next morning, during the third quadrant. The discontinuity in the population composition between the two maxima also argues strongly for factors, other than light, controlling the biomass. In addition, the decrease in nutrient values (Fig. 6b), particularly ammonia, during early morning on the first quadrant indicates a change, for example, in the pycnoclinal water mass rather than the effect of dark respiration on the same population. The lack of a strong response to light is a possible explanation for growth rates slower than the diel cycle. Arin *et al.* (2002) have reported growth rates of 1.5 d in the Alboran Sea, at higher Chl*a* concentrations, that exhibited <25% increase in biomass during the daylight hours. Hence, we conclude that the light–dark cycle was not the primary cause of the observed variability in our data.

4.4 Autotrophic Balance

According to Zaccone *et al.* (2004), the living carbon accounted for ~50% of the POC, of which about 20% was phytoplankton biomass. They found a negative correlation between the Chl*a* and the microplanktonic respiration rate, implying dominance in the autotrophic processes. As can be seen in Figure 6a, the supersaturated oxygen generated during the photosynthetic period is only partially reduced during the dark, respiration period. In fact, the magnitude of the dark–light change in oxygen in the upper portion of the DCM is less than that in the vertical between its upper and lower portions. This suggests that the upper portion of DCM remains autotrophic, whereas the lower portion is approximately balanced towards heterotrophy. Diatoms are normally strongly associated with a more productive DCM (Estrada and Salat, 1989), whereas the abundance of picophytoplankton is generally associated with a less productive DCM. One might expect then to observe a greater oxygen production during the first quadrant than in the remainder of the series. Instead, the daylight values of oxygen maximum are similar. This may be because the POC values were approximately twice as high during the first quadrant (~100 units) as those during the remainder of the series (Zaccone *et al.*, 2004). This suggests that both the photosynthetic and respiration rates were correspondingly higher during the first quadrant of the series. Consequently, changes in the strength of the DCM are strongly associated with changes in the phytoplankton community producing it, as noted by Magazzù and Decembrini (1995). Finally, the competition for nutrients between phytoplankton and heterotrophic bacteria appears to have favored the former, given that high levels of Chl*a* correspond with low levels of bacteria (cf. Sala *et al.*, 2002).

4.5 Pycnocline

The height and thickness of the pycnocline also influenced the DCM (Tab. I) which was contained within the isopycnals of 27.2–28.2 sigma-t units (Fig. 8). The 27.2-value had a mean depth of ~31 m and varied from 21 to 28 m during the two Chl*a* maxima and reached 35 m at the intervening minimum. The pycnocline depth (upper boundary) is potentially an indicator of greater exposure to light and thereby potentially of photosynthetic activity. However, as noted above, the maxima occurred at night and the minimum during the day. While light was obviously a factor in production, its manifestation in an increased accumulation of biomass would have been effected only if the mechanism, which causes the vertical movement, were synchronized with the light cycle. For example, the minimum Chl*a*, which occurred during daylight, might have created an even stronger minimum had it occurred during night-time. Furthermore, for cases in which the growth rate is slower than diurnal and/or slower than changes in light, any direct correlation will be minimized. Since the height of the pycnocline is directly related to the thickness of the pycnocline, we suggest

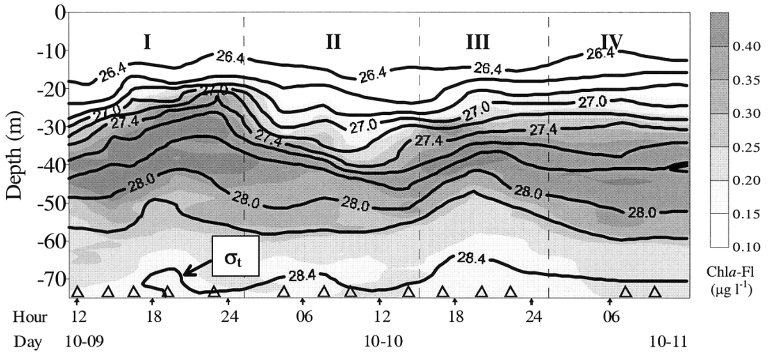

FIGURE 8 Aretusa station time series: vertical chlorophyll *a* distribution (Chl*a*-Fl, $\mu g\, l^{-1}$, background) and contour lines of water density (σ_t).

that the latter is a better indicator of changes in biomass, as also noted by Olaizola *et al.* (1993).

The thickness of the pycnocline decreased from 20 to ~10 m, between the first Chl*a* maximum and the minimum that followed (Tab. I). Likewise the amount of nutrients between these two conditions varied by roughly the same ratio, or ~50%. Raffa and Hopkins (2004) give a plausible explanation, in which the primary mechanism for increasing or decreasing the volume between two isopycnals is an advective convergence or divergence occurring between the defining isobars. A direct consequence of the pycnocline varying in the horizontal, at scales lower than that of the shelf width, is the creation of strong shears and even significant velocity peaks within the pycnocline (ibid.). These shears enhance mixing within the pycnocline and result in very different trajectories for passive particles. In essence, they belie the sense of vertical coherence in the data acquired by vertically sampling through the DCM/pycnocline.

4.6 Comparison with Offshore

The reported study was conducted on the scale of the Augusta continental shelf, and consequently we cannot report definitively on the uniqueness of our interpretation on the scale of the Sicilian coast or on the scale of the Ionian basin. However, to provide some comparison in the deep Ionian, we looked at some historical data taken ~100 km off Augusta during the late summer, as reported by Rabitti *et al.* (1994) and Leonardi (pers. comm.). With respect to our observations, these data demonstrate a deeper DCM located at ~75 m depth and a smaller biomass with levels of Chl*a* not greater than 0.15 μg m^{-3}. The orthophosphate concentrations (0.05 μM) were lower than those that we observed in the Gulf of Augusta. The physiology of the DCM plankton community offshore was characterized by degraded pigments (FEO), indicating a senescence phase of the phytoplankton cycle. In this phytoplankton community, the nanophytoplankton species prevailed (57%), dinoflagellates and coccolitophoride were present in decreasing percentage (25% and 14%, respectively), and the diatoms were the lowest group (5%). Also, there was no evidence of the MMW as a salinity minimum (<38.5 ppt) in the upper water column or of elevated nutrients greater than > 0.3 μM of NO_3 in the euphotic zone. Also, the percentage of degraded pigments relative to Chl*a* was much lower in our observations than in those of Rabitti *et al.* (1994), further indicating that the coastal community is considerably more active than that offshore, despite the fact that our observations were taken later in the season.

5 CONCLUSIONS

A preliminary study of the temporal behavior of the DCM, at its intersection with the bathymetry of the nearshore for the case of the Sicilian continental shelf off Augusta in October, revealed some interesting aspects both particular to the location and perhaps in general to the DCM processes. Particular to Augusta was the absence of any terrestrial influence, which might have enriched or impacted the surface layer, and the absence of a benthic community (Budillon *et al.*, 2003), which might have provided a different source of recycled nutrients than that provided to deeper localities.

Particular to the region is the indication that most of the eastern Sicilian shelf is provided with an intermittent source of nutrients from the enriched water mass (MMW), which is advected southward along the shelf break. The MMW is characterized by a less saline and cooler water type and by higher nutrient concentrations. Because of its cooler waters and greater nutrients, the MMW defines both the pycnocline and the DCM over the shelf. As a result of the intermittency of the physical processes drawing the MMW onto the shelf, a reservoir of MMW is maintained within the pycnoclinal layer. However, because the nutrient signature is lost much more quickly through bio-uptake than is that of the salinity minimum by mixing, the spatial distribution of nutrients within the pycnocline is quite patchy. When this distribution is moved around over the shelf by a spatially complicated and reactive circulation, it generates a large variability at any location in the temporal response of the autotrophic communities inhabiting the DCM.

The interpretation of a 48 h time series has forced us to reconsider the simplistic picture of the DCM: that is, as a single community, residing in a low-energy environment of a the pycnocline, and in a vertical balance between the availability of light from above and nutrients (new and recycled) from below. In our case, changes in the availability of nutrients and the phytoplankton composition were dominated by advection within the pycnocline. In a sense, the expected succession from a new-nutrient community to a regenerated-nutrient community undoubtedly still existed but was moved around in space. Although the eastern coast of Sicily is a rather unique case, the same dynamic might occur in frontal or other situations in which nutrients are brought into a euphotic area through isopycnal upwelling, and that process itself had some variability in the horizontal plane. Another important complication that we observed is that a strong pycnocline within the shallow waters of the shelf will be exposed to horizontal variability of its isobars, a condition that leads to strong shears and often secondary velocity peaks within the pycnocline/DCM environment. On one hand, these shears tend to isolate previously vertically coherent communities; on the other hand, they may create a useful mechanism for greater spatial dispersion of nutrients regenerated in the respiration underside of the DCM.

During the time series, the distributions of nitrogen and orthophosphate were not coincident in the vertical, presumably as a result of their differing recycling rates. Furthermore, the distribution of nitrate appeared to be linked more strongly to physical processes (advection and sedimentation) and that of the orthophosphate to be more dependent on the biological processes of regeneration. In the former case, new nitrate was made available by resupply of MMW in the pycnoclinal layer and was lost through uptake and sedimentation underlying aphotic layers. In the latter case, the correlation between AP and Chl*a* depended greatly on the planktonic community composition, e.g., strong for the case of the diatom dominance and weak for the case of picoplankton. However, both communities produced approximately the same level of AP. This situation suggests that the community structure adapts fairly efficiently to its nutrient environment. With a pulse of new nutrients (high N/P ratio), the larger diatom fraction prevails, resulting in nitrogen loss through sinking and a vigorous level of orthophosphate recycling (thus reducing the original N/P ratio). As the community ages and becomes smaller, the nitrogen loss decreases, and the orthophosphate recycling shifts to other components with the result that the N/P ratio decreases further.

Even though these conclusions and inferences were based on a data set that was limited in time, space, and variables, we feel that it was sufficient to raise some rather important questions concerning the dynamics of the DCM. For example: How does this unique mechanism of coastal eutrophication vary seasonally? What is the integrated impact on the production of the eastern Sicilian coast? How representative is a single observation of the DCM with respect to other stations in space or in time? This suggests that a broader knowledge of the temporal and horizontal variability of the DCM and of its controlling internal processes must be acquired before attempting to construct models of the DCM. A further implication needing investigation is the possibility that the intermittent nutrient enrichment of the DCM can support both pelagic and microbial carbon pathways.

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