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ORIGINAL RESEARCH ARTICLE

Spatio-temporal variability of the size-fractionated primary production and chlorophyll in the Levantine Basin (northeastern Mediterranean)

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Spatial and temporal variations in size-fractionated primary production (PP) and chl Summary a, in relation to ambient physicochemical parameters, were studied in the three distinct ecosystems of northeastern Levantine Basin namely eutrophic Mersin Bay, mesotrophic Rhodes Gyre, and oligotrophic offshore waters. These ecosystems were visited in July and September 2012 and March and May 2013. Total primary production (TPP) rates ranged between 0.22 and 17.8 mg C m⁻³ h⁻¹ within the euphotic zone, whereas depth-integrated TPP rates were in the range $21.5-348.8 \text{ mg Cm}^{-2} \text{ h}^{-1}$ (mean: $105.5 \pm 88 \text{ mg Cm}^{-2} \text{ h}^{-1}$), with the lowest rates recorded for offshore waters. Similar spatio-temporal variations were observed in chl a concentrations, ranging from 2.3 to 117.9 mg m $^{-2}$ (mean: 28.9 \pm 24.9 mg m $^{-2})$ in the study area. The Mersin Bay TPP rates have exceeded almost 8-12 times those measured in the offshore waters and the Rhodes Gyre; however, the chl a concentrations measured in coastal waters (0.343 mg m⁻³) and the Rhodes Gyre (0.308 mg m^{-3}) were only threefold larger than the offshore values. PP and chl a were dominated by picoplankton in the study area whereas small nanoplankton, being the most active, displayed the highest assimilation ratio in offshore waters (6.8) and the Rhodes Gyre (2.8). In the upper-layer waters depleted of P (0.02–0.03 μ M) of the northeastern Mediterranean, a positive correlation was observed between $NO_3 + NO_2$ and PP (and thus, chl a), which strongly suggests that reactive P and inorganic nitrogen are co-limiting factors in the production and biomass distribution of the phytoplankton community in both shelf and offshore waters. © 2018 Institute of Oceanology of the Polish Academy of Sciences. Production and hosting by Elsevier Sp. z o.o. This is an open access article under the CC BY-NC-ND license (http:// creativecommons.org/licenses/by-nc-nd/4.0/).

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1. Introduction

The eastern Mediterranean Sea is one of the world's least productive regions, with low nutrient and chlorophyll concentration (Ediger and Yilmaz, 1996; Krom et al., 1991; Psarra et al., 2005; Yucel, 2013). In general, primary production (PP) rate and chlorophyll concentration tends to decrease from west to east and north to south in the Mediterranean (Siokou-Frangou et al., 2010). Increasing oligotrophy toward the east can mainly be attributed to increasing phosphorus limitation (N/P ratio increase from 20 to 29) in the northeastern Levantine waters due to limited inputs of nutrients from external sources and the fact that its deep waters have high N/P (25–26) ratios (Krom et al., 1991, 2010; Thingstad et al., 2005; Yılmaz and Tugrul, 1998; Yucel, 2013). Atmospheric depositions supply a considerable amount of nutrients to the oligotrophic offshore waters (Guerzoni et al., 1999; Koçak et al., 2010; Krom et al., 2004). This atmospheric dry and wet deposition support new production during spring and autumn in the offshore eastern Mediterranean (Herut et al., 2005; Markaki et al., 2003). Primary production in the eastern Mediterranean is principally dominated by eddies and currents that control the distribution of nutrients in the upper-layer waters (Ediger and Yilmaz, 1996). Annual PP is estimated to vary regionally and seasonally between 20.3 and 151.2 g C m⁻² y⁻¹ (Siokou-Frangou et al., 2010 and references there in; Yucel, 2013). The lowest chlorophyll concentrations were recorded in the anticyclonic regions of the Levantine Basin during the dry period, reaching as low as 0.01-0.23 mg m⁻³ (Ediger and Yılmaz, 1996). However, concentrations reach high levels ranging 2.49- 3.1 mg m^{-3} in the Rhodes gyre and in the coastal waters enriched by terrestrial inputs (Ediger and Yılmaz, 1996; Yucel, 2013). In the basin, phytoplankton blooms are generally observed in late winter and spring, following the winter convectional mixing (Siokou-Frangou et al., 2010). Up till now, only a few PP rate estimations have been conducted for the Cilician Basin (northeastern Mediterranean) (Ediger et al., 2005; Yayla, 1999; Yılmaz, 2006; Yucel, 2013), all of which highlighted apparent major differences between coastal and offshore waters. Offshore waters are commonly known as oligotrophic (Ediger et al., 2005; Ediger and Yılmaz, 1996; Yucel, 2013). Coastal waters (Mersin and Iskenderun Bays) display a high production capacity (Tugrul et al., 2016; Yılmaz, 2006; Yucel, 2013) due to the input of nutrients from natural and anthropogenic sources (through contaminated rivers and direct discharge of partially treated domestic and industrial wastewaters). Cyclonic systems in the open Levantine Basin differ in terms of their biological, chemical, and physical properties from the surrounding waters owing to the rising of nutrient-rich deep waters toward the base of the euphotic zone (EZ) for most of the year, sometimes reaching the surface during severe winters (Ediger and Yılmaz, 1996; Ediger et al., 2005). Chlorophyll concentrations and PP rates varied between 0.02 and 1.0 mg m⁻³ and 38.5 and 268 mg C m⁻² day⁻¹ in the Rhodes Gyre (Ediger et al., 2005). In severe winter-spring periods, the highest rates of PP and Chl-a were recorded in the peripheries of the Rhodes Gyre (Ediger et al., 2005). The coastal waters of the northeastern Cilician Basin are fed by perennial rivers, namely Goksu, Tarsus, Seyhan, Ceyhan, and some other smaller rivers, with associated chemical properties (high

 $NO_3 + NO_2/PO_4$ ratios and Si/ $NO_3 + NO_2$ ratio mostly <1 in the last 2 decades) (Uysal et al., 2008). In the coastal zone, atmospheric and river inputs, winter convectional mixing, and summer unwelling events determine the surface patrices.

and summer upwelling events determine the surface nutrient concentrations and rates of the new and regenerated PP (Ediger et al., 2005; Uysal, 2006; Uysal and Köksalan, 2010; Uysal et al., 2008).

Phytoplankton composition and abundance in the sea are determined by the physicochemical characteristics of upperwater masses, rates of nutrient inputs, and also by the changes in N/P/Si ratios within the euphotic zone. Diatoms have been reported as the most abundant group in the Cilician Basin shelf waters (Eker and Kideys, 2000; Eker-Develi et al., 2003; Kıdeyş et al., 1989; Polat et al., 2000; Uysal et al., 2003; Uysal et al., 2008). However, in the Levantine offshore waters, small phytoplankton dominate the total biomass and abundance (Li et al., 1993; Siokou-Frangou et al., 2010; Uysal et al., 2004; Uysal, 2006; Yucel, 2013). Recent studies pertaining to flow cytometry and highperformance liquid chromatography have also revealed that in the oligotrophic Levantine open sea, small-sized phytoplankton is the major contributor to the total phytoplankton biomass (Li et al., 1993; Yucel, 2008, 2013). It appears that PP rate data from the Levantine shelf and open sea waters are very limited for the assessment of spatio-temporal variability in the northeastern Mediterranean (Ediger et al., 2005; Yılmaz, 2006; Yucel, 2013). This study aims to enhance the existing knowledge pertaining to PP and size-based standing biomass potential of the basin by comparing and contrasting ecosystems that extend from highly oligotrophic to eutrophic, in relation to ambient physicochemical parameters, on a seasonal basis.

2. Material and methods

2.1. Sample collection and methodology

In this study, five stations were visited for measuring chemical (phosphate, nitrite + nitrate, silicate), biological (sizefractionated chlorophyll and primary production experiments), and physical (salinity, temperature, depth, photosynthetically active radiation (PAR), fluorescence, secchi disc depth [SDD]) parameters of the water column along a transect extending from Mersin Bay to Rhodes Gyre representing the coastal, offshore, and cyclonic areas of the northern Levantine Basin (Fig. 1, Table 1) during July and September 2012 and March and May 2013. Water samples from predefined depths (1, 2, 5, 13, 25 and 39 m for coastal waters and 1, 4, 8, 20, 50, 75, 100, 150 and 200 m for offshore and Rhodes Gyre) were collected on board the r/v Bilim-2 of the Institute of Marine Sciences (METU) using Niskin bottles fitted onto a rosette sampler, coupled with Sea-Bird Electronics-911 plus CTD (conductivity, temperature, depth) probe. Profiles of temperature, salinity, PAR and fluorescence were obtained using the standard Sea-Bird data processing software.

2.1.1. Nutrient analysis

Nutrient (nitrate + nitrite, phosphate, silicate) samples from the bottle casts were collected into 100 ml highdensity polyethylene bottles that were pre-cleaned with

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Figure 1 Location of sampling stations in the northeastern Mediterranean including rivers, bathymetry and main currents (AMC: Asia Minor Current, WCE: West Cyprus Eddy, RG: Rhodes Gyre). Modified from Siokou-Frangou et al. (2010).

Table 1 List of sampling stations.					
Area	Stations	Position	Sampling depth [m]	Total depth [m]	Sampling date
Coastal Offshore Rhodes Gyre	R23 R28 R48 R50 R58	N36.700 E34.700 N36.300 E34.700 N35.871 E33.981 N35.750 E31.000 N35.500 E29.000	39 200 200 200 200 200	40 223 1006 2320 2800	July 3—8, 2012 September 20—25, 2012 March 12—21, 2013 May 6—12, 2013

10% HCl. Bottles for nitrate + nitrite and phosphate analysis were kept frozen (-20°C), whereas those for silicate were kept cool (+4°C) in the dark until the analysis. Nutrient measurements were carried out using a Bran + Luebbe model four-channel auto-analyzer, employing the standard methods described in Grasshoff et al. (1983) and Strickland and Parsons (1972). Detection limits for nitrate + nitrite, phosphate, and silicate were 0.05, 0.02, and 0.3 μ M, respectively.

2.1.2. Chlorophyll-a

Seawater samples (2 l) collected at selected depths (including deep chlorophyll maximum) within the euphotic zone (EZ:1% of surface light depth - Table 2) were then filtered onto Whatman nucleopore polycarbonate filters for size fractionation (0.2, 2.0, and 5.0 μ m pore sizes and 47 mm diameter) at a low vacuum. Organic particles collected on the filters were then extracted with the help of 5 ml 90% acetone solution through the use of an ultrasonicator (60 Hz for 1 min). The final volumes of the extracts were then adjusted to 10 ml. The homogenized samples were kept in the dark at +4°C overnight and then centrifuged at 3500 rpm for 10 min in order to remove cellular debris. Chl-a concentrations of the centrifuged samples were determined through the fluorometric method, using a Hitachi F-2500 type fluorescence spectrophotometer. The Chl-a concentration of each sample was calculated according to the formula given by Strickland and Parsons (1972).

2.1.3. Primary production

Samples for primary production (PP) experiments were taken from surface and the lower depths within the euphotic layer. taking into account the incident PAR levels (at depths where 75, 50, 25, 10, 1, and 0.1% of surface PAR levels were achieved) and additionally from the deep chlorophyll maximum depth. In situ incubation experiments were consistently carried out around noon by following the methodology forwarded by Steemann Nielsen (1952). For the determination of PP, acid-cleaned transparent polycarbonate bottles (75 ml light and dark bottles for each depth) were filled with seawater samples taken from the selected depths, and 2 μ Ci ¹⁴C-NaHCO₃ solution were added to each bottle, and then the closed bottles were incubated for three hours. After incubation, the contents of each pair of light bottles were filtered using nucleopore polycarbonate filters (0.2, 2.0 and 5.0 μ m pore sizes and 25 mm diameter) at a low vacuum pressure. The contents of the dark bottles were also filtered with the use of 0.2 μ m pore size filters as blank. In this work, three different pore size filters were used for fractionated PP experiments in order to determine the contribution of picoplankton (Pico) (0.2-2 µm); small nanoplankton (Nano) $(2-5 \mu m)$ and microplankton (larger nanoplankton and microplankton as Micro) ($>5 \mu$ m) to the total production at each depth. Filters were then transferred to scintillation vials and acidified with 1 ml 0.5 N HCl. Scintillation cocktail was added to the vials after 24 h. Radioactivity of each solution was measured using a Perkin Elmer

Table 2	Dange of his physics chamical	variables (massa m		values) in the study area
Table Z	Range of bio-physico-chemical	variables (mean, n	ninimum and maximum	values) in the study area.

Parameters	R23	R28		R48	R50)	R58
Temperature [°C]	23.00 (16.34–29	.13) 18.3	4 (16.00–29.03)	17.73 (15.98	-28.71)	17.14 (15.34–27.66)	15.91 (14.30-25.34)
Salinity	39.03 (37.95-39	.45) 39.1	0 (38.87-39.49)	39.09 (38.82	-39.59)	39.07 (38.87-39.51)	39.06 (38.84-39.50)
Secchi disc depth [m]	11.5 (8–16)	24.3	(19–27)	27.3 (22-31)		27.5 (26-31)	27.5 (24–30)
Depth of the Euphotic Zone	37 (26-bottom)	78	(61–86)	87 (70–100)	88 (83–100)	88 (77–96)
(EZ; 1% light depth)							
NO ₃ + NO ₂ [μM]	0.45 (0.05–2.66) 0.3	9 (0.05–2.48)	0.39 (0.05-	-2.41)	0.60 (0.05-3.82)	1.18 (0.05-5.51)
PO₄ [μM]	0.03 (0.02–0.07) 0.0	3 (0.02–0.07)	0.03 (0.02-	-0.08)	0.04 (0.02-0.13)	0.04 (0.02–0.17)
Si [μM]	1.76 (0.20-4.48) 0.9	0 (0.42–2.34)	0.83 (0.32-	-1.96)	0.98 (0.44-3.17)	2.21 (0.74-6.80)
N/P (in EZ)	4.4 (exclude Ma	rch 5.2	(2.3–17.5)	6.9 (2.5–24	1.5)	5.8 (1.4–29.5)	13.7 (1.7–85.7)
	2013) (1.7-88.7)					
N/Si (in EZ)	0.31 (0.06-0.92) 0.1	8 (0.07–0.79)	0.21 (0.07-	-0.63)	0.20 (0.07-1.02)	0.24 (0.05–1.34)
Total Chl [mg m ⁻³]	0.381 (0.024-1.	365) 0.1	57 (0.022-1.203)	0.162 (0.01	1–0.569)	0.087 (0.012-0.563)	0.229 (0.016-1.257)
Depth integrated	13.2 (2.3–25.8)	21.9	(14.9–27.1)	25.9 (6.5-53	8.5)	17.1 (4.1–32.1)	46.2 (8.4–118)
Chl [mg m ⁻²]							
Mean Chl (depth	0.343 (0.06–0.6	6) 0.1-	46 (0.10–0.18)	0.17 (0.04-	-0.36)	0.11 (0.03-0.21)	0.308 (0.05-0.78)
integrated/depth)							
[mg m ⁻²]							
Total primary production	5.48 (0.23–17.8	0) 0.7	6 (0.01–2.46)	0.63 (0.08-	-1.58)	0.72 (0.03-2.26)	0.42 (0.01-1.15)
$[mg C m^{-3} h^{-1}]$							
Depth integrated primary	193.3 (30.1-348	.8) 88.2	(21.54–188.5)	83.1 (29.9–1	42.9)	103 (33.9–222.8)	60 (21.9–91.7)
production [mg C m ^{-2} h ^{-1}]							
Mean PP (depth	4.95 (0.77-8.94) 0.5	9 (0.14–1.26)	0.55 (0.19–	-0.95)	0.69 (0.22-1.48)	0.40 (0.14–0.61)
integrated/depth)							
$[mg C m^{-2} h^{-1}]$							
% Contribution of groups Pie	co 36 (17—55)	73 (58–79)		67 (47-85)	59 ((35–79)	70 (59–78)
to TCHL Na	ano 31 (26–37)	9 (4–15)		10 (8–16)	10) (4–19)	9 (2–14)
Mi	icro 34 (23–48)	17 (12–26)		22 (7-37)	31 ((13–45)	21 (12–27)
% Contribution of groups Pie	co 42 (26–54)	62 (48–77)		61 (38–78)	73 ((64–86)	70 (51–86)
to TPP Na	ano 24 (21–27)	19 (16-29)		20 (11-41)	11	(6–19)	16 (6-43)
Mi	icro 34 (21–47)	18 (7–27)		18 (11-27)	15	ō (6—24)	14 (8–24)

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Tri-Carb 2810 TR Scintillation Counter. Hourly rates of production were calculated from the measurements, and then these rates were converted to depth-integrated production rates [mg C $m^{-2} h^{-1}$] using the trapezoidal method (O'reilly and Zetlin, 1998).

2.1.4. Statistical methods

Principal component analysis (PCA) was used to summarize environmental variable inter-correlations and their potential underlying environmental factor patterns/gradients. For these analyses, log transformation was first applied to all variables and then all the variables were standardized to zero mean and unit variance prior to PCA on the correlation matrix, using the r (R Core Team, 2012) package vegan's (Oksanen et al., 2012) RDA (Redundancy analysis) function.

3. Results

3.1. Hydrographic properties

Temperature and salinity profiles for each station and sampling period are presented in Fig. 2. Surface temperature ranged between 15.92 and 29.13°C in the area (Fig. 2), where relatively much cooler waters were recorded near Rhodes cyclonic Gyre. The water column was almost well mixed due to the strong winter convectional mixing as observed in March 2013 (Fig. 2). Thermal stratification in the upper layer becomes apparent after March; the warmer-surface mixed layer was observed to deepen by 60 m in September 2012 (Fig. 2). The seasonal thermocline is consistently steeper and shallower in the cyclonic Rhodes Gyre due to the upwelling of cooler deep waters (Fig. 2).

Fig. 2 clearly shows that the upper layer T and S profiles are influenced by the river inflow, especially during winter spring. In the open sea, surface salinity decreased from 39.13 to a level of about 38.0 psu in March 2013 (Fig. 2). As expected, surface salinity increased to 39.51 psu during summer—early autumn (Fig. 2) due to excess evaporation and limited freshwater input. It should be noted that less saline (\leq 38.87 psu) Atlantic waters were detected between 45 and 70 m below the seasonal halocline (20–40 m) in September 2012 at the offshore stations (St. 28-R48-R50) and Rhodes Gyre (St. R58), flowing westward in the northern Levantine sea (Fig. 2). Euphotic zone was thicker (\approx 90 m) in offshore waters and Rhodes Gyre compared to the coastal sector where light can reach the bottom (Table 2).

3.2. Nutrients

Typical nutrient profiles from the stations are presented in Fig. 3, which clearly indicate that the offshore surface waters were depleted in dissolved inorganic nutrients. Although the surface phosphate values were very low ($0.02-0.04 \mu M$) both in the coastal and offshore areas, concentrations of silicate and $NO_3 + NO_2$ were significantly higher in coastal waters of the Cilician Basin fed by NO₃ + NO₂- and Si-laden, but Pdepleted river waters (Fig. 3). Thus, concentrations for $NO_3 + NO_2$ and silicate ranged from 0.05 to 5.5 μ M and 0.2 to 6.8 μ M, in the offshore and coastal waters, respectively. Spatio-temporal variations of the physicochemical and biological parameters that were measured in this study are summarized in Table 2. Nutrient concentrations of the EZ waters were very low in the offshore waters, and concentrations began to increase and reached the highest value at 200 m depth, below the EZ in the Levantine offshore waters and Rhodes Gyre; the nutricline was markedly sharp in the Rhodes Gyre and formed at shallower depths (between 50 and 75 m) (Fig. 3). An increase was observed in phosphate concentrations, following winter convectional mixing (March 2013) in the offshore waters. The highest seasonal variations were seen in the EZ of the Rhodes Gyre, where nutrient concentrations were measured over a wide range (Table 2, Fig. 3).

Very low N/P (4.4–13.7) and N/Si (0.2–0.3) ratios were observed in EZ waters of the study area (Table 2). Higher values were found for the deeper parts of the EZ (\approx 80–100 m) in offshore waters and Rhodes Gyre. N/P values reached peak levels in the surface coastal waters in March



Figure 2 Temperature and salinity profiles at stations visited in the Levantine basin (AW: Atlantic Water salinity signature detected at stations R28 to R58). Modified from Yucel (2017).





Figure 3 Vertical distributions of dissolved nutrients at the stations visited in the Levantine basin. Modified from Yucel (2017).

2013 (88.7) and at 68 m near Rhodes Gyre in September 2012 (85.7).

3.3. Size-based chlorophyll-a

Changes in chlorophyll concentration with respect to depth for all the stations visited are presented in Fig. 4. Overall, total Chl-a concentration varied regionally and seasonally from 0.011 to 1.365 mg m^{-3} in the study area (Table 2). Surface- and layer-averaged concentrations increased in rainy seasons (March 2013) in river-fed coastal waters while concentrations inversely increased with depth in the dry season (July and September 2012) (Fig. 4). Generally, total Chl-a concentrations at offshore surface waters (St. R28, R48, and R50) remained very low, but reached elevated maxima in stations R48 (0.569 mg m⁻³, July 2012) and R28 $(1.2 \text{ mg m}^{-3}, \text{ in September 2012})$ during the stratification period. Additionally, higher values were measured near and at the bottom of the EZ during the stratification period (July and September 2012), as the deep chlorophyll maximum (DCM), a typical feature of the eastern Mediterranean (Ediger and Yılmaz, 1996; Kress and Herut, 2001; Siokou-Frangou et al., 2010), was formed between 75 and 100 m throughout the study period. However, this feature can weaken or totally disappear in winter due to the intensive vertical mixing, as was the case in March 2013, during which Chl-*a* was distributed homogeneously within the entire EZ (variations were observed $\pm 0.02-0.04$ mg m⁻³ in water column). In July 2012, higher Chl-*a* concentrations (0.514–0.569 mg m⁻³) were recorded in the much warmer upper layer of EZ (4–50 m) at St. R48, although concentrations have not generally exceeded 0.2 mg m⁻³ in the upper layer of EZ in the offshore waters of the northern Levantine Basin. Very low layer-averaged concentrations were observed in May 2013 following the spring bloom (Fig. 4). Average Chl-*a* concentration for the upper 10 m of Rhodes Gyre was calculated as low as 0.06 mg m⁻³ for the study period. While DCM was found in July 2012 (1.26 mg m⁻³) and May 2013 (0.52 mg m⁻³) within the nutricline (\approx 75–100 m), it disappeared in September 2012 and March 2013 in EZ of the cyclonic Rhodes Gyre.

Size-fractionated Chl-*a* profiles indicate picoplankton (61 \pm 19%) to be the major contributor in the EZ of the study area (Fig. 4). Contribution of small nanoplankton and microplankton to the bulk Chl-*a* were calculated as 14 \pm 10% and 25 \pm 12%, respectively. Small nanoplankton contribution increased for the total Chl-*a* in nutrient-rich upper layer of coastal waters, while the contribution was negligible for offshore waters and the Rhodes Gyre. Microplankton including larger nanoplankton formed the second dominant group in the coastal waters, DCM, and near the nutricline (50 m) in



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Figure 4 Changes in size fractionated and total chlorophyll *a* concentrations with depth at selected stations in the Levantine basin (*Note*: the different depth scales for the coastal st. R23; and different scale at R23 for March 2013 and R58 for July 2012 (*x* and *y* axes)).

Rhodes Gyre (Fig. 4). Contribution of picoplankton increased in summer and early autumn (hot and dry season) and decreased during the rainy and cold period (March 2013) in coastal waters, except in the surface waters.

3.4. Size-based primary production

Depth distributions of size-fractionated and total primary production (TPP) rates are presented in Fig. 5. TPP displayed a remarkable seasonal and regional variability between the sampling sites. TPP rates were discovered to be apparently high $(1.42-17.80 \text{ mg C m}^{-3} \text{ h}^{-1})$ in March 2013 (representing late winter—early spring conditions) at all the stations, and the productive layer was rather broad, extending down to the 0.1% light depth. The TPP rate over the basin decreased markedly to the levels of $0.13-3.32 \text{ mg C m}^{-3} \text{ h}^{-1}$ in the upper EZ (down to 25% light depth) in May 2013, when the upper layer was stratified and the available nutrients were already consumed during the spring bloom period. Principally, the TPP displayed an increasing trend in the upper layer of the EZ (10% light depth) and then decreased steadily

toward the base of the EZ, which varied from 61 m (1% light depth) to 100 m in the oligotrophic open sea for the summer—autumn period (Table 2).

In the coastal waters of the Mersin Bay (St. R23), TPP rates were maximal in March, followed by July and September, whereas the least levels were observed in May. Rates peaked at the surface during spring (March 2013) and dropped to its lowest levels (layer-averaged rate: $1.5 \text{ mg C m}^{-3} \text{ h}^{-1}$), following the major spring bloom in May 2013.

In the offshore waters of the northern Levantine Basin (St. R28, R48, and R50), rates decreased to low levels of 0.71-0.84 mg C m⁻³ h⁻¹ (EZ layer-averaged values), which are 6.7 times lower than those found for the coastal region influenced by river inputs. It should be noted that enhanced TPP rates were observed in the subsurface waters between 8 and 100 m in July and September, reaching the maximal rate upper layer of the EZ (8 m in July).

In the Rhodes Gyre (St. R58), TPP rate was found high at the depths between thermocline (10-20 m) and the base of the EZ ($\approx 100 \text{ m}$) and low in highly illuminated surface waters during summer-autumn. After the winter convectional mix-







Figure 5 Changes in size fractionated and total primary production rates with depth at selected stations in the Levantine basin (*Note*: the different depth scales for the coastal st. R23; and different scale for all station).

ing (March 2013), TPP increased at the surface waters (top 25 m), in comparison with dry and hot seasons (July and September 2012) and decreased slightly toward the lower end of the EZ. Very low (0.219 \pm 0.09 mg C m $^{-3}$ h $^{-1}$) TPP rates were measured in the water column in May 2013 in Rhodes Gyre.

Size-fractionated PP profiles indicate picoplankton to be the major contributor ($62 \pm 17\%$) at all sites throughout the study period. Contribution of picoplankton to TPP reached up to 86% in offshore waters (St. R50, September 2012) and Rhodes Gyre (March 2013), and TPP in DCM was also markedly dominated by picoplankton. Microplankton including larger nanoplankton was the second dominant group ($20 \pm 11\%$) followed by small nanoplankton ($18 \pm 11\%$) in the northern Levantine Sea, while shifting with each other in the different depth layers within EZ in the offshore waters (July and September 2012 and May 2013). EZ averages indicate small nanoplankton to be more productive than microplankton at St. R28, R48, and R58 (Rhodes Gyre). Microplankton production exceeded that of small nanoplankton only in coastal waters (47%) and made a major contribution to offshore waters, following winter convectional mixing in March 2013.

3.5. Principal component analysis (PCA)

Environmental variables were analyzed using the principal component analysis. First, 5 components were selected from Table 3 and accounted for 95% of the total variation. The loading plot of PCA of abiotic and biotic parameters is presented in Fig. 6. Component 1 (PC1) can explain 63% of the total variance and component 2 (PC2) can explain 15% of the total variance. In two dimensional space, given by F1 vs F2, variables were separated into three groups (i.e., one including NPP: nanoplanktonic PP, MPP: microplanktonic PP, TPP: total PP and PPP: picoplanktonic PP). Correlations

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are present between NPP, MPP, TPP, and PPP (Supplementary Fig. S1). Additionally, PO_4 , silicate, and $NO_3 + NO_2$ have similar trends. According to the distribution of the stations, R23 differed from other stations with high production.

Table 3Eigen values and corresponding values of percent-
age of variance for each component.

Component	Eigen value	% of variance	Cumulative %
1	12.34	63.0	63.0
2	3.08	15.7	78.7
3	1.76	9.0	87.7
4	0.92	4.7	92.4
5	0.56	2.8	95.3
6	0.30	1.5	96.8
7	0.24	1.2	98.1
8	0.14	0.7	98.8
9	0.12	0.6	99.4
10	0.05	0.3	99.7
11	0.02	0.1	99.9
12	0.01	0.0	100

Extraction method: principal component analysis.

4. Discussion

4.1. Seasonal variability in size-fractionated primary production and chlorophyll in coastal waters

In the northeastern Mediterranean Sea, regional rivers, upwelling events, and atmospheric (wet + drv) depositions are regarded as the main sources of nutrients (Kocak et al., 2010; Uysal, 2006; Uysal and Köksalan, 2010, 2017). Though the eastern Mediterranean is commonly reported to be one of the least productive basins in the world (Siokou-Frangou et al., 2010), the coastal waters of Mersin Bay display a high primary production (PP) capacity (Yılmaz, 2006; Yucel, 2013) due to high concentration of nutrients (especially silicate and $NO_3 + NO_2$) introduced by local rivers (Seyhan, Lamas, Tarsus, and some smaller brooks) (Kocak et al., 2010). Elevated surface nutrient concentrations in less saline coastal waters of Mersin Bay lead to the enhancement of dissolved inorganic and organic nutrients, total PP, algal biomass, as well as changes in algal composition as compared to the nutrientpoor Levantine offshore waters.

The total PP in the coastal waters of northern Levantine Sea was as high as 193 mg C m⁻² h⁻¹, exceeding most of the PP rates to date reported for different sub-regions of the Mediterranean (Siokou-Frangou et al., 2010; Yucel,



Figure 6 Results of principal components analysis of production, chlorophyll and environmental parameters (NPP: nanoplanktonic PP, MPP: microplanktonic PP, TPP: total PP and PPP: picoplanktonic PP, NCHL: nanoplanktonic Chl, MCHL: microplanktonic Chl, TPP: total Chl and PCHL: picoplanktonic Chl).

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2013). Exchange of productive and nutrient-rich coastal Mersin Bay waters with oligotrophic offshore waters is limited due to the blockage of westward flowing of the Asia Minor Current (AMC) present in the northeastern Levantine deep Basin. This mechanism creates highly contrasting water masses with very low and very high production capacities within the wide shelf basin of Mersin Bay on the NE Levantine basin (Yucel, 2008).

TPP rate and chlorophyll concentrations of Mersin Bay coastal waters (St. R23) have increased markedly in March 2013, when the surface salinity was measured below 38 psu and the concentrations of silicate and $NO_3 + NO_2$ at the surface were maximal, following the winter convectional mixing and pronounced river runoff (Fig. 3). Such optimum conditions have stimulated PP in coastal waters favoring microplankton + larger nanoplankton (47% of total primary production: 162.8 mg C m⁻² h⁻¹) as the dominant group. Additionally, Yucel (2013) measured the microplankton + larger nanoplankton-dominated high primary production rates in summer and autumn (October 2010, July and August, 2011) in coastal waters that were affected partially by the local river run off. Microplankton is composed mainly of diatoms that consume the majority of available nutrients in the coastal waters, compared to smaller cells. Moreover, higher silicate concentrations favor diatoms in coastal waters at concentrations above 2 µM (Egge and Asknes, 1992; Fogg, 1991). Therefore, in the present study significant positive correlations were obtained between nutrients $(NO_3 + NO_2)$ and silicate) and microplankton production and chlorophyll in coastal waters (Supplementary Fig. S1). Conversely, picoplankton was generally observed to be the dominant contributor to the bulk flora in summer and autumn, when the nutrient concentrations were relatively low in coastal waters during the course of this study (Table 2, Fig. 4). However, contrary to the dominance of diatoms in the phytoplankton composition of coastal waters that was reported in previous studies (Eker and Kideys, 2000; Eker-Develi et al., 2003; Kideyş et al., 1989; Polat et al., 2000; Uysal et al., 2003) where picoplankton was missed or not studied along with large phytoplankton groups, except some ataxonomic phytoplankton studies, recent studies indicate that phytoplankton composition was generally dominated by picoplankton (Yılmaz, 2006; Yucel, 2008; Yucel, 2013; Yucel et al., 2017). Picoplankton is a better competitor with the lower energy requirements and higher production efficiency than microplankton in nutrient-poor waters during summer and autumn in coastal waters (Finkel et al., 2005; Moutin et al., 2002). Moreover, picoplankton, the major contributor in hot and dry seasons, is more tolerant of warmer waters than microplankton, which cannot tolerate higher temperatures (Supplementary Fig. S1) (Yucel, 2013). Small nanoplankton was the least contributing group in coastal waters, where their remarkably increased contribution to TPP was only observed in very favorable environmental conditions (March 2013).

Based on very low N/P and N/Si ratios, nitrogen was suggested to be the limiting nutrient during July and September 2012 and May 2013 in coastal waters. Despite the high levels of phosphate and silicate, the lower nitrogen concentration of the water column delimited phytoplankton growth significantly during May 2013. These low $NO_3 + NO_2$ concentrations have limited the growth and shaped the phytoplankton composition in coastal waters (Yucel, 2013). Actually, changes in size groups

of the phytoplankton is highly dynamic in coastal waters and may change at short time intervals, depending on the changes in ambient physicochemical conditions, river regime, nutrient concentrations and composition, activity of cells, predation and competition (Romero et al., 2013).

4.2. Seasonal variability of size-fractionated primary production and chlorophyll in offshore waters

In offshore waters of the northern Levantine Basin, nutrient concentrations were observed to be low and distributed homogeneously at the top 100 m of the water column, and then increasing with the increasing depth down to the nutricline, which occurs between 300 and 500 m (Yilmaz and Tugrul, 1998; Yucel, 2013). Besides, small-scale upwelling events and atmospheric deposition offer a certain amount of nutrients to the oligotrophic offshore waters. Goksu River also supplies nutrients to the south and the southwestern offshore surface waters. The direct (increasing nutrients)/ indirect (increasing chlorophyll) effects of the Goksu River can reach Cyprus via currents (Fig. 1) (Uysal et al., 2008; Yilmaz and Tugrul, 1998; Yucel, 2008).

Nutrient concentrations were very low in the upper layer, covering the euphotic (EZ) (75 m) and exhibiting typical characteristics of oligotrophic environments in the northern Levantine Sea throughout the year (Ediger et al., 2005). Phosphorus was near the detection limit (0.02 μ M) and $NO_3 + NO_2$ was also very low within the EZ (Table 2); the nutrient profiles displayed a gradual increasing trend below the EZ. Phosphorus is utilized faster than nitrate and silicate in the oligotrophic eastern Mediterranean (Krom et al., 2005). Although it is widely accepted that phosphorus is the limiting nutrient for primary production, low N/P (6 \pm 0.8) and N/Si (0.195 \pm 0.015) ratios also indicated nitrogen limitation or nitrogen + phosphorus co-limitation in the offshore waters (Yucel, 2013). Since phosphorus concentration of the upper layer of EZ was at very low levels (Table 2), no clear relationship appeared between the biological parameters and the phosphorus concentration throughout the study period in the offshore waters of northern Levantine Sea (Supplementary Fig. S1). Phosphorus supplied from the Plimited Levantine intermediate depths is utilized rapidly and phosphorus concentration declines below 0.03 µM (undetectable by conventional colorimetric method) in the offshore EZ as the inorganic N (NO₃ + NO₂ + NH₄) enters the system with higher N/P ratio. Therefore, inorganic N can be measured at background levels (0.1–0.2 μ M) in the EZ in summer-autumn period. Following intense winter convectional mixing, higher PP levels were observed all over the northern Levantine offshore waters (top 75 m), due to nutrient supply from the intermediate depths.

In the early spring period, the surface NO₃ + NO₂ was observed to as low as levels of 0.05–0.23 μ M whilst phosphorus was at hardly detectable (detection limit) levels of 0.02–0.04 μ M due to consumption of nutrients supplied from deep waters by photosynthesis in the EZ internal sources (Ediger and Yılmaz, 1996; Krom et al., 1991). Thus, the low concentrations of NO₃ + NO₂, PO₄ and the low N/P ratio (<15) strongly suggest that N and P co-limited production during the post-bloom period in the Levantine basin.

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In the offshore waters where the seasonal thermocline was located at shallow depths (about 10-50 m) 10-25 m in July 2012, higher concentrations of chlorophyll and PP values displayed broad vertical distribution, vanishing at the base of the thermocline. In the more productive thermocline zone, PP was dominated by picoplankton (Fig. 5) and nutrient concentrations were low, ranging between 0.07 and 0.08 μ M for NO₃ + NO₂ and 0.02-0.03 μ M for PO₄ (St. R48, Fig. 3). Picoplankton dominated PP and low nutrient concentrations in the thermocline depth range of EZ indicate that the PP was stimulated by nutrients mainly generated from small-size detritus accumulated with the thermocline zone (Ediger et al., 2005) and also labile forms of the colloidal and dissolved organic nutrients in the oligotrophic and mesotrophic marine environments (Berman and Bronk, 2003; Bronk et al., 2007; Roussenov et al., 2006; Torres-Valdes et al., 2009).

In the 2013 late spring, when there was no apparent seasonal thermocline formation in the upper layer, nutrients available in the EZ were almost consumed by phytoplankton; the NO₃ + NO₂ and PO₄ were very low (0.05–0.07 μ M and 0.02–0.02 μ M, respectively). Low Chl-*a* and PP values measured in the spring indicate that the majority of nutrients supplied to the EZ during the winter mixing period have been consumed and the system had the background nutrient levels of the Levantine EZ waters.

No close relationship was observed between the water column PP and the chlorophyll concentration. Chlorophyll peaks (DCM) were observed below the high PP zone at the same station (Figs. 4 and 5). The formation of DCM is well known to develop in the light-limited depths of the offshore EZ extending the seasonal thermocline, depending on the depths of the seasonal thermohaline feature, limited nutrient supply from the EZ boundary and rate of nutrients regenerated in the thermohaline feature near the base of the EZ where the DCM was formed during summer-early autumn period (Fig. 4). High light condition could stimulate primary productivity in the upper layer of EZ (10–75 m), far above the nutricline in offshore waters. In addition, intrusion of nutrients into the base of EZ may provoke low light adapted phytoplankton (Ediger et al., 2005) in DCM, which was dominated by picoplankton consisting mainly of Synechococcus and Prochlorococcus in the eastern Mediterranean. Although phytoplankton composition was not available for this study, Li et al. (1993) found Prochlorococcus to be more abundant than Synechococcus in the water column of offshore waters in the eastern Mediterranean. Ghiglione et al. (2008) also observed high concentration of Prochlorococcus at the base of the DCM, while Synechococcus was observed in the upper 40 m in the Gulf of Lions. Furthermore, Yucel (2013) found that contribution of Prochlorococcus to total picoplankton increase was below 30-40 m in eastern Mediterranean offshore waters.

Picoplanktonic primary production (65%) and bulk chlorophyll (66%) dominated phytoplankton composition in offshore waters of the northern Mediterranean (Table 2).

Microplankton + larger nanoplankton formed the second dominant group in the nutrient-depleted offshore waters. All previous studies indicated that phytoplankton composition shifted from microplankton to picoplankton with increasing oligotrophy and picoplankton has been considered to dominate the phytoplankton in the oligotrophic offshore waters of the eastern Mediterranean (Li et al., 1993; Siokou-Frangou et al., 2010; Uysal, 2006; Uysal and Köksalan, 2010; Yucel, 2013). The contribution of picoplankton to the total primary production exceeded 70% in Levantine offshore waters (Yucel, 2013). Low N/P ratios can be ascribed to rapid utilization of available nitrogen by picoplankton (cyanobacteria and prochlorophytes), which have high affinity to nitrogen species in offshore waters. Cyanobacterial production can be satisfied significantly by the scarce amount of nitrogen sources (Karl et al., 1997; Moore et al., 2002; Pantoja et al., 2002). Moreover, picoplankton has more advantages, with the high surface to volume ratio to reaching low concentrations of nutrients and photoprotectant pigments to survive excess light conditions, compared to microplankton (Finkel et al., 2009; Yucel, 2013). Excess input of phosphate in early spring also provoked micro- and nanoplanktonic production and biomass in offshore waters (Figs. 3-5).

4.3. Seasonal variability of size-fractionated primary production and chlorophyll in Rhodes Gyre

In Rhodes Gyre, nutrient concentrations started to increase rapidly in the base of the EZ in this study (Fig. 3). Since the nutricline was located just above the EZ seasonally variable amounts of nutrients have been pumped by upwelling processes from the nutricline depths to the lower depths of the EZ (Ediger and Yılmaz, 1996). This phenomenon stimulates primary productivity in the EZ (1% light depth: 59–80 m) throughout the year. In the Levantine Basin, nitracline was formed at shallower depths than phosphacline, even in Rhodes Gyre; for example, $NO_3 + NO_2$ gradient started at 50 m whereas the PO_4 gradient was observed at 75 m in the Rhodes Gyre because of either the selective accumulation of labile $NO_3 + NO_2$ or the selective removal of reactive phosphate by sinking particle (Yılmaz and Tugrul, 1998).

In the gyre the upper layer is thermally stratified during late spring-autumn period. Therefore, limited nutrients are supplied from the nutricline depths to the upper mixed depths of EZ (50 m), which leads to consumption of available nutrients via photosynthesis and thus low nutrient $(NO_3 + NO_2, PO_4)$ concentrations with low N/P (\approx 5), as observed in the Levantine offshore waters during the study period (Table 2). However, chlorophyll concentrations measured in the upper layer of cyclonic Rhodes Gyre in July 2012 and May 2013 have exceeded those observed in both coastal (salinity: 37.9-39.4 psu) and offshore waters (salinity: 38.9-39.59 psu) (Fig. 4). In the Gyre waters, chlorophyll profiles were broader (25-100 m) in July 2012, reaching higher concentrations at the EZ base (75 and 100 m) in May 2013, which indicates the role of nutrient inputs from the shallower nutricline (50-75 m), keeping chlorophyll concentrations at the levels of coastal waters partly fueled by terrestrial inputs during dry period. Consequently, low nutrient high chlorophyll (LNHC) condition was observed in the upper part of the EZ during the summer (July 2012). High nutrient low chlorophyll (HNLC) condition could develop in the core of the Rhodes Gyre, as observed in March 1992 (Ediger et al., 2005), due to the dilution of organic matter produced in the upper layer by upwelling water masses. However, such a condition was as not observed in March

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2013, as the less saline deep water could not replace the more saline, warmer surface layer within the Gyre (Fig. 2). Therefore, very low phosphate (0.04 μ M), NO₃ + NO₂ (0.69 μ M), and chlorophyll (<0.23 mg m⁻³) concentrations were measured at top 150 m in March 2013, following the winter convectional mixing. The March 2013 data strongly suggest that low PP rates may represent post-bloom phase in the surface waters of the region, with low nutrient concentrations. However, the chlorophyll was higher in the Rhodes Gyre than in the Cilician basin waters, due presumably limited nutrient inputs from the density gradient zone situated at the base of the EZ and regenerated of nutrients in the light-limited zone of the EZ. High levels of POC/Chl-a ratio in the EZ determined by Ediger et al. (2005) was attributed to detritus and heterotrophic activity-dominated in the EZ during nutrient depleted spring-autumn periods over the Levantine basin. In addition, lowest nutrient concentrations and low PP rates were observed in top 50 m at the end of spring (May 2013), while total chlorophyll reached 0.525 mg m^{-3} at the DCM formed at 75 m (Fig. 4). In summer (July 2012), the DCM formed was broader, extending down to 100 m, with slightly higher nutrient concentrations than in May 2013.

Picoplankton was the major contributor (65%) to total PP within EZ, including DCM, as observed in offshore waters, followed by microplankton + larger nanoplankton. Total chlorophyll was also dominated by picoplankton (70%) in the Rhodes Gyre (Table 2). The contribution of larger cells ($>5 \mu$ m) was maximal (0.581 mg m⁻³ and 0.274 mg C m⁻³ h⁻¹) in July 2012 at the 50–75 m depth range at nutricline, with high phosphate, NO₃ + NO₂, and Si concentrations being pumped from the lower layer of the EZ. It seems that microplankton cannot compete with picoplankton in Rhodes Gyre under low nutrient conditions, as it was seen in coastal and offshore waters, but an increase was seen in their contribution in high nutrient conditions (in July 2012 in coastal waters and March 2013 in Rhodes Gyre), which provoke microplanktonic growth (Egge and Asknes, 1992; Fogg, 1991).

4.4. Longitudinal variability of size-fractionated primary production, chlorophyll, and assimilation ratio

Along the east-west transect (from St. R28 to R58), PP showed a gradual decrease from 0.588 mg C $m^{-3}\,h^{-1}$ to



Figure 7 Depth integrated (A) and mean (B) chlorophyll *a* values calculated for all stations and sampling periods. (*Note*: the different integration depth for the coastal st. R23).

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0.402 mg C $m^{-3} h^{-1}$ in the area (Fig. 8B). In addition, depthintegrated PP (DIPP) also decreased from 193.3 mg C $m^{-2} h^{-1}$ in coastal waters to 60 mg C m⁻² h⁻¹ in Rhodes Gyre. In contrast to the east-west decreasing trend in PP, concentration of chlorophyll increased toward Rhodes Gyre (from 0.146 mg m⁻³ in St. R28 to 0.308 mg m⁻³) and DICHL chlorophyll) fluctuated (depth-integrated between 13.2 and 46.2 mg C m⁻² in the study area. The PP rate and the chlorophyll concentration were not in accordance in the northern Levantine Sea during the study period which was discussed above (Figs. 7 and 8). Studied areas of northern Levantine Basin are well known to have different bio-physicochemical characteristics and dynamics (Ediger and Yılmaz, 1996; Ediger et al., 2005; Yılmaz and Tugrul, 1998). Chlorophyll concentrations in the Rhodes Gyre were close to those of the coastal waters (0.343 mg m^{-3}), where riverine nutrient inputs feed the coastal ecosystem. As usual, very high primary production rates were recorded for whole study area after the intense winter convectional mixing, which determines the nutrient budget of the EZ in March 2013 (Fig. 8A). After the bloom period in late spring (May 2013), very low PP rates and chlorophyll were measured when phosphate and $NO_3 + NO_2$ were almost depleted in the area.

The coastal waters of the northern Levantine Sea had different characteristics and were separated statistically from the other stations with high production capacity (4.955 mg C m⁻³ h⁻¹) (Fig. 6). Although Rhodes Gyre and offshore waters had some similar features, Rhodes Gyre was also separated from others due to its distinct-high nutrient (below 50 m) and chlorophyll concentrations in the euphotic layer (below 50 m). All results showed that coastal waters were affected by river input, while offshore waters and cyclonic Rhodes Gyre were influenced by convective winter mixing and continual upwelling events, respectively.

Contribution of all groups to TPP slightly decreased toward the west, while all groups increased their contribution to total chlorophyll from R28-the most eastern part of offshore waters to R58-Rhodes Gyre. While contribution of smaller cells (<2 μ m) to DICHL increased from the east to the west in the northern Levantine Basin, DIPP rates decreased throughout the transect. Conversely, the opposite trend (low chlorophyll and high PP of picoplankton) was observed in the cyclonic West Cyprus Eddy (WCE) (St. R50), with small scale nutrient intrusions below the EZ (less than Rhodes Gyre). Moreover, the contribution of microplankton to DICHL increased from eastern part of the offshore waters to the WCE and Rhodes Gyre, where EZ layer-averaged nutrient concentration increased along the transect, while it was not observed in DIPP. Small nanoplankton was the least



Figure 8 Depth integrated (A) and mean (B) primary production values in the five stations and four seasons studied (*Note*: the different integration depth for the coastal st. R23 and "break" line of B axis at 2–3).

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Figure 9 Distribution of seasonal (A) and mean (B) assimilation ratios at the stations.

contributor in DICHL and DIPP in the northern Levantine Sea during the study period.

The physiological state of an individual cell can be different according to the stages of a bloom in different marine ecosystems (Falkowski and Raven, 2007). Although chlorophyll defines the size of the standing stock, PP just indicates the carbon assimilation capacity of the flora. High level of chlorophyll does not necessarily correspond to high PP or physiological activity, as it is dependent on the stage of the bloom. Moreover, there is no linear relationship between chlorophyll and carbon assimilation capacity due to the complex effects of light, temperature and nutrient on phytoplankton physiology (Wang et al., 2009).

In the northern Levantine Sea, assimilation ratio (AR: mg carbon assimilated per mg chl *a*) was calculated at the lowest (1.3) for Rhodes Gyre (St. R58) and the highest (14.6) for coastal waters (St. R23) (Fig. 9). Assimilation ratio (6) was found higher than other offshore stations at St. R50, which also had higher production capacity due to the relatively higher nutrient concentrations in comparison with other offshore stations. St. R50 was in the center of the cyclonic West Cyprus eddy, which transfers nutrients from the aphotic layer to the EZ and may stimulate productivity. Phytoplankton in the Rhodes Gyre were found to be the least active (low PP, low nutrient concentrations and high chlorophyll [LNHC]

in the periphery of the gyre where the nutrients were quickly utilized and converted to biomass by phytoplankton) compared to other stations. As expected, assimilation ratios of picoplankton were not found to be the highest, as it was seen in DICHL and DIPP at all the stations (Fig. 9). Although picoplankton assimilate carbon more efficiently than nanoplankton and microplankton (Finkel et al., 2005), their lifespan may be shorter than the decomposition duration of chlorophyll content. Though the contribution of small nanoplankton to PP (<0.024 mg C m⁻³ h⁻¹) and chlorophyll $(<0.055 \text{ mg m}^{-3})$ was minor, they were observed to be the most active group in the northern Levantine Sea. Nanoplankton comprises different trophic types of groups (mixotrophic, heterotrophic, and phototrophic) in the aquatic ecosystem (Riemann et al., 1995). A mixotrophic nanoplankton may have a better carbon assimilation ratio with low chlorophyll high production capacity in the eastern Mediterranean. This could be one way of expressing their high assimilation ratio in the oligotrophic offshore waters and cyclonic Rhodes Gyre.

5. Conclusions

In the northern Levantine Sea, the rate of primary production and phytoplankton species composition in the coastal and

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open sea are determined by the seasonally varying rates of river inflows, availability and inputs rates of nutrients by dry + wet atmospheric depositions, upwelling events and regenerated from slowly sinking detritus of nano + picoplankton produced in the EZ. Temperature varying seasonally between 16 and 29°C is also another important factor that regulates the success and composition of the pelagic flora. Picoplankton was the most dominant phytoplankton group in the northern Levantine Sea. High nutrient concentrations (nitrogen and silicate) trigger productivity of microplankton in the river-fed (with $Si/NO_3 + NO_2 < 1.0$) coastal waters during the rainy season (March) and in cyclonic Rhodes Gyre during the summer. Low N/P in the nutrient-depleted $(NO_3 + N O_2 < 0.15 \ \mu$ M; $PO_4 < 0.03 \ \mu$ M) euphotic zone indicated nitrogen and possibly P co-limitation in the northern Levantine Basin in July and September 2012 and May 2013. The seasonal averaged total primary production rates observed in coastal waters was 8-12 times higher than those observed in offshore waters and the Rhodes Gyre, respectively. However, the mean total Chl-a values display less spatial variability. ranging from 0.14 mg m $^{-3}$ in the offshore waters to the levels of 0.34 mg m^{-3} in the more productive Levantine coastal waters and 0.31 mg m^{-3} in Rhodes Gyre.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.oceano.2017. 12.003.

References

- Berman, T., Bronk, D.A., 2003. Dissolved organic nitrogen: a dynamic participant in aquatic ecosystems. Aquat. Microb. Ecol. 31, 279– 305, http://dx.doi.org/10.3354/ame031279.
- Bronk, D.A., See, J.H., Bradley, P., Killberg, L., 2007. DON as a source of bioavailable nitrogen for phytoplankton. Biogeosciences 4, 283–296, http://dx.doi.org/10.5194/bg-4-283-2007.
- Ediger, D., Tuğrul, S., Yılmaz, A., 2005. Vertical profiles of particulate organic matter and its relationship with chlorophyll-*a* in the upper layer of northeastern Mediterranean. J. Mar. Syst. 55 (3–4), 311– 326, http://dx.doi.org/10.1016/j.jmarsys.2004.09.003.
- Ediger, D., Yılmaz, A., 1996. Characteristics of deep chlorophyll maximum in the North-eastern Mediterranean with respect to

environmental conditions. J. Mar. Syst. 9 (3–4), 291–303, http://dx.doi.org/10.1016/s0924-7963(96)00044-9.

- Egge, J.K., Asknes, D.L., 1992. Silicate as regulating nutrient in phytoplankton competition. Mar. Ecol. -Prog. Ser. 83, 281–289, http://dx.doi.org/10.3354/meps083281.
- Eker, E., Kideyş, A.E., 2000. Weekly variations in phytoplankton community structure of a harbour in Mersin Bay (north-eastern Mediterranean). Turk. J. Bot. 24, 13–24.
- Eker-Develi, E., Kideyş, A.E., Tuğrul, S., Yılmaz, D., Ediger, D., 2003. Phytoplankton dynamics in the Northeastern Mediterranean with respect to relative dust deposition. In: Yılmaz, A. (Ed.), Proceedings of the Second International Conference on "Oceanography of the Eastern Mediterranean and Black Sea: Similarities and Differences of Two Interconnected Basins", 14–18 October 2002. METU Cultural and Convention Center, Tubitak Publ., Ankara, Turkey, 686–694, (in Turkish).
- Falkowski, P., Raven, J.A., 2007. Aquatic Photosynthesis, 2nd ed. Princeton Univ. Press, ISBN-13: 978-0691115511, 500 pp.
- Finkel, Z.V., Katz, M.E., Wright, J.D., Schofield, O.M.E., Falkowski, P. G., 2005. Climatically driven microevolutionary patterns in the size of marine diatoms over the Cenozoic. Proc. Natl. Acad. Sci. U. S. A. 102 (25), 8927–8932, http://dx.doi.org/10.1073/ pnas.0409907102.
- Finkel, Z.V., Beardall, J., Flynn, K.J., Quigg, A., Rees, T.A.V., Raven, J.A., 2009. Phytoplankton in a changing world: cell size and elemental stoichiometry. J. Plankton Res. 32 (1), 119–137, http://dx.doi.org/10.1093/plankt/fbp098.
- Fogg, G.E., 1991. The phytoplanktonic ways of life. New. Phytol. 118 (2), 191–232, http://dx.doi.org/10.1111/j.1469-8137.1991.tb00974.x.
- Ghiglione, J.F., Larcher, M., Lebaron, P., 2008. Spatial and temporal scales of variation in bacterioplankton community structure in the NW Mediterranean Sea. Aquat. Microb. Ecol. 40 (3), 229–240, http://dx.doi.org/10.3354/ame040229.
- Grasshoff, K., Ehrhardt, M., Kremling, K., 1983. Methods of Seawater Analysis. Verlag Chemie, Weinheim, 237 pp.
- Guerzoni, S., Chester, R., Dulac, F., Herut, B., Loye-Pilot, M.D., Measures, C., Migon, C., Molinaroli, E., Moulin, C., Rossini, P., Saydam, C., Soudine, A., Ziveri, P., 1999. The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea. Prog. Oceanogr. 44 (1–3), 147–190, http://dx.doi.org/ 10.1016/s0079-6611(99)00024-5.
- Herut, B., Zohary, T., Krom, M.D., Mantoura, R.F.C., Pitta, P., Psarra, S., Rassoulzadegan, F., Tanaka, T., Thingstad, T.F., 2005. Response of East Mediterranean surface water to Saharan dust: on-board microcosm experiment and field observations. Deep-Sea Res. Pt. II 52 (22–23), 3024–3040, http://dx.doi.org/ 10.1016/j.dsr2.2005.09.003.
- Karl, D., Letelier, R., Tupas, L., Dore, J., Christian, J., Hebel, D., 1997. The role of nitrogen fixation in biogeochemical cycling in the subtropical North Pacific Ocean. Nature 388 (6642), 533–538, http://dx.doi.org/10.1038/41474.
- Kıdeyş, A.E., Ünsal, M., Bingel, F., 1989. Seasonal changes in net phytoplankton off Erdemli, northeastern Mediterranean, DOĞA. Turk. J. Bot. 13 (1), 45–54.
- Koçak, M., Kubilay, N., Tuğrul, S., Mihalopoulos, N., 2010. Atmospheric nutrient inputs to the northern Levantine basin from a long-term observation: sources and comparison with riverine inputs. Biogeosciences 7 (12), 4037–4050, http://dx.doi.org/ 10.5194/bg-7-4037-2010.
- Kress, N., Herut, B., 2001. Spatial and seasonal evolution of dissolved oxygen and nutrients in the Southern Levantine Basin (Eastern Mediterranean Sea): chemical characterisation of the water masses and inferences on the N:P ratios. Deep-Sea Res. Pt. I 48 (11), 2347–2372, http://dx.doi.org/10.1016/S0967-0637(01) 00022-X.
- Krom, M.D., Emeis, K.C., Van Cappellen, P., 2010. Why is the Eastern Mediterranean phosphorus limited? Prog. Oceanogr. 85 (3-4), 236–244, http://dx.doi.org/10.1016/j.pocean.2010.03.003.

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- Krom, M.D., Kress, N., Brenner, S., Gordon, L.I., 1991. Phosphorus limitation of primary productivity in the eastern Mediterranean. Limnol. Oceanogr. 36 (3), 424–432, http://dx.doi.org/10.4319/ lo.1991.36.3.0424.
- Krom, M.D., Herut, B., Mantoura, R.F.C., 2004. Nutrient budget for the Eastern Mediterranean: implications for P limitation. Limnol. Oceanogr. 49 (5), 1582–1592, http://dx.doi.org/10.4319/ lo.2004.49.5.1582.
- Krom, M.D., Woodward, E.M.S., Herut, B., Kress, N., Carbo, P., Mantoura, R.F.C., et al., 2005. Nutrient cycling in the south east Levantine basin of the Eastern Mediterranean: results from a phosphate starved system. Deep-Sea Res. Pt. II 52 (22–23), 2879– 2896, http://dx.doi.org/10.1016/j.dsr2.2005.08.009.
- Li, W.K.W., Zohary, T., Yacobi, Y.Z., Wood, A.M., 1993. Ultraphytoplankton in the eastern Mediterranean Sea: towards deriving phytoplankton biomass from flow cytometric measurements of abundance, fluorescence and light scatter. Mar. Ecol. -Prog. Ser. 102, 79–87, http://dx.doi.org/10.3354/meps102079.
- Markaki, Z., Oikonomou, K., Kocak, M., Kouvarakis, G., Chaniotaki, A., Kubilay, N., Mihalopoulos, N., 2003. Atmospheric deposition of inorganic phosphorus in the Levantine Basin, eastern Mediterranean: spatial and temporal variability and its role in seawater productivity. Limnol. Oceanogr. 48 (4), 1557–1568, http://dx. doi.org/10.4319/lo.2003.48.4.1557.
- Moore, L.R., Post, A.E., Rocap, G., Chisholm, S.W., 2002. Utilization of different nitrogen sources by the marine cyanobacteria *Prochlorococcus* and *Synechococcus*. Limnol. Oceanogr. 47 (4), 989– 996, http://dx.doi.org/10.4319/lo.2002.47.4.0989.
- Moutin, T., Thingstad, T.F., Wambeke, F.V., Mariei, D., Raimbault, P., Slawyk, G., Claustre, H., 2002. Does competition for nanomolar phosphate supply explain the predominance of the cyanobacterium Synechococcus? Limnol. Oceanogr. 47 (5), 1562–1567, http://dx.doi.org/10.4319/lo.2002.47.5.1562.
- Oksanen, J., Blanchet, F.G., Kindt, R., Legendre, P., Minchin, P.R., O'Hara, R.B., Simpson, G.L., Solymos, P., Stevens, M.H.H., Wagner, H., 2012. Vegan: Community Ecology Package, Version 2.0-4, http://cran.r-project.org/web/packages/vegan//index.html.
- O'reilly, E.J., Zetlin, C., 1998. Seasonal, horizontal and vertical distribution of phytoplankton chlorophyll Northeast US continental shelf ecosystems. Report NMFS 139. A Tech. Rep. the Fishery Bulletin. U.S. Department of Commerce, Seattle, WA, 126 pp.
- Pantoja, S., Repeta, D.J., Sachs, J.P., Sigman, D.M., 2002. Stable isotope constraints on the nitrogen cycle of the Mediterranean Sea water column. Deep Sea Res. Pt. I 49 (9), 1609–1621, http:// dx.doi.org/10.1016/s0967-0637(02)00066-3.
- Polat, S., Avşar, D., Işık, O., Çiçek, E., 2000. Interrelationships between phytoplankton abundance and physico-chemical parameters in Yumurtalık Bight, northeastern Mediterranean. J. Fish. Aquat. Sci. 17 (3–4), 129–142.http://www.egejfas.org/ download/article-file/57255.
- Psarra, S., Zohary, T., Krom, M.D., Mantoura, R.F.C., Polychronaki, T., Stambler, N., Tanaka, T., et al., 2005. Phytoplankton response to a Lagrangian phosphate addition in the Levantine Sea (Eastern Mediterranean). Deep Sea Res. Pt. II 52 (22–23), 2944–2960, http://dx.doi.org/10.1016/j.dsr2.2005.08.015.
- R Core Team, 2012. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, https://www.gbif.org/tool/81287/ r-a-language-and-environment-for-statistical-computing.
- Riemann, B., Havskum, H., Thingstad, F., Bernard, C., 1995. The role of mixotrophy in pelagic environments. In: Joint, I. (Ed.), NATO AS1 Series, Molecular Ecology of Aquatic Microbes, vol. 38. Springer-Verlag, Berlin, 87–114, http://dx.doi.org/10.1007/978-3-642-79923-5_6.
- Romero, E., Peters, F., Guadayol, Ò., 2013. The interplay between mild physicochemical forcing and plankton dynamics in a coastal area. Limnol. Oceanogr. 58 (3), 903–920, http://dx.doi.org/ 10.4319/lo.2013.58.3.0903.

- Roussenov, V., Williams, R.G., Mahaffey, C., Wolff, G.A., 2006. Does the transport of dissolved organic nutrients affect export production in the Atlantic Ocean? Glob. Biogeochem. Cycles 20, GB3002, http://dx.doi.org/10.1029/2005GB002510.
- Siokou-Frangou, I., Christaki, U., Mazzocchi, M.G., Montresor, M., Ribera d'Alcalá, M., Vaqué, D., Zingone, A., 2010. Plankton in the open Mediterranean Sea: a review. Biogeosciences 7 (5), 1543– 1586, http://dx.doi.org/10.5194/bg-7-1543-2010.
- Steemann Nielsen, E., 1952. The use of radioactive carbon (C14) for measuring organic production in the sea. ICES J. Mar. Sci. 18 (2), 117–140, http://dx.doi.org/10.1093/icesjms/18.2.117.
- Strickland, J.D.H., Parsons, T.R., 1972. A practical handbook of seawater analysis. Bull. Fish. Res. Board. Can. 167, 1–130.
- Thingstad, T.F., Krom, M.D., Mantoura, R.F.C., Flaten, G.A.F., Groom, S., Herut, B., Kress, N., Law, S.C., Pasternak, A., Pitta, P., Psarra, S., Rassoulzadegan, F., Tanaka, T., Tselepides, A., Wassmann, P., Woodward, E.M.S., Wexels Riser, C., Zodiatis, G., Zohary, T., 2005. Nature of phosphorus limitation in the ultraoligotrophic eastern Mediterranean. Science 309 (5737), 1068–1071, http:// dx.doi.org/10.1126/science.1112632.
- Tugrul, S., Yucel, N., Akçay, I., 2016. Chemical oceanography of the northeastern Mediterranean. In: Turan, C., Salihoğlu, B., Özgür-Özbek, E., Öztürk, B. (Eds.), The Turkish Part of Mediterranean Sea Marine Biodiversity, Fisheries Conservation and Governance. Turkish Marine Research Foundation (TUDAV), Istanbul, 15–29. http://www.tudav.org/images/2016/documents/ MEDITERRANEAN SEA 2016.pdf.
- Torres-Valdes, S., Roussenov, V.M., Sanders, R., Reynolds, S., Pan, S., Mather, R., Landolfi, A., Wolff, G.A., Achterberg, E.P., Williams, R.G., 2009. Distribution of dissolved organic nutrients and their effect on export production over the Atlantic Ocean. Glob. Biogeochem. Cycles 23 (4), GB4019, http://dx.doi.org/ 10.1029/2008GB003389.
- Uysal, Z., Senichkina, L., Kuzmenko, L., Georgieva, L., Altukhov, D., 2003. Weekly changes in phytoplankton species composition, diversity, abundance, and biomass across the northern Levantine basin shelf waters. In: Yılmaz, A. (Ed.), Proceedings of the Second International Conference on "Oceanography of the Eastern Mediterranean and Black Sea: Similarities and Differences of Two Interconnected Basins, 14–18 October 2002. METU Cultural and Convention Center, Tubitak Publ, Ankara, 680–686, (in Turkish).
- Uysal, Z., Yıldız, Y.Ç., Tuğrul, S., 2004. Levantin baseni pikoplankton (heterotrofik bakteri ve cyanobakteri) içerik ve dinamikleri. Tubitak Publ, Ankara, 67 pp., (in Turkish).
- Uysal, Z., 2006. Vertical distribution of marine cyanobacteria *Synechococcus* spp. in the Black, Marmara, Aegean, and eastern Mediterranean seas. Deep Sea Res. 2 Top. Stud. Ocanogr. 53 (17–19), 1976–1987, http://dx.doi.org/10.1016/j.dsr2.2006.03.016.
- Uysal, Z., Latif, M.A., Özsoy, E., Tuğrul, S., Kubilay, N., Beşiktepe, Ş. T., Yemenicioğlu, S., Mutlu, E., Ediger, D., Beşiktepe, Ş., Ediger, V., Ak Örek, Y., Örek, H., Demirel, M., Tunç, Ş.Ç., Terbıyık, T., 2008. Kilikya Baseni Kıyısal Ekosisteminde Dolaşım. Taşınım ve Ötrofikasyon Araştırmaları Project No: 104Y277. Erdemli-Mersin, (in Turkish).
- Uysal, Z., Köksalan, İ., 2010. Synechococcus dynamics in the Levantine basin shelf waters (northeastern Mediterranean). Mediterr. Mar. Sci. 11 (2), 277–294, http://dx.doi.org/10.12681/mms.77.
- Uysal, Z., Köksalan, İ., 2017. Short term temporal and spatial fluctuations in marine cyanobacterium *Synechococcus* abundance in oligotrophic deep shelf water (northeastern Mediterranean). Fresenius Environ. Bull. 26 (8), 5115–5124.
- Wang, X.J., Behrenfeld, M., Le Borgne, R., Murtugudde, R., Boss, E., 2009. Regulation of phytoplankton carbon to chlorophyll ratio by light, nutrients and temperature in the Equatorial Pacific Ocean: a basin-scale model. Biogeosciences 6, 391–404, http://dx.doi. org/10.5194/bg-6-391-2009.
- Yayla, M.K., 1999. Primary Production, Availability and Uptake of Nutrients and Photo-Adaptation of Phytoplankton in The Black

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Sea, The Sea of Marmara and the Eastern Mediterranean. (M.Sc. thesis). Institute of Marine Science, Middle East Technical Univ, Mersin, Turkey, 128 pp.

- Yılmaz, A., Tugrul, S., 1998. The effect of cold- and warm-core eddies on the distribution and stoichiometry of dissolved nutrients in the Northeastern Mediterranean. J. Mar. Syst. 16 (3–4), 253–268, http://dx.doi.org/10.1016/s0924-7963(97)00022-5.
- Yilmaz, D., 2006. Temporal Variation of Phytoplankton in the Northeastern Shelf of Mediterranean Sea: Composition, Pigment Signature and Production. (Ph.D. thesis). Institute of Marine Science, Middle East Technical Univ, Mersin, Turkey, 165 pp.
- Yucel, N., 2008. Phytoplankton Pigment Distribution in the Cilician Basin (Northeastern Mediterranean). (M.Sc. thesis). Institute

of Marine Science, Middle East Tech. Univ, Mersin, Turkey, 175 pp.

- Yucel, N., 2013. Monthly Changes in Primary and Bacterial Productivity in the North-Eastern Mediterranean Shelf Waters. (Ph.D. thesis). Institute of Marine Science, Middle East Tech. Univ, Mersin, Turkey, , 179 pp., http://etd.lib.metu.edu.tr/upload/ 12616125/index.pdf.
- Yucel, N., 2017. Seasonal and spatial variation of bacterial production and abundance in the northern Levantine Sea. Mediterr. Mar. Sci. 18 (1), 97–106, http://dx.doi.org/10.12681/mms.1627.
- Yucel, N., Uysal, Z., Tugrul, S., 2017. Variability in phytoplankton pigment composition in Mersin Bay. Turk. J. Aquat. Sci. 32 (1), 49–70, http://dx.doi.org/10.18864/tjas201705.