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On the production, elemental composition (C, N, P) and distribution of photosynthetic organic matter in the Southern Black Sea

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Abstract

Chemical oceanographic understanding of the southern Black Sea has been improved by recent measurements of the optical transparency, phytoplankton biomass (in terms of chlorophyll-a and particulate organic matter) and primary productivity. During the spring-autmun period of 1995–1996, light generally penetrated only into the upper 15–40 m, with an attenuation coefficient varying between 0.125 and 0.350 m^{-1}. The average chlorophyll-a (Chl-a) concentrations for the euphotic zone ranged from 0.1 to 1.5 $\mu g\ l^{-1}$. Coherent sub-surface Chl-a maxima were formed near the base of the euphotic zone only in summer. Production rate varied between 247 and 1925 in the spring and between 405 and 687 mgC $m^{-2}\ d^{-1}$ in the summer-autumn period. The average POM concentrations in the euphotic zone varied regionally and seasonally between 3.8 and 28.6 μm for POC, 0.5 and 3.1 μm for PON and 0.02 and 0.1 μm for PP. Atomic ratios of C/N, C/P and N/P, derived from the regressions of POM data, ranged between 7.5 and 9.6, 109 and 165, and 11.2 and 16.6, respectively. In the suboxic/anoxic interface, the elemental ratios change substantially due to an accumulation of PP cohering to Fe and Mn oxides. The chemocline boundaries and the distinct chemical features of the oxic/anoxic transition layer (the so-called suboxic zone) are all located at specific density surfaces; however, they exhibit remarkable spatial and temporal variations both in their position and in their magnitude, which permit the definition of long-term changes in the biochemical properties of the Black Sea upper layer.

Introduction

The Black Sea, a relatively large, deep, landlocked basin, is connected to the Sea of Marmara through the narrow and shallow Bosphorus Strait (Figure 1). Low saline Black Sea waters are transported to the Mediterranean while a counterflow in the Bosphorus introduces more saline Mediterranean waters into the Black Sea via the Sea of Marmara. There exists a permanent and strong halocline at depths of 50–150 m, shoaling in the cyclonic gyres and deepening in the coastal regions. Continuous transport of biogenic particles from the productive surface to the lower layers, combined with limited vertical ventilation through the permanent halocline, provides the major reasons for the anoxic and sulphidic condition of the subhalocline waters.

In addition to these natural processes, the increasing input of nutrients and organic matter from the land via the rivers and the discharge of wastes have, during the last two decades, generated dramatic changes in the Black Sea ecosystem, especially in the wide northwestern shelf (Mee, 1992; Bologa, 1985/1986; Bologa et al., 1995; Cociasu et al., 1996, 1997). Long-term modifications and collapses of the biological structure of the ecosystem have been well documented

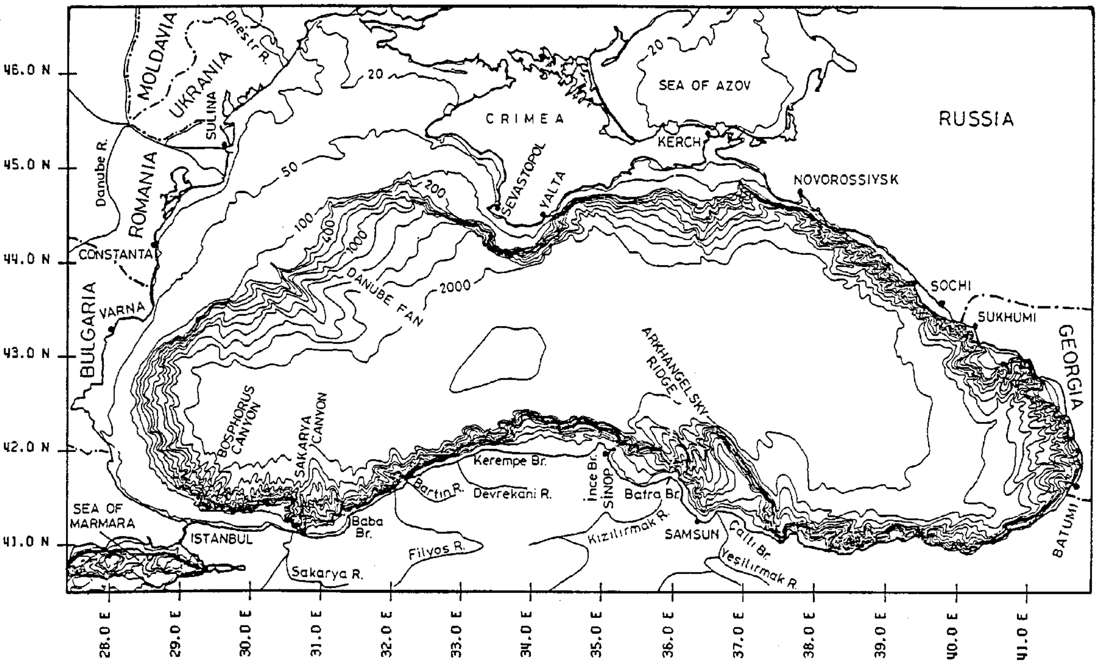

Figure 1. Bathymetry and location map of the Black Sea.

(Bodeanu, 1992; Mee, 1992; Shuskina et al., 1990; Smayda, 1990; Vinogradov et al., 1989; Bologa et al., 1995). However, the lack of good quality historical data of high resolution impairs understanding of how the recent anthropogenic inputs and climatic changes have influenced nutrient and organic carbon pools of the Black Sea. Nevertheless, comparison of the limited earlier measurements with the high-resolution data obtained since 1988 has enabled several workers to address the magnitude of the long-term changes in the nutrient and oxygen profiles from the upper layer down to the sulphide-bearing waters of the deep basin (Murray et al., 1989, 1991, 1994; Kempe, 1991; Cadispoti et al., 1991; Tuğrul et al., 1992; Baştürk et al., 1994). Similar changes have been observed in the nutrient chemistry of the waters of the polluted northwestern shelf (Cociasu et al., 1997).

According to Sorokin (1983) and Vedernikov & Demidov (1993), primary production in the Black Sea displays two phytoplankton maxima throughout the year; the major one occurs in early spring while a secondary peak appears in autumn. Recently, additional summer blooms have frequently been observed in both the coastal and open waters (Hay & Honjo, 1989; Hay et al., 1990, 1991; Sur et al., 1996). Primary production is relatively low in the open sea (50–200 gC m^{-2} y^{-1}) compared to the northwestern shelf area (up to 400 gC m^{-2} y^{-1}) (Vedernikov & Demidov, 1993; Bologa et al., 1985/1986), where there are riverine discharges of nutrients (Cociasu et al., 1997). Since input of nutrients from the anoxic layer through the permanent pycnocline is limited both by denitrification and by oxidation-reduction processes occurring in the oxic/anoxic transition layer, the major nutrient source for the open system is the input from the nutricline (Murray et al., 1995). New production in the open waters of the Black Sea is therefore dominated by the input from the nutricline/coinciding with the oxycline/riverine input via surface circulations and atmospheric transport probably being of secondary importance; consequently the rates of new production in the Black Sea are low (Murray et al., 1995; Oğuz et al., 1996).

In the present paper, we have evaluated high-resolution hydrographic data, light penetration phenomena, dissolved oxygen and hydrogen sulphide, dissolved inorganic nutrients, the elemental composition (C, N, P) of particulate organic matter and the photosynthetic carbon production rates measured seasonally in 1995 and 1996. In this context, we discuss the magnitudes of the spatial and temporal changes in the principal chemical and biological features of the Black Sea upper layer down to the sulphide-bearing waters.

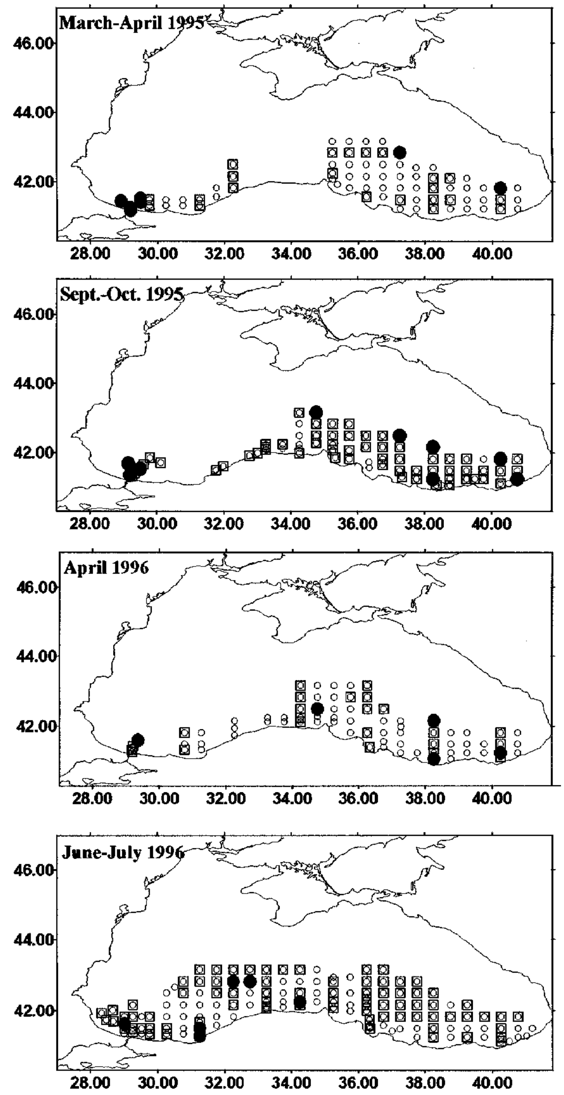

Figure 2. Station networks of the 1995–1996 cruises conducted in the southern Black Sea. Symbols denote different sampling strategies: ○ = Hydrophysical stations, □ = Hydrochemical stations and ● = Biological stations.

Methodology

Area of Study: Basin-wide cruises in the southern Black Sea surveyed the Turkish Economic Zone in March–April 1995, September–October 1995, April 1996 and June–July 1996. The cooperative marine science programmes (CoMSBlack and NATO TU-Black Sea) between the Black Sea riparian countries were initiated in early 1990s and the basinwide data are published by the joint groups. The station networks of the four cruises are illustrated in Figure 2. Hydrographic measurements were carried out on a regular 0.5° grid system for determining the physical boundaries of the cyclonic and anticyclonic circulations and the sub-basin scale variations of the hydrography. The locations of stations for biochemical studies were selected both by reference to observations from earlier years and by examining real-time CTD measurements. Previous studies clearly demonstrate the physical oceanography of the Black Sea upper layer to be dominated by the quasi-permanent cyclonic gyres in the the eastern and western halves of the basin (Figure 3). The two gyres are separated from a series of anticyclonic eddies in the coastal zone by the cyclonically undulating Rim current (Oğuz et al., 1991, 1993). The influence of the freshwater input, mainly from the Danube, Dnepr and Dnester rivers at the northwestern shelf, can be traced down to the Bosphorus region (Sur et al., 1996).

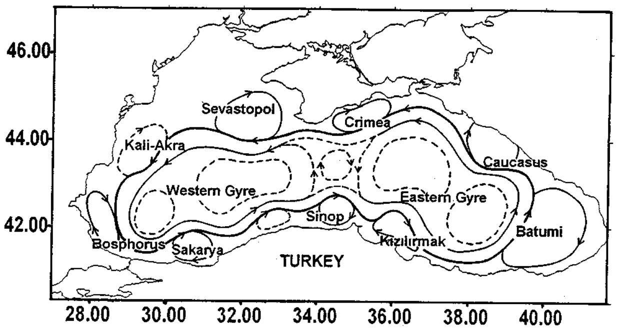

Figure 3. Schematic representation of the main features of the upper layer general circulation of the Black Sea (After Oğuz et al., 1993).

Sampling and analysis: The hydrographic data were collected using a Sea-Bird Model 9 CTD probe. A Licor 185 Model quantameter was used for solar irradiance measurements in the euphotic zone. This instrument measures Photosynthetically Active Radiation (PAR) within the range of 400–700 nm, in μE m^{-2} s^{-1} unit. Water samples were collected with General Oceanic Go-Flo Rosette bottles attached to the CTD. The analyses of nutrient samples – kept frozen in HDPE for a few weeks – were carried out using a Technicon Model two-channel Autoanalyzer. The colorimetric methods followed were similar to those described by Strickland & Parsons (1972) and Grasshoff et al. (1983). Chlorophyll-a (Chl-a) samples were collected from the euphotic zone down to the depth of 0.1% of surface light. Samples concentrated on GF/F filters were extracted with 90% acetone solu-

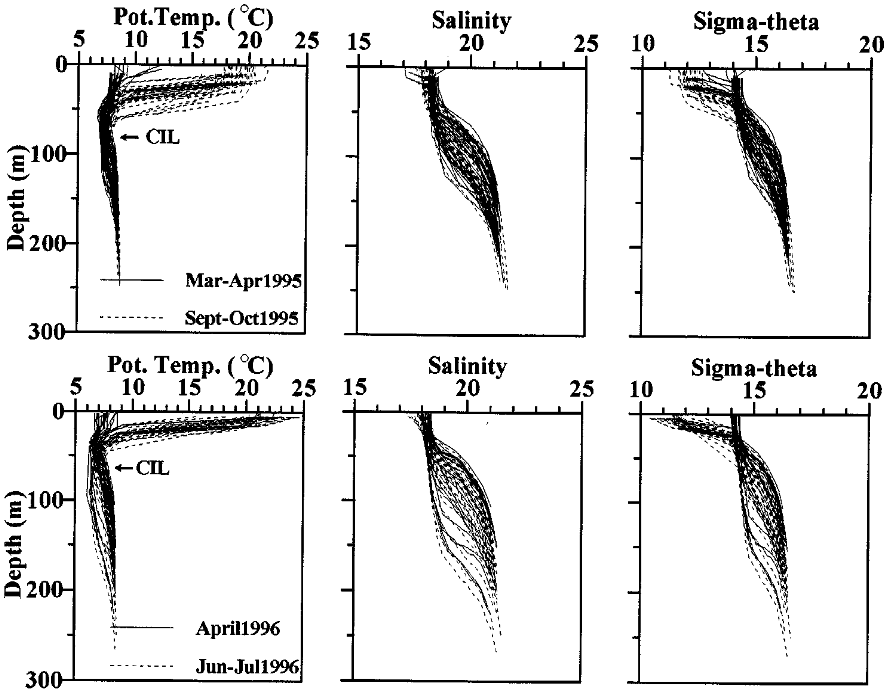

Figure 4. Potential Temperature (˚C), Salinity and Sigma-theta profiles in the upper layer of the southern Black Sea for the 1995–1996 period (unpublished data, METU, Institute of Marine Sciences, Physical Oceanography Section).

tion. The fluorescence intensity of clear extracts was then measured (Strickland & Parsons, 1972; Holm-Hansen & Riemann, 1978), using a Hitachi F-3000 Model spectrofluorometer. A commercially available Chl-a standard obtained from Sigma was used to quantify the sample intensities. Particulate organic matter (POM) collected on GF/F filters (pre-combusted at 450–500 ˚C) for carbon (POC) and nitrogen (PON) and phosphorus (PP) measurements were kept frozen until processing on land. The POC and PON samples were dried at 50–60 ˚C overnight and then exposed to concentrated HCl fumes to remove inorganic carbonates. Filters were dried again and kept in a vacuum desiccator until analysis by the dry combustion method (Polat & Tuğrul, 1995), using a Carlo Erba Model 1108 CHN analyzer. The PP samples were first exposed to dry combustion at 500 ˚C for 2 h and then treated with 10 ml of 2N HCl for 10 h and filtered (Polat & Tuğrul, 1995). After the adjustment of pH to 8.0, the oxidized phosphorus in the solution was determined colorimetrically by the routine ortho-phosphate method. Dissolved oxygen (DO) and H_2S concentrations were determined by conventional Winkler and iodometric titration (Baştürk et al., 1994) while low H_2S concentrations were determined by the colorimetric method (Cline, 1969). The rates of carbon fixation by phytoplankton in the samples taken from the surface and from 90%, 75%, 50%, 25%, 10%, 1% and 0.1% surface light depths were determined by tracing the conversion of dissolved inorganic radioactive carbon (^{14}C) into particulate organic carbon. The original methodology (Steemann-Nielsen, 1952) was followed with slight modifications (Richardson, 1991). Incubator experiments were performed under artificial growth conditions.

Results

Hydrographic properties: The composite depth profiles of Potential Temperature, Salinity and Density (Sigma-$\theta = \sigma_t$) from the southern Black Sea demonstrate that throughout the seasons of stratification a nearly isohaline and relatively cool, isothermal water mass exists below the seasonal pycnocline (Figure 4). This prominent and persistent feature of the Black Sea, termed the Cold Intermediate Layer (CIL), possesses a temperature minimum which is characterised by the 8 ˚C limiting isotherms (Oğuz et al., 1991). The thickness of the CIL is larger (up to 100 m) in the anticy-

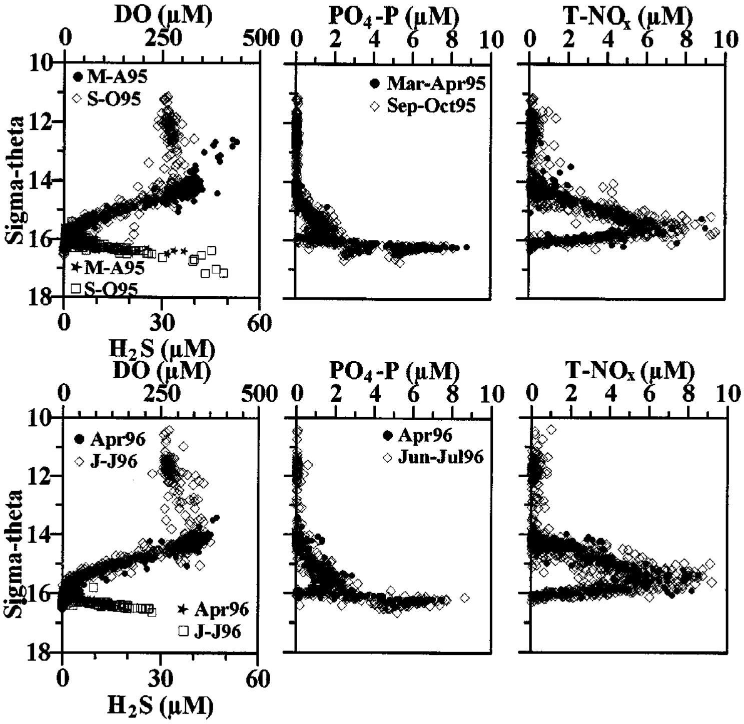

Figure 5. Vertical distribution of Dissolved Oxygen (DO) – H_2S and Dissolved Nutrients (PO_4–P and Total Oxidized Nitrogen = T–NO_x) in the upper layer of the southern Black Sea for the 1995–1996 period. Sigma-theta was used instead of depth on the vertical scale.

clonic regions (ACR) than in the cyclonic regions (CR) (about 50 m). The σ_t = 14.8 isopycnal surface defines not only the temperature minimum within the CIL but also the upper boundary of the permanent pycnocline in the Black Sea (Buesseler et al., 1994; Murray et al., 1991). In the CIL, the salinity varies slightly from nearly 18.5 to 20.1 ppt. The profiles illustrated in Figure 4 show that, in winter, when the surface waters cool down to 6–7 °C, the upper layer is thoroughly homogenized by convective mixing down to the σ_t = 14.7–14.8 isopycnal surfaces. With the advent of heating in spring and summer, the surface temperatures rise to 20–25 °C and the CIL becomes topped by a warm surface layer (Figure 4). Below the CIL, the temperature gradually rises from 8 °C to 8.7 °C at the base of the permanent pycnocline; this is observed at different depths (Figure 4). The subhalocline waters possess similar temperatures at similar density surfaces over the entire deep basin though isohalines appear at different depths from the deep to the coastal regions. Composite density profiles demonstrate coherent seasonal changes in the surface layer due to the significant changes in the surface temperature during the year. On the contrary, the density of the water masses below the CIL is mainly determined by their salinity. This salinity-determined density gradient (the permanent pycnocline) is located at shallower depths in cyclonic but at much deeper layers in anticyclonic regions. Below the permanent pycnocline the density increases very slowly with depth, the values being similar at any given depth whatever the region (Figure 4).

Chemical properties: The composite chemical profiles down to the anoxic waters were plotted relative to water density (rather than depth) as a vertical scale (Figure 5). As recently indicated by Tuğrul et al. (1992), Baştürk et al. (1994) and Murray et al. (1995), composite profiles from hydrodynamically different regions exhibit characteristically similar vertical features below the euphotic zone down to the upper anoxic layer.

Dissolved Oxygen (DO): Figure 5 shows the surface layer down to the temperature minimum in the CIL to be nearly saturated with dissolved oxygen (DO = 250–450 μM). The lower DO values in the productive surface waters are due to the decreasing solubility at higher temperatures during stratification. The concentra-

Table 1. Average nutrient [phosphate (PO_4-P) and total oxidized nitrogen (T-NO_x = NO_3 + NO_2-N)] concentrations [(μM), from the surface down to σ_t = 14.5] in the southern Black Sea.

Location	Mar–Apr 1995		Sept–Oct 1995		April 1996		June–July 1996	
	PO_4-P	T-NO_x	PO_4-P	T-NO_x	PO_4-P	T-NO_x	PO_4-P	T-NO_x
Bosphorus	0.04	0.42	0.08	1.07	0.24	0.56	0.12	0.55
Western Cyclone	–	–	–	–	–	–	0.15	0.26
Eastern Cyclone	0.05	0.24	0.06	0.28	0.21	0.63	0.04	0.16
Batumi Anticyclone	0.05	0.55	0.03	0.43	0.35	0.76	0.07	0.98
Off Sakarya	0.09	0.79	–	–	0.08	1.48	0.03	0.53
Off Sinop	–	–	0.05	0.34	0.06	0.52	0.06	0.84

tions decrease steeply in the upper depths of the permanant pycnocline from 200–250 μm at the σ_t = 14.2–14.8 density surfaces to suboxic concentrations of 20–30 μm at the σ_t = 15.4–15.6 surfaces, these surfaces defining the upper and lower boundaries of the main oxycline. Throughout summer and autumn, stratification limits the normal ventilation of the CIL by vertical mixing. Under these circumstances, as recently indicated by Baştürk et al. (1997a), the oxycline commences at greater density surfaces (σ_t = 14.4–14.5) but at shallower depths (35–40 m) in cyclonic regions (CR), than in the frontal zones of the Rim Current (RCFZ) or in anticyclonic regions (ACR) where the onset is located at σ_t = 14.2–14.3 (70–100 m). Below the main oxycline, DO declines slowly to < 5 μm at σ_t = 15.9–16.0, and can no longer be detected at the σ_t = 16.15–16.20 density surfaces where sulphide concentrations are 1–3 μm (Figure 5). This DO-deficient water, formed within the oxic/anoxic transition layer with DO < 20 μM and $H_2S < 1$ μM, is called the suboxic zone. Sulphide-bearing waters were consistently observed at density surfaces of $>$ 16.15–16.2 over the entire deep basin. In the upper anoxic layer, the H_2S concentration increased steadily with depth (Figure 5), showing insignificant spatial or temporal variation at any density surface.

Phosphate (PO_4) and T-NO_x (NO_3 + NO_2) Distributions: As previously emphasized by Baştürk et al. (1994), Bingel et al. (1993) and Codispoti et al. (1991), the surface waters of the southern Black Sea are always poor in nutrients during the seasons when these waters are stratified. In the spring-autumn period of 1995–1996, average concentrations in the euphotic zone ranged regionally and seasonally from 0.16 to 1.5 μm for T-NO_x (mainly NO_3) and from 0.03 to 0.35 μm for phosphate (Table 1). The limited nutrient data from previous years (Bingel et al., 1993) together with modelling studies (Oğuz et al., 1996) indicate that intense vertical mixing in winter provides input from the nutricline which may increase surface nitrate concentrations 5–10-fold so that primary productivity becomes light-limited. Composite profiles of T-NO_x and phosphate indicate that, below the euphotic zone, nutrient concentrations increase with increasing density down to the base of the main oxycline (Figure 5). The nitrate concentrations display a well-defined maximum of 5–9 μm between the 15.4–15.6 density surfaces defining the upper boundary of the suboxic zone where DO concentrations decrease to 20–30 μm. In the suboxic zone, due to denitrification, nitrate concentrations decline steadily to 0.1–0.2 μm at the suboxic/anoxic interface. Nitrate then becomes reduced by sulphide in the upper anoxic waters until to undetectable levels. Phosphate concentrations increase within the oxycline to a maximum in the upper suboxic zone or at the σ_t = 15.6–15.7 isopycnal surfaces. Below this broad maximum, phosphate concentrations decline steeply in the cyclonic regions (CR), forming a pronounced minimum (0.05–0.10 μm) at the σ_t = 15.85–15.90 isopycnal surfaces. This feature is less marked in coastal regions and it is nearly imperceptible within the RCFZ. Nevertheless, throughout the deep basin phosphate profiles always increase steeply within the sulphidic water interface and reach peak values of 5–8 μm at σ_t = 16.2 isopycnal surface. Phosphate concentrations decrease slightly in the upper anoxic layer and then increase again slightly with depth. The occurrence throughout the deep basin of the marked maximum at the sulphidic boundary probably results from dissolution of phosphate-associated Fe- and Mn-oxides in the anoxic waters (Shaffer, 1986; Codispoti et al., 1991).

Primary productivity and related parameters: Vertical profiles of POC, PON and PP in the upper water column show remarkable variations with depth, region

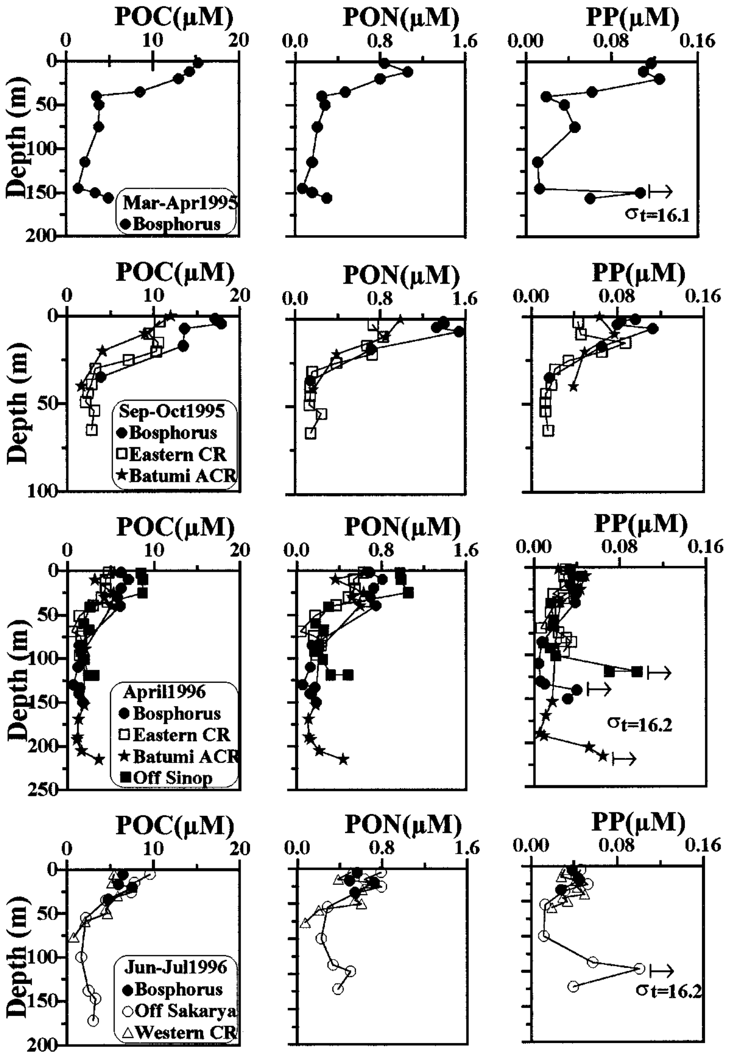

Figure 6. Vertical profiles of Particulate Organic Carbon (POC), Nitrogen (PON) and Total Particulate Phosphorus (PP) obtained in the southern Black Sea for the 1995–1996 period.

Table 2a. Average POM concentrations (μM) in the euphotic zone of the southern Black Sea.

Location	Mar–Apr 1995			Sept–Oct 1995			April 1996			June–July 1996		
	POC	PON	PP	POC	PON	PP	POC	PON	PP	POC	PON	PP
Bosphorus	28.6	3.1	0.115	12.6	1.03	0.075	6.3	0.74	0.036	6.2	0.58	0.038
Western Cyclone	–	–	–	–	–	–	–	–	–	5.5	0.56	0.034
Eastern Cyclone	–	–	–	8.7	0.59	0.046	3.8	0.48	0.024	–	–	–
Batumi Anticyclone	–	–	–	8.2	0.73	0.065	4.6	0.55	0.035	–	–	–
Off Sakarya	–	–	–	–	–	–	–	–	–	7.4	0.65	0.043
Off Sinop	–	–	–	–	–	–	8.6	1.00	0.039	–	–	–

Table 2c. POM elemental composition (molar ratios calculated from individual data) for the euphotic zone of the southern Black Sea.

Location	Mar–Apr 1995			Sept–Oct 1995			April 1996			June–July 1996		
	C/P	C/N	N/P	C/P	C/N	N/P	C/P	C/N	N/P	C/P	C/N	N/P
Bosphorus	231	11.2	22.6	168	12.2	13.7	175	8.5	20.0	168	10.8	15.6
Western Cyclone	–	–	–	–	–	–	–	–	–	131	10.2	16.1
Eastern Cyclone	–	–	–	193	15.6	13.1	158	7.9	20.0	–	–	–
Batumi Anticyclone	–	–	–	126	11.2	11.1	131	8.3	15.7	–	–	–
Off Sakarya	–	–	–	–	–	–	–	–	–	170	10.6	16.2
Off Sinop	–	–	–	–	–	–	220	8.6	25.0	–	–	–

Table 2b. POM elemental composition (derived from regression analysis) for the euphotic zone of the southern Black Sea.

Date	Regression	r^2	*n*
March–April, 1995	POC = 253.6 PP - 0.6	0.93	12
	POC = 7.8 PON + 4.4	0.98	
	PON = 32.0 PP - 0.6	0.92	
September–October 1995	POC = 109.3 PP + 3.4	0.36	35
	POC = 8.8 PON + 3.3	0.81	
	PON = 11.2 PP + 0.1	0.37	
April, 1996	POC = 111.8 PP + 1.7	0.29	25
	POC = 7.5 PON + 0.3	0.90	
	PON = 14.2 PP +0.2	0.30	
June–July, 1996	POC = 164.5 PP + 0.3	0.82	28
	POC = 9.6 PON + 0.6	0.88	
	PON = 16.6 PP ± 0.0	0.84	

Table 3. Average light indices in the southern Black Sea: Depth [*D*(m)] of 1% Surface Light and Downward Attenuation Coefficient [K_d (m^{-1})].

Location	Mar–Apr		Sept–Oct		April		June–July	
	1995	1995	1996	1996				
	D	K_d	*D*	K_d	*D*	K_d	*D*	K_d
Bosphorus	35	0.152	15	0.250	–	–	34	0.139
Western Cyclone	–	–	–	–	–	–	40	0.125
Off Sakarya	–	–	–	–	–	–	35	0.128
Off Sinop	–	–	–	–	21	0.230	–	–

and season (Figure 6 and Table 2a). In 1995–1996, the average particulate concentrations in the euphotic zone estimated for different regions of the southern Black Sea ranged between 3.8 and 28.6 μm for POC, 0.5 and 3.1 μm for PON and 0.02 and 0.1 μm for PP (Table 2a). In April and June, the euphotic zone concentrations were lower in 1996 than in the previous year. On a regional basis, the highest concentrations were observed in the coastal waters near the Bosphorus exit, in April 1995 (Table 2a). Below the euphotic zone, the concentrations declined to their background levels (POC = 1–4 μM, PON = 0.1–0.3 μM, PP = 0.01–0.03 μM) – excluding the coherent maxima which appear in the suboxic/anoxic interface at the density surfaces of $\sigma_t = 16.1$–16.2 (Figure 6). It should be noted that the increases in PP concentration within the interface were more pronounced than in POC and PON (Figure 6).

In order to estimate the relative elemental composition of POM collected in the surface water, regression analyses of basin-wide particulate data were carried out on a seasonal basis (Table 2b). The atomic N/P ratio lines ranged seasonally between 11.2 and 16.6 whereas the estimated ratios of C/P and C/N were in the range of 109–164 and 7.5–9.6 for the 1995–1996 period, excluding the anomalously high ratios from the Bosphorus region in March–April 1995. The euphotic zone averages of the particulate ratios, calculated from the individual data displayed in Table 2c, also exhibit marked variations with region and season. In April 1996, the C/N ratio ranged regionally between 7.9 and 8.6, which were less than those for other periods of 1995–1996 (Table 2c). Interestingly, the summer-96 ratios decreased slightly below the euphotic zone to values similar to those in the euphotic zone in April 1996. The estimated C/P ratios (between 126–231) are consistently higher than the Redfield ratio of 106 (Table 2c). In the suboxic/anoxic interface the C/P and N/P ratios of seston were found to be as low as 33 and 4, respectively, due to the less pronounced increases in the POC and PON contents of the interface (Figure 6).

The observed light penetration in the upper water column of the southern Black Sea during 1995–1996 indicated the thickness of the euphotic zone (practically defined as the depth of 1% of the surface light) to range between 15 and 40 m (Figure 7 and Table 3). The less energetic, high wavelength component of the incoming light was absorbed in the upper surface layer (the top 10m), where the highest (downward) attenuation coefficient (K_d = 0.125–0.350 m^{-1}) was calculated. Below this layer the solar light penetrated with a constant K_d, which varied seasonally and regionally between 0.125 and 0.250 m^{-1}. The highest estimated K_d values were 0.250 m^{-1} observed in the Bosphorus region during Sept–Oct., 1995 and 0.230 m^{-1} observed in the RCFZ off Sinop in April, 1996, corresponding to a euphotic layer of 15 m and 21 m, respectively. Similar light penetration characteristics were displayed throughout the southern Black Sea in June–July 1996, with K_d estimates in between 0.125 and 0.139 m^{-1}, corresponding to a euphotic zone thickness of 34–40 m (Figure 7, Table 3). The 1% light depth always extended below the seasonal thermocline formed at 30–50 m in September 1995 and 20–30 m in July 1996 (Figures 4 and 7).

Seasonal Chl-a data from different regions of the southern Black Sea are displayed in Figure 7 and Table 4. In June–July 1996, the concentrations in the euphotic zone were generally low ($<$ 0.5 μg l^{-1}) with the lowest values in the surface mixed layer, and a subsurface Chl-a maximum was formed near the base of the euphotic zone and/or below the seasonal thermocline, corresponding to the depths of 0.5–2% of the surface light (Figure 7). However, the Sept–Oct 1995 profiles indicated an apparent increase in the Chl-a concentration in the surface mixed layer, when the mixed layer depth was greater than that of the euphotic layer (Figures 4 and 7). During the spring–autumn period of 1995–1996 Chl-a concentrations ranged from 0.1 to 0.6 μg l^{-1} in the Batumi ACR whilst the concentrations in the western CR, the Bosphorus region and off Sinop (RCFZ) ranged from 0.3 to 1.5 μg l^{-1}. Interesingly, relatively low concentrations (0.1 to 0.5 μg l$^{-1)}$ were determined in the March–April period of 1995–1996, showing almost uniform vertical distributions.

Primary productivity (P) profiles were similar throughout the southern Black Sea; the highest rates, which varied seasonally and regionally between 1 and 10 mgC m^{-3} h^{-1} (or 10 and 180 mgC m^{-3} d^{-1}), were always determined in the upper euphotic zone down to the 10% light intensity depth or the top 10–20 m of the water column. Below this layer, the rate decreased markedly with depth and dropped to negligible rates at the 1% light intensity depth (Figure 7). In order to determine the maximum rates of production, P(M), under adequate light intensity, samples taken from different depths of the euphotic zone were exposed to the full artificial light conditions in the incubator. The estimated maximum rates, P(M), were comparable or almost constant down to the depths of 1% surface light intensity but varied seasonally and regionally between 1 and 20 mgC m^{-3} h^{-1}. The depth-integrated P rates ranged from 1925 mgC m^{-2} d^{-1} in the RCFZ off Sinop in April 1996 to 194 mgC m^{-2} d^{-1} in the Bosphorus region in June–July 1996, yielding an average of 472 mgC m^{-2} d^{-1} for the stratification seasons of 1995–1996 (Table 5).

Table 4. Euphotic zone average Chlorophyll-a concentrations (μg l^{-1}) in the southern Black Sea.

Location	Mar–Apr 1995	Sept–Oct 1995	April 1996	June–July 1996
Bosphorus	0.66	0.86	0.27	0.82
Western Cyclone	–	–	–	0.54
Eastern Cyclone	0.13	0.99	0.07	0.50
Batumi Anticyclone	0.12	0.30	0.09	0.48
Off Sakarya	–	–	–	0.62
Off Sinop	–	–	0.37	–

Table 5. Daily primary production rates [P(D) (mgC m^{-2} day^{-1})] integrated for the euphotic zone in the southern Black Sea.

Location	Mar–Apr 1995	Sept–Oct 1995	April 1996	Jun–July 1996
Bosphorus	247	405	–	194
Western Cyclone	–	–	–	687
Off Sakarya	–	–	–	603
Off Sinop	–	–	1925	–

Discussion

The chemocline boundaries and the characteristic features (nitrate, phosphate maxima and phosphate minimum) of the oxic/anoxic transtion layer have consistently appeared at specific density surfaces during the spring-autumn period of 1995–1996 (Figure 5). The oxycline was much thicker in the ACR and RCFZ because of the thicker CIL which forms the upper part of the permanent pycnocline. The suboxic zone formed below the main oxycline (or at σ_t = 15.4–15.6) extended consistently down to the σ_t = 16.15–16.2 density surfaces throughout the deep basin. Comparison of present and past data shows the suboxic zone to have displayed no vertical movement since 1988 (Tuğrul et al., 1992; Baştürk et al., 1994 and Murray et al., 1995).

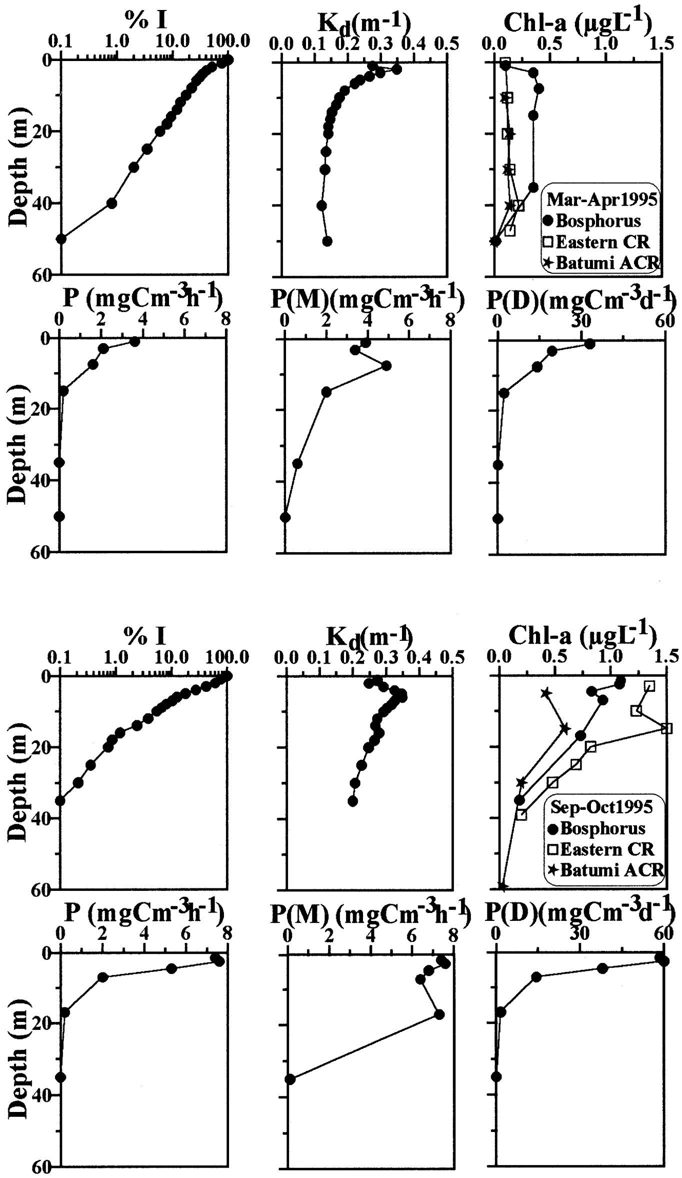

Figure 7a.

Figure 7. Vertical profiles of Light Penetration [as % of surface light (% I) and downward attenuation coefficient (K_d)], Chlorophyll-a (Chl-a) and Primary Production Rates [True noon production = P, Maximum Production = P(M), and Daily Production = P(D)] for the southern Black Sea for the spring–autumn periods of (a) 1995 and (b) 1996.

Nevertheless, its upper boundary deepens slightly during intense winter mixing and then shoals again by 0.1–0.2 density units during the stratification seasons when vertical ventilation of the oxycline is limited (Baştürk et al., 1997a). Unexpectedly, in the summer of 1992, the suboxic boundary was temporarily modified within the western cyclone; it became shifted upwards by nearly 0.3–0.4 density units (about 5–10 m), as compared to its position in the summer of 1991. The characteristic nitrate profile depicted in Figure 5 was also eroded markedly by intense denitrification resulting in an apparent removal of nitrate from the charactersitic

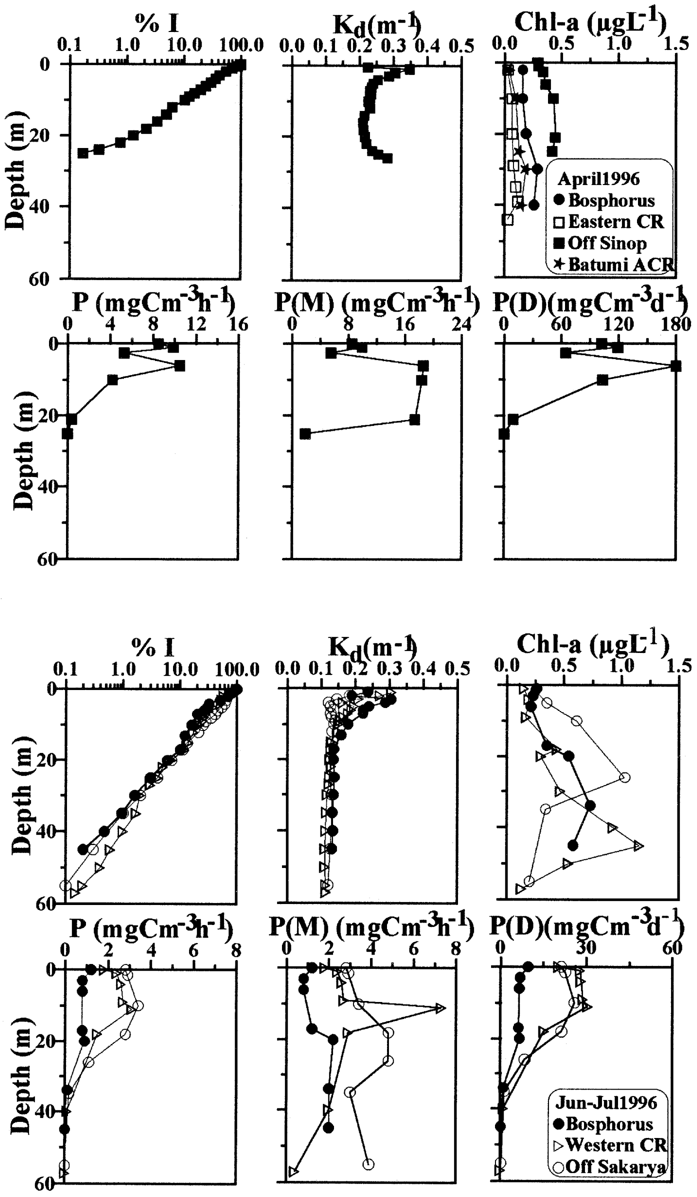

Figure 7b.

chemocline (Baştürk et al., 1997b). In the summer of 1992 the nitrate in the upper layer (down to $\sigma_t = 15.5$) decreased from its characteristic maximum concentration of 5–9 μm, to < 2 μm. In late 1992 the eroded chemical features appeared to recover though with lower nitrate concentrations at the NO_3 maximum depth (S. Konovalov, pers. com.).

High-resolution data obtained in the present study and during the Knorr-88 cruise (Codispoti et al., 1991) indicate significant regional changes in the characteristic features of vertical nutrient profiles. The upper CIL situated in the ACR between the $\sigma_t = 14.1$–14.4 surfaces has a distinctive chemical structure; it is now relatively enriched in nitrate (increasing vertically from 0.5 to 2.5 μm) whereas the phosphate concentrations remain almost constant with depth (but varying regionally between < 0.02 and 0.1 μm). Thus, the atomic N/P ratios (T-NO_x/PO_4) in the P-deficient upper

CIL appear to be anomalously high (between 40–80). This ratio decreases markedly to the levels of 4–8 at the base of the oxycline. Similar high N/P ratios have been reported for the bottom waters of the northwestern shelf (Cociasu et al., 1997), where the CIL, entrapped by the associated eddy fields, appears to be formed by winter cooling and becomes introduced into the southwestern coastal waters by the Rim current (Oğuz et al., 1992). Interestingly, such anomalies in the CIL were not encountered during the Atlantis 1969 cruise (Brewer, 1971); on the contrary, if the debatable ammonia data are ignored, the CIL appears to have been impoverished in nitrate and thus to have possessed anomalously low N/P ratios (between 1–5). It should be noted here that the Levantine Intermediate Water (LIW) which forms during winter cooling of the surface waters and sinks down to intermediate depths in the eastern Mediterranean, is enriched in nitrate but poor in reactive phosphate, resulting in anomalously high N/P ratios (Krom et al., 1992; Yılmaz & Tuğrul, 1997). It is as yet unclear what processes selectively remove reactive phosphate from the water column or cause the accumulation of nitrate in the Black Sea CIL and the Mediterranean LIW.

Because of the formation of a thicker CIL in the ACR, the chemical gradients in the oxycline are nearly a half of those in the CR where the CIL is very thin. Throughout 1995 and 1996 the gradients of DO and nitrate in the oxycline were estimated to be 9.8 μM m^{-1} and 0.26 μM m^{-1}, respectively, for the CR, and 4.2 and 0.1 respectively for the ACR and RCFZ, values which are consistent with those reported by Baştürk et al. (1997a, 1997b) for the early 1990's. Whereas phosphate gradients were comparable, the present nitrate gradient is much higher than that (0.015–0.03 μM m^{-1}) estimated from the 1969 data due to the unexpectedly low nitrate content of the oxycline (Tuğrul et al., 1992).

The phosphate minimum formed in the lower suboxic zone at the $\sigma_t = 15.85$–15.90 is a permanent feature of the CR (Tuğrul et al., 1992; Baştürk et al., 1994; Murray et al., 1995) and it is less distinct towards the coastal margins. Interestingly, this minimum was less pronounced (most probably due to coarse sampling intervals) and located at greater density surfaces – by about 0.1–0.15 density units (or 10-15 m) – in the late 60's (Tuğrul et al., 1992). This apparent shift coincides with the long-term upward expansion of the suboxic zone by about 0.3–0.4 density units since 1969 (Tuğrul et al., 1992; Codispoti et al., 1991; Murray et al., 1995). Long-term changes in the Black Sea ecosystem appear to have resulted from the increasing input of nutrients and labile organic matter by rivers; thus the enhanced primary productivity of the surface waters has led to a decrease in water transparency – the Secchi disk depth – markedly from 9–27 m in the 60's to 2–16 m in the 90's (Vladimirov et al., 1997). The contribution of climatic changes to the deterioration of the Black Sea ecosystem is still poorly understood. The deep phosphate maximum, formed in the sulphidic water interface has remained constant at a precise, specific density surface since the late 60's. This finding suggest that small-scale fluctuations observed in the suphidic water boundary are principally the result of the poor reliability of sulphide data (Tuğrul et al., 1992; Romanov et al., 1997).

The elemental composition of marine POM is relatively uniform (Copin-Montegut & Copin-Montegut, 1983) as compared to those of lakes (Hecky et al., 1993). In fact, the C/N/P ratios of POM in marine waters depend on the hydrography of the different marine regions, nutritional status, growth rates of marine phytoplankton and grazing pressure (Copin-Montegut & Copin-Montegut, 1983). The examination of sestonic ratios is a simple tool for understanding the composition of marine particles as well as the correlation between POM and environmental factors. The C-N and N-P regressions demonstrate that seasonal cycles of the sestonic ratios in the Black Sea euphotic zone take place within a limited range of ratios (C/N = 7.5–9.6; N/P = 11.2–16.6), corroborating the conclusion reached by Copin-Montegut & Copin-Montegut (1983). In other words, the relatively low inorganic nutrient concentrations of the surface waters during stratification seasons (Table 1) modified the sestonic ratios slightly relative to the mean planktonic ratio (N/P = 16). However, the C/P ratios were more variable due to the fast cycling of particulate phosphorus and P-deficient POM synthesis in the P-depleted surface waters. For instance, the C/P and N/P ratios of the Bosphorus region were unexpectedly high in March–April 1995. In June–July 1996, POM was deficient both in P and N elements, whilst the N/P ratio was similar to Redfield ratio, implying the assimilation rate of carbon to exceed those of N and P. Moreover, the small intercepts presented in Table 2b indicate low concentration of carboneceous (N- and P-deficient) organic compounds in the total seston, as well as weak limitation of inorganic nutrients on the chemical composition of POM of mostly regenerative origin as previously suggested by Copin-Montegut & Copin-Montegut (1983). The intercepts of PON/PP regressions are very low, suggesting the increases in particulate nutrients to occur in the same proportions in the living and non-living POM content of the euphotic zone.

In March–April 1995, the Bosphorus region phytoplankton was adapted to low P-supply as confirmed by low production rates and low Chl-a concentrations obtained in this period. These P-limited seston ratios are similar to those of moderately P-limited lakes (Hecky et al., 1993) but higher than the seston ratios of the P-limited eastern Mediterranean surface waters. Nevertheless, the present ratios are comparable to the C/N ratios of the fast-sinking POM collected by sediment traps in summer 1988 by Karl & Knauer (1991).

Altough the POM in the surface waters possesses a mean N/P ratio of about 14, similar to the Redfield ratio of 16, the molar NO_x/PO_4 ratios are always as low as 4–8 in the oxic/anoxic interface. Such anomalous N/P ratios indicate the nitrate loss from the suboxic waters via denitrification which exceeds the phosphate export from this layer to the sulphidic waters via the absorption on to Fe- and Mn oxides and subsequent sedimentation (Shaffer, 1986; Codispoti et al., 1991).

Production (P) rates determined in the present study are similar to those reported for the open part of the northwestern shelf and off the Romanian coast (Bologa, 1985/1986) and exceed those observed in the central Black Sea (Vedernikov & Demidov, 1993). The highest P rates were observed in April 1996 and June–July 1996, although the Chl-a concentrations were less pronounced in April, 1996. The inconsistency between the P rate and the Chl-a concentrations obtained in April 1996 generated relatively high assimilation numbers (30 mgC $mgChl^{-1}$ h^{-1}) suggesting that the light was not a limiting factor since the intensity of solar radiation exceeded the seasonal averages in this period. The estimated assimilation numbers were in the range of 2-15 mgC $mgChl^{-1}$ h^{-1} for the other seasons. Relatively high P rates in June–July 1996 are consistent with the occurrence of short summer blooms in the Black Sea additional to the characteristic spring and autumn blooms (Sorokin, 1983; Bologa, 1985/1986; Vedernikov & Demidov, 1993; Hay & Honjo, 1989; Hay et al., 1990; 1991; Sur et al., 1996). The highest carbon production rates and assimilation numbers were observed in the upper layer of the euphotic zone (above the 10% light depth). In general, the thickness of the euphotic zone was lower (with relatively high K_d) in the CR and the RCFZ than in the ACR due to relative increase of phytoplankton abundance, as also reported by Vidal (1995). The transparency of the water column in the Black Sea is also affected by the presence, besides phytoplankton, of a large variety of particles (inorganic particles, detritus, microzooplankton and even jelly fish) all of which have relatively high stocks in the Black Sea compared to other temperate seas such as the Mediterranean.

The springtime POC concentrations being relatively high or comparable to summer–autumn concentration and low Chl-a concentrations observed in the open waters in the spring, gave rise to relatively high C/Chl ratios (ranging between 400–600, mean = 550 w/w). This indicates the majority of the seston to have been composed of detritus and/or microzooplankton developed after the phytoplankton bloom. Probably the spring cruises took place after the completion of the characteristic bloom in the Black Sea. In summer and autumn both biomass indices (Chl-a and POC) were significantly high and the C/Chl ratios were relatively low (ranging between 100–300 for Sept.–Oct. 1995 and between 100–200 for June–July 1996). The decrease in the C/Chl ratio in the stratification seasons confirms the occurrence of a healthy phytoplankton bloom in this period. Uysal et al. (1997) also observed relatively high phytoplankton (mainly dominated by dinoflagellates) biomass (10^5 cells l^{-1}) in summer 1996 and the populations were comparable to those in spring (10^6 cells l^{-1}).

The Bosphorus exit was always relatively rich in phytoplankton biomass (in terms of Chl-a) because of the nutrient and POM-enriched surface waters from the northwestern shelf entrained by the alongshore currents. Interestingly, during the Sep.–Oct. 1995 and June-July 1996 cruises, relatively high concentrations from the eastern and western cyclones dominated the spatial distribution of Chl-a. This resulted partly from the intermittent influx of nutrients from the nutricline located at the base of the euphotic zone in the CR via diffusive processes and mainly by regenerative processes in the upper layer. Accordingly, in July 1996, the prominent deep Chl-a maximum in the CR was formed at the base of the euphotic zone and nearly coincided with the nutricline onset at the $\sigma_t = 14.5$–14.6 density surface. In the ACR, the nutricline is located much below the euphotic zone and thus the input from the nutricline generally occurs during winter mixing. Therefore, during the stratified seasons, Chl-a increase in the coastal ACRs is dominated by the input from rivers which is transported to the associated eddy fields via the Rim current.

It should be emphasized that the pattern of primary productivity in most of the Black Sea is determined by the material transported via the cyclonic boundary

Rim current and the frontal and jet instabilities between the Rim current and the interior eddy fields. Riverine input contributes to new production mainly in coastal and offshore areas by such a mechanism, though the more common mechanism of nutrient transport from the nutrient rich lower layer to the euphotic zone by winter mixing in the central regions of the Black Sea which is limited by the strong stratification. In comparison, the role of atmospheric sources of nutrients appears to be marginal (Kubilay et al., 1995).

On the other hand, due to the anoxic conditions in deep waters in the Black Sea, source and sink terms for nutrients (mainly for nitrate) immediately below the euphotic zone are unusual compared to conditions in the central cyclones. In the Black Sea anoxic conditions start at shallower depths (50–100 m) and, unlike the open ocean, below the oxic-anoxic interface the waters are enriched in ammonia and devoid of NO_3 and NO_2. Thus the transition suboxic layer laying below the euphotic zone and above the anoxic layer provides an environment condusive to photosynthetic production in the euphotic zone; nutrients are transported from this suboxic layer by diffusional processes as well as by winter mixing. The f-ratio has therefore been estimated to be as low as 0.1 (Murray et al., 1995; Cadispoti et al., 1991) and according to Dortch (1990) in such systems the f-ratio is mainly determined by the availability of ammonia. The one-dimensional physical-biological model of Oğuz et al. (1996) suggest that 40 and 60% of the annual primary production in the Black Sea is supported by NO_3 and NH_4, respectively. In this case the ratio of regenerated nitrogen to total nitrogen utilized is about % 75, yielding an effective f-ratio of about 0.25.

Conclusions

High-resolution data reveal that, as a result of as yet undefined processes, the upper CIL down to the temperature minimum depth in the ACR is enriched with nitrate but drastically poor in phosphate. There are thus very high N/P ratios in the upper nutricline and an apparent shift in the nutricline onset in the CIL. Since these P-limited CIL waters are mixed vertically with the surface waters of the ACR in winter and early spring, bloom in such areas is probably limited by phosphorus. Nitrate-limited production occurs in the CR due the low N/P ratios of the chemocline established just below the euphotic zone. The relatively high atomic N/P ratios of POM indicate that the anomalously low ratio of nitrate/phosphate in the oxic/anoxic interface of the entire deep basin is due to nitrate removal via denitrification, greatly exceeding P-export from the suboxic waters.

In addition to characteristic spring and secondary autumn blooms, summer phytoplankton blooms are significantly observed in the Black Sea and such blooms are mainly driven by the transport of material via the cyclonic Rim current and its interaction with the eddy fields in the central parts of the Black Sea. Riverine input contributes to new production mainly in coastal and partly offshore areas. In the central region of the Black Sea new production is also supported by the nutrient transport from the nutricline located below the euphotic zone and from the suboxic zone, such transport being significant during winter mixing.

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