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Surface and mid-water sources of organic carbon by photoautotrophic and chemoautotrophic production in the Black Sea

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Abstract

The multilayered surface waters of the Black Sea contain aerobic, suboxic and anoxic layers that support both photoautotrophic (PP) and chemoautotrophic (ChP) biological production. During the R/V *Knorr* cruise in May–June 2001, phytoplankton biomass (represented as chlorophyll-*a*), photoautotrophic and chemoautotrophic production (ChP) rates were determined in the western Black Sea. Integrated chlorophyll-*a* concentrations in the euphotic zone were as low as $2.2\,mg\,m^{-2}$ in the central gyre, while they were as high as $19.9\,mg\,m^{-2}$ in the NW shelf region. Integrated photoautotrophic production rates ranged from 112 to $355\,mg\,C\,m^{-2}\,d^{-1}$. The lowest values were determined in the central gyre and the highest values were found at the shelf-break station near the Bosphorus, the NW shelf/shelf-break area and in the Sevastopol eddy. Primary production and chlorophyll-*a* data revealed that post-bloom conditions existed during this sampling period. Bioassay experiments showed that under optimum light conditions, photoautotrophic production was nitrogen-limited. ChP increased in the redox transition zone and coincided with the lower boundary of the fine particle layer. The maximum values were shallower (at $\sigma_\theta = 16.25$) in the central gyre and deeper (at $\sigma_\theta = 16.5$) in the shelf-break region near Sakarya Canyon. Integrated ChP rates were 63 and $1930\,mg\,C\,m^{-2}\,d^{-1}$, which were equivalent to 30% and 89% of the overall water-column production for the central gyre and Sakarya Canyon regions, respectively.

Keywords: Black Sea; Chlorophyll-*a*; Photoautotrophic and chemoautotrophic productions; Post-bloom conditions

1. Introduction

Nutrients in the surface waters of coastal regions of the Black Sea are principally fed by river input and by lateral as well as vertical nutrient transport mechanisms (Yılmaz et al., 1998a, b and the references cited therein). In the open, central gyre ecosystem, which is dominated by the cyclonic eddy, primary production is mainly sustained by the diffusive influx of nutrients from oxic/suboxic interface by wind-induced vertical mixing processes, especially in winter (Oğuz et al., 2004). The permanent pycnocline coincides with the oxic–anoxic

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transition zone, where intense denitrification and redox-dependent processes limit nitrogen and phosphorus input to the surface productive layer in the Black Sea (Baştürk et al., 1994).

Nutritional statuses of waters on the NW shelf and of whole Black Sea have changed significantly over the past few decades (Codispoti et al., 1991; Tuğrul et al., 1992; Cociasu et al., 1996; Konovalov and Murray, 2001; Cociasu and Popa, 2002). The NO_3/PO_4 ratio in surface waters near the Danube River was 11.7 in the 1970s and 22–33 for 1988–1992 (Cociasu et al., 1996). The ratio continued to increase (to as high as 100) until 1995 due to net decrease in inorganic phosphate input. After 1996 it decreased significantly (e.g., down to 20 in 2000) due to a decrease in inorganic nitrogen input (Cociasu and Popa, 2002). On the other hand, low NO_3/PO_4 ratios in the nutricline below the euphotic zone resulted in nitrogen-limited photoautotrophic production in open waters (Baştürk et al., 1997; Yılmaz et al., 1998b; Yayla et al., 2001). These low ratios were due to nitrate removal via denitrification. The depletion of dissolved reactive silicate in surface waters during the 1970s and 1980s also has been found to have important impacts on the Black Sea ecosystem. This caused dramatic shifts in phytoplankton species compositions from siliceous (mainly diatoms) to non-siliceous species (mainly coccolithophores and flagellates) (Humborg et al., 1997; Cociasu et al., 1996). Recent changes in the nutrient concentrations of river input (Cociasu and Popa, 2002) have resulted in hydrochemical changes in the coastal waters. Concentrations of nitrate decreased considerably, and concentrations of silicate increased in the oxic layer and decreased in the anoxic zone in 1990s (Konovalov et al., 1999; Konovalov and Murray, 2001; Cociasu and Popa, 2002).

Changes in the nutrient regimes also caused changes in the magnitude of primary production in the Black Sea. Long-term data obtained since 1960s have shown that primary production in the Black Sea generally displayed two maxima throughout the year; the major one occurred in early spring (mainly diatoms) while a secondary peak appeared in autumn (mainly coccolithophorids) (Sorokin, 1983; Vedernikov and Demidov, 1993). More recently, additional summer and autumn blooms (dominated by dinoflagellates and coccolithophorids) have been observed frequently in both coastal and open waters (Hay et al., 1990; Yılmaz et al., 1998a, b; Çoban Yıldız et al., 2003; Oğuz et al., 2003). During 1960–1991 primary production ranged from 570 to 1200 $mg\,C\,m^{-2}\,d^{-1}$ on the NW shelf, between 320 and 500 $mg\,C\,m^{-2}\,d^{-1}$ in the region of the continental slope, and between 100 and 370 $mg\,C\,m^{-2}\,d^{-1}$ in the central deep water regions (Vedernikov et al., 1996). Similar rates of primary production (247–1925 $mg\,C\,m^{-2}\,d^{-1}$ for spring and 405–687 $mg\,C\,m^{-2}\,d^{-1}$ for summer/autumn period) were estimated for the southern Black Sea in 1995–1996 (Yılmaz et al., 1998b). Production data collected on the NW shelf in the 1970s and 1980s showed that these waters were highly eutrophic (Bologa et al., 1999). In the first half of the 1990s, these shelf waters became increasingly eutrophic, and more frequent and intense phytoplankton blooms were reported (Bologa et al., 1999). Average production values in the central gyres increased by approximately a factor of two in the 1980s and in the first half of the 1990s (Vedernikov and Demidov, 1993; Yunev et al., 2002). After 1992, the deep-water ecosystem of the Black Sea showed positive signs of recovery, since both chlorophyll-*a* concentrations and rates of primary production decreased (Yunev et al., 2002). After the mid-1990s the major late winter–early spring maximum in phytoplankton biomass either weakened or disappeared, depending on local meteorological and oceanographic conditions (Oğuz et al., 2003). Changes also occurred in nutrient regimes reflecting changes in input (both in quantity and character) from land-based sources.

In addition to photoautotrophic production in the surface layer, stratified water columns underlain by anoxia, like the Black Sea and Cariaco Basin, support multiple layers of biological production (Jørgensen et al., 1991; Sorokin et al., 1995; Taylor et al., 2001). There is a complex microbial food web at the oxic/anoxic interface in such multi-layer systems and productive microbial communities live on the residual chemical energy (H_2S, CH_4, NH_4^+, H_2, low molecular weight organics) that originates from the anoxic layer (Brewer and Murray, 1973). This chemoautotrophic production (ChP) enhances the bacterial biomass and elemental cycling. Previously measured rates of ChP in the Black Sea ranged from 24 to 324 $mg\,C\,m^{-2}\,d^{-1}$, which was equivalent to 10–32% of the surface primary production in the Black Sea (Jørgensen et al., 1991; Sorokin et al., 1995). The range of ChP in the Cariaco Basin was 312–1884 $mg\,C\,m^{-2}\,d^{-1}$, and this was equivalent to 10–333% surface primary production (Taylor et al., 2001).

This study presents further new data on the surface-layer photoautotrophic and mid-water ChP in the Black Sea for May–June 2001. For this purpose, phytoplankton biomass (represented as chlorophyll-*a*), photoautotrophic (PP) and Chemoautotrophic (ChP) rates were determined in the western Black Sea.

2. Materials and methods

2.1. Study area

A bathymetric map of the western Black Sea and the station network where photoautotrophic (PP) and Chemoautotrophic (ChP) measurements were made during the R/V *Knorr* cruise in May–June 2001 is presented in Fig. 1. The station locations and measurements are listed in Table 1.

2.2. Sampling and analysis

2.2.1. Supporting parameters

Hydrographic data were collected using Sea-Bird CTD probes mounted on a 24-10L bottle rosette. Data are available on the R/V *Knorr* 2001 web page (*oceanweb.ocean.washington.edu/cruises/Knorr2001*). Light transmission and in situ fluorescence data were collected using a Sea Tech single-beam (660 nm) light transmissometer and a Chelsea-type in situ fluorometer attached to the CTD probe. A quantameter (combination of LI-1000 data logger and LI-192SA underwater quantum sensor) was used to measure irradiance levels in the water column. Dissolved oxygen and hydrogen sulfide (H_2S) concentrations were determined by conventional Winkler and iodometric back titration methods, respectively (Baştürk et al., 1994), while low H_2S concentrations were determined by the colorimetric method (Cline, 1969).

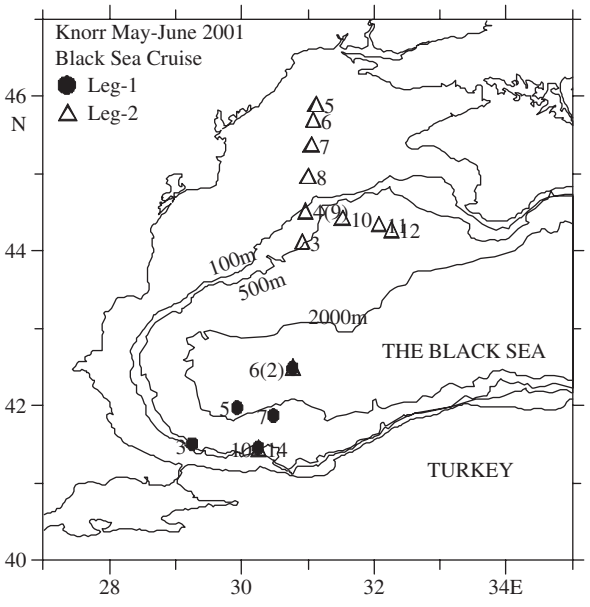

Fig. 1. Bathymetric map of western Black Sea and station network for May–June 2001 R/V *Knorr* cruise. Filled symbols represent the stations visited during Leg 1 and open symbols denote the stations visited during Leg 2.

2.2.2. Chlorophyll-a, primary production and bioassay tests

Discrete chlorophyll-*a* samples were collected down to 1% I_0 isolume (or down to 0.1% I_0 isolume at some stations). In situ fluorescence profiles from previous rosette casts were taken into account for selection of the sampling depths. Chlorophyll-*a* analyses were performed using the fluorometric method described in UNESCO (1994). The fluorescence by phaeopigments-*a* also was determined by acidifying the samples, but only data for active chlorophyll-*a* are presented here (abbreviated as Chl). The analytical precision for Chl was 8% and the detection limit was 0.01 mg m^{-3}. The accuracy of our Chl data was confirmed by the acceptable results obtained through an international inter-comparison exercises performed recently (Quasimeme, 2003).

Primary production was measured using the ^{14}C method (Steemann-Nielsen, 1952; UNESCO, 1994). Samples were routinely collected from the 60%, 36%, 22%, 12-8%, 6-5%, 3%, 1% and 0.1% I_0 isolumes. An additional sample from the subsurface fluorescence maximum was generally included in the sample set. Hundred microliter of ^{14}C-bicarbonate solution (2 μCi) was added into 100-mL light and dark bottles filled with the seawater samples. Bottles were incubated for 24 h in a plexyglass water tank on deck exposed directly to sunlight during the day and dark during the night (Hama et al., 1983; Joint and Pomroy, 1986; Rey et al., 2000). Circulating surface seawater was used to keep the temperature constant. Samples were placed in natural screen bags in order to simulate the light levels, from which the samples were collected. After recovery, samples were filtered through cellulose nitrate, 0.2-μm pore size membranes. Filters were exposed to concentrated HCl fumes for 5 min to purge unassimilated ^{14}C, and then to formaldhyde (37%) fumes for 2 min to stop all biological activity. Finally, filters were suspended in

Table 1
Station-based inventory for the measurements of chlorophyll-*a* (Chl), primary production (PP), chemoautotrophic production (ChP) and bioassay tests

Station no./Leg no.	Station ID	Coordinates Lat. (N), Long. (E)	Chl (CTD no.)/PP (CTD no.)	Bioassay test	ChP (CTD no.)
Sta. 3/Leg 1	Bosphorus shelf break	41° 30′N 29° 15′E	CTD 6/CTD 6	CTD 6	
Sta. 5/Leg 1	Transit to gyre	41° 58′N 29° 56′E	CTD 11/CTD 11		
Sta. 6/Leg.1	Western central gyre	42° 29′N 30° 46′E	CTD 17/CTD 22	CTD 22	CTD 19-20-21
Sta. 7/Leg 1	Turkish transect	41° 52′N 30° 29′E	CTD 39/CTD 39		
Sta. 10/Leg 1 (shallow)	Turkish shelf	41° 25′N 30° 15′E	CTD 44/CTD 44		
Sta. 10/Leg 1 (deep)	Turkish shelf break	41° 27′N 30° 15′E	CTD 53/CTD 53		CTD 51
Sta. 2/Leg 2	Western central gyre	42° 30′N 30° 46′E	CTD 2/CTD 2		
Sta. 3 /Leg 2	NW slope	44° 07′N 30° 55′E	CTD 11/CTD 11		
Sta. 8 /Leg 2	NW shelf	44° 58′N 31° 00′E	CTD 22/CTD 22	CTD 22	
Sta. 12/Leg 2	Sevastopol eddy	44° 21′N 32° 04′E	CTD 26/CTD 26		

Information on samples for surface Chl measurements and Chl profiles obtained rather than these stations are represented in Table 2.

liquid scintillation cocktail and radiocarbon counts were performed. The effect of ^{14}C discrimination, because the uptake of ^{14}C is 5% slower than that of ^{12}C, was taken into account during calculation. Carbon uptake rates were normalized to $mg\,C\,m^{-3}\,d^{-1}$ by multiplication with the concentration of total dissolved CO_2. Total alkalinity was measured utilizing a multi-point hydrochloric acid titration (Dickson, 1981) and the calculation of the carbonate parameters, e.g., total dissolved CO_2 from alkalinity, was performed as reported in Millero et al. (1993). As the incubation period was 24 h long, some of the organic matter produced was used for respiration so the results yielded net primary production (Steemann-Nielsen, 1952). Dark carbon uptake rates due to non-photoautotrophic carbon fixation (e.g., bacterial activity) were separately determined for each depth and these values were subtracted from the primary production values. Only net photosynthetic primary production rates are presented in this study and symbolized as PP for simplicity. Vertical profiles of PP rates were integrated down to 1% I_0 isolume to yield the rates as per unit area in units of $mg\,C\,m^{-2}\,d^{-1}$.

Bioassay tests were performed by artificial addition of extra nutrients in order to determine the limiting nutrient. These experiments were conducted at three stations (Sta. 3, Bosphorus shelf break and Sta. 6, central gyre; Leg 1 and Sta. 8, NW shelf; Leg 2). Water samples were collected from the fluorescence maximum (11 m/Sta. 3, 25 m/Sta. 6) and from the surface in the case where the in situ fluorescence in the surface mixed layer was homogeneous (1 m/Sta. 8). Initial nutrient concentrations were adjusted according to the concentration levels observed in the upper nutricline (0.25–0.50 μM for PO_4, 2.5–5 μM for NO_3, 1–2 μM for NH_4, and 5–10 μM for Si). For adaptation purposes, bioassay samples were incubated for 1 d without any nutrient addition under simulated in situ conditions (i.e. in the plexyglass tank and in appropriate screen bags when the samples were collected below the surface) as described above in the section of primary production measurements. Then, 100-mL aliquots were enriched either with all nutrients (PO_4, NO_3, NH_4 and Si), with combination of four nutrients (PNS), and the cocktail was prepared using PNS with the addition of iron in which, initial Fe concentrations were adjusted to 0.005 and 0.01 μM. Two control samples were processed without any nutrient addition and incubated under the same conditions. After incubation in the tank

for 1 d, ^{14}C tracer was added and they continued to incubate. After 3 d, the samples were filtered and processed in the same way as the primary production samples. Such prolonged incubation periods for bioassay tests commonly have been used to study the effects on growth and production rates and to determine the limiting nutrients (Balode et al., 1998 and the references cited therein).

2.2.3. Chemoautotrophic production (ChP)

Chemoautotrophic assimilation of inorganic carbon was measured by ^{14}C-bicarbonate incorporation into particles as described by Taylor et al. (2001). Discrete water samples were collected from 16 depths at Sta. 6 and 23 different depths at Sta. 10-Deep. Vertical sampling intervals were small, e.g., 2–4 m for the whole water column for Sta. 6, and 2–10 m for the upper water column down to fine particle layer (FPL) at Sta. 10-Deep. Features in the light transmission profiles were taken into account during sampling in order to find reliable proxies for microbial activity near the oxic/anoxic interface. The Black Sea has a very pronounced density structure, therefore specific density surfaces also were taken into account for identification the chemical and microbiological features such as ChP (Murray et al., 1995). Unfortunately less frequent sampling (i.e. 50-m depth intervals) was performed below the oxic–anoxic interface at Sta. 10-Deep, therefore not all features within the water column were individually sampled. Samples were drawn from Niskin bottles through silicon tubing which was placed at the bottom of 1-L dark polyethylene bottles. The water was allowed to overflow for 1–2 volumes to prevent oxygenation. Samples were quickly (maximum 1 h after sampling) dispensed from these bottles (carefully and slowly poured) into 100-mL Yena glass-stoppered bottles without head space after overflowing. In general, duplicate, and for some specific depths (for example, samples from the oxic/anoxic interface) triplicate, samples were processed. Hundred microliter of ^{14}C-bicarbonate (2 μCi) in an alkaline brine (pH = 9.5; salinity = 60 ppt) were injected into the bottom of each bottle before sealing with a glass stopper. Samples were incubated at 8–10 °C (in the refrigerator) and in the dark (all bottles were covered with aluminum foil) for 24 h. After incubation, particles were collected on 0.2-μm cellulose nitrate membranes and prossesed as for the primary production samples. The chemoautotrphic production rates were integrated for specific layers (e.g., chemosynthetically active layer) in order to estimate the contribution of ChP to surface layer or overall water-column carbon production.

3. Results and discussion

3.1. Spatial distribution of chlorophyll-a and primary production

Data for Chl and PP are shown in Table 2 and the spatial distributions are illustrated in Fig. 2. Surface Chl data were obtained at almost all stations visited during both legs and provided an extensive spatial distribution. Surface Chl concentrations ranged from 0.03 and 1.92 mg m^{-3} for the whole study area (Table 2, Fig. 2A) and were almost 64 times higher on the NW shelf than at the deep-water stations. The surface Chl concentrations did not change much from one leg to the other. For example, the surface Chl concentrations remained within the range of 0.06–0.11 mg m^{-3} at the central gyre station during both legs covering a 9-d period. Spatial distribution of integrated Chl (to 1% I_0 isolume) exhibited similar trends (Table 2, Fig. 2B). Integrated Chl concentration ranged from 2.2 and 19.9 mg m^{-2} and the maximum concentrations were observed on the NW shelf (e.g., Leg 2-Sta. 6). Previous data have shown that the NW shelf always has high Chl concentrations. The average integrated Chl in the euphotic zone was 16.9 mg m^{-2} for late spring 1984, 45 mg m^{-2} for early spring 1988, 60 mg m^{-2} for mid winter 1989, 28 mg m^{-2} for summer 1989, and 54.6 mg m^{-2} for autumn 1992. The values in the open central areas were usually lower (e.g., 9.9 and 12.6 mg m^{-2} in the eastern and western gyres, respectively, for late spring 1984; 13.7 and 16 mg m^{-2} for summer 1989; and 23.3 and 30.1 g m^{-2} for autumn 1992) (Sorokin, 2002 and references therein). The spatial difference also was clearly seen in recent data (1990–1996) from Yılmaz et al. (1998a). The maximum water-column Chl concentration was 34.0 mg m^{-3} in the shelf waters (mainly in the NW shelf) while the deep region values only averaged 2.5 mg m^{-3}. The strong contrast between the open and shelf waters also was recorded during the bloom periods in the late winter and early spring. Finally, integrated Chl concentrations ranged from 4.9 to 20.1 mg m^{-2} with an average value of 14.2 ± 5.8 mg m^{-2} in the open central and southern Black Sea coastal waters for summer 1997, late spring 1998 and autumn 1998 periods (Yayla, 1999). These results show that the

Table 2
Stations and their coordinates, 1% I_0 isolume, surface chlorophyll-*a* (S-Chl), integrated chlorophyll-*a* (Int-Chl), integrated primary production (Int-PP) in the Black Sea during May–June 2001 cruise

Date	Station no./Leg no.	Latitude (N)	Longitude (E)	1% I_0 isolume (m)	S-Chl ($mg\,m^{-3}$)	Int-Chl ($mg\,m^{-2}$)	Int-PP ($mg\,C\,m^{-2}\,d^{-1}$)
24 May 2001	Sta. 3/Leg 1	41° 30′	29° 15′	18	0.16	2.6	355
25 May 2001	Sta. 5/Leg 1	41° 58′	29° 56′	20	0.18	3.3	319
26 May 2001	Sta. 6/Leg 1	42° 29′	30° 46′	20	0.06	2.2	145
29 May 2001	Sta. 7/Leg 1	41° 52′	30° 29′	20	0.03	2.3	211
30 May 2001	Sta. 10 (shallow)/Leg 1	41° 25′	30° 15′	18	0.24	4.8	119
31 May 2001	Sta. 10 (deep)/Leg 1	41° 27′	30° 15′	20[a]	0.28	9.6	237
3 June 2001	Sta. 2/Leg 2	42° 30′	30° 46′	25	0.11	4.2	112
4 June 2001	Sta. 3/Leg 2	44° 07′	30° 55′	20	0.21	7.1	280
4 June 2001	Sta. 4/Leg 2	44° 31′	30° 58′	—	0.21	—	—
4 June 2001	Sta. 5/Leg 2	45° 54′	31° 07′	—	1.42	—	—
5 June 2001	Sta. 6/Leg 2	45° 42′	31° 05′	15[a]	1.92	19.9	—
5 June 2001	Sta. 7/Leg 2	45° 23′	31° 03′	15–20[a]	0.63	9.9	—
5 June 2001	Sta. 8/Leg 2	44° 58′	31° 00′	20	0.26	6.2	258
6 June 2001	Sta. 9/Leg 2	44° 31′	30° 58′	20–22[a]	0.61	11.9	—
6 June 2001	Sta. 10/Leg 2	44° 26′	31° 31′	21[a]	0.42	10.1	—
6 June 2001	Sta. 11/Leg 2	44° 21′	32° 04′	—	0.50	—	—
7 June 2001	Sta. 12/Leg 2	44° 21′	32° 04′	30	0.34	7.3	317
9 June 2001	Sta. 14/Leg 2	41° 27′	30° 15′	20–25[a]	0.33	9.3	—

Integration has been performed from surface down to 1% I_0 Isolume for both Chl and PP.
[a]1% I_0 isolume has been estimated from in situ fluorescence and light transmission data.

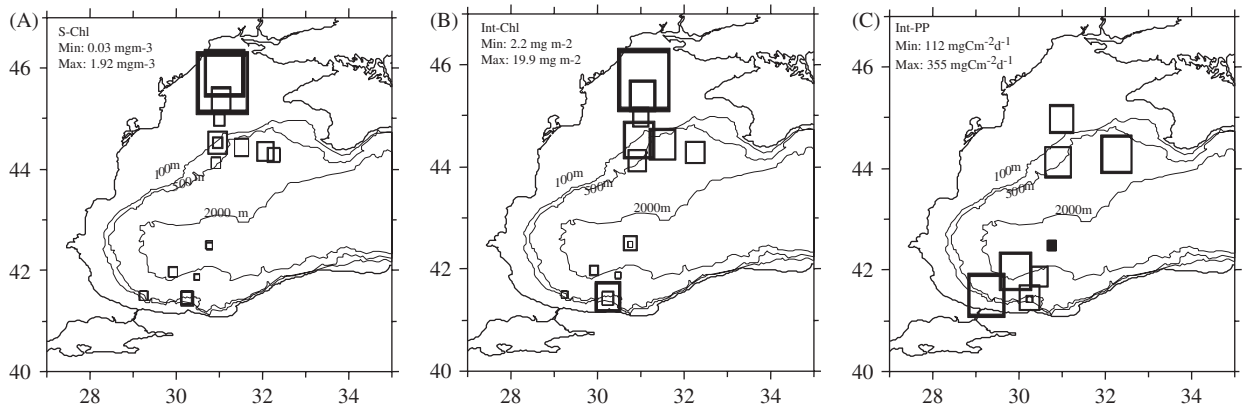

Fig. 2. Spatial distribution of chlorophyll-*a* for the surface chlorophyll (S-Chl) (A); integrated chlorophyll-*a* (Int-Chl) (B) and integrated primary production (Int-PP) (C) within the layer down to 1% I_0 isolume in the Black Sea for May–June 2001 period.

spatial distribution in the Black Sea is a well-known feature and the new data in this paper are consistent with this picture, which is the strong contrast in Chl levels between the NW shelf and the open Black Sea. The comperatively low Chl concentrations observed in this study (Table 2) represent post bloom conditions in the Black Sea and elevated detrital component (e.g., particulate organic carbon, POC). Abnormally high POC/Chl ratio (Çoban Yıldız et al., 2006a) might be the reason for the shallow 1% I_0 isolume in spite of the relatively low Chl concentrations observed for May–June 2001.

Primary production ranged from 112 to $355\,mg\,C\,m^{-2}\,d^{-1}$ for the whole study period. The lowest rates were measured in the central western gyre stations (112 and $145\,mg\,C\,m^{-2}\,d^{-1}$ for Sta. 2-Leg 2 and Sta. 6-Leg 1, respectively). Higher values were observed on the NW shelf, at the south shelf/shelf-break areas and in the Sevastopol eddy ($258\,mg\,C\,m^{-2}\,d^{-1}$ for Sta. 8-Leg 2, $355\,mg\,C\,m^{-2}\,d^{-1}$

for Sta. 3-Leg 1 and 312 mg C m^{-2} d^{-1} for Sta. 12-Leg 2) (Table 2, Fig. 2). The PP rates were slightly lower (PP was 22% less at the central gyre station) during the second leg in June, which showed that post-bloom conditions were continuing. These new PP data were relatively low compared with historical data and provided further understanding of the spatial distribution. New (2001) and historical (1960–1998) data collected in the Black Sea waters by different groups are given in Table 3.

All Chl and PP data show that NW shelf waters are relatively productive waters compared with the open Black Sea. The reason for the high Chl and PP in the NW shelf area has been linked to input from land-based nutrient sources via the major rivers (Mee, 1992; Mee et al., 2005; Cociasu et al., 1996; Sorokin, 2002 and references therein), strong nutrient coupling between shelf sediments and overlying waters, efficient nutrient cycling in the water column by strong regenerative processes (Grégoire and Friedrich, 2004) and vertical winter mixing enhanced by Cold Intermediate Water formation (Oğuz et al., 1992).

The comparatively low PP values obtained in the present study suggest that our samples were collected during a post-bloom period. Primary production per unit Chl was relatively high (i.e. 98 mg C mg Chl d^{-1}) during Leg 1 but was lower (34 mg C mg Chl d^{-1}) during Leg 2 showing post-bloom conditions were a progressive phenemenon (Fig. 3). This ratio was the lowest (25 mg C mg Chl d^{-1}) in Sakarya Canyon (Deep) station.

All indices in our study suggested that we sampled during a post-bloom condition. Historical data show that the structure of the classical major spring peak of phytoplankton biomass and primary production observed prior to mid 1990s either weakened or disappeared in the Black Sea. This was probably caused by the stronger stratification and reduced upward nutrient supply from the nutricline due to the observed warming that occurred in the Black Sea from 1995–96 to 2002. The recent seasonal distributions indicated by SeaWiFS data show a gradual decrease of biomass from a maximum in November towards summer. The autumn bloom, although weaker, lasts longer compared to its counterparts before the mid-1990s

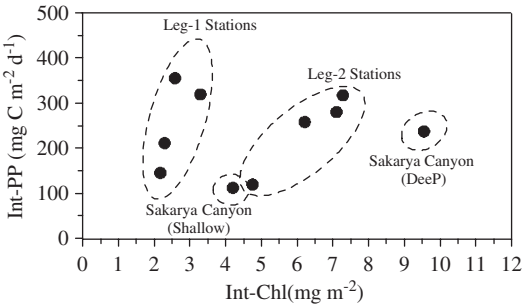

Fig. 3. Integrated primary production (Int-PP) vs. integrated chlorophyll-*a* (Int-Chl) represented both for Leg-1 and Leg-2 stations. The data were clustered for different legs and specially marked for Sakarya Canyon stations.

Table 3
Long-term primary production data in the Black Sea

Period	Location	Primary production (mg C m^{-2} d^{-1})	Reference
May–June 2001	Western Black Sea	112–355	Present study
May–June 2001	Central western gyre	112–145	Present study
May–June 2001	NW and southern shelves, shelf break regions	258–355	Present study
1964–86	Open waters	112±54	Yunev et al. (2002)
1986–92	Open waters	587±35	Yunev et al. (2002)
1992–96	Open waters	319±116	Yunev et al. (2002)
Spring 1995	Bosphorus region	194	Yılmaz et al. (1998b)
Autumn 1995	Bosphorus region	405	Yılmaz et al. (1998b)
Summer 1996	Sakarya Canyon region	603	Yılmaz et al. (1998b)
Spring–autumn 1998	Southern Black Sea	516±97	Yayla et al. (2001)
Summer 1960	NW shelf	1600	Sorokin (2002)
Autumn 1960	NW shelf	1520	Sorokin (2002)
Summer 1972	NW shelf	1540	Sorokin (2002)
Late spring 1982	Danube estuary	2140	Sorokin (2002)
Spring 1988	Western Bulgarian coast	1030	Sorokin (2002)
Late winter 1991	Western Bulgarian coast	1000	Sorokin (2002)

(Oğuz et al., 2003). The most notable effect of this warming is the increased limitation of bottom–up transport of nutrients for driving biomass production and primary production rates (Oğuz et al., 2003). Reduced nutrient supply from the nutricline due to weaker turbulent mixing and stronger stratification during mild winters from 1995 to 2002 period resulted in less pronounced early-spring blooms and less new production, which was followed by less regenerated production during the rest of the spring (Nezlin, 2001; Oğuz et al., 2003). Relatively low Chl concentrations and PP rates have been recorded for May–June 2001 period compared with data from the same seasons for the 1980s and for the first half of the 1990s.

3.2. Vertical distribution of chlorophyll-a and primary production

The Chl concentrations in the euphotic zone (defined as 1% I_0 isolume at 18–20 m) ranged from 0.05 to 0.25 mg m^{-3} in the Turkish shelf break (Sta. 3, Leg 1) and at a station located between central gyre and the shelf break (Sta. 7, Leg 1) (Fig. 4A). The vertical distribution was homogeneous with slight sub-surface maxima. Concentrations were relatively high at light deficient depths (i.e. at 30 m). In the shelf and shelf-break regions, the formation of a well-defined subsurface maximum is often prevented due to strong currents (e.g., Rim current) and vertical mixing (Yılmaz et al., 1998b). PP was maximum at the surface or in the range of 25–45 mg C m^{-3} d^{-1}. PP rates decreased with increasing depth to <5 mg C m^{-3} d^{-1} at the bottom of the euphotic zone (Fig. 4A).

In the region of Sakarya Canyon, well-defined subsurface Chl and in situ fluorescence maxima were observed at 10–5% I_0 isolume (5–10 m) in the upper thermocline (Fig. 4B). The maximum was more intense (>1 mg m^{-3}) for the Chl profile than for the fluorescence profile. Chl concentrations decreased gradually with depth in the euphotic zone. The Chl integrated to 1% I_0 isolume was twice as large (9.6 mg m^{-2}) over the deep part of the canyon (Sta. 10-Deep, Leg 1) than over the to shallower part (Sta. 10-Shallow, Leg 1), where the integrated Chl was 4.8 mg m^{-2} (Table 2). Similar trends were observed in PP data, lower areal primary production (119 mg C m^{-2} d^{-1}) was measured for the shallow station, and the rate was 2-fold higher (237 mg C m^{-2} d^{-1}) at the deeper Sakarya Canyon station (Table 2). These Sakarya stations also had well-defined subsurface maxima in PP. At the Sta. 10 Shallow the maximum was near the surface (at 40–35% I_0 isolume at 1.5–2 m) while at Sta. 10-Deep the maximum coincided with the in situ fluorescence and/or Chl maxima (Fig. 4B). At these stations there was relatively high carbon uptake rates at low light levels (10–5% I_0 isolume equivalent to a light intensity of 50–100 micro-Einstein m^{-2} s^{-1}). Lateral transports of water masses, having different physical, chemical and biological characteristics influence the subsurface layers and may cause the vertical variability seen in both Chl and PP. Similar subsurface maxima have been reported previously in the Black Sea for late spring–early summer. These were attributed to a deepening of the euphotic zone in the summer (Sorokin, 2002). This may explain the relatively high integrated values of primary production in the shelf-break regions (Table 2).

The depth of the euphotic zone (1% I_0) was relatively deeper in the central gyre (20 m for Sta. 6, Leg 1 and 25 m for Sta. 2, Leg 2), and the Chl and in situ fluorescence profiles both had deep maxima (Fig. 4C). In the upper euphotic zone both in situ fluorescence and Chl were almost constant and low (i.e. Chl concentration was in between 0.1 and 0.2 mg m^{-3}). The Chl concentration at the maximum was relatively low when compared with the maximum concentrations measured at Sakarya Canyon and the NW shelf stations. Previous work has shown that the deep Chl maxima is a well known characteristics of open Black Sea waters for the stratification seasons (Sorokin, 2002; Yılmaz et al., 1998b; Yayla et al., 2001). Surface PP rates were relatively low (10–20 mg C m^{-3} d^{-1}) and the values decreased with depth. There was no subsurface maximum in PP coinciding with deep Chl maximum (Fig. 4C).

The vertical distributions of Chl and in situ fluorescence were different in the NW shelf and slope region (Fig. 4D) where the surface values were relatively high (>0.2 mg m^{-3}). A maximum (0.45 mg m^{-3}) was observed at low light levels (8–5% I_0 isolume at 10–12 m). Chl concentrations and in situ fluorescence values were high in the euphotic zone, and the vertical profiles showed a broad maximum and/or homogeneous type of structure in the mixed layer. PP rates ranged from 20 to 30 mg C m^{-3} d^{-1} at the surface and did not change or even increased slightly at low light levels in the euphotic zone. Below this depth PP rates decreased steadily and below 1% I_0 isolume values

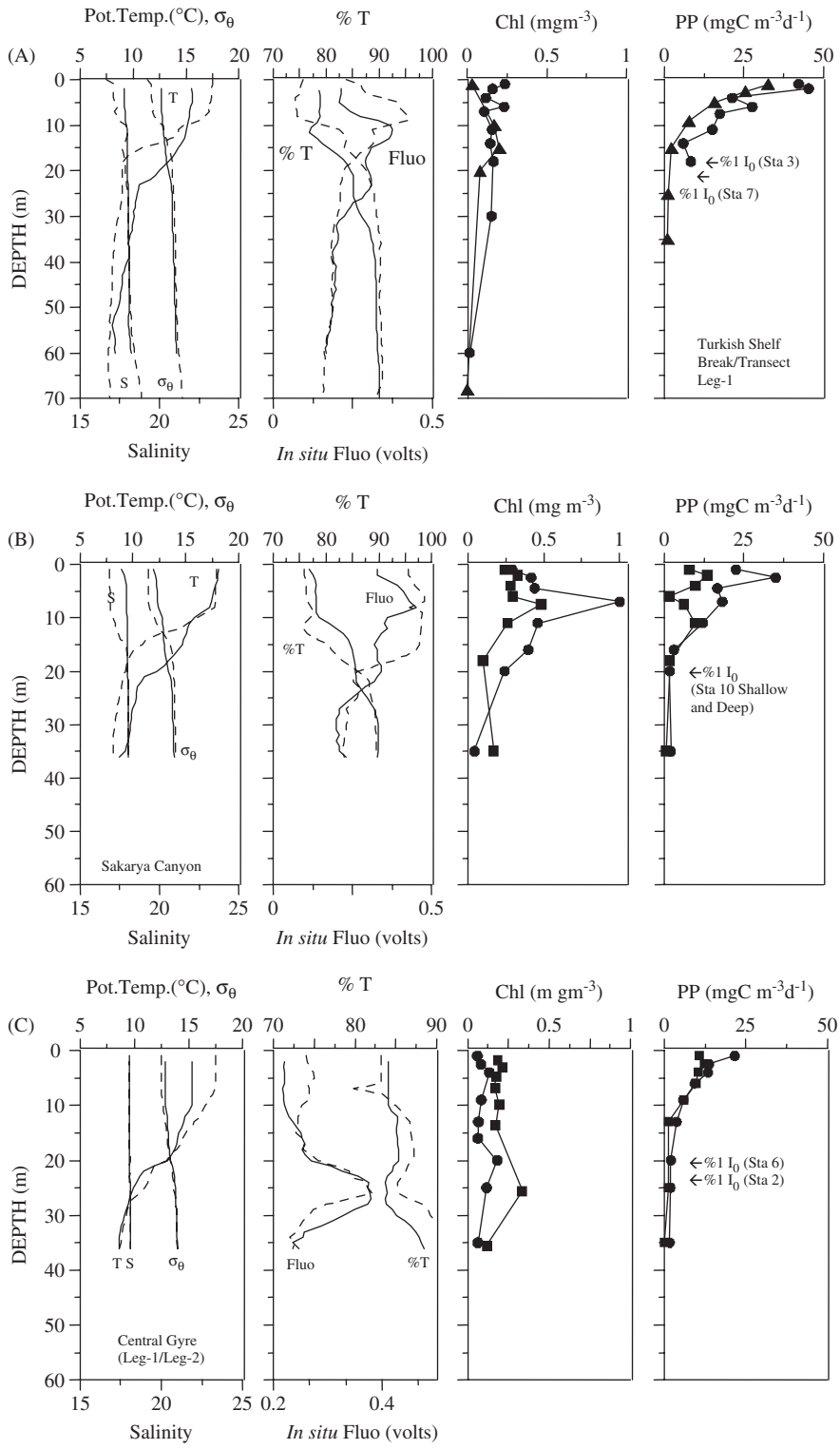

Fig. 4. Vertical profiles of hydrographic parameters (potential temperature, $T = {}^{\circ}\mathrm{C}$; salinity, $S = ‰$; and sigma–theta, σ_θ), light transmission ($\%T$), in situ fluorescence (In situ Fluo = volts), chlorophyll-a ($\mathrm{Chl} = \mathrm{mg\,m^{-3}}$), and primary production ($\mathrm{PP} = \mathrm{mg\,C\,m^{-3}\,d^{-1}}$) for: (A) Turkish shelf-break region (Leg 1-Sta. 3; ____/●) and for a station within transect between Turkish shelf and central cyclone (Leg 1-Sta. 7;_____/▲), (B) Sakarya Canyon region (Leg 1-Sta. 10: Shallow; _____/■ and deep stations; ____/●), (C) Central cyclone (Leg 1-Sta. 6; ____/● and Leg 2-Sta. 2; _____/■), (D) Northwestern shelf/slope region (Leg 2-Sta. 3; ____/● and Sta. 8; _____/■), (E) Sevastopol eddy region (Leg 2-Sta. 12; ____/●). The depth of euphotic zone (or 1% I_0 isolume) was shown by thick arrow for each station.

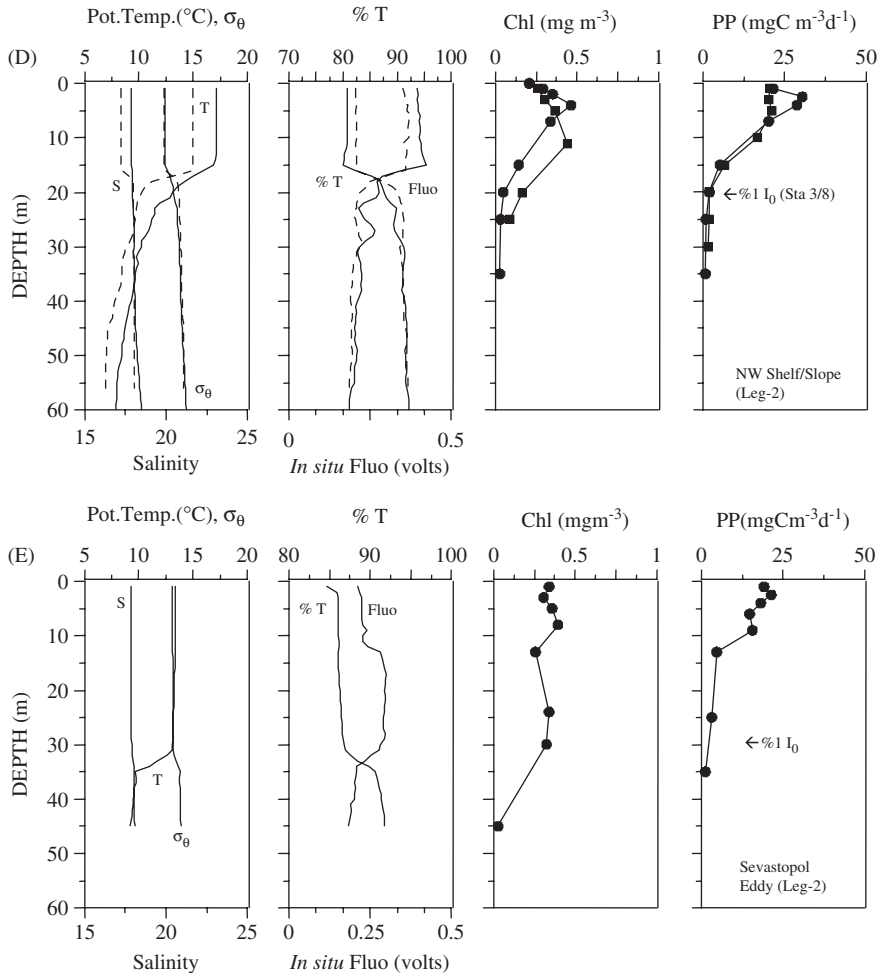

Fig. 4. (*Continued*)

were low. The relatively high phytoplankton biomass (e.g., Chl concentration) and primary production rates suggest that there was no nutrient limitation for the photoautotrophically active biomass in this region (Fig. 4D).

The station located in the Sevastopol eddy region (Sta. 12, Leg 2) was completely different from the other stations in terms of hydrography and upper-layer biological processes (Fig. 4E). The mixed layer was deeper (30–35 m) and coincided with the 1% I_0 isolume. In situ fluorescence and Chl profiles were homogeneous down to the bottom of the euphotic zone at 30 m. The average Chl concentration in the mixed layer was $0.35\,mg\,m^{-3}$. PP rates were also constant at $\sim 20\,mg\,C\,m^{-3}\,d^{-1}$ in the surface layer (0–10 m or 7% I_0). Although PP rates decreased sharply below the 1% I_0 isolume, the homogeneous vertical structure and relatively thick euphotic zone resulted in higher estimates of integrated primary production in the eddy. Such vertical distributions of Chl and PP result from homogenization of photoautotrophic organisms by intense vertical mixing in the eddy.

3.3. Primary production and nutrient limitation

Nutrient enrichment bioassays using ^{14}C were performed in the Turkish shelf-break area (Sta. 3), in the central gyre (Sta. 6) during Leg 1, and in the NW Shelf (Sta. 8) during Leg 2 (Fig. 5), in order to stiumulate carbon uptake rates and to determine the limiting nutrients. Rates increased after addition of NO_3 and NH_4, but PO_4 and Si addition had no affect. When all nutrients (PNS) were available, the uptake rates increased significantly to values almost three times higher than in the control samples. An

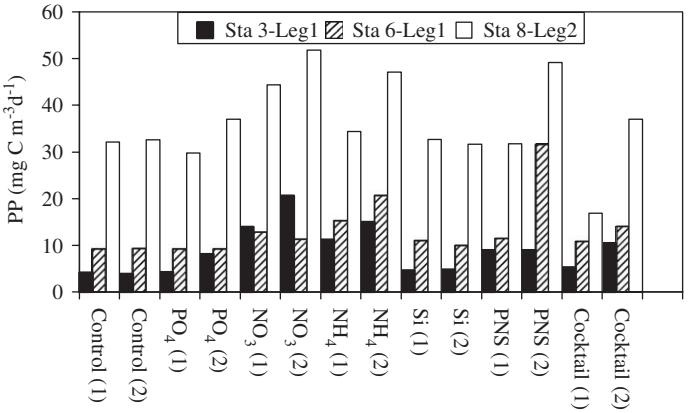

Fig. 5. The results of nutrient bioassay tests using ^{14}C technique for Turkish shelf break (Leg1-Sta. 3), western central cyclone (Leg 1-Sta. 6) and for NW shelf area (Leg 2-Sta. 8). Sampling depths for bioassay tests were 11 m for Sta. 3, 25 m for Sta. 6 (fluorescence maximum) and surface (1 m) for Sta. 8. Nutrients were added separately (as PO_4, NO_3, NH_4 and Si), all nutrients together (PNS) and all nutrients plus iron (cocktail). Numbers in parenthesis (1 and 2) denotes the different concentration levels (see methodology for the initial concentrations before the bioassay). Primary production (PP) is given as mg C m^{-3} d^{-1}.

enrichment with all four major nutrients and iron did not show significantly higher uptake rates. Comparison of the results obtained from the PNS (all nutrients but no Fe) and cocktail (all nutrients and Fe addition) indicated that growth stimulation was less pronounced with the iron addition. This observation could be the result of the response exhibited by the phytoplankton population to high iron concentration (See methodology) and/or due to complex formation by iron. The iron addition experiments did not exhibit consistent results. These findings support the conclusion that Black Sea waters are nitrogen-limited as was previously suggested by Yayla et al. (2001). The NO_3/PO_4 ratio is low (<3) in the euphotic zone and at the top of the nutricline (between 2.5 and 6.5) in both the central gyre and the peripheral regions in the Black Sea (Baştürk et al., 1997). As a result, vertical mixing of these waters results in nitrogen limitation (Yılmaz et al., 1998b).

On the NW shelf (Sta. 8, Leg 2), the bioassay results showed that phytoplankton uptake rates changed slightly with addition of nutrients, both separately and in combined mixtures (PNS and cocktail) (Fig. 5). The increase in carbon uptake rates in the bioassay tests on the NW shelf was in the range of 10–50% with respect to non-enriched samples. There was a significant increase of the NO_3/PO_4 ratio in the Danube riverine input over the past three decades. The ratio was 11.7 in the 1970s (Almazo, 1961, cited in Cociasu et al., 1996) and 22–33 in 1988–1992 (Cociasu et al., 1996). The ratios were even higher (>50) in the 1990s and reached 100 in 1996. These increases were due to the net decrease in phosphate. After 1996 the ratio decreased to 20 (still higher than the Redfield ratio of 6.6) in 2000 due to the sharp decrease in inorganic nitrogen (Cociasu and Popa, 2002). The nutritional status of the NW shelf area may have resulted in phosphorus limitation of primary production in the 1980s and 1990s, but the bioassay tests during *Knorr* 2001 did not show clearly P-limitation on the shelf (Fig. 5). This was probably because of the sharp decrease in the NO_3/PO_4 ratio of the Danube riverine input at the beginning of the 2000s.

The depletion of dissolved reactive silicate in surface waters was determined to have been an important characteristic of the Black Sea ecosystem during the 1970s and 1980s, while anthropogenic impact was causing an increase in N and P input to the Black Sea in the same period. These changes in input fluxes resulted in dramatic shifts in phytoplankton species composition from siliceous (mainly diatoms) to non-siliceous species, mainly to coccolithophores and flagellates (Cociasu et al., 1996; Humborg et al., 1997). The significant changes in riverine input (i.e. annual nitrate input from the Danube decreased from 770 thousand tons in 1991 to 108.9 thousand tons in 2000) (Cociasu and Popa, 2002) resulted in hydrochemical changes in the Black Sea. Concentrations of nitrate decreased considerably, and concentrations of silicate increased in the oxic and decreased in the anoxic zone in 1990s (Konovalov et al., 1999; Cociasu and Popa, 2002). Therefore silicate may not be a critical

element for limiting primary production considering the significant changes in nitrate and phosphate concentrations in the Danube River and the Black Sea over the past decades. The bioassay tests performed at the shelf and open-water sites in May–June 2001 showed that silicate addition did not stimulate carbon uptake rates (Fig. 5). Microscopic analysis performed during this cruise supported these findings, since the bulk of the total phytoplankton biomass (91%) was made up of dinoflagellates and coccolithophores (Soydemir et al., 2003).

3.4. Mid-water ChP

ChP rates were measured at two stations during Leg 1 (Sta. 6, Central Gyre and Sta. 10-Deep, Sakarya Canyon). The results are presented as vertical profiles together with the photoautotrophic production, hydrographic, light transmission, in situ fluorescence, dissolved oxygen, and hydrogen sulfide data (Fig. 6). ChP rates increased in the redox transition zone in the water column, in the depth intervals between 108 and 131 m in the central gyre (Sta. 6, Leg 1) and between 175 and 262 m (or 275 m by extrapolation) in the Sakarya Canyon station (Fig. 6A and 6B, Table 4). The maximum for ChP at Sta. 6 corresponded to the $\sigma_\theta = 16.1-16.3$ with the peak at $\sigma_\theta = 16.25$ (123 m), which coincided with the lower boundary of FPL (Fig. 6A). ChP rates were significantly higher at the Sakarya Canyon location (almost 8 times higher at the maximum depth) and the broad peak corresponded to $\sigma_\theta = 16.35-16.7$. The maximum was located at $\sigma_\theta = 16.5$ (210 m) and again coincided with the lower boundary of FPL (Fig. 6B). The chemoautotrophic layer was located at a shallower depth or at a $\Delta\sigma_\theta = 0.25$ lower isopycnal surface in the central gyre station compared with the Sakarya Canyon region. The comparisons of light transmission and ChP between the central gyre and Sakarya Canyon regions are clearly observed in Fig. 6C. The depth of maximum ChP was in the sulfide zone just below the O_2–H_2S interface (Fig. 6A and 6B) as has been previously observed in the Black Sea (Sorokin et al., 1995) and Cariaco Basin (Taylor et al., 2001).

The presence of the chemoautotrophic layer in the Black Sea also was confirmed by the vertical distribution of particulate $\delta^{15}N$ (Çoban-Yıldız et al., 2006a). At the base of the suboxic zone, suspended particulate organic matter was depleted in heavier isotope suggesting formation of newly formed particles. The minimum in $\delta^{15}N$ occurred at the suboxic–anoxic interface, where suspended particulate concentrations increased (Çoban-Yıldız et al., 2006a). The depth of maximum ChP also coincided with the secondary maxima in total bacterial abundance and biomass at the central gyre station (Morgan et al., 2006). A maximum in bacterial biomass occurred at $\sigma_\theta = 16.1$ (110 m) and maximum bacterial production rates were observed at $\sigma_\theta = 16.2$ (118 m). Higher chemoautotrophic activity was observed at the interface ($\sigma_\theta = 16.4$–16.7) in Sakarya Canyon (Sta. 10-Deep, Leg 1), which coincided with the higher heterotrophic bacterial biomass and abundance (e.g., at $\sigma_\theta = 16.6$–16.7, at Sta. 14, Leg 2) (Morgan et al., 2006). The increase in bacterial biomass and production may be related to the increase in chemoautotrophy, through the transfer of recently assimilated inorganic carbon to heterotrophic bacterial populations. The value of particulate $\delta^{13}C$ was also higher in the same layer, consistent with the tendency for heavier ^{13}C to be preferentially converted from DOC to POM by bacterial activity (Çoban Yıldız et al., 2006a). Dark carbon uptake at the interface is the sum of chemoautotrophy and bacterial heterotrophy (Karl and Knauer, 1991). Similar trends were observed in the Cariaco Basin (Taylor et al., 2001). In the Cariaco Basin, the fraction of heterotrophic bacterial production based on dissolved inorganic carbon (parallel to dissolved organic carbon) was about 2.2% of the total uptake. Chemoautotrophy fueled by upward fluxes of reduced sulfur species from anoxic waters amounted to 97% of the total dark uptake. By comparison, in the Black Sea lower bacterial production rates were determined at the O_2–H_2S interface both at the central gyre and Sakarya Canyon shelf break. Heterotrophic bacterial biomass and abundances were significantly higher (especially at shelf-break station) (Morgan et al., 2006).

Areal ChP for the central gyre station was 63 mg C m^{-2} d^{-1} for the maximum (between 108 and 131 m) at the oxic–anoxic interface and was 93 mg C m^{-2} d^{-1} for the whole water column down to anoxic layer (from 60 and 164 m) (Table 4). This ChP was equivalent to 43% of the surface photoautotrophic production or 30% of overall carbon production (photoautotrophic plus ChP) for the whole water column from the surface down to the anoxic layer (Table 4). Our data showed that ChP in Sakarya Canyon (Sta. 10-Deep) was as high as 1930 mg C m^{-2} d^{-1} in the chemoautotrophic layer

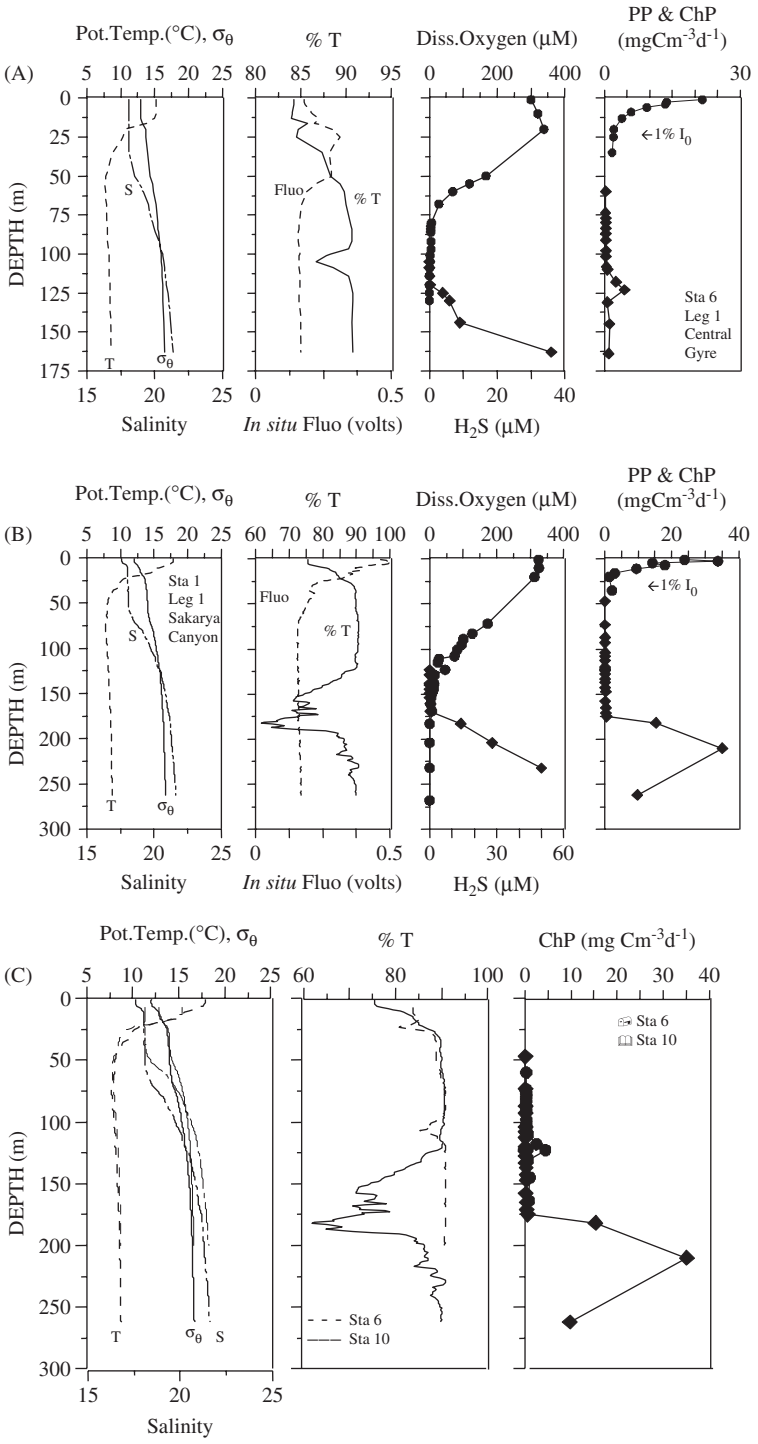

Fig. 6. Vertical profiles of hydrographic parameters (potential temperature, $T = {}^{\circ}\mathrm{C}$; salinity, $S = ‰$; and sigma–theta, σ_θ), light transmission (%T), in situ fluorescence (In situ Fluo = volts), dissolved oxygen (μM, ●), hydrogen sulfide (H_2S, μM, ◆), primary production (PP, mg C m^{-3} d^{-1}; ●), and chemoautotrophic production (ChP, mg C m^{-3} d^{-1}; ◆), and 1% I_0 isolume (←, %1 I_0) for: (A) western central gyre (Leg 1-Sta. 6), (B) Sakarya Canyon region (Leg 1-Sta. 10-Deep), (C) chemoautotrophic production rates of these two stations (Sta. 6, ● and Sta. 10-Deep, ◆) were combined in the same graph. Solid line represents the Sakarya Canyon station (Sta. 10-Deep) whereas dashed line represents the central gyre station (Sta. 6).

Table 4
Integrated primary production (Int-PP) and chemoautotrophic production (ChP) rates in the Black Sea during May–June 2001

	Sta. 6/Leg-1 (western central cyclone)	Sta. 10-deep/Leg-1 (Sakarya Canyon)
Int-PP (down to 1% I_0 isolume)	145 mg C m^{-2} d^{-1}	237 mg C m^{-2} d^{-1}
Chemoautotrophic layer	108–131 m	175–262 m
σ_t interval for chemoautotrophic layer	16.1–16.3	16.4–16.7
Maximum ChP located at	$\sigma_\theta = 16.25$ Depth = 123 m	$\sigma_\theta = 16.5$ Depth = 210 m
Maximum ChP at peak point	4.5 mg C m^{-3} d^{-1}	35.2 mg C m^{-3} d^{-1}
Int-ChP (whole water column) (60–164 m/Sta. 6 and 47–262 m/Sta. 10)	93 mg C m^{-2} d^{-1}	1951 mg C m^{-2} d^{-1}
Int-ChP (chemoautotrophic layer) (108–131 m/Sta. 6 and 175–262 m/Sta. 10)	63 mg C m^{-2} d^{-1}	1930 mg C m^{-2} d^{-1}
Contribution to surface production (ChP/PP)	43%	814%
Contribution to water column production (ChP/PP + ChP)	30%	89%

(almost 30 times higher than observed at the central gyre station), which was equivalent to 814% of the surface production or 89% of total (photoautotrophic and chemoautotrophic) carbon production in the whole water column (Table 4). These areal ChP rates might be overestimated because of irregular sampling at the oxic/anoxic interface. Dark uptake rates above the chemoautotrophic layer due to anaplerotic reactions of heterotrophs and phototrophs were insignificant ($=21$ mg C m^{-2} d^{-1}) at Sta. 10-Deep, and overall dark carbon uptake rates corresponded to 1951 mg C m^{-2} d^{-1}. Areal ChP rates given for the Black Sea (24–324 mg C m^{-2} d^{-1}) are in good agreement with our new data, especially if one considers the values given previously for the open waters by Jørgensen et al. (1991) and Sorokin et al. (1995). ChP rates were calculated as 10–32% of surface photoautotrophic production in the Black Sea. Heterotrophic bacterial production was low and approximately equal to the rate of ChP at the interface in the central Black Sea region during the 1988 *Knorr* cruise which was the only time simultaneous measurements were performed (Jørgensen et al., 1991; Karl and Knauer, 1991). The range of ChP for the Cariaco Basin was determined as 312–1884 mg C m^{-2} d^{-1}, and this level of ChP was equivalent to between 10% and 333% of the surface primary production (Taylor et al., 2001). Though this discussion is based on only two data points in the Black Sea, the results suggest that ChP is extremely important, thus it is imperative to collect more data of this type. The ChP rates (1930 mg C m^{-2} d^{-1}) estimated for Sakarya Canyon region (Sta. 10-Deep, Leg 1) seem to be extremely high compared with the previous findings in the Black Sea, and these need to be verified.

Anomalies in dissolved oxygen above and in the suboxic layer were not very significant for the Sakarya Canyon station (Fig. 6B) (when compared to those of the shelf-break station/Sta. 3, Leg 1), but the multiple maxima in the FPL at the lower boundary of suboxic zone indicated the importance of lateral transports or intrusions of oxygenated Mediterranean waters in this region. Lateral advection of biogenic particles from more productive regions to the chemoautotrophic layer at this station is possible since the lateral intrusion of Mediterranean-origin water masses have characteristics of the Turkish shelf and shelf-break regions (Oğuz et al., 2001; Konovalov et al., 2003). The sandwiched water layers (oxygenated and sulfur-containing waters located layer by layer at intermediate depths corresponding to suboxic layer at certain isopycnal surfaces) have been often observed in the Sakarya Canyon region during the recent field studies (1997 summer, 1998 late spring and autumn 1999) (Yayla, 1999; Yayla et al., 2001; Oğuz et al., 2001; Çoban Yıldız et al., 2006a, b). But, these examples observed in the Sakarya Canyon region in May–June 2001 seem to be less significant for the transport of high amount of particles from the slope since the anomalies in temperature, salinity and dissolved oxygen were not very significant. On the other hand, dissolved oxgen pumped by lateral intrusions might be immediately used in aerobic heterotrophy, nitrification, or abiotic oxidation of redox sensitive element (S, Mn and Fe). The energy source for the observed high chemoautotrophy is H_2S, whether by direct utilization or through intermediate oxidation products like elemental sulfur, $S_2O_3^{2-}$, or SO_3^{2-}, which may be produced extensively by these intrusion processes (Oğuz et al., 2001; Konovalov

et al., 2003). Çoban Yıldız et al. (2006a) showed that particulate organic matter was depleted in heavier nitrogen isotope ($\delta^{15}N \approx -10‰$) at the suboxic/anoxic interface, confirming the dominance of newly formed particles. In other words particle organic-matter production exceeds the decomposition. The largest increases in particulate organic-matter concentrations corresponded to the largest depletions in particulate $\delta^{15}N$ at the interface (Çoban-Yıldız et al., 2006a). The other observation is the presence of elemental sulfur (S_8 and S_6) at the interface, which has been confirmed by bulk compositional analysis using a pyrolysis GC–MS technique for the suspended particles collected over the whole water column (Çoban-Yıldız et al., 2006b). As suggested by Lewis and Landing (1991) and Murray et al. (1995), lateral transport of oxygenated waters may stimulate the oxidation of H_2S to elemental sulfur and intensive microbial activity and oxidation processes because advective transports play an important role in providing the e-donors for the chemoautotrophic activity. Thus the broad and relatively strong peak observed in the ChP rates at the Sakarya station might be related to the strong in situ microbial production. Water in the Bosphorus Plume contains oxygen and lateral ventilation by the Bosphorus Plume along isopycnals produces oxygen anomalies at mid-water depths at the shelf break (Latif et al., 1991; Murray et al., 1995). Consequently, one would expect higher contribution of organic carbon production at intermediate depths along the southern shelf-break area of Black Sea since the advective mechanisms and lateral transports seem to be more important than vertical transport of enough H_2S to fuel chemoautotrophic activities.

4. Conclusions

Present data on chlorophyll-*a* (representing phytoplankton biomass) and primary production in the Black Sea showed that NW shelf waters and southern shelf/shelf-break regions are usually more productive than the central part of the sea. However, the values for the May–June 2001 period were considerably lower, indicating most probably the post-bloom conditions. On the other hand, Nezlin (2001) and Oğuz et al. (2003) argued that nutrient supply from the nutricline was not efficient due to strong stratification and weak turbulent mixing during the mild winters that occurred from 1995 to 2002. This resulted in less pronounced early-spring blooms and/or low new production. A gradual decrease in biomass from a maximum in November towards summer was observed and summer/autumn blooms, although weaker, lasted longer as compared to their counterparts before the mid-1990s. Therefore relatively low chlorophyll-*a* concentrations and low primary production rates were observed in May–June 2001 compared with data from the same seasons in the 1980s and the first half of the 1990s. Vertical distributions of phytoplankton biomass were influenced by water-column dynamics. There is a homogenous distribution on the shelf, a well-defined sub-surface maxima at the shelf break, and deep chlorophyll-*a* maxima in the central gyre. Bioassay experiments performed for both shelf and open waters in May–June 2001 revealed that silicate was not a critical element for limiting carbon uptake rates. Nitrogen was determined to be the limiting nutrient especially for the open Black Sea waters. Chemoautotrophic production (ChP) rates in the water column increased in the redox transition zone, which coincided with the lower boundary of fine particle layer. The chemoautotrophic layer was located at shallower depths or at 0.25 sigma–theta unit shallower isopycnal surface in the central gyre compared to the shelf-break region in Sakarya Canyon. Integrated ChP at the interface was equivalent to 30% and 89% of the total water-column production in the central gyre and Sakarya Canyon regions, respectively. Chemoautotrophic activities reflect the more intense microbial activity at the suboxic–anoxic transition layer, especially shelf-break regions of the southwestern Black Sea where the partial aeration is performed by Bosphorus plume. Thus, multilayer systems having anoxia, support multiple layers of biological in situ production and the Black Sea represents a unique environment for such processes.

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