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Surface and midwater sources of organic carbon by photo- and chemo-autotrophic production in the Black Sea

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Abstract - Multilayer systems having anoxia like the Black Sea, support multiple layers of biological production. During R/V Knorr May-June 2001 cruise, chlorophyll-a concentration, photosynthetic and chemosynthetic production rates have been determined in the western Black Sea. The primary production and chlorophyll-a data revealed that the post-bloom conditions were prevailing during the sampling period. Dark uptake rates measured down to anoxic layer showed that, bacterial chemoautotrophic production within the interface makes significant contribution to overall organic carbon pool in the Black Sea.

Keywords- Black Sea, photosynthetic and chemosynthetic production, chlorophyll-a, post-bloom conditions

Introduction

Input from the rivers especially in the northwestern shelf is the main source of nutrients in the Black Sea (Cociasu *et al.*, 1996). As has been reported previously (Yılmaz *et al*, 1998; the references cited therein), the coastal waters of the Black Sea are principally fed by the riverine input and by the lateral as well as the vertical nutrient transport mechanisms. In the open ecosystem, which is dominated by the cyclonic eddies, primary production is mainly sustained by the influx of nutrients from the oxic/suboxic lower layers mainly by vertical mixing processes especially in winter. However, the input from the anoxic layer is limited due to the presence of a permanent pycnocline in the Black Sea. The pycnocline coincides with the oxic-anoxic transition zone where intense denitrification and redox-dependent processes also limit nitrogen and phosphorus input to the productive layer (Baştürk *et al.,* 1994). In comparison, the contribution of atmospheric nutrient input appears to be marginal(Kubilay *et al.*, 1995). Long-term data obtained since 60's have shown that primary production in the Black Sea generally displayed two phytoplankton maxima throughout the year; the major one occurred in early spring (mainly diatoms) while a secondary peak appeared in autumn (mainly coccolithophorids) (Vedernikov and Demidov, 1993). More recently, additional summer (in the late 1980s and early 1990s) and more significant autumn blooms (in the second half of 1990s) which are dominated by dinoflagellates and coccolithophorids) have frequently been observed in both the coastal and open waters (Hay *et al.*, 1990; Yılmaz *et al.*, 1997; Yılmaz *et al.*, 1998; Çoban Yıldız et al., this volume; Yunev *et al.*, 2002; Oğuz et al., 2003). Estimations of primary production have ranged from 570 to 1,200 mg C m^{-2} d^{-1} at the NW shelf, between 320 to 500 mg C m^{-2} d^{-1} in the regions of continental slope, and between 100 to 370 mg C m^{-2} d^{-1} in the open regions during 1960-1991 period (Vedernikov *et al.*, 1996). Similar primary production rates (247-1,925 mg C m^{-2} d^{-1} for spring and 405-687 mgC $m^{-2}d^{-1}$ for summer/autumn period) have been estimated for the southern Black Sea for 1995-1996 period (Yılmaz *et al.*, 1998).

Chemoautotrophic production were calculated as 10%-32% of the surface primary production in the Black Sea during Knorr 1988 Cruise (simultaneous measurements, Jorgensen et al., 1991; Karl and Knauer, 1991). The range of chemoautotrophic production was determined as 312-1884 mg C m^{-2} d^{-1} for Cariaco Trench which is one of the well known anoxic basins and this level of chemosynthetic production was equivalent to between 10% and 333% surface primary production (Taylor *et al.*, 2001). Oxic-anoxic interface and sub-oxic layer provides active microbial food web in anoxic basins. Chemoautotrophic production may provide new labile organic matter in this zones in anoxic environments where dark inorganic carbon uptake rates increase and this process is well defined in the Cariaco Trench and in the Black Sea systems (Sorokin *et al.*, 1995; Jorgensen *at al.*, 1991; Karl and Knauer, 1991; Taylor *et al.*, 2001).

Materials and Methods

Hydrographic data were collected using a Sea-Bird CTD probe. Light transmission and *in situ* fluorescence data were collected using Chelsea type *in situ* fluorometer and a Sea Tech single beam light transmissometer (660 nm), attached to the CTD probe. A quantameter (LI-COR, LI-1000 Data Logger and LI-192SA Underwater Quantum Sensor) was used for irradiance measurements in the water column. Dissolved oxygen (DO) and hydrogen sulfide (H_2S) concentrations were determined by conventional Winkler and Iodometric Back Titration methods (Baştürk *et al.*, 1994) while low H_2S concentrations were determined by the colorimetric method (Cline, 1969). Chlorophyll-a (Chl-a) was determined fluorometrically within acetone extracts using Sigma Chl-a standard for calibration purposes (JGOFS, 1994). Photosynthetic carbon uptake rates were measured by standart ^{14}C radio-isotope technique (JGOFS, 1994). Samples were regularly collected from 60%, 36%, 22%, 12-8%, 3%, 1% and 0,1% light depths and after radiactive carbon addition, the samples were incubated at simulated *in situ* conditions for 12-24 hrs. Trends and the peaks in the light transmission profiles were taken into account during sampling for dark uptake

measurements in order to find reliable proxies for bacterial maxima at the oxic-anoxic interface. Similar radiocarbon tracing technique was applied for the chemosynthetic production measurements but samples were incubated at 8-10 °C in the dark for 24 hrs (Taylor *et al.*, 2001). Carbon assimilation rates were normalized to mg C m^{-3} d^{-1} by the multiplication with total dissolved $^{12}CO_2$ concentrations.

Results and Discussion

Photosythetic production (plus chlorophyll-a concentration) and chemosynthetic production or dark inorganic carbon uptake rates were estimated at 10 stations in the western Black Sea (including northwestern shelf) but only 2 representative stations (one at the central gyre and one in the coastal station near Sakarya Canyon) were presented here (Tables 1,2; Figs. 1,2). Overall evaluation revealed that, euphotic zone integrated chlorophyll-a concentration was as low as 2.2 mg m^{-2} in the central gyre while it was as high as 19.9 mg m^{-2} in the NW shelf region. Areal net photosynthetic production rates were in between 119 and 376 mgC m^{-2} d^{-1}.

Table 1. Locations of the stations, Euphotic Zone depth (EZ), Euphotic Zone Integrated Active Chlorophyll-a, Average Net Primary Production (PP), and Dark Uptake rates for the upper lighted zone in the Black Sea during May-June 2001 cruise.

Date	Station	Latitude	Longitude	EZ (m)	Int- Chl-a (mg m^{-2})	Ave-Net Integr. PP (mgC$m^{-2}d^{-1}$)	Dark Uptake (mgC$m^{-2}d^{-1}$)
26.05.01	Leg1-6	42,48	30,77	20	2,2	154	19
03.06.01	Leg2-2	42,50	30,77	25	4,2	119	22
	Central Gyre						
31.05.01	Leg1-10 (Deep)	41,45	30,25	20*	9,6	250	20
	(Shallow)	41,42	30,25	18	4,8	126	24
	Sakarya Canyon						

* *Estimated from biological data*

Vertical Distribution of Chlorophyll-a (CHL) and Primary Production (PP)

CHL and PP together with *in situ* relative fluorescence, light transmission and hydrographical data have been represented as vertical profiles in Fig. 1. Euphotic zone (depth of 1% light with respect to surface) was relatively deeper in the central western gyre (20m for St 6, Leg-1 and 25m for St. 2, Leg-2) and CHL and *in situ* fluorescence profiles showed deep CHL maxima locating at the bottom of the euphotic zone or at 1% light depth (Fig. 1). In the upper euphotic zone both *in situ* fluorescence and CHL concentration were almost constant (between 0.1-0.2 mg m^{-3}). CHL concentration at the maximum was relatively low (2-5 times) when compared with the peak concentration observed at Sakarya canyon and NW shelf stations. Previous work also showed that deep chlorophyll-a maxima is well known characteristics of open Black

Sea waters for the stratification seasons (Sorokin, 2002 and the references cited there; Yilmaz et al., 1998). Surface PP rates were the lowest (10-20 mg C m^{-2} d^{-1}) among all measured PP rates and the vertical distribution showed a regular decreasing trend with decreasing light intensity.

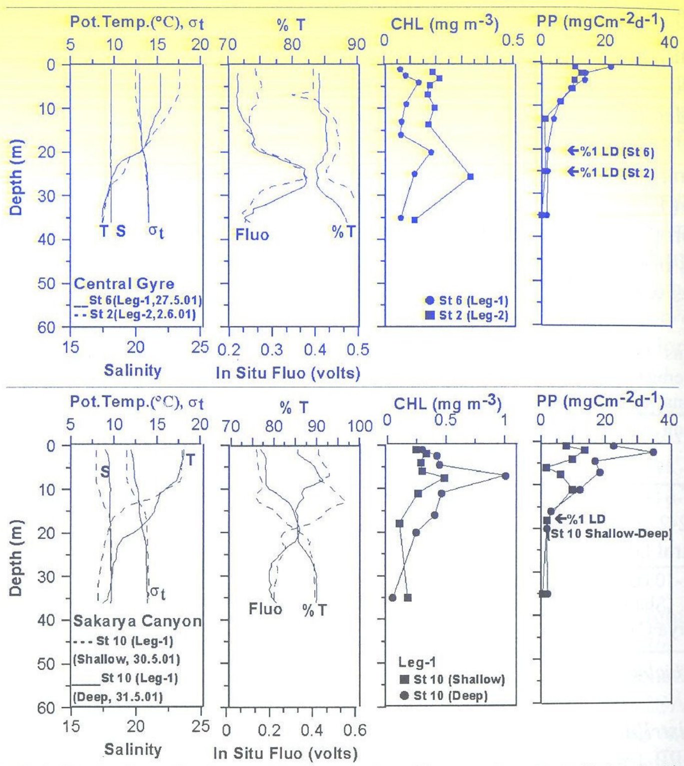

Fig. 1. Vertical distribution of hydrographical parameters (Temperature, T; Salinity, S; Sigma-theta, σ_t), *in situ* fluorescence (Fluo), Chlorophyll-a (CHL) and Average Daily Primary Production (PP) in the euphotic zone (defined as 1% light depth, LD) at the central gyre (Sta 6, Leg-1 and Sta 2, Leg-2) and Sakarya Canyon region (Sta 10, shallow and deep sections, Leg-1) during May-June 2001.

In Sakarya Canyon region, a well defined subsurface *in situ* fluorescence and CHL maxima (>1 mg m^{-3}) were observed at 10-5 % light depth or 5-10m (Fig. 1). The CHL concentrations above and the below the maximum were very similar (0.25 mg m^{-3}) in the euphotic zone. The areal concentration integrated down to 1% light depth was almost double (9.6 mg m^{-2}) at the deep part of the canyon (St 10-Deep, Leg-1) with

respect to shallower part (St 10-Shallow, Leg-1) where the areal concentration was as low as 4.8 mg m^{-2} (Table 1). The similar trends were observed in PP data, and lower areal primary production rates (126 mg C m^{-2} d^{-1}) was estimated for the shallow station while the rates were X2 times higher (250 mg C m^{-2} d^{-1}) at deep Sakarya canyon station. Two well defined subsurface peaks were defined in the vertical profiles of PP and the first one was at near surface (at 35-40% light depth or 1.5-2m) while the secondary one coincided with the *in situ* fluorescence and/or CHL maxima. Relatively high carbon uptake rates at low light levels (%10-5 light depth (or at 50-100 E m^{-2} s^{-1} light intensity) with respect to surface exposing to intense solar light (1020 E m^{-2} s^{-1}) were observed. Such vertical structures observed both in CHL and PP confirm the presence of lateral transports where the water masses having different physical, chemical and biological characteristics which may interfere the subsurface layers.

Chemoautotrophic mid-water production

Dark inorganic uptake rates as representing mainly the chemosynthetic production, increased in the redox transition zone in the water column, at the depth interval of 108-131 m in the central gyre (St 6, Leg-1) and of 175 - <262 m in the Sakarya Canyon (Fig 2, Table 2). The peak point for chemosynthetic production corresponded to the sigma-theta interval of 16.1-16.3 (the maximum located at σ_t=16.25 or at 123m) and coincided with the lower boundary of fine particle layer (FPL), where the light transmission decreased down to 86 % at σ_t =16.1 at St 6 (Fig. 6a). On the other hand, dark inorganic carbon uptake rates were significantly high in the Sakarya Canyon region (almost X8 times higher at the maximum depth) and a broad peak corresponded to the sigma-theta interval of 16.35 - <16.7 (the maximum has located at σ_t=16.5 or at 210m) and coincided again with the lower boundary of FPL where the light transmission decreased down to 62 % at σ_t =16.4. Chemosynthetic layer located at shallower depth and or 0.25 sigma-theta unit lighter isopycnal surface in the central gyre station when compared to the shelf break station in Sakarya canyon region. In general, the depth of maximum chemosynthesis was determined below the O_2-H_2S interface or at the lower boundary of sub-oxic layer (Fig. 2) as was observed in Cariaco Trench (Taylor *et al.,* 2001). Increase in bacterial biomass might be related to the increase in chemoautotrophy, through the transfer of recently assimilated inorganic carbon to heterotrophic bactial populations since the higher chemosynthetic activity observed at the interface (e.g. at σ_t = 16.4 – 16.7) in Sakarya canyon region (St 10-Deep, Leg-1) overlapped with the higher bacterial biomass and abundance (e.g. at σ_t = 16.6-16.7 or at 250m, at St 14, Leg-2) (Morgan *et al.*, unpublished data). Bacterial biomass and abundance were relatively low at the interface where the maximum was observed at σ_t = 16.1 (or at 110m) and the bacterial production rates were relatively significant at σ_t = 16.2 (or at 118m) (Morgan *et al.*, unpublished data) again coinciding with the chemosynthetic active layer in the central gyre (St 6, Leg-1) (Table 2). At the interface, dark carbon uptake is the sum of chemoautotrophy and partly bacterial heterotrophy (Karl and Knauer, 1991). In Cariaco Trench, the fraction of heterotrophic bacterial production on dissolved inorganic carbon (parallel to dissolved organic carbon) is almost %2.2 of the total uptake or chemoautotrophy amounts 97% of the total dark uptake fueled by upward fluxes of reduced sulfur species from anoxic waters.

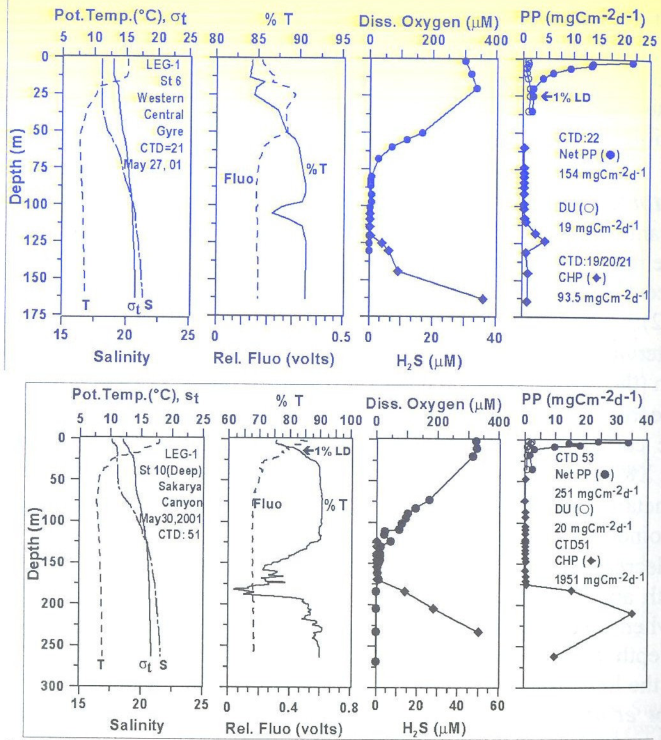

Fig. 2. Fig. 1. Vertical distribution of hydrographical parameters (Temperature, T; Salinity, S; Sigma-theta, σ_t), in situ fluorescence (Fluo), Light Transmission (%T), Dissolve Oxygen (DO), Hydrogen Sulfide (H_2S), Average Daily Primary Production (PP) and Dark Uptake rates (DU) in the euphotic zone (defined as 1% light depth, LD) and Chemosynthetic Production (CHP) at the central gyre (Sta 6, Leg-1) and Sakarya Canyon region (Sta 10, deep section, Leg-1).

Areal inorganic dark carbon uptake rates at the interface was determined as 93.5 mg C $m^{-2}d^{-1}$ for central gyre station and this production was equivalent to 54 % of the surface photosynthetic production or 35 % of overall carbon production

(photosynthetic plus chemosynthetic production) in the whole water column from surface down to anoxic layer (Table 2). The areal inorganic dark uptake rates was overestimated in Sakarya Canyon region (St 10-Deep) due to non-frequent sampling at the interface, but the present data showed that areal dark inorganic uptake rates was as high as 1951 mg C $m^{-2}d^{-1}$ (almost X20 times higher rates than those observed in the central gyre station) and it was equivalent to 722 % of the surface production or 88 % of overall carbon production in the whole water column (Table 2). Areal dark carbon uptake rates given for the Black Sea (24-324 mg C $m^{-2}d^{-1}$) are in good agreement with the present data especially if one considers the values given for the open waters (Jorgensen *et al.,* 1991; Sorokin et al., 1995). Chemoautotrophic production were calculated as 10%-32% of surface primary production in the Black Sea and heterotrophic bacterial production was low approximately equal to the rate of chemoautotrophic production at the interface in the central Black Sea region during 1988 Knorr Cruise when simultaneous measurements were performed (Jorgensen *et al.,* 1991; Karl and Knauer, 1991). The range of chemoautotrophic production was determined as 312-1884 mg C $m^{-2}d^{-1}$ for Cariaco Basin and this level of chemosynthetic production was equivalent to between 10% and 333% surface primary production (Taylor *et al.,* 2001). On the other hand, the chemosynthetic production rates (1951 mg C $m^{-2}d^{-1}$) estimated for Sakarya canyon region (St 10-Deep, Leg-1), seems to be extremely high when compared with the previous findings in the Black Sea.

Table 2. Integrated Photosynthetic (PP) and Chemosynthetic (CHP) production rates in the Black Sea during May-June 2001

	St 6 (W. Central Gyre)	St 10-Deep (Sakarya Canyon)
Integrated Gross PP (down to 1% light depth)	173 mg $Cm^{-2}d^{-1}$	270 mg $Cm^{-2}d^{-1}$
Chemosynthetic Layer	108 – 131 m	175 - <262 m
σ_t Interval for Chemosynthetic Layer	16.1 – 16.3	16.35 - <16.7
Maximum Peak Point of CHP located at σ_t = / Depth =	16.25 / 123m	16.5 / 210m
Max. Peak Value of CHP	4.5 $mgCm^{-2}d^{-1}$	35.2 $mgCm^{-2}d^{-1}$
Integrated CHP (down to anoxic layer)	93.5 $mgCm^{-2}d^{-1}$	1951 $mgCm^{-2}d^{-1}$
Contribution to Surface Production (CHP/PP)	54 %	722 %
Contribution to Water Column Production (CHP/CHP+PP)	35 %	88 %

Conclusions

Present data showed that, chemoaototrophic production at O_2-H_2S interface is relatively high in the Black Sea and it seems it is potential midwater source of sedimentary biogenic particles for the basin related to the microbial activities and redox processes which are persistent features in the Black Sea ecosystem. Bacterial chemoautotrophic production within the interface makes significant contribution to overall organic carbon production, influence elemnetal cycling at this layer and may influence the chemical quality of the sedimentary flux. Lateral transports of oxygenated waters from coastal areas enhance the chemoautotrophic production, even the carbon produced at midwater depths may exceed the surface photosynthetic production in shelf break areas.

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