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Carbon and nitrogen isotopic ratios of suspended particulate organic matter (SPOM) in the Black Sea water column

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Abstract

Carbon and nitrogen isotopic ratios (δ^{15}N and δ^{13}C) of suspended particulate organic matter (SPOM) in the water column of the Black Sea were measured at a total of nine stations in September–October (autumn) 1999 and May 2001. For comparison, a station in the Mediterranean Sea and one in the Sea of Marmara were sampled in October 1999. Large-sized particle samples, as well as samples of surface sediment were also collected for N and C isotopic analysis.

The results revealed important vertical and regional variations in N and C isotopic composition. Seasonal variations in SPOM δ^{15}N and δ^{13}C were not apparent. SPOM in the euphotic zone (EZ), oxycline, and suboxic/anoxic interface layers of the water column was characterized by distinct isotopic composition. In the EZ, the N and C isotopic ratios of SPOM were in the range typically observed for plankton-derived SPOM in the surface ocean (EZ means ranged from 2.7‰ to 5.9‰ for δ^{15}N and from −24.0‰ to −21.5‰ for δ^{13}C). Shelf region SPOM had higher δ^{15}N and lower δ^{13}C (EZ means of 5.9‰ and −24.0‰, respectively). Large-sized particles (LPOM) collected by zooplankton net tows had ~3‰ higher δ^{15}N values compared to SPOM, indicating fractionation during trophic transfer of nitrogen. SPOM in the oxycline increased by 3–6‰ for δ^{15}N, while δ^{13}C decreased by −2‰ to −4‰, which may be attributed to greater lipid content. In the suboxic/anoxic interface zone, SPOM isotopic ratios (δ^{15}N as low as 0.0‰ to −8.0‰) suggest chemoautotrophic production leading to dominance of new, in situ produced organic matter. The location of the most negative δ^{15}N values indicates that chemoautotrophic production is most intense at the shelf-break regions, possibly enhanced by mixing of oxygenated and nitrate-rich Mediterranean inflow waters with suboxic/anoxic Black Sea water.

Keywords: Black Sea; Mediterranean Sea; Marmara Sea; Organic matter; δ^{15}N; δ^{13}C

1. Introduction

The Black Sea is a semi-enclosed marine basin with net estuarine circulation. The large inputs of freshwater primarily from the Danube and Dnieper rivers are far in excess of regional evaporation. Accordingly, relatively fresh surface water leaves the Black Sea through the Bosporus, and deeper and relatively salty Mediterranean water enters at

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intermediate depths. Strong stratification caused by this large salinity difference between upper and lower layers severely limits ventilation of the Black Sea's interior. This results in permanent anoxic conditions in subsurface waters throughout the Black Sea. Its correspondingly well-defined oxic, suboxic and anoxic layers, with sharp chemical gradients along isopycnal surfaces (Codispoti et al., 1991; Tuğrul et al., 1992), have been an important natural laboratory for understanding marine redox processes.

The Mediterranean Sea and Black Sea are connected via the inland Sea of Marmara (Fig. 1). The near-surface environment of the eutrophic/mezotrophic Sea of Marmara is strongly influenced by the Black Sea upper-layer inflow (Polat and Tuğrul, 1995) as well as anthropogenic inputs (Orhon et al., 1994). The Northeastern Mediterranean is known to be an oligotrophic marine environment (Yılmaz and Tuğrul, 1998; Kress and Herut, 2001 and references therein) and is the dominant influence on the deep Sea of Marmara. As a result of strong two-layer stratification caused by counter-flows of the waters of Black and Mediterranean Seas, O_2 concentrations in the lower layer of the Sea of Marmara decline from saturated levels near its Mediterranean outlet to 30–50 μM, at the southern end of the Bosporus. Lower layer-flow entering the Bosporus remains oxic due to low residence time of this water mass (Beşiktepe et al., 1994). Despite its importance as the communication route between the Black and the Mediterranean Seas, there is limited published information on the chemical/biological oceanography of the Sea of Marmara (Sorokin et al., 1995; Polat and Tuğrul, 1995; Polat et al., 1998; Çoban-Yıldız et al., 2000a). To the best of our knowledge, there are no C or N isotopic measurements on suspended particulate organic matter (SPOM) from the Sea of Marmara.

Key to predicting the Black Sea's future and explaining the causes of its environmental variability (see, e.g., Bologa, 1985/1986; Murray et al.,

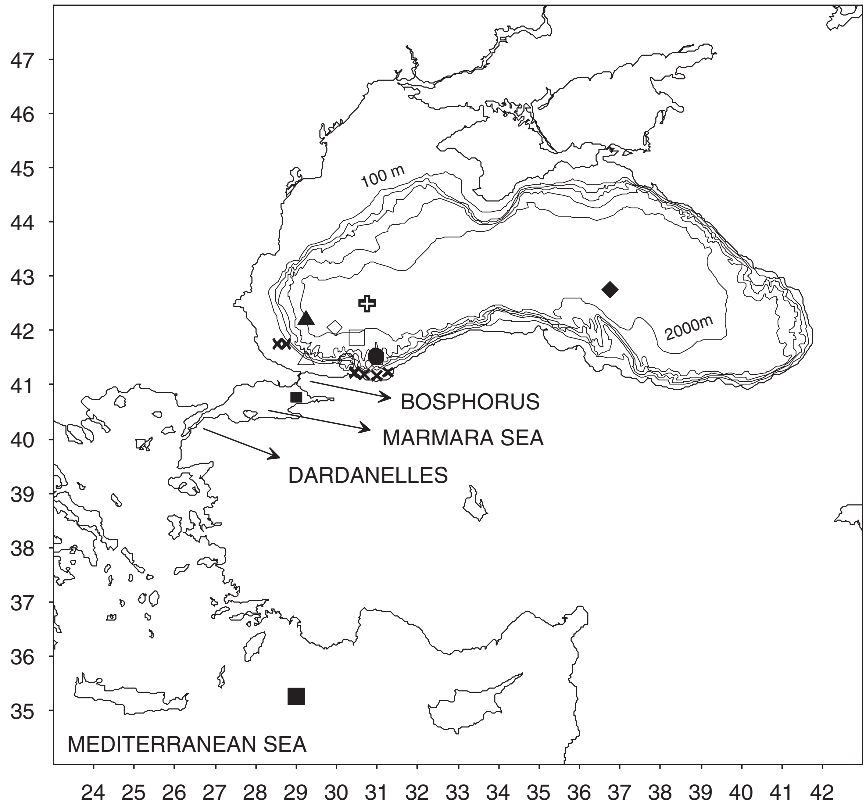

Fig. 1. Station locations visited in autumn 1999 (solid symbols labeled with 'A'; ●: A1, ◆: A2; ▲: A3) and May 2001 (open symbols, labeled with 'M'; △: M3, ◇: M5; □: M6; ✣: M7; ○: M10; ☆: M11) for SPOM sampling in the Black Sea. Station symbols for SPOM are as presented in Fig. 3 and Table 1. Sampling locations surface sediments along the south-western shelf (✕) for the Black Sea in 1988–1989 also are shown. SPOM samples for the Mediterranean and the Marmara Seas (■) were collected in autumn 1999.

1989; Bologa et al., 1999; Hay et al., 1990; Codispoti et al., 1991; Konovalov and Murray, 2001; Finenko et al., 2001; Kıdeyş, 2002; Yunev et al., 2002) is an understanding of the biogeochemical processes and mechanisms involved in production, consumption, decay and transformation of carbon and nitrogen species in the oxic, suboxic, and anoxic compartments of the ecosystem. The aim of the present study, therefore, is to identify the most important water-column formation and transformation processes influencing the SPOM pool of the Black Sea. Two contrasting marine environments, the Mediterranean Sea and the Sea of Marmara, also were investigated for comparison.

POM is operationally characterized as being either as small and suspended in the water column (SPOM) or large and rapidly sinking (LPOM). SPOM in the euphotic zone (EZ) is composed of phytoplankton, microzooplankton, aggregates of bacteria, and detrital matter with relative contributions depending on season and region. Below the EZ of the Black Sea, SPOM is both produced and decomposed by bacteria. In this study, focus is on SPOM as the largest pool of particulate organic matter reflecting the biogeochemical processes associated with each distinct layer.

We examine variations in the stable C and N isotopic composition of SPOM to trace processes through the water column. Isotopic fractionation occurs when specific reaction rates vary for chemical species containing the different isotopes of an element. Usually, the lighter isotope tends to react faster than the heavier one, which causes enrichment in the product and depletion in the reactant of the lighter isotope. This is valid for almost every step of biochemical reactions. In general, light isotopes (^{14}N and ^{12}C) are more easily assimilated by living organisms than heavier isotopes (Wada and Hattori, 1991; Altabet, 1996; Waser et al., 1998). Therefore, during initial formation of organic matter from inorganic precursors, a depletion of ^{15}N and ^{13}C is observed in newly formed SPOM relative to the isotopic ratio of the DIN and DIC pool, though the degree of isotopic fractionation is likely to vary between different autotrophic processes (e.g., photosynthesis vs. chemosynthesis).

2. Sampling and analytical methods

SPOM samples were collected in the Black Sea at three stations in September–October (autumn) 1999 aboard the R/V *BİLİM* and at six stations in May 2001 aboard the R/V *KNORR* (Fig. 1). The sampling locations were selected by examining real-time CTD measurements and by considering the previously known circulation of the basin (Fig. 2; Korotaev et al., 2003). The circulation of the surface layer of the Black Sea is dominated by the meandering cyclonic Rim-Current system encircling the basin, four cyclonic gyres distributed within the interior, and several anticyclonic eddies shoreward of the Rim Current (Oğuz et al., 1993; Korotaev et al., 2003). The Black Sea also has a narrow continental shelf and steep continental slope

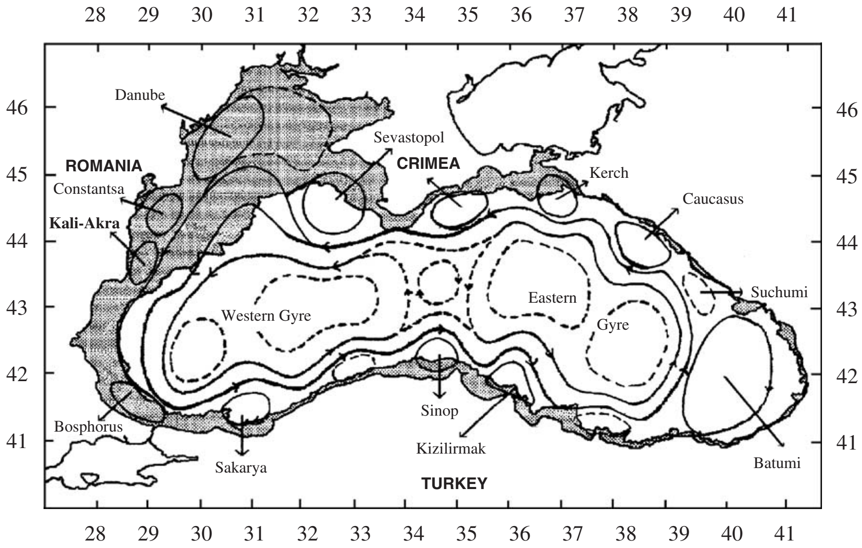

Fig. 2. Scheme of the Black Sea circulation (from Korotaev et al., 2003).

in the southwestern region (Fig. 1). Sampling was carried out in the central, shelf break, and continental shelf regions of the Black Sea, including stations within the Rim Current. All water samples were filtered through a 200-μm nylon mesh to remove larger particles. Particulate samples were collected on pre-combusted GF/F filters (0.7 μm pore size). Two to 40 l of water were filtered, depending on the location and depth of the sample. Since sampling was also distributed temporally, we were able to examine both seasonal and regional variations in SPOM composition. Collections also were made in the northeastern Mediterranean (Rhodes Gyre) and the Marmara Seas during the autumn 1999 R/V *BİLİM* cruise (Fig. 1). For comparison with SPOM, larger particles in the 200–2000 μm size range were collected by zooplankton net tows hauled vertically from suboxic depths to the surface during the May 2001 Black Sea cruise. In addition, a smaller number of surface sediment samples collected a decade earlier were analyzed for their C and N content and isotopic ratios. Sediment samples collected in 1988–1989 from two locations at the western coast NW of the Bosporus and from four locations off Sakarya (Fig. 1; see Ergin et al., 1996 for sampling details) were provided by Dr. V. Ediger (IMS-METU).

Samples were first acid-fumed to remove carbonates and then prepared for mass spectrometer analysis by encapsulation in tinfoil cups. Isotopic ratio measurements were done using an automated system consisting of an elemental analyzer coupled to an isotope-ratio mass spectrometer for isotopic analyses in continuous flow mode (Owens and Rees, 1989). Standardization was by combustion of solid materials of known isotopic composition (ACA) for ^{13}C, and by injection of atmospheric N_2 into the helium carrier gas for ^{15}N. Isotope ratios were expressed in per mil deviations from the standard as defined by the following equation:

$$\delta^{15}\mathrm{N} \text{ or } \delta^{13}\mathrm{C}\ (‰) = (R_{\mathrm{sample}}/R_{\mathrm{standard}} - 1) \times 1000,$$

where $R = {}^{15}\mathrm{N}{:}{}^{14}\mathrm{N}$ or ${}^{13}\mathrm{C}{:}{}^{12}\mathrm{C}$.

Reproducibility for δ^{15}N and δ^{13}C (based on standards) was better than 0.2‰.

Dissolved inorganic nutrient concentrations were measured by the shipboard autoanalyzer system following protocols described by Strickland and Parsons (1972) and Grasshoff et al. (1983). Dissolved oxygen (O_2) and H_2S concentrations were determined by conventional Winkler and iodometric titration, respectively (Baştürk et al., 1994), while low H_2S concentrations were determined by the colorimetric method (Cline, 1969). Chlorophyll-*a* concentrations were measured fluorometrically after extraction with 90% acetone solution (Strick land and Parsons, 1972; Holm-Hansen and Riemann, 1978).

3. Results

3.1. The Black Sea

3.1.1. Hydrographic characteristics of the study sites

A strong permanent pycnocline is found at intermediate depths ($\sigma_\theta > 14$) in the Black Sea. Examining temperature and salinity as a function of σ_θ (Fig. 3) shows the permanent pycnocline created by intrusion of relatively saline Mediterranean water underneath lower-salinity surface waters. The top of the permanent pycnocline corresponds to the cold intermediate layer (CIL), which is characterized by a temperature minimum at $\sigma_\theta \sim 14.5$. The vertical extent of the CIL was typically broader at the Rim-Current stations than in the central region. Below the CIL, temperature gradually increases with depth from 8 to 8.7 °C, as observed previously (Oğuz et al., 1991; Murray et al., 1991). Recent intrusions of Mediterranean water via the Bosporus plume can be observed most easily by the fluctuations in temperature (Fig. 4): the Bosporus plume produces warm anomalies.

The depth of the surface mixed layer and its interaction with the light field in controlling production varies seasonally. In autumn-99, a sharp thermocline was found between 15 and 23 m, but the EZ depth was deeper. The 1% and 0.1% surface light levels (I_o) were 25–5 m and 45–50 m, respectively (Table 1), suggesting that light did not limit phytoplankton production. In May 2001, spring warming of surface waters already had taken place and the depth of the surface mixed layer was between 10 and 24 m. The EZ was shallower compared to autumn-99 (1% $I_o = 18$–20 m, 0.1% $I_o = 30$–35 m) (Table 1). At this time, light limitation also was not evident.

3.1.2. Biogeochemical characteristics

Nutrient concentrations in the EZ of the Black Sea were low during both autumn 1999 and May 2001 (Table 1). For both seasons, stratification limited vertical exchange between the SML and the nitracline. Composite vertical profiles of [O_2],

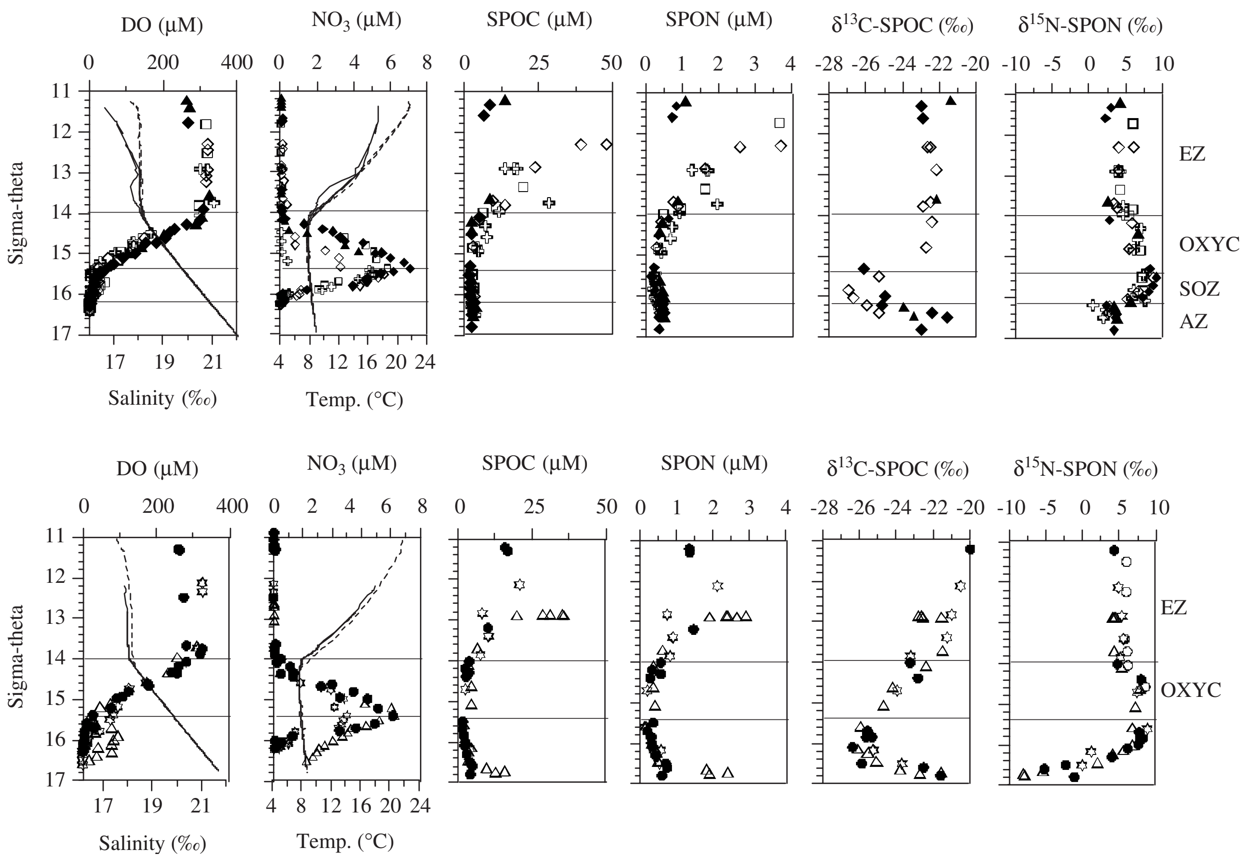

Fig. 3. Composite profiles of nitrate (NO_3^-) and dissolved oxygen (DO) concentrations, temperature and salinity profiles, suspended particulate organic carbon (SPOC) and nitrogen (SPON) concentrations, and N and C isotopic ratios of SPON and SPOC, against density. Upper: central stations. Lower: shelf-break stations. Temperature and salinity profiles are shown by solid lines for May 2001 and by dashed lines for autumn 1999, respectively. For other parameters, solid and open symbols represent stations visited in autumn 1999 and May 2001, respectively. Station symbols are as presented in Fig. 1 and Table 1 (Autumn 1999: ●: A1, ♦: A2; ▲: A3 and May 2001: △: M3, ◇: M5; □: M6; ✣: M7; ○: M10; ☆: M11). EZ: Euphotic zone, OXYC: oxycline, SOZ: suboxic zone, AZ: anoxic zone.

[NO_3^-], [SPOC], δ^{13}C-SPOC and δ^{15}N-SPON, as a function of σ_θ show a number of features common to all stations (Fig. 3). The EZ, oxycline, suboxic and anoxic zones are marked by features in the NO_3^- and O_2 concentration profiles tied to specific σ_θ surfaces, as reported previously (Codispoti et al., 1991; Tuğrul et al., 1992; Murray et al., 1995). Below the EZ, nitrate concentrations increase with depth and density. A well-defined NO_3^- maximum is found at the base of the oxycline ($\sigma_\theta \approx 15.4$). Below this density surface suboxia leads to denitrification and reduction of [NO_3^-] to typically undetectable levels at the suboxic–anoxic interface at $\sigma_\theta \approx 16.0$ (i.e, Murray et al., 1995; Yılmaz et al., 1998). Concentrations of NO_3^- at the maximum varied regionally and seasonally from 5 to 8 μM; Figs. 3 and 4.

Anomalous vertical NO_3^- distributions relative to this general pattern, however, were observed. At a shelf-break station in May 2001 (M3, Figs. 3 and 4b) relatively high [NO_3^-] and [O_2] were observed at greater than normal $\sigma_{\theta,}$ and this was likely associated with recent intrusions of Mediterranean water. The significance of this observation is discussed in detail below.

3.1.3. SPOM concentration

Concentrations of SPOM carbon and nitrogen in the EZ of the Black Sea exhibit regional and seasonal variations, presumably as a function of nutrient supply supporting SPOM production as well as its consumption and downward transport to aphotic layers (Figs. 3 and 4). Inventories of SPOC and SPON in the EZ were remarkably high and

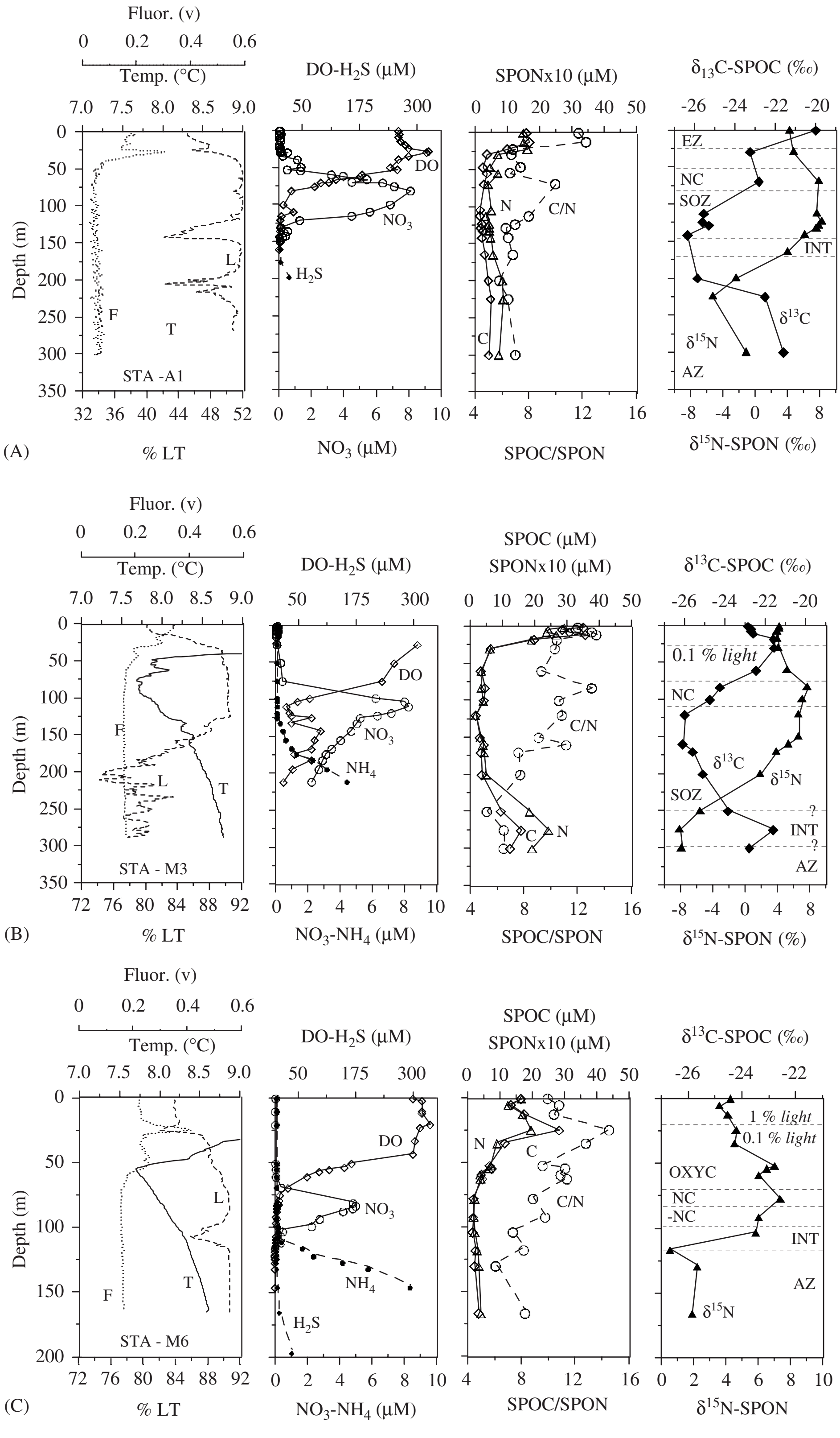

Fig. 4. Vertical variation of temperature (T), in-situ fluorescence (F), light transmission (L), nitrate (NO_3^-), dissolved oxygen (DO), hydrogen sulfide (H_2S), suspended particulate organic carbon (SPOC, ◇) and nitrogen (SPON, △) and their elemental ratios (dashed line, ○), $\delta^{15}N$ (▲) and $\delta^{13}C$ (◆) in SPOM in the Black Sea. (A) Autumn 1999, station A1, (B) May 2001 station M3, (C) May 2001 station M6.

Table 1
Euphotic zone properties of the stations visited in autumn 1999 and May 2001. Station names are as presented in Figs. 1 and 3. Euphotic zone thickness is defined as 0.1% surface light depth. R: rim current, P: peripheral region, G: cylonic gyre

Season	Region	Station code	SSS (‰)	SST (°C)	Depth of NO_3-max (m)	Thickness of SML (m)	Thickness of EZ (m)	EZ integrated			EZ average			
								SPOC (mmol C m^{-2})	SPON (mmol N m^{-2})	Chl-a (mg m^{-2})	δ^{13}C-SPOC	δ^{15}N-SPON	NO_3+NO_2 (μM)	PO_4 (μM)
Aut-99 Black Sea	R	A1	17.5	22.2	80	18	45	450.2	47.0	19.7	−21.6	4.5	0.18	0.04
	P	A2	18.0	20.9	75	15	50	275.9	30.4	12.9	−22.9	2.7	0.25	0.03
	G	A3	17.7	21.5	80	23	50	381.2	37.6	12.4	−21.8	3.4	0.1	0.06
Cruise mean		—	17.7	21.5	—	19	48	369.1	38.3	15.0	−22.1	3.5	0.2	0.04
May 2001 Black Sea	R	M3	17.9	15.6	110	20	30	709.3	59.4	4.7	−22.3	4.3	0.08	0.02
		M11	17.6	18.0	100	10	35	394.8	37.9	12.0	−21.5	5.3	0.04	0.03
	Shelf	M10	16.9	17.7	—	10	35	1222.7	94.6	7.1	−24.0	5.9	—	—
	P	M5	17.3	15.4	85	24	32	835.6	59.2	5.4	−22.5	4.3	0.13	0.02
		M7	17.1	17.5	93	10	35	740.3	65.4	4.5	−23.0	5.4	0.06	0.06
	G	M6	18.1	15.3	80	15	35	679.4	55.5	3.5	—	4.3	0.06	0.02
Cruise mean		—	17.5	16.6	—	15	34	763.7	62	6.2	−22.7	4.9	0.07	0.03
Aut-99 Med. Sea	G	F	39.3	21.6	—	20	80	227.8	32.0	10.6	−22.8	2.2	0.14	0.02
Aut-99 Mar. Sea	—	K	21.6	20	—	18	30	249.3	41.0	18.9	−20.0	3.3	3.9	0.37

regionally variable in May 2001 compared to autumn 1999 (Table 1 and Fig. 3). The highest SPOC and SPON concentrations were measured in the shelf region (M10), and SPOM concentrations were generally higher in rim-current and peripheral regions as compared to the cyclone centers. Cruise means of depth-integrated SPOC and SPON concentrations for the EZ were 369.1 and 38.3 mmol m^{-2}, respectively, in autumn 1999. Mean EZ SPOC and SPON inventory increased in May 2001 to 763.7 and 62 mmol m^{-2}, respectively. These higher SPOM concentrations reduced light penetration and euphotic depth (Table 1). Chlorophyll-*a* concentrations, however, were relatively low in May 2001, leading to abnormally high SPOC/chlorophyll-*a* ratios. Such high C/Chl ratios are an indicator of substantial heterotrophic biomass (Yılmaz et al., 1998). Microscopic analyses showed that phytoplankton populations were dominated by dinoflagellates during this period (Soydemir et al., 2003), suggesting the possibility of mixotrophy in the EZ.

Below the EZ, SPOC and SPON concentrations decreased at all stations (Fig. 3). The lowest SPOC and SPON concentrations (1.35–1.86 μM for SPOC and 0.13–0.35 μM for SPON) were found at the base of the oxycline or in the upper suboxic zone, nearly corresponding to the depth of NO_3^- maximum (Fig. 3). In contrast to the EZ, there was no distinct regional or seasonal variation in SPOM concentrations at these depths. SPOM concentrations increased slightly with depth through the suboxic zone forming a local maximum at the suboxic/anoxic transition layer. This maximum in SPOM in the suboxic/anoxic transition layer is regionally variable, being more pronounced in the shelf-break region of the southwestern Black Sea (with maximum values as high as 15.89 and 2.43 μM for SPOC and SPON, respectively, at STA M3).

The C/N ratio of EZ SPOM was substantially higher than the Redfield ratio of 6.6; cruise means were 9.6 for autumn 1999 and 12.3 for May 2001 (Table 1). Usually SPOM C/N increases below the EZ in response to early diagenesis (Altabet, 1996). In the Black Sea, however, SPOM C/N decreased through the base of the EZ and into the oxycline. Values near the Redfield ratio were observed in the suboxic/anoxic transition zone at the local SPOM maximum of Rim Current Stations (Figs. 4A and B).

3.1.4. SPOM isotopic composition

The isotopic composition of EZ SPOM was similar at all stations despite distinct seasonal and regional variations in SPOM and chlorophyll-*a* (Fig. 3 and Table 1). EZ means for δ^{15}N-SPOM were 3.5‰ in autumn 1999 and 4.9‰ in May 2001, a difference of only 1.4‰ between the two seasons. Mean SPOC δ^{13}C was −22.1‰ and −22.7‰ for autumn 1999 and May 2001, respectively. While these δ^{15}N and δ^{13}C values are in agreement with values previously reported for Black Sea SPOM (Calvert and Fontugne, 1987; Fry et al., 1991; Kodina et al., 1996), aliasing of seasonal variability may have occurred given our low temporal resolution. Spatial variability was evident during each cruise, with higher δ^{15}N (along with higher SPOM) closer to shore (Fig. 5). For example, shelf station M10 in 100 m water depth had both the highest SPOM concentrations and δ^{15}N values (but the lowest δ^{13}C) (Table 1).

Below the EZ, the isotopic composition of SPOM was similar during both seasons and at all stations. With decreasing SPOM concentration, δ^{15}N increased from 2.7–5.4‰ to 7.2–9.1‰ and δ^{13}C decreased from (−23.0‰)–(−21.5‰) to (−27.0‰)–(−25.2‰), excluding the shelf station. The lowest SPOM concentrations at the base of the oxycline

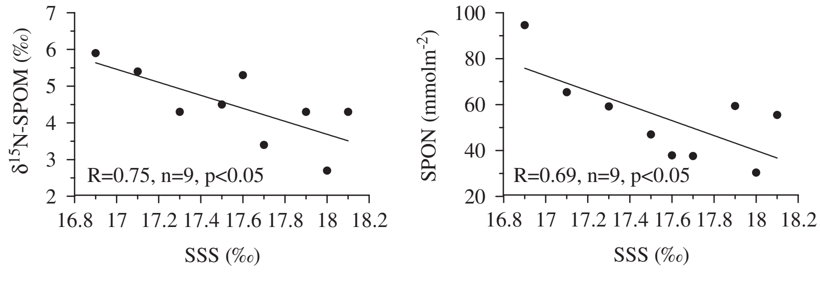

Fig. 5. Suspended particulate organic nitrogen (SPON) concentrations integrated for the euphotic zone and their mean isotopic composition (δ^{15}N-SPOM) versus sea-surface salinity (SSS) for nine stations investigated in the Black Sea.

within the NO_3^- maximum (5.0 and 8.3 µM) generally corresponded to the highest δ^{15}N-SPOM values (7.2–9.1 ‰).

In sharp contrast to oxic open-ocean sites, the SPON δ^{15}N values decreased and SPOM concentrations increased with depth within the suboxic zone ($\sigma_\theta \approx 16.2$) (Fig. 3). SPOM at the sulfide interface zone had the lowest δ^{15}N values in almost every profile though the magnitude of this minimum varied regionally. The modest suboxic zone SPOM δ^{15}N minima in the western cyclone were in agreement with the earlier studies (Fry et al., 1991). However, in the rim current/shelf break regions, δ^{15}N-SPOM reached unusually negative values that corresponded to elevated SPOM concentrations (Figs. 3 and 4). In general, the greatest ^{15}N depletions corresponded to the highest SPOM concentrations and lowest C/N ratios (Figs. 3, 4A and B).

LPOM collected in May 2001 had much higher δ^{15}N values (7.9‰, with a standard deviation of 0.8‰, $n = 9$) than SPOM samples of the same season, probably due to the presence of higher trophic-level zooplankton.

3.2. The Mediterranean (Rhodes cyclone) and the Marmara Seas

3.2.1. The Mediterranean Sea (station F)

As expected, the Mediterranean (Rhodes Gyre) and Marmara Seas differed from the Black Sea with respect to hydrography as well biogeochemistry. Warm (21.6 °C), salty (39.3‰) surface waters in the Rhodes cyclone were separated from deeper layers by a strong seasonal thermocline at 20 m (Table 1 and Fig. 6). The EZ extended to 80 m below this shallow SML (Table 1 and Fig. 6). A broad fluorescence peak was observed in the light-limited zone between the 1% and 0.1% light depths, coincident with the chlorophyll-*a* maximum and nitracline (Fig. 6). Below 175 m, lower temperature (13.8 °C) and salinity (38.8‰) and higher NO_3^- and PO_4^{-3} characteristic of Levantine deep-water were observed (Fig. 6).

Though the Rhodes Gyre is typically more productive than average for the Mediterranean due to cyclonic nutrient pumping, very low productivity was measured during our observations in late-summer. Nutrients in the EZ were at undetect-

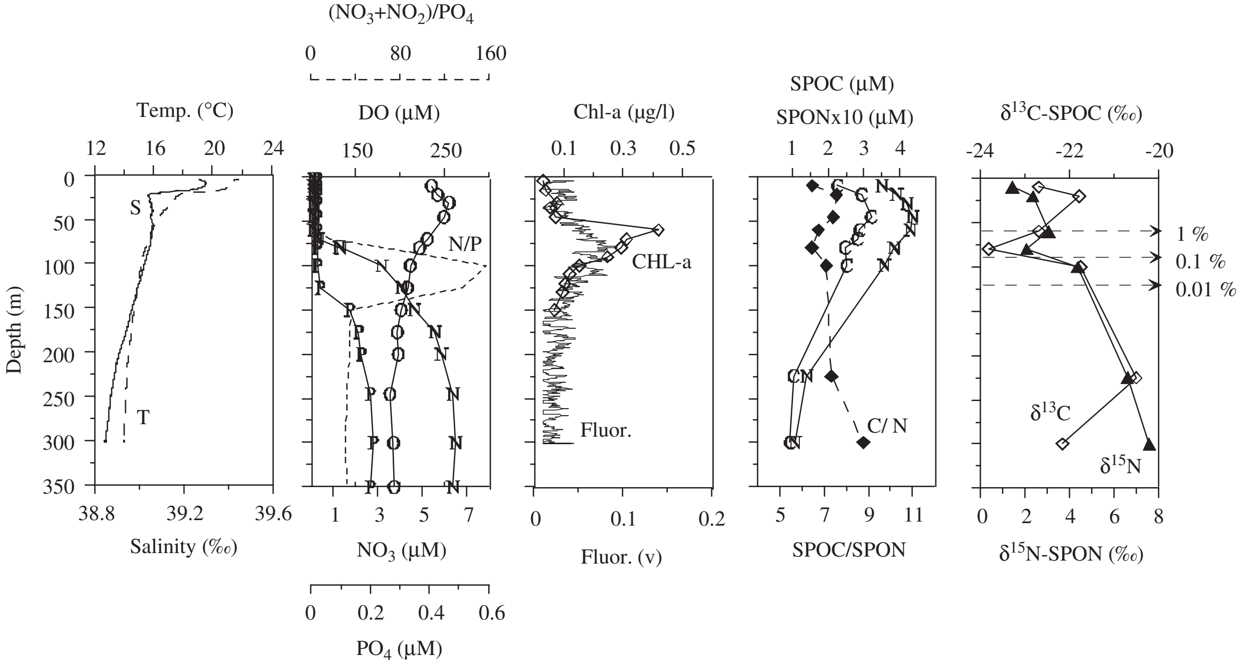

Fig. 6. Oceanography of the Rhodos Gyre (35°15′N, 29°0′E) in September 1999 expressed as depth profiles of salinity (solid line); temperature (dashed line), dissolved oxygen (DO, symbol: O), nitrate (NO_3^-, symbol: N), phosphate (PO_4^{3-}, symbol: P) and $(NO_3^- + NO_2^-)/PO_4^{3-}$ atomic ratio (dashed line), fluorescence, total chlorophyll-*a* (Chl-*a*), suspended particulate organic carbon and nitrogen (SPOC, symbol: C and SPON, symbol: N) and their elemental ratios (dashed line, C/N), δ^{15}N (▲) and δ^{13}C (◇) in SPOM. Horizontal dashed lines represent 1%, 0.1% and 0.01% light depths.

able levels. Consistent with prior observations (Krom et al., 1991), PO_4^{-3} limitation was suggested by the 50-m deeper PO_4^{-3}-cline compared to the nitracline. Accordingly, the N/P ratio in the nitracline was extremely high (in the range of 60–160). At depths below 250 m, the dissolved N/P ratio was almost 32 (twice the Redfield ratio), as reported previously (Ediger et al., 2005). As this deep water is pumped upward, and phytoplankton uptake of NO_3^- and PO_4^{-3} at Redfield ratio, tends to drive the remaining dissolved nutrients to even higher N/P ratios, which is consistent with our observations.

In the EZ, both SPOM and chl-*a* concentrations were much lower than those observed in the Black Sea in autumn, though integrated values were comparable due to a thicker EZ of the Mediterranean Sea (Table 1). Depth-integrated SPOM inventory in the EZ was 227.8 and 32.0 mmol m^{-2} for C and N, respectively. The C/N ratio of SPOM in the EZ was uniform with a mean of 6.9. Below the EZ, the C/N ratio increased to 8.8 at 300 m. The δ^{15}N of SPOM was lower than measured in the Black Sea (Table 1) and consistent with other recent observations from the E. Mediterranean (Pantoja et al., 2002). Values were as low as 1.4‰ in the surface mixed layer (Fig. 6). As observed in other nutrient-depleted environments (Altabet and McCarthy, 1986; Eadie and Jeffrey, 1973), a subsurface minimum in δ^{15}N (2.01‰) and δ^{13}C (−23.83‰) was found at the base of the EZ, coinciding with the chlorophyll maximum zone (Fig. 6). Below the EZ, δ^{15}N increased steadily with increasing depth to 7.6‰ at 300 m. δ^{13}C-SPOM tended to parallel these vertical variations in δ^{15}N.

3.2.2. The Sea of Marmara (station K)

The Sea of Marmara is the body through which interchange between the Black and Mediterranean Seas occurs, and it is expected to share characteristics of both. In autumn-99, an 18-m thick warm (20 °C) and low-salinity ($S = 21.6$) surface mixed layer of Black Sea origin was separated from a deeper layer of Mediterranean origin by a strong halocline/thermocline (Fig. 7 and Table 1). Nutrients were depleted in the surface mixed layer while O_2 concentration was at atmospheric saturated (Fig. 7). The 0.1% light depth in the Sea of Marmara was below the nutricline (30 m), in contrast to observations for the Black and the Mediterranean Seas. The EZ of the Marmara Sea also had higher mean NO_3^- and PO_4^{3-} concentrations (Table 1). O_2 concentrations decreased with depth and NO_3^- concentrations increased sharply, though reversals coincident with the particle maxima (light transmission minima) suggested inter-

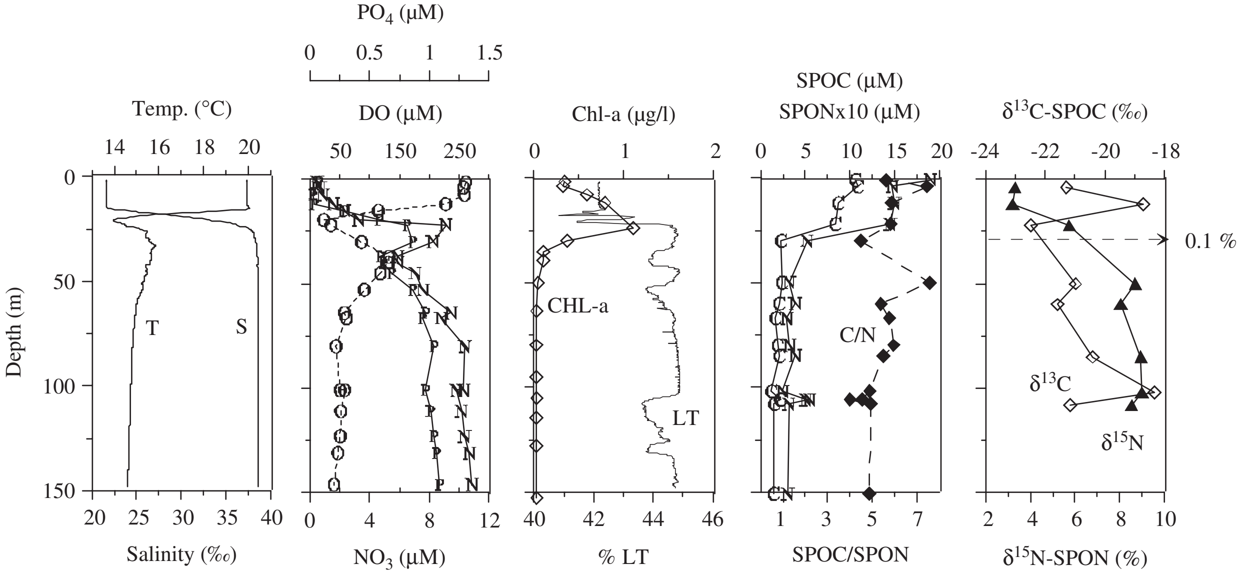

Fig. 7. Oceanography of Marmara Sea (40°46′N, 29°00′E) in September 1999 expressed as depth profiles of salinity (S); temperature (T), dissolved oxygen (DO, symbol: O), nitrate (NO_3^-, symbol: N), phosphate (PO_4^{3-}, symbol: P), light transmission (LT), total chlorophyll-*a* (Chl-*a*), suspended particulate organic carbon and nitrogen (SPOC, symbol: C and SPON, symbol: N) and their elemental ratio (dashed line, C/N), δ^{15}N (▲) and δ^{13}C (◇) in SPOM. Horizontal dashed line represents 0.1% light depth.

leaving of water masses (Fig. 7). Deep water O_2 concentrations of ~50 μM and NO_3^- and PO_4^{3-} concentrations of 10–11 μM and ~1 μM were typical of sub-halocline values for the eastern basin of the Marmara Sea (Polat et al., 1998).

Chlorophyll-*a* concentrations increased from 0.35 μg l^{-1} at the surface to 1.1 μg l^{-1} at the base of the halocline and within the steep nitracline (Fig. 7). The increase in chlorophyll concentrations was consistent with fluorescence and particle maximum (not shown; Fig. 7). Below the halocline, the chlorophyll concentrations decreased sharply to undetectable levels.

Similarly, the near-surface SPOC and SPON concentrations were high, comparable to the Black Sea (compare Figs. 4 and 7), decreasing to background values of 1.5–2.3 and 0.3–0.5 μM, respectively, below the halocline. In the upper EZ, C/N ratios were similar to the Redfield ratio. Below the EZ, the C/N ratios increased only slightly and decreased back to ~5 below 100 m (Fig. 7).

SPOM isotopic ratio in the SML was similar to the autumn 1999 Black Sea surface values (Table 1). δ^{15}N-SPOM was low (3.1–3.2‰) at the surface, where NO_3^- concentrations were in the range of 0.45–1.3 μM (Fig. 7). δ^{15}N-SPOM increased with depth to 5.8‰ at the base of the EZ and to 8‰ and 9‰ at depth. δ^{13}C was as low as −22.5‰ in the chl-*a* layer and increased to −18.5‰ at depth (Fig. 7).

4. Discussion

4.1. The Black Sea

In May 2001, biochemical composition of surface SPOM differed from the expected characteristics for spring (Krivenko et al., 1998; Çoban-Yıldız et al., 2000a). The EZ had low chlorophyll-*a* but very high SPOC and SPON concentrations (Table 1), with high C/N ratios (Table 1). These findings indicate that an intense spring bloom took place just before the May-01 cruise and consumed nearly all the biologically available nutrients. Such intense spring blooms have not been observed since 1996 (Oğuz et al., 2003). Low uptake rates of inorganic C and N (Çoban-Yıldız et al., 2003) suggest that the high organic matter content of the EZ was not directly supported by autotrophy but by herbivory, mixotrophy, and/or detrital sources. Consistent with this conclusion, pyrolysis of EZ SPOM yielded a ratio of carbohydrate and chlorophyll markers much higher than expected for phytoplankton (Çoban-Yıldız et al., 2006).

Despite the seasonal and regional variation of SPOM concentrations in the EZ, both C and N isotopic ratios varied little in comparison to sub-EZ values (range of δ^{15}N; 2.7–5.9‰, range of δ^{13}C; −24‰ to −21.6‰, Table 1). As the sampling for this study was carried out during periods of strong stratification with very low surface nitrate concentrations, winter data are needed to clarify the extent of seasonality in δ^{15}N of bulk POM in the EZ. A relationship between NO_3^- concentration and isotope fractionation, during uptake and assimilation of NO_3^- by phytoplankton, is well documented (e.g., Altabet and McCarthy, 1985; Altabet, 1988, 1996; Altabet and Francois, 1994, 2001). The observed depletion in ^{15}N (low δ^{15}N) in POM relative to NO_3^- was greatest when high NO_3^- inputs and/or low NO_3^- uptake resulted in little relative NO_3^- depletion. The lowest δ^{15}N values for marine POM (−4‰ to −5‰) have been reported in the regions where there is little depletion of surface NO_3 as in HNLC regions (Altabet and Francois, 1994, 2001). When DIN utilization is complete, the δ^{15}N of the POM produced should be the same as the δ^{15}N of the DIN utilized (Altabet, 1988, 1996). Thus, there should be large seasonal variation in δ^{15}N corresponding to the drawdown of surface layer NO_3^-. For example, large temporal variations in δ^{15}N of PON have been recorded in warm-core rings along the Gulf Stream before and after stratification (Altabet and McCarthy, 1985). The low seasonal variation in surface δ^{15}N-SPOM observed in this study therefore was most probably due to consistently low NO_3^- concentrations in the EZ during our observation periods and rapid recycling. Larger particles (LPOM) collected by zooplankton tow at the same stations in May 2001 had δ^{15}N values that were ~3‰ higher than SPOM, which is explained by isotopic fractionation during trophic transfer of nitrogenous compounds.

The δ^{13}C of phytoplankton and, by extension, surface layer SPOM reflects both the δ^{13}C of the DIC and isotopic fractionation during carbon fixation. The latter is influenced by an interplay between CO_2 concentration, growth rate, cell surface to volume ratio, and biochemical pathway (Fogel and Cifuntes, 1993; Laws et al., 1994; Altabet, 1996). Typically, small phytoplankton with low surface to volume ratios and high growth rates and low external [CO_2] exhibit the least fractionation and highest δ^{13}C. Chemoautotrophic bacteria can exhibit fractionation effects both higher and lower than found in photoautotrophs depending on enzyme system used to fix carbon (House et al., 2003). In our study, the δ^{13}C of near-surface SPOM (Table 1) was well within the range observed for marine phytoplankton (Michener and Schell, 1994). Nevertheless, it is important to note that the most negative δ^{13}C belonged to the surface SPOM of the shelf station, where the less-saline surface waters ($S = 16.9$) had higher concentrations of SPOM (Table 1). The high C/N ratio for this station (10) suggests that the contribution of isotopically lighter refractory terrestrial organic matter from river discharges to the coastal margin may be an important component of SPOM pool (Fry and Sherr, 1984; Hedges et al., 1997; Sailot et al., 2002).

As expected, SPOM concentrations decrease below the seasonal thermocline in response to decreasing primary production with light limitation and respiration (Yılmaz et al., 1998, 2006). However, δ^{15}N-SPOM displayed little variation from the SML to the base of the EZ, despite recent estimations based on productivity and sediment flux data that only 25% of the particulate material produced in the EZ sinks below 60 m, into the oxic/anoxic transition zone while the rest is remineralized above (Karl and Knauer, 1991). Evidently, there is sufficient primary production to consume remineralized nitrogen, thereby preventing any increase in the isotopic ratio of SPON (Altabet, 1996). Indeed, the C/N ratios of SPOM in the deeper parts of the EZ were generally closer to the Redfield ratio (Fig. 4). Direct measurements of dissolved inorganic nitrogen uptake rates have shown that 22–43% of the EZ nitrogen productivity is based on NH_4, remineralized within the EZ (Çoban-Yıldız et al., 2003).

Increasing δ^{15}N below the EZ as a result of selective remineralization of the lighter nitrogen isotope is consistent with decomposition of particulate organic matter (Saino and Hattori, 1980; Saino and Hattori, 1987; Altabet and McCarthy, 1986; Fry et al., 1991). δ^{15}N-SPOM increased on average by 3.7‰ from the EZ to the depth of the nitrate maximum, in agreement with observations of increases by 3–4‰ during early oxidative degradation of dead phytoplankton and zooplankton (Wada, 1980). In contrast, SPOM in the oxycline is depleted in ^{13}C (Figs. 3 and 4). This may be due to the dominance of more refractory, lighter lipid components in the residual SPOM pool, as a result of decomposition (Eadie and Jeffrey, 1973). High δ^{15}N and C/N ratios and lower δ^{13}C values are found across both regions and seasons indicating that the SPOM pool in the oxycline is dominated by partly decomposed, refractory organic material. Supporting this conclusion, recent studies have shown that lipids consistently dominate the SPOM pool of the Black Sea oxycline (Çoban-Yıldız et al., 2000b).

An exception was found at the central station in May 2001 (Fig. 4C). An increase in the C/N ratio of SPOM in the oxycline relative to the EZ was not observed, in agreement with the SPOM lipid to protein ratio (Çoban-Yıldız et al., 2006). This was mainly because the C/N ratio of SPOM at the base of the EZ was relatively high (Fig. 4C). Most likely, higher C/N ratios originating in SPOM of the surface mixed layer reflected the beginning of a transitional phase from bloom to post-bloom period. The source particles for SPOM in the oxycline probably originated from the EZ earlier in the season with relatively low C/N.

SPOM below the oxycline in the Black Sea exhibited unique behavior as compared to oxygenated water columns (including the Marmara and the Mediterranean Seas) in terms of both concentration and isotopic composition (e.g., Saino and Hattori, 1980; Jeffrey et al., 1983; Altabet and McCarthy, 1986; Pantoja et al., 2002; also compare depth profiles of SPOM concentrations and isotopic compositions in Figs. 4, 6 and 7). Below the suboxic zone, low δ^{15}N values and C/N ratios were observed at all Black Sea stations (Fig. 3), possibly indicating the dominance of newly formed biogenic particles. Minimum δ^{15}N values were observed at the suboxic–anoxic transition zone, where particulate concentrations increased to various extents (Fig. 3 and 4) in agreement with minima in light transmission (Fig. 4). The largest increases in SPOM concentrations coincided with the largest depletions in δ^{15}N. In our study, the lowest δ^{15}N-SPOM values observed in the interface zone of the central regions were still positive, similar to the observations of Fry et al. (1991). At the two shelf-break regions (A1 and M3), however, the δ^{15}N values of SPOM were as low as ~ -5‰ and -8‰ (Figs. 3 and 4). These data along with substantial dark DIC uptake (Yılmaz et al., 2006) strongly suggest intense microbial activity in the suboxic/anoxic layer of the shelf break regions of SW Black Sea. Indeed, the minimum of δ^{15}N in SPOM in the interface zone was previously attributed to fractionation during bacterial NH_4^+ uptake (Fry et al., 1991).

Another striking feature observed at these shelf-break stations was the lateral intrusion of oxygenated waters by the Mediterranean input via the Bosporus plume, as clearly observed at station M3. The intrusion of 'new water' to intermediate depths can be traced by modified vertical profiles of O_2 and nitrate (Figs. 3 and 4) as well as fluctuations in temperature profile (Konovalov et al., 2003) (Fig. 4). Intrusions of oxygenated Mediterranean water carried along the shelf break by the Rim Current have been suggested to be the main physical process causing partial ventilation of sub-halocline waters of the Black Sea (Konovalov and Murray, 2001; Murray et al., 2003; Tuğrul and Salihoğlu, 2003). Our particulate data from the anoxic interface indicate that chemoautotrophic and heterotrophic activities are enhanced by the intrusion of this oxygenated and nitrate-rich water via the Bosporus plume. This hypothesis is corroborated by the chemistry data of Tuğrul and Salihoğlu (2003). They observed secondary broad nitrate maxima below the main nitrate profile vanishing steadily in the interface zone of SW Rim Current and Black Sea open waters. These deeper nitrate maxima coincided perfectly with the coherent nitrite maxima formed in the same zone, where concurrent oxidation/dilution of ammonia, dissolved manganese, and hydrogen sulfide were recorded as compared to their characteristic profiles in the upper anoxic layer of the central basin (Tuğrul and Salihoğlu, 2003). The observation of higher POM and higher DIC uptake rates in this zone, together with the remarkable modifications in redox-sensitive chemical parameters, corroborate biologically catalyzed oxidation-reduction chemical reactions as suggested by Murray et al. (1995).

In addition, re-suspension of surface sediments at the shelf-break regions under the rim current probably produced a convenient substrate for the growth of microorganisms. Isotopic ratios of surface sediments on the continental shelf of the southwestern Black Sea (Fig. 1) were measured to check the possibility that they contributed directly to the unique geochemical signals observed in the suboxic/anoxic transition zone. This was ruled out, as the δ^{15}N values of surface sediments were 3.6–5.4‰, similar to the δ^{15}N EZ SPOM, rather than the chemoautotrophic signal observed at suboxic/anoxic transition region. Furthermore, the C/N ratios in surface sediments were 9.2–11.0, significantly higher than found for SPOM in the transition layer of shelf-break regions. This large difference in δ^{15}N and C/N between surface sediments and SPOM at the suboxic/anoxic transition layer suggests the dominance of water-column processes rather than sediment re-suspension.

Similar observations have been made in the Baltic Sea, where the δ^{15}N of SPOM decreased from 8‰ to 1.1‰ as a result of microbial activity stimulated by the occasional intrusion of dense, oxygen and nitrate-rich water into the deep anoxic zone (Voss et al., 1997). δ^{15}N values for ammonium in the anoxic layer of the Black Sea range from 1.1‰ to 3.8‰ (Fry et al., 1991), and fractionations of 11–14‰ have been estimated for the bacterial uptake of NH_4^+ (Voss et al., 1997; Hoch et al., 1992). Based on these values, chemoautotrophic bacteria utilizing NH_4^+ as their dominant N source should have δ^{15}N values of −13‰ to −7‰, comparable to the values measured in this study at the shelf-break regions of the southwestern Black Sea.

We note that the low δ^{15}N values we hypothesize to be associated with chemoautotrophic production are coincident with δ^{13}C maxima (Figs. 3 and 4). This observation appears to conflict with the common perspective that chemosynthesis should produce low δ^{13}C (Ruby et al., 1987; Thiel et al., 2001). However, recent culture studies show that depending on biochemical pathway for carbon fixation, isotopic fractionation can be either less or more intense than for the RuBP carboxylase pathway used by most photoautotrophs (House et al., 2003). A likely reason for the local ^{13}C enrichment in SPOM is the production of relatively fresh organic matter with isotopic fractionation similar to EZ carbon fixation. Recall that lowered δ^{13}C below the EZ is associated with diagenetic enrichment of ^{13}C-depleted lipids.

4.2. The Mediterranean Sea

POM suspended in the EZ of the Rhodes Cyclone in autumn 1999 was more depleted in ^{15}N than the Black Sea SPOM, yielding EZ and surface mixed-layer averages of 2.2‰ and 1.4‰, respectively, and consistent with recent reports (as low as 2.5‰ in Struck et al., 2001; −0.3‰ ± 0.5‰ in Pantoja et al., 2002). In nutrient-poor surface waters like the Mediterranean Sea, which is also likely P limited (Krom et al., 1991), low δ^{15}N values have generally been explained to be as a result of either nitrogen fixation (Struck et al., 2001; Pantoja et al., 2002) or preferential consumption of excreted NH_4^+ depleted in ^{15}N (Checkley and Miller, 1989). Nitrogen fixing organisms may dominate the SPOM pool in the surface layers of the Eastern Mediterranean Sea (Rabitti et al., 1994; Moutin et al., 2002; Pantoja et al., 2002). These organisms are known to produce biomass with nitrogen isotopic ratio of −2‰ to 0‰ (Minagawa and Wada, 1986; Carpenter et al., 1997). However, in agreement with recent studies (Pantoja et al., 2002), we observed the δ^{15}N of deep-water NO_3^- to be between 1.9‰ (200 m) and 3.3‰ (400 m), significantly lower than the open-ocean average of near 5‰ (Sigman et al., 2000). While the low δ^{15}N for deep-water NO_3^- may reflect a basin-wide importance for N_2 fixation, its direct and complete utilization by phytoplankton following upward advective/diffusive transport is a likely explanation for the low δ^{15}N of EZ SPOM in the Rhodes gyre. One additional explanation for the low δ^{15}N-SPOM in the surface waters of the Rhodes cyclone could be the consumption of isotopically light DON. However, there are no published data on δ^{15}N values for DON in the Mediterranean Sea for us to test this hypothesis.

At the base of the EZ (depth of the 0.1% light level), where onset of nitracline was located, a subsurface minimum was observed for both δ^{13}C and δ^{15}N (Fig. 6). Lower δ^{15}N and δ^{13}C of SPOM is consistent with the light-limited conditions at the base of the EZ where there is only partial NO_3^- utilization (enhanced N-isotopic fractionation) at low phytoplankton growth rates (enhanced C-isotopic fractionation). Subsurface minimum in δ^{15}N of SPOM has been observed in previous studies (Saino and Hattori, 1980, 1987; Altabet and McCarthy, 1985).

4.3. The Sea of Marmara

EZ organic matter production is confined to the low-salinity upper layer (Polat et al., 1998), as can be observed by higher SPOM and chlorophyll-*a* concentrations (Fig. 7). The O_2 minimum in the halocline, which coincides with the temperature minimum, likely reflects entrainment of low-O_2 subsurface Black Sea water (Fig. 7).

At the base of the halocline, chlorophyll concentrations increased probably due to nutrient availability. Although low C/N ratios of SPOM accompanied with higher chlorophyll-*a* concentrations suggest increased photosynthetic activity, there was no associated increase in SPOM concentrations. Therefore, higher chlorophyll concentration in this layer was due to higher chlorophyll content per photoautotrophic cell as a result of light limitation, without net organic matter production. As above, a decrease in δ^{13}C suggests low phytoplankton growth rates (Laws et al., 1994).

Nutrient-poor and oxygen-rich Aegean (Mediterranean) water is introduced to the lower layer of the Marmara Sea via the Strait of Dardanelles (Fig. 1). During its easterly transport, it becomes enriched in nutrients and depleted in oxygen due to the oxidation of sinking organic matter (Polat et al., 1998). SPOM composition at the sub-halocline waters is determined not only by downward flux of organic matter from the EZ, but also by the properties of the Mediterranean SPOM. SPOC concentrations from the sub-halocline waters of the Marmara Sea (~1.5–2 μM) are almost two-fold higher than the SPOC concentrations of the Mediterranean lower layer (~1 μM), indicating partial contribution of POM sinking from the upper layer of the more productive Marmara Sea to its lower layer. C and N isotopic ratios of SPOM for sub-halocline layers, however, were similar to those measured in the aphotic layers of the Mediterranean Sea.

The fluctuating light transmission profile and slight variations in C/N in the lower layer suggest the intrusions of different water masses with different ages and/or composition flowing across the basin from the Straits of Dardanelles. Unfortunately, the sampling resolution for isotopic measurements was insufficient to characterize these water masses. An exception is at 102 m, where δ^{13}C-SPOM increased to a high value of −18.3‰ (Fig. 7). Associated increase in SPOM concentrations, consequent decrease in C/N ratio, and in situ light transmission strongly suggest the existence of a transitional zone between two different water layers.

5. Summary and conclusions

Important biogeochemical processes occurring in the Black Sea produce telltale variations in the C and N isotopic composition of SPOM. This study was carried out during stratification of the upper water column when low EZ DIN concentrations and rapid recycling prevented isotopic fractionation during phytoplankton assimilation of DIN. Accordingly, N isotopic ratios for average EZ SPOM varied over a narrow range (2.7–5.9‰) despite seasonal and regional variations in its concentration, probably reflecting a common source for new nitrogen within this range in δ^{15}N. The moderately higher δ^{15}N values in May 2001 relative to autumn 1999 (1.5‰ greater) likely reflect greater contribution of herbivorous and detrital material to the SPOM pool after the spring bloom. Supporting this inference, larger particles (LPOM) collected by zooplankton net tows had ~3‰ higher δ^{15}N values compared to SPOM, indicating fractionation during trophic transfer of nitrogenous compounds. A future time-series study with seasonal resolution covering the winter period should resolve the influence of phytoplankton blooms on these observations. δ^{13}C values for EZ SPOM also varied modestly (−24‰ to −21.5‰), reflecting only small changes in the parameters influencing isotopic fractionation during phytoplankton carbon fixation (CO_2 concentration, growth rate, cell geometry). The lowest EZ values were found in the shelf region, perhaps resulting from the contribution of refractory terrestrial matter low in δ^{13}C.

SPOM below the EZ and within the oxycline of the Black Sea was characterized by lower SPOM concentrations and heavier N and lighter C isotopic ratios; the latter may indicate the dominance of refractory lipid components. Whereas in oxygenated marine water columns (as shown in this study in the Mediterranean and the Marmara Seas) these trends in δ^{15}N and δ^{13}C continue with depth, in the Black Sea, below the oxycline, unique observations were made for SPOM concentration and composition. SPOM concentration in the Black Sea generally increased through the suboxic zone, reaching a secondary maximum at the suboxic/anoxic interface zone. In this zone, isotopic ratios were characterized by depletion in ^{15}N and enrichment in ^{13}C. The greatest depletions in δ^{15}N coincided with the greatest increases in SPOM concentrations, a strong indication of mid-water chemoautotrophic production in the interface zone. Based on the most negative δ^{15}N values, chemoautotrophic production appears to be most intense at the shelf-break regions, possibly enhanced by mixing of oxygenated and nitrate-rich Mediterranean inflow waters with suboxic/anoxic Black Sea water. The high δ^{13}C values can be explained by bacterial DIC assimilation in the suboxic/anoxic interface zone producing fresh organic matter with isotopic fractionation similar to EZ carbon fixation.

In summary, organic material in the Black Sea EZ is produced under stratified, nitrogen-limiting conditions for most of the year with little variation in nitrogen isotope ratio. Below the EZ and within the oxycline, diagenesis increases δ^{15}N and reduces δ^{13}C, the latter due to accumulation of refractory lipids. In the suboxic–anoxic interface zone, chemoautotrophic production possibly leads to dominance of new, in situ produced organic matter, with distinct SPOM isotopic ratio. This chemo-auto and perhaps chemo-heterotrophic bacterial activity is regionally variable and more intense on the shelf/break.

SPOM in the EZ of the Mediterranean Sea (mean $\delta^{15}N = 2.2‰$) had lower δ^{15}N as compared to the Black Sea (mean $\delta^{15}N = 3.5‰$ for autumn and 4.9‰ for May). Given that utilization of NO_3^- was complete in the EZ, this observation likely reflects the low $\delta^{15}N\text{-}NO_3^-$ for Mediterranean deep water as compared to the open-ocean average. Low Mediterranean δ^{15}N values may reflect basin-wide importance of N_2 fixation as a new nitrogen source and/or the lack of water column denitrification.

SPOM composition in the EZ of the Sea of Marmara Sea is similar to the Black Sea. SPOM composition at the sub-halocline waters is determined not only by downward flux of organic matter from the EZ but also by the properties of the Mediterranean SPOM. At these sub-halocline waters, different water masses with different age and composition flowing across the basin from the Straits of Dardanelles also were marked by the variations in the light transmission profile and C/N elemental ratio.

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