EFFECTS OF CIRCULATION ON THE SPATIAL DISTRIBUTIONS OF PRINCIPLE CHEMICAL PROPERTIES AND UNEXPECTED SHORT- AND LONG-TERM CHANGES IN THE BLACK SEA

Ö. BAŞTÜRK, S. TUĞRUL, S. KONOVALOV,* İ. SALIHOĞLU. Middle East Technical University -Institute of Marine Sciences, Erdemli, Turkey

* Marine Hydrophysical Institute, Sebastopol, Ukraine.

Abstract. Past and present biochemical data, starting from R/V J. Elliott Pillsbury August-1965 cruise till R/V Bilim April-1994 cruise, were compared in terms of density dependent profiles for the dynamically different regions of the Black Sea. Examining of these data sets revealed that the suboxic zone has expanded since late 60's. An unusual event in July-1992, during which an intense blooming of planktonic organisms was observed and concurrent dissimilatory nitrate reduction occurred within the offshore waters of the western Black Sea, has been evaluated in terms of biochemical and physical properties. During this unusual period, the nitracline was eroded down to the σ_{θ} = 15.4 density surface where conventional nitrate peak has been observed during the last decade. In the meantime, the dissolved oxygen concentration of 25 µM, which was expected to be attained at the 15.40 density surface was observed to shift to the σ_{θ} = 14.9-15.0 surfaces in July,1992. In a similar manner, the onset of the phosphate gradient layer for the cyclonic regions of the Black Sea appeared to have deepened from σ_{θ} = 14.5 density surface in September-1991 to 14.9-15.0 surfaces in July-1992, whereas the position of sulfidic layer ($H_2S > 1 \mu M$) has remained unchanged, between the density surfaces of 16.15-16.20 during recent decades.

1. Introduction

The Black Sea, a land-locked deep basin connected to the Mediterranean through the Bosphorus, is occupied with the oxygenated brackish waters in the surface layer and more saline, sulfide-bearing waters below 150-200 m depths. The permanent pycnocline, separating these two layers, permits to continuous snow of biogenic particles to the subhalocline waters but prevents the ventilation of deep layers of Mediterranean origin. Therefore, distinctive chemical features have established in the oxic/anoxic transition layer of the basin due to the complicated redox-dependent biochemical reactions, and the vertical mass fluxes in the redox-gradient zone (1). Specifically, a preeminent suboxic zone is formed permanently in the lower pycnocline

where DO < 20 μ M and H2S < 1 μ M throughout the whole deep basin (2,3). In addition to natural processes sustaining the anoxia in the deep waters, large riverine inputs of biochemically labile chemicals and direct wastewater discharges to coastal waters have led to dramatic changes in the productive ecosystem of the upper layer of the Black Sea during last 30 years (4,5); intense eutrophication and collapse of living resources being much more pronounced in the wide western shelf. Though damages in the biological component of the marine ecosystem have been well documented (6,7,8), long-term changes in its chemical properties are still poorly understood due to the lack of high-quality and high-resolution historical data.

Basin wide studies conducted since 1988 have led to a better understanding of major processes dominating the Black Sea oceanography (9,10,11,12). Limited winter data indicate that the upper layer may be homogenised thoroughly down to depths of the σ_{θ} =14.7-14.8 surfaces by intense vertical mixing (12,13) and down to the σ_{θ} =15.7-15.8 surfaces by lateral advection processes in winter (14). The interannual stability of the permanent pycnocline has permitted us to collate old and recent chemical data relative to water density, so as to understand the behaviour of the principal hydrochemical features of the upper layer in the hydrodynamically different regions of the Black Sea (3,15,16). The density-dependent chemical profiles have also led us to distinguish seasonal variations from long-term changes in the Black Sea chemical oceanography since late 60's.

2. Material and methods

The data obtained during the R/V J. Elliott Pillsbury August-1965, R/V Atlantis April-March-1969 and R/V Knorr August-1988 cruises were taken from technical reports (17,18,19). These data sets were utilised for the visualisation of the present day situation in the Black Sea in conjunction with the past data. The coordinates of stations for R/V Bilim September-1991cruise were given elsewhere (2,3), whereas those of the stations visited during the July-1992 cruise of R/V Bilim are given in Table 1, for three different regions.

3. Results and Discussions

3.1. BIOCHEMICAL PROPERTIES

Density dependent vertical profiles for the dissolved oxygen (DO), oxidized forms of nitrogen ($TNO_x = NO_3 + NO_2$) and phosphate (o-P04) from dynamically different regions of the Black Sea were discussed by utilizing recent and past data (2,3). It has been shown that the prominent chemical features and the onset of chemical gradient layers appeared at different density surfaces, depending on the water circulation in the basin (3). The density dependent variations of past and present DO concentrations within the cyclonic (CR) and the anticyclonic regions (ACR) and rim current frontal

zone (RCFZ) were displayed in Figure 1a-c, and those of TNO_x and o- PO_4 for CR and ACR in Figure 2 for R/V J. Elliot Pillsbury August-1965, R/V Atlantis March-April-1969, R/V Knorr July-August-1988 cruises, and September-1991 and April-1994 cruises of the R/V Bilim. The profiles

TABLE 1. Names and coordinates of the stations grouped according to the shape of the density dependent vertical profiles of the TNO_x in July-1992

		REGI	ONI		
Sta. No	Latitude	Longitude	Sta. No.	Latitude	Longitude
N10P45	43° 10' N	32° 45' E	M50S45	42° 50' N	35° 45' E
N10T45	43° 10' N	36° 45' E	M30P15	42° 30' N	32° 15' E
M30T15	42° 30' N	36° 15' E	M30N15	42° 30' N	31° 15' E
M50T45	42° 50' N	36° 45' E	M50N15	42° 50' N	31° 15' E
M30N45	42° 30' N	31° 45' E	M10N45	42° 10' N	31° 45' E
M10M15	42° 10' N	30° 15' E	L50M15	41° 30' N	30° 15' E
M50R15	42° 50' N	34° 15' E	M50V45	42° 50' N	37° 45' E
M50P15	42° 50' N	32° 15' E			
		REGI	ON II		
Sta. No.	Latitude	Longitude	Sta. No	Latitude	Longitude
L30V45	41° 30' N	37° 45' E	L35T45	41° 35' N	36° 45' E
L50T45	41° 50' N	36° 45' E	L15X15	41° 15' N	39° 15' E
L30X15	41° 30' N	39° 15' E	L50W15	41° 50' N	38° 15' E
L30W15	41° 30' N	38° 15' E	L30V15	41° 30' N	37° 15' E
L15V15	41° 15' N	37° 15' E			
		REGI	ON III		
Sta. No.	Latitude	Longitude	Sta. No	Latitude	Longitude
L30X45	41° 30' N	39° 45' E	L30Y15	41° 30' N	40° 15' E
L30Z10	41° 30' N	41° 10' E	L50Y45	41° 50' N	40° 45' E
L50Y15	41° 50' N	40° 15' E	L50X15	41° 50 N	39° 15' E
M30S45	42° 30' N	35° 45' E	L30Y45	41° 30' N	40° 45' E
L30K45	41° 30' N	28° 45' E	L30M45	41° 30' N	30° 45' E
M15R15	42° 15' N	34° 15' E	M30R15	42° 30' N	34° 15' E
M30R45	42° 30' M	34° 45' E	N10Q45	43° 10' N	33° 45' E

displayed in Figures 1 and 2 represent the normal, expected vertical distributions of the biochemical parameters. Vertical profiles for the unusual period July-1992 were displayed separately in Figures 3-5 for all the three groups of stations denoted by Region-I, -II and -III, based on the appearances of TNO_x profiles, rather than the general circulation. Region-I (see Fig.3) represents a group of stations where TNO_x concentrations were abnormally low (< 2 μ M) down to σ_{θ} = 15.40 surface, whereas the Region-II (see Fig.4) represents another set of stations where the nitracline onset is located at its expected density surface as it has been given by Baştürk et al. (3) but with

eroded peak values. The stations located in sites named as Region-III (Fig. 5) possess normal vertical profiles of nutrients.

3.1.1. Dissolved oxygen (DO).

The DO vs. density profiles (Figure 1) clearly show that a permanent and steep oxycline is established below the DO-enriched (250 - 350 μ M) surface waters. However, the onset of the DO gradient which varies regionally from σ_{θ} = 14.2 to 14.5 density surfaces, depending on the dynamic characteristics of the region during the spring-autumn period. The oxycline, and thus nutricline, commences at greater density surfaces (σ_{θ} =14.4-14.5) but at smaller depths in the cyclonic regions (CR) than its position (σ_{θ} = 14.2-14.3) in the anticyclonic regions (ACR) and the rim current frontal zones (RCFZ)(2).

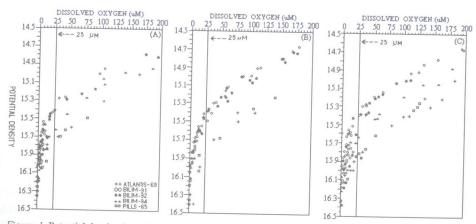


Figure 1. Potential density dependent variations of dissolved oxygen in (A): cyclonic, (B): anticyclonic and (C): rim current systems of the Black Sea for different periods.

The gradient also displays an apparent variability in space and time due to short-and long-term changes in the rates of DO input and consumption by biochemical reactions in the upper pycnocline. The DO depletion rate in the CR (7-8 μ M/m) was shown to be nearly two-fold the estimates of 3.5-4.5 μ M/m for the ACR and RCFZ, due to apparently increasing thickness of the CIL in the ACR and RCFZ (3). The main oxycline, with a regionally varying gradient, extends down to the σ_{θ} =15.4-15.6 density surfaces, where the DO concentration drops to the suboxic levels of 20-25 μ M. DO profiles for R/V Bilim April-1994 cruise, representing a post-winter condition, do not fit well to those profiles of R/V Atlantis-1969 and R/V Pillsbury-1965 profiles; the latter two profiles well coincide with each other (Fig. 1a-c) even though they represented spring and mid-summer periods, respectively. Interestingly, the thickness of DO gradient was apparently greater in the 60's due to the establishment of the suboxic boundary at greater density surface. 20 μ M dissolved oxygen level observed in the σ_{θ} =15.95-16.0 layer in the 60's has shoaled to the σ_{θ} =15.4-15.6 in 90's; indicating a coherent long-term shoaling of the suboxic zone in the Black Sea, by

nearly 0.3-0.4 σ_{θ} units, since late 60's. In the suboxic zone, the DO declines slowly to < 5 μ M at σ_{θ} =15.9-16.0, and vanishes at the sulfidic boundary (σ_{θ} .= 16.15-16.20) where H_2S = 1-3 μ M. High-resolution H_2 S data obtained by calorimetric technique indicated that the sulfide-bearing waters have always appeared at about 16.15-16.20 density surfaces throughout the deep basin (3,10,20). In other words, a remarkable spatial and temporal consistency of the modern H_2S data from the interface strongly suggests that the large scattering observed in the sulfidic water boundary was most probably due to the analytical artifact rather than the environmental factors.

Although the onset of the oxycline has remained unchanged since late 60's, its slope (μM DO / σ_{θ}) has increased during last decade (3,9) (see Figs. 1a-c). This long-term change in the DO gradient has been observed throughout the basin especially during summer periods, no matter the region is cyclonic or anticyclonic in character. Although the April-1994 data indicate some short-term modification of the oxycline by both vertical mixing and horizontal advection down to the upper surface of the sub-oxic zone (σ_{θ} =15.7), still the long-term expansion of the suboxic zone is apparent since August-1965 and March-April, 1969 periods (Figs, 1a-c), in comparison with the April-1994 profiles.

An unforeseen event observed in July-1992 was the measurements of anomalously low levels of dissolved oxygen (Fig. 4b) at the conventional oxycline depths of the western cyclonic gyre. DO concentrations dropped to 20-30 μ M at around 14.9-15.0 density surfaces and almost vanished at around the 15.4 density surface (Fig. 3b) where the well established TNO_x maxima (Fig. 2a) with DO levels of 20-30 μ M (Fig. 1a) was located before 1992 summer. Although the onset of the oxycline in July-1992 coincided with that observed in September-1991 (Fig. 1a) within the interior of western cyclonic gyre, its concentration rapidly decreased in the upper pycnocline resulting in a coherent enlargement of the suboxic zone, as well as the erosion of the upper slope of TNO_x maxima due, probably, to dissimilatory nitrate reduction (denitrification). However, within the ACR and RCFZ regions, oxycline kept its normal feature (Figs. 4b and 5b) where suboxic levels of DO were detected at around 15.40 density surface.

3.1.2. Nutrient Distributions.

The concentrations of inorganic nutrients in the productive surface waters ranged between $<0.02\text{-}0.2~\mu\text{M}$ for o-PO₄ and $<0.1\text{-}0.5~\mu\text{M}$ for the TNO_x species (Fig.2). Remarkably high values were recorded in the shelf waters, especially in the northwestern shelf area, due to the riverine inputs, accompanied with relatively high N:P ratios (3,7). In the open waters, the molar ratios of particulate nutrients in sestons were in range of 11-25 over the basin in 1995-1996, mostly comparable to the mean ratio (N:P=16) given for oceanic plankton (21). Below the euphotic zone, very characteristic nutrient profiles inherent to the Black Sea are seen. The nutricline, coinciding with pycnocline, was shown to commence, consistently at greater density surfaces in the CR than in the ACR and RCFZ, due to the shoaling of the pycnocline to nearly the base of the euphotic zone in the CR (2,3).

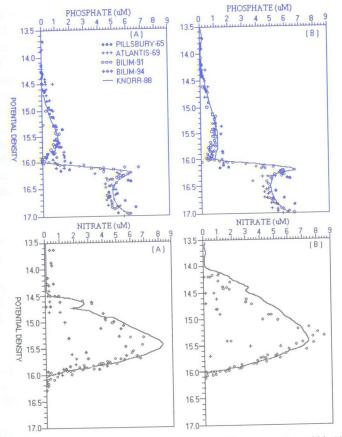


Figure 2. Potential density dependent variations of PO₄ and TNO_x concentrations within (A): cyclonic and (B): anticyclonic regions of the Black Sea for different periods.

In the oxycline, the inorganic nutrient concentrations increase steadily with depth (Fig. 2). The TNO_x profiles display distinct maxima between the specific density surfaces of σ_{θ} = 15.4 and 15.6 within the oxic/suboxic interface. Interestingly, the TNO_x maxima were located at greater density surfaces by about 0.3-0.4 density units, but with markedly lower peak values during the 60's (Fig.2a).

In July-1992, typical TNO $_x$ profiles displayed the characteristic maxima (6-8 μ M, see Fig. 2a) at around 15.4-15.6 density surfaces in the ACR and RCFZ. Unexpectedly, the concentration at the depth of the TNO $_x$ maximum dropped to less than 2 μ M in the western CR (Region I, Fig. 3a). During this period a short-term summer bloom was observed within the CR. Dramatic decreases in the maximum TNO $_x$ concentrations to <2 μ M in July-1992 period also resulted in a concurrent increase in the NO $_2$ concentrations within the upper layer of the suboxic zone (Fig. 3f) with the two intense maxima. The upper peak values as high as 0.6-0.8 μ M were observed at around 14.2-14.3 density surfaces where the onset of nitracline was

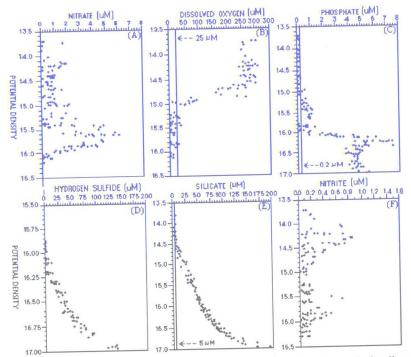


Figure 3. Density dependent plots of biochemical parameters at stations where abnormal nitracline were observed in July-1992 (Region -I, see Table 1. and Fig. 6 for station locations)

located, due to intermediate steps in nitrification process, whereas the deeper but less intense peak (0.4-0.5 μM) at 15.8-15.9 surfaces was due to the dissimilatory nitrate reduction processes. These peak values are obviously higher than those observed in September-1991 survey. Disregarding the short-term local modifications, the TNOx concentrations decrease steeply in the lower suboxic zone and drops to $<0.1\text{-}0.2~\mu M$ levels at the sulfidic boundary due to denitrification and oxidation-reduction reactions in the suboxic/anoxic interface.

Close examination of the TNO_x profiles for the Region-II (Fig. 4a) which specifies the RCFZ for July-1992, reveals that, even the nitracline onset has remained constant at 14.2-14.3 density surfaces as compared to September-1991 profiles (2,3), the maximum concentration was reduced from 6-7 μ M in 1991 down to < 2 μ M in July-1992. Suboxic dissolved oxygen levels (DO < 25 μ M) in this region were observed at the same density surfaces (σ_{θ} = 15.4-15.5) in July-1992 as was in September-1991. NO₂ distribution in this region (Fig. 4f) displays a broad, but less intense, single peak (<0.3 μ M) within the oxic and suboxic layer, whereas the two peaks were observed in the Region-I (CR, Fig. 3f). Within the Region-III (ACR, Fig. 5), TNO_x profiles display the expected vertical distribution; ie. the onset being at 14.2-14.3 density surfaces and peak values at around 15.4 - 15.5 density surfaces where suboxic (< 25 μ M) DO concentrations were reached; implying that this part of the basin was not affected by the physical and biochemical processes modifying the profiles of

biochemical properties within the other regions. Moreover, the density dependent profile of the NO₂ (Fig. 5f) displays a uniform distribution in this region.

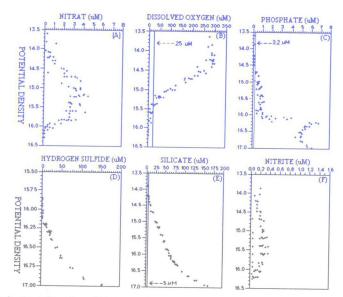


Figure 4. Density dependent plots of biochemical parameters at stations where nitracline onset was normal, but its peak value has been eroded (Region - II, see Table 1 and Fig. 6 for station locations).

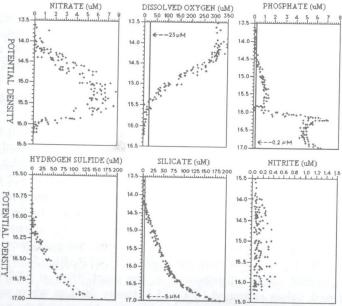


Figure 5. Density dependent plots of biochemical parameters at stations where nitracline onset and peak values are normal (Region - III, see Table 1. and Fig. 6 for station locations).

TABLE 2. Depth integrated totals of basic biochemical parameters within the Regions -I, -II and - III for different density intervals for July-1992 period in units of x10⁻³ mmoles.m⁻². (*): Number of data points

	REGION I (Cyclonic Region)						
	Param.	11.0-14.5	14.50-15.41	15.41-15.95			
	DO	6412 (42)	1501 (38)	161 (29)			
	PO ₄	2.10	4.96 (38)	25.04			
	TNO _X	14.13	15.77	70.87			
	Si	(42) 91.14 (38)	(38) 308.45	(30) 697.22 (26)			
į	TNO _X /PO ₄	91.14 308.45 (32) (32) (32) (37) (38) (32) (32) (37) (38) (39) (39) (39) (39) (39) (39) (39) (39					
	REGION II (Rim Current Region)						
	Param.	11.0-14.3	14.30-15.41	15.41-15.95			
	DO			249			
ij	PO ₄	1.68	17.53	16.14			
	TNO _x	(20) 15.64	(34)	(19) 47.54			
	Si	(19) 53.47	(34) 398.53	(19) 531.64			
	TNO _X /PO ₄	(8) 9.31	(17) 5.97	(10) 2.95			
	REG	ION III (Ant	icyclonic Regi	ion)			
	Param.	11.0-14.3	14.30-15.41	15.41-15.95			
	DO PO ₄	10179 (43) 2.49	8844 (67) 54.71	193 (26) 13.77			
	TNO _X	(46) 17.45	(66) 230.13	(25) 58.07			
	Si	(43) 148.00 (46)	(66) 893.31	(23) 788.09			
	TNO _X /PO ₄	7.01	(66) 4.21	(26) 4.22			

Phosphate profiles also exhibit a basin wide increasing trend within the oxycline and the upper suboxic zone down to σ_θ = 15.6-15.7 surface depths. Below, it possesses a prominent minimum (0.05-0.10 μ M) at the σ_θ = 15.85-15.90 surfaces of the cyclonic regions (CR) only. This feature weakens markedly within the coastal regions and nearly disappears within RCFZ (3). Nevertheless, the profiles always display a steep increase within the sulfidic water interface of the entire basin (Figs. 2a,b), reaching to peak values of 5-7 μ M at σ_θ = 16.20-16.25 surfaces. Then, the concentration decreases

slightly in the upper anoxic water and increases again slightly with the increasing depth in the anoxic layer. However, the phosphocline onset in the Region-I (Fig. 3c) during July-1992 period is detected at larger density surfaces (σ_{θ} = 14.9-15.0) with a concurrent decrease in DO concentrations (Fig. 3b) down to the suboxic levels at the same density surfaces. This apparent shift was most probably the result of adsorption of o-P0₄ on to the biogenic particles intensively during the summer bloom and/or utilisation in the anthropogenic processes in the denitrification zone developed in the upper nutricline. Phosphocline onset within the Region-II (Fig. 4c), which resembles the feature of RCFZ in September-1991 (2,3), was also shifted from 14.2-14.3 density surface to 14.5-14.7 surfaces in July-1992, but not as much as the shift in the Region-I. The sub-surface o-P0₄ maximum and suboxic minimum are not clearly evident in this region.

Depth integrated totals, given as $x10^{-3}$ mmoles.m⁻² for the biochemical parameters for different density intervals within the above mentioned three regions are given in Table 2 for July-1992 period.

Table 3. Depth integrated total ($x10^{-3}$ mmoles.m⁻²) of biochemical parameters between the surface and 15.95 density surfaces of different regions of the Black Sea.

CYCLONIC REGIONS					
Cruise	TNO _X	PO ₄	Si	TNO _x /PO ₄	
Knorr-1988 ⁽¹⁾		33.9	2193.3	7.46	
Bilim-1991 ⁽²⁾	283.4	37.2		7.63	
Bilim-1992 ⁽³⁾	100.8	32.1	1485.9	3.14	
	ANTICYCLO	NIC REG	LONS		
Cruise	TNOX	P04	Si	TNO _x /PO ₄	
Knorr-1988	551.4	76.2	2866.1	7.24	
Bilim-1991 ⁽¹⁾	395.7	46.3		8.54	
Bilim-1992 ⁽²⁾	305.7	71.0	2318.6	4.31	
	l l				

(1): R/V Knorr, Cruise No.4; (2): September,1991
(3): July, 1992

Depth integrals between 14.30 - 15.41 density surfaces indicate that Region-III (ACR) and Region-II (RCFZ) have higher (230.1 and 104.6 totals of TNO_x) compared to the integral for 14.50 - 15.41 surfaces within the Region-I (15.8) where permanent cyclonic eddy was formed, even though the depth integrated totals extended down to the σ_θ = 14.5 surface for the latter surface. However, the depth-integrated totals in the surface layer down to the nitracline onset were 14.1, 17.5 and 15.6 x 10^{-3} mmoles.m⁻² for Regions I, II and III, respectively. Table 2 also indicates an intense denitrification

within the Region-I during the July-1992 period. When the overall depth-integrated values of the TNO $_x$ from surface down to the 15.95 density surfaces of three regions for three different periods are compared (Table 3.), it is clearly evident that the total TNO $_x$ in the CR in July-1992 (100.8 x10⁻³ mmoles.m⁻²) decreased to 1/3 of the values for the summer periods of 1988 and 1991 (253.1 x10⁻³ and 283.4 x10⁻³ mmoles.m⁻² , respectively).

However, in the ACR it remained nearly constant (305.6 - 395.3 x10⁻³ mmoles.m⁻²) during the summers of 1991-1992 which were about 10% lower than the estimate for 1988 (551.4 x10⁻³ mmoles.m⁻²). The depth-integrated values for R/V Knorr-1988 are always higher than the estimates from the R/V Bilim-1991 integrals due to the continuity of the data sets in the former cruise (pump-cast data) whereas discrete type (bottle-cast) data were available for the latter cruise. Comparison of the combined nutrient profiles of the CR and the ACR together with the N:P ratios reveals that the rations were decreased from 7.2 - 8.5 in 1988 and 1991 periods down to 3.1 - 4.82 during the summer of 1992.

Sestons were determined to have N:P ratios of greater than 10; then, the anomalously low N:P ratios determined within the oxic/suboxic interface strongly suggest that the nitrate losses by denitrification in the suboxic zone (DO < 20 μM) of the system exceed the phosphate export to the anoxic waters by redox-dependent sedimentation processes. However, this suggestion is insufficient to explain very low TNO_x/PO₄ molar ratios observed in the oxycline in 60's, when the suboxic zone was very thin in comparison with that observed since 1988.

3.2 PHYSICAL PROPERTIES

During the July-1992 cruise of R/V Bilim, intensity of the fluorescence adjusted to the Chll-a wavelengths was also measured by using an in situ fluorimeter attached to a Sea Bird CTD probe. The magnitude of the sub-surface fluorescence maximum intensities, in arbitrary units, plotted over the southern half of the basin is displayed in Figure 6. The positions of the stations which were designated as Region-I, -II and -III are also shown in the same figure to clarify the discussions.

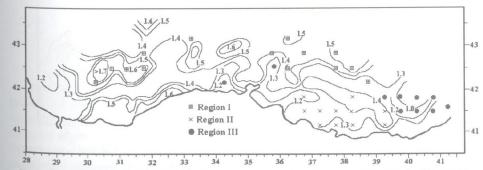


Figure 6. Horizontal distribution of sub-surface fluorescence maximum intensity within the mixed layer of the Black Sea in July-1992 (R/V Bilim - 1992).

As is seen from the Fig. 6, the highest fluorescence intensities (>1.5 units) were measured mainly within the offshore waters of the western Black Sea where the main cyclonic gyre was located (Figs. 7a,b), whereas some patchy distributions are observed within the offshore waters of the central Black Sea. Fluorescence intensities varying between 1.4 - 1.5 units were also detected in the region located between the RCFZ and the coastal zones of the southwestern Black Sea. Within the fluorescence maximum regions, the Secchi disk transparency of water column was measured to be as low as 3-5 m, whereas it was relatively high (8-10 m) in the other regions. Although it is not shown here, the percent light transmission of these more productive surface waters were measured to be as low as 50-60 % within Region-I, but ranged between 75-85 % in other two regions.

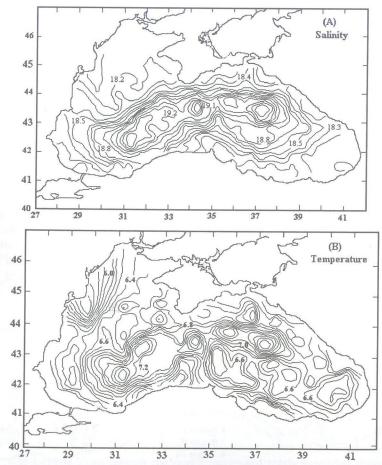


Figure 7. Horizontal distributions of (A): salinity and (B): potential temperature at 50 db level in July-1992. (reproduced from Oğuz et al., 1993)

If sub-surface maximum fluorescence distribution (Fig. 6) is examined in conjunction with the temperature (Fig. 7a), salinity (Fig. 7b) and potential density distributions (Fig. 7c), it appears that the region of maximum fluorescence intensities coincides with the water masses having higher temperature (>7.2°C) and salinity (>19.2) at 50 db level. This relatively warmer and more saline water masses were found to be formed by the local generation of Cold Intermediate Layer (CIL) within the cyclonic region which does not replenish the CIL in the convergence zones (15,16). The averaged CIL temperature in July-1992 was shown to be cooler than in September-1991, with the most noticeable differences being confined to the $\sigma_{\theta} = 14.4-15.0$ range (15), and the maximum density gradient has shifted to the 15.3 σ_{θ} level in April-May-1994 which was confined to the 14.9 σ_{θ} level in 1991 (16). The July-1992 period was also shown to possess less intense meanders and offshore filaments as was observed in 1991 (22). RCFZ was shown to be distinctly different from that of 1991 period during which RCFZ was situated roughly over the upper topographic slope near the shelf break, which in turn allowed considerable interactions between the shelf and interior water masses. This zone is shifted further offshore and confined to the lower topographic slope (22).

TABLE 4. Average physical properties of the water columns of the Regions I, II and III at specific density surfaces for a summer period. (D: Depth, T: Potential temperature, S: Salinity, ST: Sigma-theta)

		Septem I	ber-1991 III	j j	ULY-1992 III	
14.20 surface	D T S	33.4 8.42 18.37	54.3 7.23 18.21	27. 8.7 18.4	3 6.93	
Core of CIL	D T S	44.9 6.95 18.60 14.54	72.4 6.94 18.39 14.37	43. 6.3 18.6 14.6	6.43 69 18.35	
15.40 surface	D T S	67.0 7.82 19.82	117.0 7.83 19.82	59. 7.7 19.7	0 7.76	
15.95 surface	D T S	90.6 8.25 20.59	144.4 8.27 20.59	87. 8.3 20.5	8.23	

However, if the average physical properties of the Regions-I & III in July-1992 period is examined in comparison with those for September-1991 period (Table 4), it is seen that the average temperature and the salinity at the 14.20 density surface of cyclonic region (Region I) in July-1992 (8.73°C and 18.42) are higher than that of September-1991period (8.42°C and 18.37), respectively. In contrast to above mentioned changes, the properties at the temperature minimum depth in the core of CIL are colder but more saline in July-1992, implying that the isopycnal mixing

affected the water column down to these depths. On the other hand, the temperature and salinity values at the 15.40 density surface, where TNOx maxima were observed, are lower than those observed during September-1991. Changes in the average salinity at 14.20 σ_{θ} surface of the Region-III is less intense (0.03 salinity units) compared to that in the Region-I)0.07 salinity units). When the average temperature and salinity values of the 15.40 σ_{θ} surface are compared, it will be seen that both properties have the same values in both regions in September-1991. On the other hand, the average temperature measured in 1992 period was larger in Region-I but smaller in Region-III than those obtained in 1991; whereas average salinity values in both regions and periods were insignificant.

4. Conclusions

Evaluation of the hydrographic measurements performed in July-1992 in conjunction with the past data shows that the interannual as well as intra-annual variations triggered by different driving forces affect the general water circulation, and hence the coastal-offshore interactions and vertical mixing processes. These forces may influence the density dependent profiles of biochemical properties of the upper layer down to the anoxic boundary due to the intensity of the vertical as well as horizontal winter mixings and thus the regions of CIL formation which controls the supply and cycles of nutrient elements in the euphotic and oxic/anoxic interface. In July-1992, these processes provided sufficient nutrients into the photic layer of the cyclonic gyre where light intensity and the water temperature were suitable for the intense summer bloom which has lead to apparent reductions in the concentrations of o-PO₄ and TNO_x in the oxycline, and reductions in the DO concentrations due to the oxidation of the increased sinking flux of organic matter. Thus, the main chemocline in the CR has been modified as a result of intense, local denitrification processes. However, these processes in July-1992 did not modify the suboxic/anoxic interface in the CR (σ_{θ} = 15.95 - 16.10) because such physical processes were effective down to the depth of TNO_x maxima ($\sigma_{\theta} = 15.4-15.6$).

5. Acknowledgements. This study has been made possible by the supports of Turkish Scientific and Technical Research Council (TUBİTAK), Ukrainian Agency of Marine Research and Technologies, CoMSBlack and NATO TU-Black Sea Programs.

References

- Murray, J.M., Codispoti, L.A. and Freiderich, G.E. (1993): Redox Environments: The suboxic zone in the Black Sea. IN: C.P. Huang, C.R. O'Melia and J.J. Morgan (eds), Aquatic Chemistry, American Chemical Society, ACS Advances in Chemistry Series No: 244, 157-176...
- Basturk ,O., Saydam, C., Salihoğlu, I., Eremeev, L.V., Konovalov, S.K., Stoyanov, A., Dimitrov, A., Cociasu, A., Dorogan, L. and Altabet,M (1994):. Vertical variations in the principle chemical properties of the Black Sea in the autumn of 1991. Marine Chemistry, 45, 149-165.

- Baştürk, Ö., Tuğrul, S., Konovalov, S.K and Salihoglu, I. (1997): Variations if the vertical chemistry within three hydrodynamically different regions of the Black Sea. IN: Sensitivity of the North Sea, Baltic Sea and Black Sea to Anthropogenic and Climatic Changes, Kluwer Academic Publishers, Dordrecht, NATO ASI Series, 183-196.
- 4. Mee, L.D. (1992): The Black Sea in Crisis: The need for concerted international action, Ambio, 21, 278-286.
- Murray, J.M., Jannasch, H.W., Honjo, S., Anderson, R.F., Reeburgh, W.S., Top, Z., Freiderich, G.E. Codispoti, L.A. and Izdar, E. (1989): Unexpected changes in the oxic/anoxic interface in the Black Sea, Nature, 338, 411-413.
- 6. Bodeanu, N. (1992): Algal blooms and development of the main planktonic species at the Romanian Black Sea littoral in conditions of intensification of the eutrophication process. IN: R.A. Wollenwider, R. Marchetti and R.V. Viviani (eds.), Marine Coastal Eutrophication, Elsevier Publishers, Amsterdam, pp:891-906.
- Smayda, T.J. (1990): Novel and nuisance pytoplankton blooms in the sea: Evidence for a global epidemic. IN: E. Granelli, B. Sudsstroem, L. Elder and D.M. Anderson (eds.), Lund, Sweden, 26-30 June, 1989, pp:29-40
- 8. Shushkina, Eh.A. and Musaeva, Eh.I. (1990): Structure of planktonic community from the Black Sea epipelagic and its changes as the result of the introduction of a ctenophore species, *Oceanology*, **30(2)**, 306-310
- Tuğrul, S., Baştürk, O., Saydam, C. and Yılmaz, A. (1992): Changes in the hydrochemistry of the Black Sea inferred from water density profiles, *Nature*, 359, 137-139.
- Codispotti, L.A. Friederich, G.E. Murray, J.W. and Sakamoto, C.M. (1991) Chemical variability in the Black Sea: Implications of continous vertical profiles that penetrated the oxic/anoxic interface. *Deep-Sea Res.* 38(Suppl. 2): S691-S710.
- 11. Saydam, C., Tuğrul, S., Baştürk, O. and Oğuz, T. (1993): Identification of the oxic/anoxic interface by isopycnal surfaces in the Black Sea, *Deep-Sea Res.*, 40(7), 1405-1412.
- Murray, J.M., Top, Z. and Özsoy, E. (1991): Hydrographic properties and ventilation of the Black Sea. Deep-Sea Res. 38(2), S663-S690.
- 13. Buesseller, K.O. Livimgstone, H.D., Ivanov, L., and Romanov, A. (1994): Hydrographic properties and ventilation of the Black Sea. *Deep Sea Res.* 41(2), 283-296.
- Özsoy, E., Ünlüata, Ü. and Top, Z. (1993): The evolution of Mediterranean water in Black Sea: Interior mixing and material transport by double diffusive intrusions. Prog. Oceanogr. 31, 275-320.
- 15. Ivanov, L.I., Besiktepe, Ş. and Özsoy, E. (1997a): The Black Sea Cold Intermediate Layer. IN: Sensitivity of the North Sea, Baltic Sea and Black Sea to Anthropogenic and Climatic Changes, Kluwer Academic Publishers, Dordrecht, NATO ASI Series, 253-264.
- Ivanov, L.I., Besiktepe, S. and Özsoy, E. (1997b): Physical Oceanography Variability in the Black Sea Pycnocline. IN: Sensitivity of the North Sea, Baltic Sea and Black Sea to Anthropogenic and Climatic Changes, Kluwer Academic Publishers, Dordrecht, NATO ASI Series, 265-274.
- 17. World Ocean Data Center-A
- Brewer, P.G. (1971): Hydrographic and chemical data from the Black Sea, Woods Hole Oceanogr. Inst. Technical Report, Reference No:71-65
- 19. Friederich, G.E., Codispoti, L.A. and Sakamato, C.M. (1990): Bottle and pump cast data from the Black Sea expedition, Monterey Aquarium Res. Inst. Tech. Report. No:90-3, 224 pp.
- Serap, G. (1996). A Comparative Study for the Determination of Hydrogen Sulfide in the Suboxic Zone of the Black Sea. M.S. Thesis, IMS-METU, Erdemli.
- Takahashi, T., Broecker, W.S. and Langer, S. (1985): Redfield ratio based on chemical data from isopycnal surfaces. Jr. Of Geophysical Research, 90, 6907-6924.
- 22. Oğuz, T., L. Ivanov, Ş. Beşiktepe, E. Demirov and V. Diacanu. (1998). Basinwide circulation and thermohaline characteristics of the Black Sea during July 1992. (this issue)
- Oğuz, T., Ş. Beşiktepe, Ö. Baştürk, İ. Salihoğlu, D.G. Aubrey, A. Balcı, E. Demirov, V. Diacanu, L. Dorogan, L. Ivanov, S. Konovaşov, A. Stoyanov, S.Tuğrul, V. Vladimirov and A. Yılmaz (1993): CoMSBlack'92A Physical and Chemical Intercalibration Workshop. I.M.S. METU, 15-29 January 1993. IOC Workshop Report No. 98.