Seasonal variation of nutrients in the exchange flows between the Black and Marmara Seas through the Bosphorus Strait

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Abstract- Hydro-chemical data measured in the two-layer flow regimes of the Bosphorus Strait between 1990-2001 have been examined to assess ranges of seasonal variations of both concentrations and fluxes of nutrients exchanged between the Marmara and Black Sea. The Black Sea flow into the Marmara via the Bosphorus exhibits remarkable seasonality both in its volume flux and nutrient concentrations. Saltier waters in the Marmara lower, layer flows into the SW Black Sea shelf, showing remarable seasonality in its volume flux but small changes in its chemical properties. The counter-flows in the strait increase in the spring-early summer and then weaken markedly in the autumn, depending on fresh water input to the Black Sea. Nitrate and phosphate concentrations of the Black Sea inflow drops to the lowest levels in the late spring-autumn period and then rise by 10-50 fold in late autumn and winter months. However, the seasonality in the particulate nutrient content of the Black Sea inflow is much less pronounced. Thus, the lowest nitrate and phosphate fluxes occur in autumn when flow and concentrations both are markedly low in the surface flow. However, the annual export of dissolved inorganic and particulate nutrients from the Black Sea are comparable. Nutrient export from the Marmara lower layer waters principally occurs principally takes place in dissolved inorganic (nitrate and phosphate) forms and their flux rates are dependent upon the flow regime of the Bosphorus undercurrent.

Keywords- Bosphorus strait, nutrient exchange, Black Sea, Marmara Sea

Introduction

The Black Sea, an inland sea having sulphide-bearing waters below a depth of 100-200m (Sorokin, 1983), is connected to the world ocean system via the Turkish Strait System including the Sea of Marmara, Bospgorus and Dardanelles straits. Accordingly, its brackish waters (S=17-18 ppt) flowing out through the Bosphorus and occupy the Marmara upper layer for some months (Besiktepe et al., 1993) with the associated biochemical properties before eventually reaching the Dardanelles and passing through to the Mediterranean (Polat et al., 1998). Recent estimates have show that nutrient input from the Black Sea principally determines the Marmara Sea ecosystem (Tuğrul and Polat, 1995). A counterflow in the Bosphorus permits the salty Mediterranean waters to flow into the SW Black Sea shelf waters with high nitrate and phophate concentrations (Polat and Tuğrul, 1995). Since late 80's two-layer flow regimes of the Bosphorus have been investigated extensively, permitting us to estimate seasonal volume and nutrient (dissolved inorganic and particulate forms) fluxes for the first time no data, using long-term hydro-chemical data obtained in the Bosphorus and adjacent seas in the last decade.

Experimental

Field studies were carried out using the research vessel of METU, R/V BILIM, water samples for nutrient analysis were collected at the southern and northern entrances of the Bosphorus, using a 12-bottle Rozette system attached on a CTD probe. Phosphate and nitrate (indeed, the sum of nitrate + nitrite) concentrations were determined by a Technicon model 3-channel auto-analyzer. Water samples for particulate organic carbon (POC), nitrogen (PON) and particulate phosphorus (PP) determinations were filtered through pre-ignited GF/F filters under low vacuum and kept frozen until analysis. PON and POC analyses were carried out by a Carlo Erba Model 1108 CHN analyzer. Particulate phosphorus collected on filters was measured by the dry-combustion and colorimetric method described elsewhere (Polat and Tuğrul, 1995).

Results and Discussion

The seasonal volume fluxes calculated for the first time by Tugrul et al. (2002) show that the highest and lowest rates of exchange flows in the Bosphorus Strait occur in spring and autumn, respectively, changing by about 2-fold seasonally (Table 1).

Table 1. Seasonal and annual averages of concentrations and fluxes of nitrate and phosphate in the two-layer flow regimes of the Bosphorus Strait.

Flow Type (layer)	Period	Volume Flux ($*10^9 m^3$)	NO_3 conc. ($mmol/m^3$)	NO_3 flux ($*10^8$mol)	PO_4 conc. ($mmol/m^3$)	PO_4 flux ($*10^7$ mol)	N/P Ratio
Upper	Spring	200	1.32	2.64	0.05	1.0	26.0
Upper	Summer	158	0.42	0.66	0.03	0.47	14.0
Upper	Autumn	105	0.22	0.23	0.05	0.52	4.4
Upper	Winter	145	3.2	4.64	0.14	2.03	23.0
Upper	Annual	608	1.29	8.17	0.07	4.02	18.0
Lower	Spring	94	9.17	8.62	0.92	8.64	9.9
Lower	Summer	76	10.46	7.95	0.99	7.52	10.5
Lower	Autumn	49	9.34	4.58	0.91	4.45	10.2
Lower	Winter	68	9.81	6.67	1.07	7.27	9.2
Lower	Annual	287	9.7	27.8	0.97	27.9	10.0
U/L Ratio	Annual	2.1	0.13	0.29	0.07	0.14	10.0

Dissolved inorganic nutrient (DIN, DIP) concentrations also display remarkable seasonal variations in the Black Sea inflow to the Marmara upper layer whereas the seasonality is much less pronounced in the salty Mediterranean water entering the strait (Table 1, Fig. 1) as previously emphasized by Polat and Tuğrul (1995) and Polat et al. (1998).

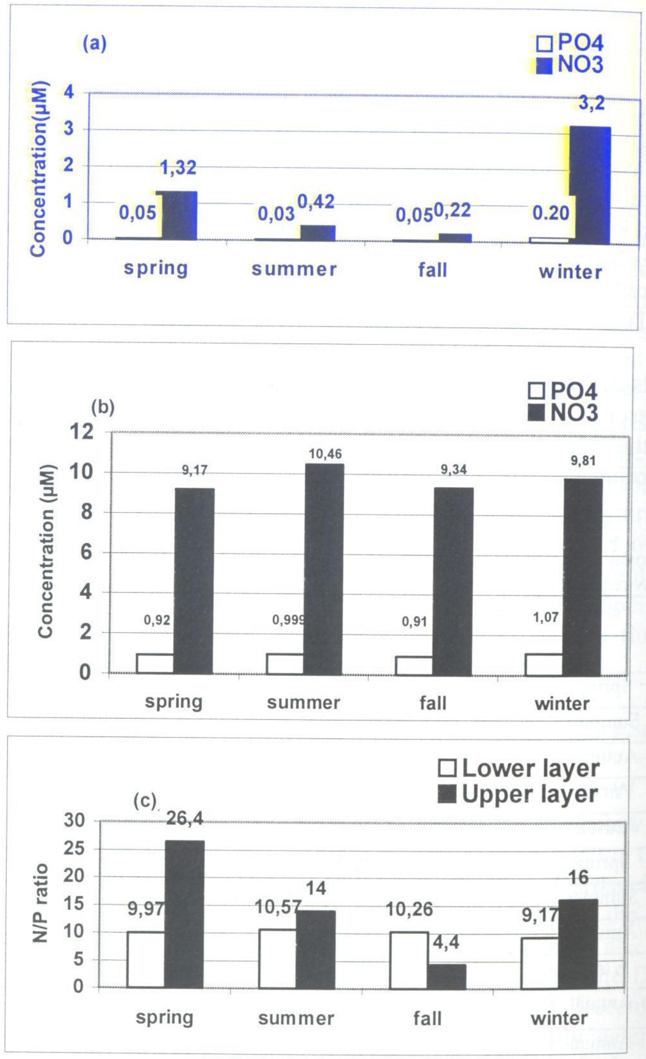

Fig. 1. Seasonal variations of nitrate, phosphate concentrations and their molar ratios in the Bosphorus two-layer flows: (a): Upper layer, (b):Lower layer,(c): NO_3/PO_4 molar ratios in the counter-flows at the strait entrances.

Nitrate content of the Black Sea inflow is as low as 0.1-0.2 µM in summer-autumn period but markedly rises to levels of 5-7 µM in winter whilst the phosphate ranges between 0.02-0.05 µM, then increasing 0.2-0.4 µM levels in winter (Polat and Tuğrul, 1995) when the nutrient input rate to the Black Sea surface waters much exceeds their removals via photosynthesis (Cociasu et al., 1996). Accordingly, the particulate nitrogen and phosphorus constituents of Bosphorus surface low exceed the nitrate and phosphate values in the ambient water during spring- autumn period when the surface waters become more productive and depleted in DIN and DIP (Fig. 1a). On the annual basis, DIN content of the Black Sea inflow is slightly less than the PON in the inflow. Seasonally variable DIN/DIP ratios calculated from the long-term data consistently increase in winter, displaying an opposite trend with the N/P ratio of suspended particles in the Black Sea inflow to the Marmara upper layer (Fig. 1c). On the other hand, the salty Mediterranean waters aged in the Marmara lower layer and thus enriched in DIN and DIP for several years, leave the basin via the Bosphorus with very high nitrate (8-11 µM) and PO4 (0.8-1.1 µM) values and almost constant N/P ratios (Fig. 1) but with very low POM to the limitation of photosynthesis to the Marmara upper layer during the year.

Nutrients loads exchanged between the adjacent seas via the Bosphorus, calculated from seasonal estimates of volume fluxes and concentrations for the exchange flows, vary markedly with season. The Black Sea DIN input to the Marmara upper layer increases by 20-fold from autumn to winter whereas the total of DIN+PON fluxes changes merely by 5-fold (Fig. 2). Seasonally variable Black Sea DIP input constitutes a small fraction of the annual load of total-P input whereas the seasonal PP influx, forming the major fraction of the Black Sea TP input, increases by about 3-fold from autumn to spring (Fig. 2). A similar seasonality appears in the nutrient input from the Marmara basin to the SW Black Sea intermediate depths, due principally to the variation of seasonal volume flux (Table 1). Assuming the system at steady state on a yearly time scale, the DIN export from the Marmara basin apparently exceed Black Sea (DIN+PON) input to the Marmara upper layer (Table 1 and Fig. 2). However, the annual load of DIP exported From the Marmara to the Black Sea via the Bosphorus undercurrent is roughly compensated by the Black Sea (DIP+PP) input to the Marmara upper layer.

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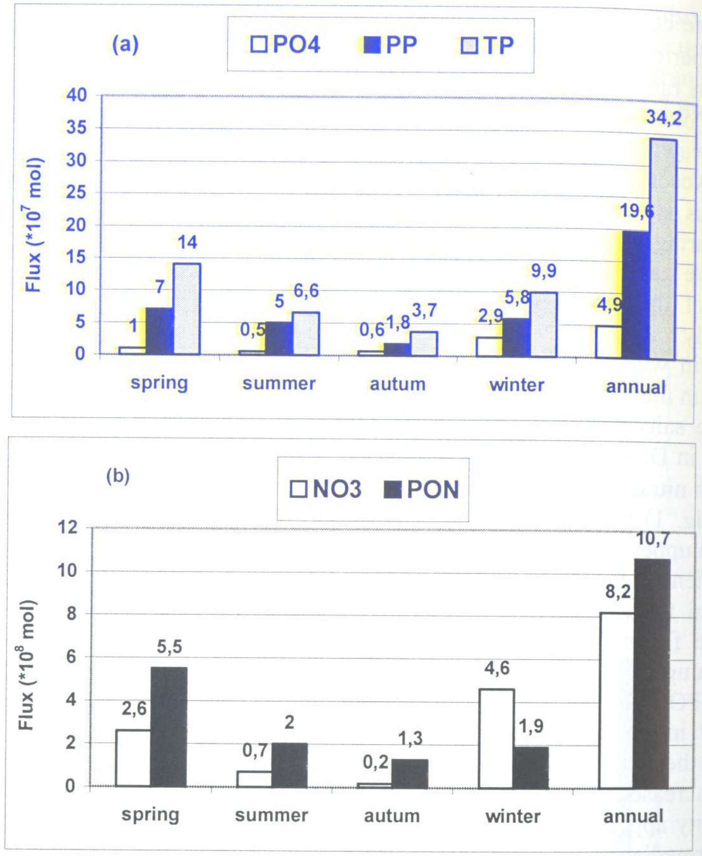

Fig. 2. Seasonal and annual influxes of nutrients from the Black Sea to the Marmara upper layer via the Bosphorus surface flow: (a) reactive phoshate, particulate-P (PP) and total- P (TP), (b): nitrate, particulate organic nitrogen (PON)

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Time series analysis of nutrients in Southwestern Black Sea and the Sea of Marmara

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Abstract- Spatio-temporal fluctuation of nutrients during 1996-2001 period in the Black Sea and the Sea of Marmara was evaluated in this study. Inorganic phosphate concentrations of the upper layer was stable while maximum concentrations were detected in unfavorable winter conditions for primary production. On the other hand, strong depletion of nitrogenous nutrients was detected in the upper layer. Chlorophyll *a* concentrations of both stations displayed increasing pattern, particularly significant in the northern part of the strait. Lower layer nitrite concentrations significantly increased since due to the enhanced domestic discharge load in the Strait. The blockage occurred in February 1998 at the northern part of the strait yielded in homogenous distribution of nutrients in the water column.

Keywords- nutrients, monitoring, Bosphorus, The Sea of Marmara

Introduction

The Sea of Marmara is a semi-enclosed sea, connecting the Black Sea to the Aegean Sea via Turkish Strait System. The Strait of Istanbul (Bosphorus) is a narrow channel, connecting the Black Sea to the Sea of Marmara. The two-layered stratification is driven by the density gradient between brackish waters of the Black Sea (16.5-18.5 psu) upperflow and salty Mediterrenaean underflow (38 psu) in the strait and Marmara Sea. Studies in the area revealed that the northwestern shelf originated waters reach the strait in about 1-2 months (Sur *et al.*, 1994), carrying high amounts of nutrients (Polat and Tuğrul, 1995) and trasported to the Marmara Sea where water renewal is estimated as at least twice a year by Black Sea inflow (Ünlüata *et al.*, 1990; Beşiktepe *et al.*, 1991). In addition to Black Sea originated waters, upper layer of the Marmara Sea had been also under the influence of surface discharges of Istanbul recently (Tuğrul and Polat, 1995; Doğan *et al.*, 2000, Okuş *et al.*, 2002). Lower layer renewal on the other hand, was estimated as about 6-7 years (Ünlüata *et al.*, 1990; Beşiktepe *et al.*, 1991) where nutrient poor waters enriched 10 folds during their travel from the Dardanelles to Bosphorus (Tuğrul, 1993). In addition, lower layer receives great amounts of deep-disposals that generally reaches to the anoxic layers of the Black Sea (Doğan *et al.*, 2000, Okuş *et al.*, 2002; Aslan-Yılmaz, 2002).

To collect continuous data and find out the influence of discharges on the ecology and water quality in the strait and Marmara Sea a monitoring project began in 1996. The aim of this paper is to figure out the recent state of nutrient composition, especially after discharge control at the area according to the data obtained during 1996-2001 surveys with R/V *Arar*.

Materials and Methods

Samples were collected by General Oceanics rosette system equipped with twelve 5 L Niskin bottles and a SBE 9/11 CTD. Samples for nitrite+nitrate (N_{ox}), total nitrogen (TN), ortho-phosphate, total phosphate (TP) and silicate (Si) were collected from surface (0.5 m), 5 m and followed by 10 m depth intervals and stored in polyethylene bottles and deep frozen (-20 °C). For total organic carbon (TOC) determination, samples were collected from same depths and stored at 4 °C. Particulate organic carbon (POC) samples were collected from 0.5, 10, 20 m and bottom depths and filtered through precombusted GF/F filters (Whatman) on board then deep frozen. For chlorophyll *a* analysis, seawater was filtered through 0.45 µm membrane filters (Sartorius) and deep-frozen. All further analyses of frozen samples were performed in the land-based laboratory. Nitrite was analyzed on board immediately after the collection of the samples, according to (Parsons *et al.*, 1984). The analyses of N_{ox}, TN, o-PO_4, TP and Si were performed by Technicon A-II Model autoanalyser (Technicon Industrial Method a, b, 1977). POC was measured by LECO model carbon instrument and TOC by TOC-500 model organic carbon measurement instrument (APHA, 1999). Chlorophyll *a* measurements were performed according to acetone extraction method (Parsons *et al.*, 1984).

The locations of the stations were given in Fig. 1. In this text, mainly the two of them are focused on. One is located at the northern exit of the Strait of Istanbul (K0) and the latter is at the southern exit (M8). These two stations are crucial since they represent the nutrient exchange between Black Sea and the Sea of Marmara.

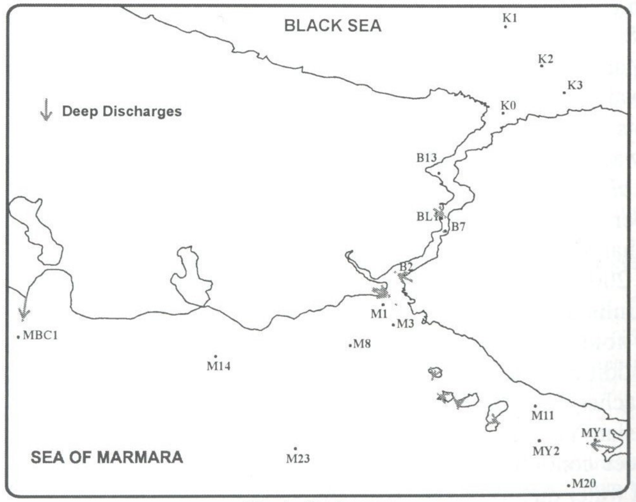

Fig. 1. Study area

Upper Layer

In the northern exit of the strait, inorganic phosphate concentrations ranged between 0.03-1.02 µM between 1996-2001 and high values generally detected in winter periods (Fig. 2). Minimum and maximum particulate phosphate values detected throughout the study were 0.05-0.35 µM and total phosphate was 0.14-3.06 µM. On the other hand, inorganic phosphate concentrations ranged between 0.05-1.57 µM, whilst particulate phosphate was 0.05-0.33 µM and total phosphate was 0.28-1.58 µM at the southern part of the strait. Mean PO_4 values were 3.2 folds higher in southern exit than northern part, indicating that phosphate poor Black Sea originated waters were enriched by surface discharges during its travel through the strait. Although phosphate forms displayed stable trend generally, the concentrations lessened during late 1999-2001 period (Fig. 2). Highest PO_4 value was 0.38 µM at the southern exit in 2001. Thus, recent studies on discharge contamination of the area had shown that connecting many surface discharges to deep disposals decreased the pollution effect of strait (Aslan-Yılmaz, 2002).

Contrary to Black Sea- Marmara Sea transects, coastal Marmara Sea stations displayed increasing upper layer means with time. Uncontrolled surface discharges in to the Marmara Sea (mainly Kadıköy-Tuzla and Ahırkapı-Küçükçekmece regions), resulted in increasing of phosphate.

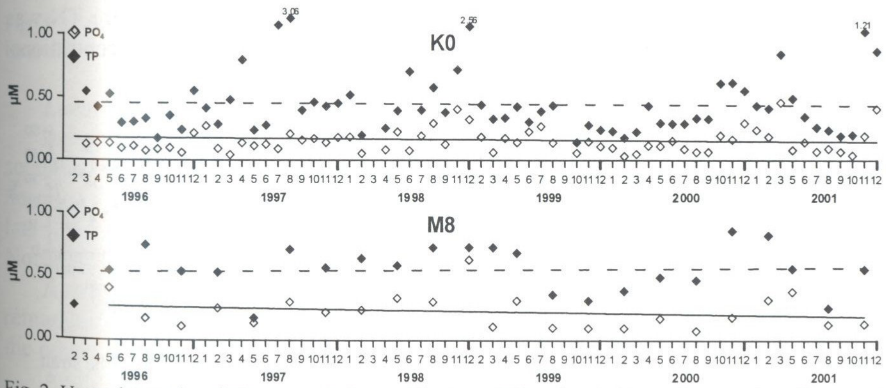

Fig. 2. Upper layer phosphate concentrations of the two stations located in northern and southern part of the strait in 1996-2001 period.

Nitrate+nitrite concentrations on the other hand, significantly decreased within five years. In northern exit of the strait, maximum value was 6.01 µM in 1996, this value decreased to 0.45 µM in 2001, excluding December 2001. In December, heavy (64 mm) rainfall resulted in high nutrient concentrations throughout the study area. On the other hand, total nitrogen distributions displayed inverse pattern; higher TN concentrations were detected with time. In 1996, maximum TN value was 15.75 µM whilst 25.90 µM was the highest value of 2001, excluding December 2001 value (43.82 µM).

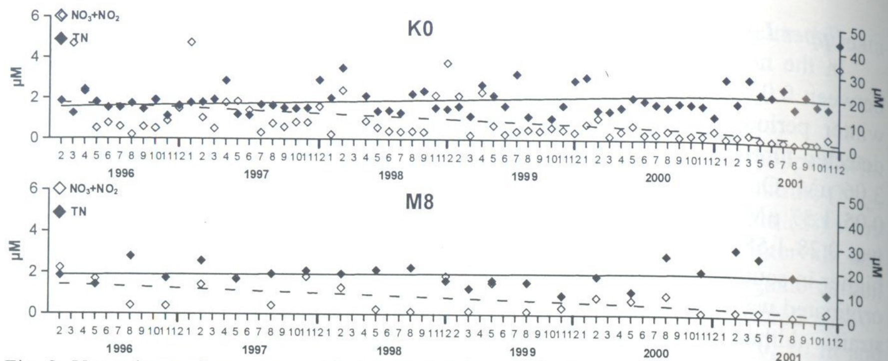

Fig. 3. Upper layer nitrogenous nutrient concentrations of the two stations located in northern and southern part of the strait in 1996-2001 period.

Upper layer NO_x and TN annual concentrations at the northern strait are given in Table 1. Decreasing trend of labile nitrogen but increasing of TN is concluded as increasing pattern of organic nitrogen forms at the area. High values of TN were partly seen in low salinity periods at the Black Sea entrance (Fig. 4). Moderate but significant (n=64, p=0.012) negative correlation between surface salinity and TN concentrations indicates that nutrient input from northwestern shelf affect strait upper layer. Lowest salinity was detected in July 1999 (14.9 psu) where TN was 31.14 µM. Southern strait also displayed similar pattern in nitrogen concentrations. NO_x decreased significantly, whilst TN increased.

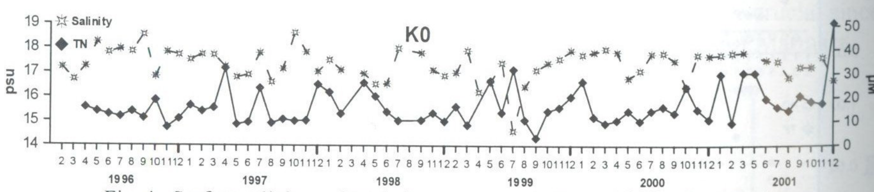

Fig. 4. Surface salinity and total nitrogen concentrations at the northern strait.

Table 1. Annual means of upper layer oxidized and total nitrogen at the northern part of the strait.

	K0	
	NO_x	TN
1996	1.56±1.96	13.60±2.75
1997	1.29±1.56	14.86±4.62
1998	1.20±1.41	16.06±5.62
1999	1.03±1.74	16.05±6.54
2000	0.44±0.31	14.86±3.92
2001	0.19±0.13	21.96±8.16

Organic carbon data displayed increasing pattern with time. Remarkably close values were detected at both parts of the strait. The mean value of POC was 23.94±13.05 µM at northern exit and 29.76±13.56 µM at southern exit. POC reached maximum value in May 2001 (67.18 µM) at northern part.

Chlorophyll *a* values were the highest in October 2000 (10.08 µM) at the northern part. In general, concentrations reached maximum in late autumn and early spring. In 2000 on the other hand, high values were detected throughout the year. This abnormality was specific for 2000 and was not observed in the following year. Relation between particulate organic carbon and chlorophyll *a* were significant (r=0.48, p<0.001, n=64).

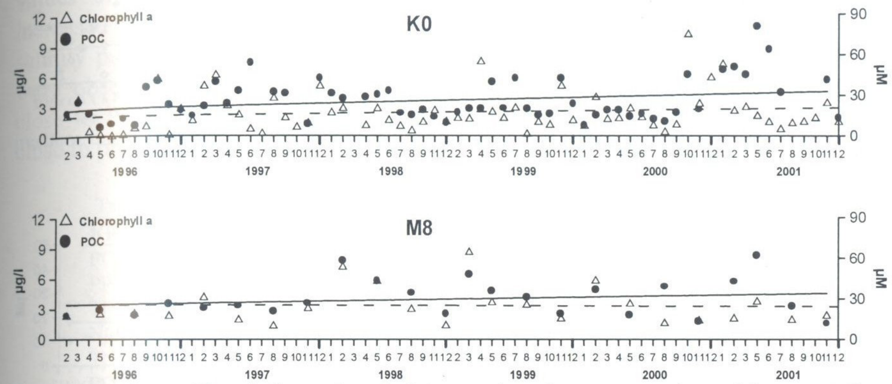

Fig. 5. Upper layer chlorophyll *a* and particulate organic carbon concentrations of the two stations located in northern and southern part of the strait in 1996-2001 period.

Lower Layer

Inorganic phosphate concentrations remarkably decreased within five years at southern strait. Highest PO_4 value was 1.07 µM in 1996, whilst this value decreased to 0.63 µM in 2001. This decreasing pattern is mainly significant after late 1999. Total phosphate on the other hand, displayed more stable pattern. Northern strait values were close to southern strait.

Among nitrogenous compounds, similar to upper layer, nitrate+nitrite remarkably decreased with time (Fig. 7) in lower layer. According to nitrite data on the other hand, an increasing pattern was observed.

Additionally, significant increasing trend of TN in six years at northern strait were detected and concluded as the effect of increasing amount of deep-disposals in the strait, dominated by organic forms of nitrogen, nitrite and probably ammonia. Fig. 8, represents the change in nitrite concentrations with time at the northern part of the strait. Mean nitrite concentrations were approximately 1.5 folds higher in 2001 than 1996.

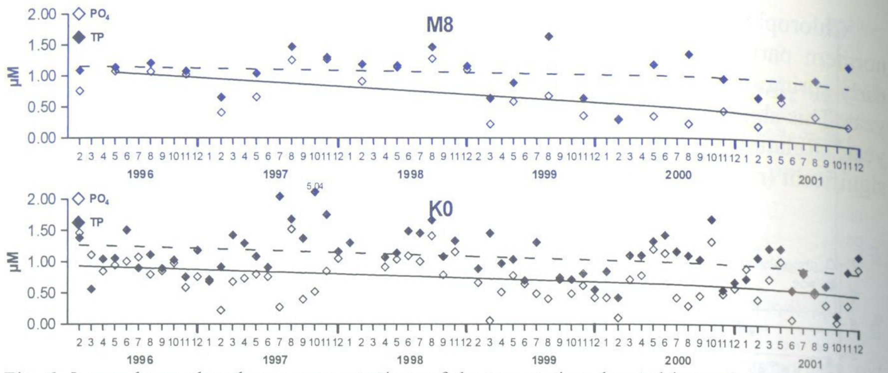

Fig. 6. Lower layer phosphorus concentrations of the two stations located in northern and southern part of the strait in 1996-2001 period.

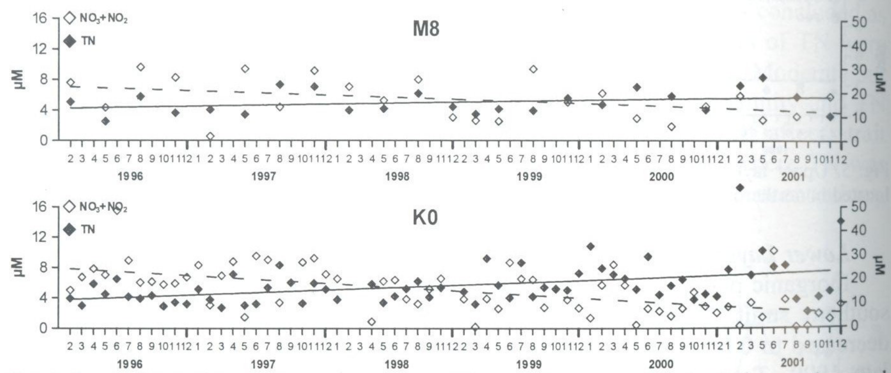

Fig. 7. Lower layer nitrogenous nutrient concentrations of the two stations located in northern and southern part of the strait in 1996-2001 period.

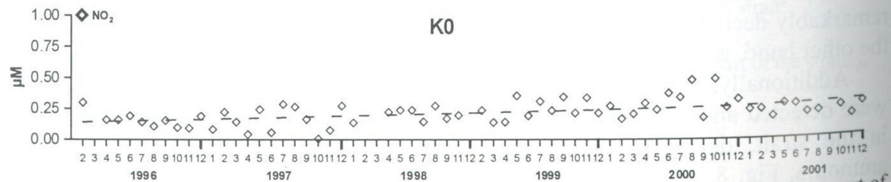

Fig. 8. Lower layer nitrite concentrations of the two stations located in northern and southern part of the strait in 1996-2001 period.

Discussion

Polat and Tuğrul (1995) stated that inorganic phosphate annual means were 0.18 µM in 1986-1992 period at northern exit of the Bosphorus. Our results had shown that inorganic phosphate concentrations did not changed much with time (Table 2). Mean o-PO_4 concentration was calculated as 0.16±0.14 µM in 1996-2001 period. However, higher values were detected in late autumn-winter periods due to unfavorable conditions for primary production. In addition to inorganic phosphate, particulate and total phosphate means were also very close to 1986-1992 period data. The amount of phosphorus originated from the Black Sea rivers is rather low since the polyphosphate concentrations were remarkably decreased in 80's (Weilguni and Humpesch, 1999).

On the other hand, oxidized nitrogen forms decreased mainly after 1999. Mean values of NOx were lower than 1986-1992 period (Table 2). TN however, increased significantly during six years, reaching maximum values mainly in low-salinity periods ($r=0.40$, $p=0.012$, $n=64$), (Fig. 4). Although an increasing pattern were observed in TN concentrations during 1996-2001 study, mean values are close to Polat and Tuğrul's findings. In addition, organic carbon data was very close to previous study.

Table 2. Comparison of the mean nutrient concentrations between two periods.

K0 Upper Layer	**1986-1992***	**1996-2001**
PO4	0.18±0.18	0.16±0.14
PP	0.15	0.15±0.07
TP	0.56	0.49±0.46
NO3+NO2	1.6±1.6	0.98±1.23
TN	21.8	16.19±5.95
POC	17.0	23.94±13.05
TOC	212.0	214.26±45.97
M8 Lower Layer	**1986-1992***	**1996-2001**
PO4	0.99±0.07	0.69±0.07
PP	0.05	0.05±0.03
TP	1.09	1.05±0.32
NO3+NO2	9.6±0.5	5.37±2.68
TN	13.20	15.69±4.84
POC	4.70	5.02±4.10
TOC	77.30	97.00±44.89

* Polat and Tuğrul, 1995

In southern strait, lower layer inorganic phosphate means significantly decreased. Connecting of several surface discharges to deep-disposals resulted in low amounts of sinking phosphates from the upper layer. All nitrogen and phosphate forms displayed great alteration with time, as many surface discharges were connected to deep-disposals. ANOVA results for these parameters were given in Table 3.

Table 3. Results of analysis of variance at northern part of the strait lower layer.

df=5	F	p
NO_2	5.58	<0.01
NO_3	4.88	0.001
TN	3.37	0.010
PO_4	4.99	0.001
TP	2.88	0.022
PP	4.37	0.002

The permanent stratification prohibits the deep-discharge rise to the upper layer. However, blocking of upper layer flow driven by meteorological conditions may result in vertical mixing in the strait. In February 1998, strong southerly winds caused blockage and lower layer salinity decreased to 22-23 psu. Vertical distribution of NO_x and PO_4 was rather homogenous compared to other sampling periods that no blockage was observed. Besides, this situation lasted for a couple of days and nutrient profile became normal in the next sampling.

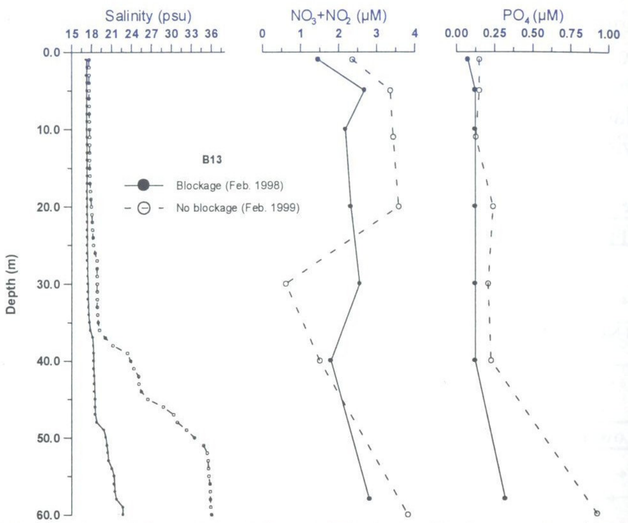

Fig. 9. Vertical distribution of the salinity, $N0_x$ and PO_4 during blockage and no blockage periods in the station B13.

Understanding ecosystem structure and discovering recent changes is meaningful unless continuous data is collected. In the Black Sea example, such data is available since 1960's (Cociasu *et al.*, 1996). Contrary to northern shelf, long-term data from southwestern Black Sea is relatively few and very limited studies exist about the Black Sea and Istanbul effect on the Strait and Marmara Sea ecosystem. Long-term monitoring studies in the area is expected to answer the questions about the area in the future. Humborg *et al.*, (1997) suggested that the man-induced changes in the Black Sea ecosystem such as construction of dam on Danube resulted in alterations of species composition. The remarkable decrease in nitrate concentrations at the euphotic zone of the Black Sea might be another signal for such responses to either man-deterioration or changes of inner pool dynamics of the ecosystem.

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