EUTROPHICATION IN THE SEA OF MARMARA

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1. Introduction

The entry of wastes into marine environment not only changes water quality parameters but also increases the risk of eutrophication, leading to dramatic changes in+ food chain, including planktonic, pelajik and demersal habitats, benthic organisms and, thereby, causes the area to become susceptible. The Urban Wastewater Treatment Directive (UWTD; EC 1991), therefore, defines the term of "eutrophication" as the "enrichment of water by nutrients, especially compounds of nitrogen and/or phosphorus, causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms present in the water and to the quality of the water concerned".

Eutrophication is the most extensively studied marine pollution problem observed especially in enclosed seas, bays fed by organic matter and nutrient-polluted rivers and direct wastewater discharges (Karydis 2009). Nutrient enrichment is followed by alterations in the phytoplankton community structure, growth of excessive algal biomass and possible toxic algal blooms; if the accumulated organic matter exceeds system's carrying capacity, the hypoxia can lead to a decline in fisheries and shellfisheries yields, poor water quality and ecosystems deterioration (Karydis 2009).

The Sea of Marmara an enclosed sea connecting the Black Sea the Mediterranean via the two shallow and narrow straits, has a severely deteriorated marine habitat, due to large nutrient inputs from the Black Sea and direct waste water discharges mainly from the city of Istanbul in recent decades (Tuğrul and Polat 1995). Massive localized eutrophication in the NW Black Sea expectedly collapsed Black Sea ecosystem and fisheries, and has led to appear similar changes in the Sea of Marmara since 1980's (Mee 1992; Polat and Tuğrul 1995).

Accoring to the first estimates of annual nutrient loads entering the Marmara Sea in 1990's (Polat and Tuğrul 1995), the Black Sea inputs dominate the Marmara Ecosystem; however, large increases in population of major cities of Marmara region drastically chemical inputs to the Marmara, reaching the levels of Black influxes (MEMPIS 2007).

Since the Marmara basin is occupied by the two-layer water masses, the permanent halocline formed between 15-30m markedly limits vertical mixing and thus, ventilation of salty deep waters of Mediterranean origins. Development of eutrophic conditions over the Marmara basin has increased POM export to the lower layer, resulting in the formation of suboxic conditions, subsurface oxygen minimum just below the halocline, and other processes of eutrophication have appeared in the Marmara ecosystem (Tuğrul and Polat 1995).

There have been a number of studies focused on the levels of nutrients and physicochemical variables of the water column in the Sea of Marmara (Tuğrul *et al.* 1995; Polat and Tuğrul 1995; Polat *et al.* 1998; Balkıs 2007; Tuğrul *et al.* 2015; Balcı *et al.* 2014). Very few published data are available on eutrophication in the Marmara Sea (Tuğrul and Morkoç 1990; Morkoç *et al.* 1997; Balkıs *et al.* 2012; Tuğrul *et al.* 2015).

A national monitoring programme has only been performed since 2009 in the Marmara Sea with the support of Ministry of Environment. Institute of Marine Sciences and Management of İstanbul University, Institute of Marine Sciences of METU and Marmara Research Center of TÜBİTAK have been carried out oceanographic and monitoring cruises in the Marmara Sea since 1986 to collect data for different projects supported by TUBITAK, EU, ministries and the municipalities. The data collected during these cruises have been the basis to understand the oceanography and as well as the eutophication status of the Marmara Sea.

2. General Aspects of the Sea of Marmara

The Sea of Marmara an intercontinental basin with shallow and narrow straits connects the Black and Mediterranean Seas and together with its two straits İstanbul (Bosphorus) and Çanakkale (Dardanelles) constitutes an oceanographic system called the “Turkish Strait System” (TSS) which provides the exchanges of salty and less saline waters between the Aegean and the Black Seas. The Marmara basin itself is a transitory site between these two adjacent basins and the straits determine the two-layer flow regime in the TSS due to great density differences between the Black Sea and the Mediterranean.

There is a permanent two-layer flow in the straits and the Marmara Sea with the halocline formed between the depths of 15-30 m, displaying seasonal and regional variations (Ünlüata *et al.* 1990; Besiktepe *et al.* 1994). The chemical oceanography of the Marmara upper layer is dominated by the Bosphorus inflow carrying the brakish surface waters of Black Sea with the associated biochemical properties (Polat and Tuğrul 1995).

Concentrations of nutrient species in the surface layer of the Marmara Sea are determined primarily by the chemical properties of the inflowing Black Sea waters and by the chemically modified salty waters of Mediterranean origin entrained into the upper layer during the winter mixing and from the counter flow regime in the Bosphorus region (Polat and Tuğrul 1995).

The Sea of Marmara region is densely populated and industrialized with more than Turkey's 20% population and 50% industry located in its drainage basin. The municipal and industrial inputs from its drainage basin, together with nutrients, organic inputs from the Black Sea, have polluted the Marmara Sea since the 1970's (Orhon *et al.* 1994; Polat and Tuğrul, 1995).

Before the 1980's, anthropogenic inputs had secondary importance for the open waters (Tuğrul and Polat 1995) but have a critical influence on primary production in coastal regions and semi-enclosed bays where water exchange with the open sea is relatively weak (Tuğrul and Morkoç 1990). The influences of anthropogenic input have increased markedly in the last two decades (Orhon *et al.* 1994), reaching the levels comparable with the Black Sea influxes (MEMPIS 2007).

The metropolitan area of İstanbul with a population of about 13.5 million is the most important pollution source for the Marmara Sea, with other important sources located in the İzmit, Gemlik and Bandırma Bays and Tekirdağ area, and from small rivers such as the Susurluk carrying important agricultural loads. Large fractions of partly treated wastewaters are discharged into the lower layer of Marmara (Tuğrul *et al.* 2015).

Changes in environmental and hydrographic conditions determines the intensity of phytoplankton production in the Marmara Sea. Nutrient inflow from land based sources and entrainment contribute to the increase of nutrient concentrations in surface layer and thus winter blooms occur in the Marmara Sea. During summer, the phytoplankton production fluctuates more or less randomly, depending on supply of nutrients from internal and external sources and grazing pressure.

Algal production is confined to the first 20m (the euphotic zone thickness) in the upper layer of the Marmara Sea throughout the year. Maximum chlorophyll-a values were generally observed in surface layer. However, a sub-surface chlorophyll-a maximum is formed at the upper halocline boundary, varying locally between 10-20m and coinciding perfectly with the nutricline over the basin. The annual algal production in the Sea of Marmara estimated from chlorophyll-a data is nearly 100 $gC/m^2/y$ (Ergin *et al.* 1993). In October 1991 and March 1992, the primary production was estimated by the ^{14}C technique as 45 and 95 gC/m^2/y at the central Marmara Sea. The annual primary production measured at a location close to the İzmit Bay by ^{14}C technique was about 170 gC/m^2/y (Tuğrul *et al.* 1989).

Dissolved oxygen (DO) concentrations are at saturated levels in the thin upper layer waters of Black Sea origin and then decrease steeply in the permanent pycnocline which coincides with the nutricline because algal production is confined to the upper layer for most of the year (Figures 1 and 2). DO concentrations, as high as 10-12 mg/L during cold season in surface layer, diminish drastically to suboxic levels of 1-2 mg/L in the lower layer waters over deep basins (Figure 1). The steep halocline separating the upper and lower layer highly limits ventilation of the deep waters. The major source of DO for the deep basin is the inflow of oxygen rich Mediterranean waters via the Dardanelles undercurrents. Therefore, DO deficiency in the Marmara lower layer waters increases from the Dardanelles-Marmara exit to the eastern basin. In the last decades, DO has decreased further in the deep Çınarcık basin due to insufficient ventilation of deep waters and increased organic matter inputs from the surface layer (Figure 1). The lowest DO values have been recorded in the enclosed bay of İzmit polluted by land-based inputs (Ediger *et al.* 2016). The renewal time of the brakish upper layer is about 4-5 months surface waters whilst the average residence time of the deep basin waters is estimated to be 6-7 years (Ünlüata *et al.* 1990; Beşiktepe *et al.* 1994).

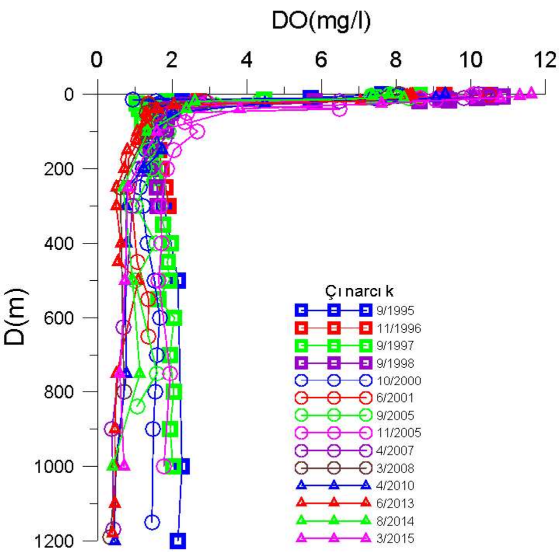

Figure 1. Vertical distribution of DO in Çınarcık Basin.

The Marmara upper layer is constantly supplied with nutrient inputs from the Black Sea, the bottom layer waters by mixing especially at the Bosphorus-Marmara Junction, direct wastewater discharges and fresh waters inflows from the its drainage basin. However, most of these nutrients are used in photosynthesis. Therefore, the upper layer concentrations of nitrate and phosphate are generally low during the year (Figure 2). Seasonally, the upper layer concentrations increase in winter due to enhanced inputs and lower uptake rate in photosynthesis. The lowest values of inorganic nutrient are reached during the summer-autumn period. Therefore, nutrients export from the Marmara to Aegean Sea occurs in the form of organic compounds.

The nutricline is located at depths of 15-25m, coinciding with the permanent halocline (Figure 2). Thus the concentrations of nitrate and phosphate increase steeply with depth in the interface, displaying a broad subsurface maximum below the halocline. In this zone, expectedly, the DO profiles exhibit a subsurface minimum.

The Mediterranean salty waters entering the Marmara deep basin originally have very low nutrients but almost saturated levels of DO concentrations (Polat and Tuğrul 1995). These salty waters are highly enriched (about 10-fold) in nutrients while losing the dissolved oxygen during their residency for almost seven years in the Marmara deep basin (Ünlüata *et al.* 1990; Beşiktepe *et al.* 1994; Tuğrul *et al.* 2002).

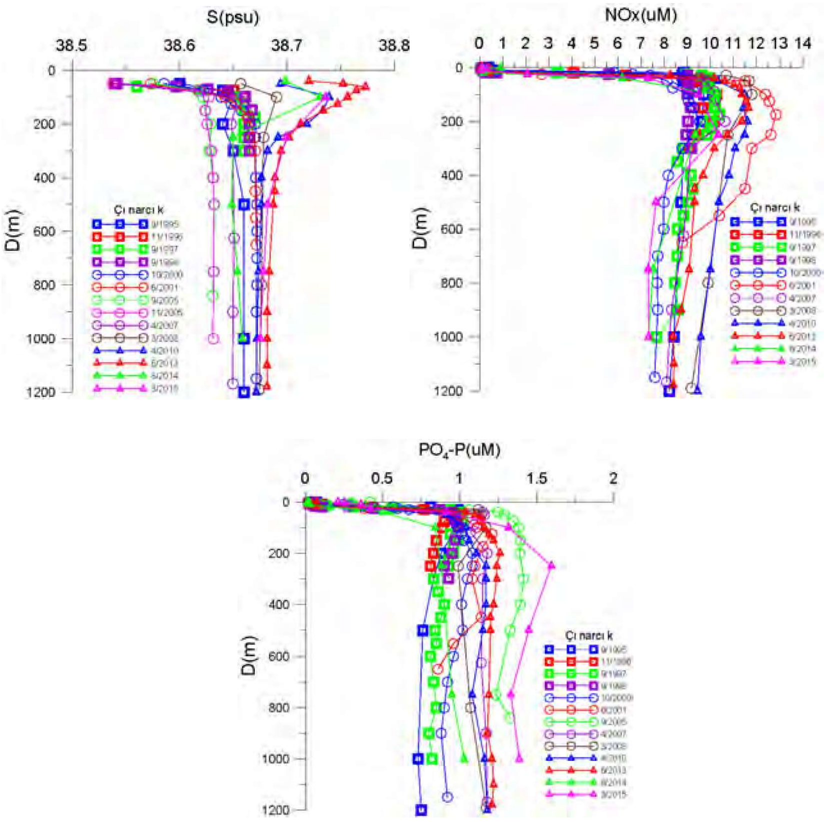

Figure 2. Vertical distribution of salinity and nutrients in Çınarcık Basin.

The Black Sea inflow via the Bosphorus surface flow increases during spring-early summer period when the river inflows to the Black Sea reaches the maximum levels and decreases markedly in late summer-autumn period (Özsoy *et al.* 1998). Therefore, chemical transport via the Bopshorus surface flow display similar a seasonal trend (Polat and Tuğrul 1995; Altıok *et al.* 2014).

The concentrations of inorganic nitrate and phosphate and their seasonal/annual fluxes through the Bosphorus and Dardanelles Straits were calculated by Polat and Tuğrul 1995 (Table 1). The winter and spring fluxes by the Bosphorus surface flow are much greater than summer and autumn fluxes, accounting for about 80% of the annual nutrient fluxes. Nutrients export from the Marmara to the Black Sea via the Bosphorus undercurrent are less variable, but have maximum values in spring and summer when the volume flux increases. It can also be noted that the lower layer nutrient fluxes are 3-6 times greater than the mass fluxes via the upper layer flow (Table 1). The nutrients influx to Black Sea from the Marmara lower layer occur mainly in dissolved inorganic form whilst the majority of nutrient from Black Sea are transported in dissolved organic form (Polat 1995, Polat and Tuğrul 1995).

In the Bosphorus Strait, the upper layer nitrate and phosphate concentrations (N/P ratio: 14-26) and fluxes are much higher in winter. The lowest mass flux occur in autumn. Though the lower layer fluxes display seasonality, the N/P ratio of the Bosphorus deep waters is almost constant (9-10.5) throughout the year (Tuğrul *et al.* 2015).

The salty Mediterranean water enters the Marmara deep basin via the Dardanelles undercurrent, with very low nitrate and phosphate but nearly saturated levels of oxygen concentrations (Table 1). These salty waters are enriched by about 10-fold (nitrate: 8-12 µM; phosphate: 0.7-1.2 µM) during about 6-7 year stay in the basin. The nutrient out fluxes from the Marmara via the Dardanelles surface layer flow also display seasonal variations, increasing in winter is observed in the Bosphorus surface fluxes (Table 1).

The Secchi Disk Depth (SDD) measured between 1986-1994 in the Marmara Sea regionally and seasonally ranged from 8 to 14m (Ediger and Yılmaz, 1996) and then the period 2009 to 2014 ranged from 4-10m. The lowest SDD values were expectedly measured in the highly polluted and eutrophic coastal waters and semi-enclosed bays, especially in the İzmit Bay. It appears that the photosynthesis has been limited to thin upper layer over the basin, reaching the upper halocline and thus nutricline depths when the surface waters being depleted nutrients during summer-autumn period (Sur *et al.* 2009, 2010; Tutak *et al.* 2012; Ediger *et al.* 2013; Polat-Beken *et al.* 2015).

The Chl-a parameter is used as indicator of eutrophy or water quality in many studies (Harding 1994 in Harding and Perry 1997; Boyer *et al.* 2009) and its concentration represents a simple, integrative measure of phytoplankton community responding to nutrient enrichment in aquatic environments (Devlin *et al.* 2007). Throughout the oceanographic studies in the Sea of Marmara (1986-2014) concentration of Chlorophyll-a values were recorded to vary between 0,2-18 µg/L (Göçmen 1988; Baştürk *et al.* 1990; Polat *et al.* 1998; Sur *et al.* 2009, 2010; Balkıs *et al.* 2012; Polat-Beken *et al.* 2015), displaying apparent spatial increasing trend from the Dardanelles to the enclosed bay of İzmit polluted by land-based inputs.

Table 1. Seasonal and annual fluxes of nitrate and phosphate exchanged between the adjacent seas through the Bosphorus and Dardanelles Straits for the period of 1990-2000 (after Tuğrul *et al.* 2015). Upp: upper Low: lower

		BOSPHORUS					DARDANELLES				
Flow type	Season	Vol. flux (*10^9 m^3)	NO3 conc. (mmol /m^3)	NO3 flux (*10^8mol)	PO4 conc. (mmol /m^3)	PO4 flux (*10^7 mol)	Vol. flux (*10^9 m^3)	NO3 conc. (mmol /m^3)	NO3 flux (*10^8 mol)	PO4 conc. (mmol /m^3)	PO4 flux (*10^7 mol)
Upp	Spring	200	1,32	2,64	0,05	1	307	0,2	0,61	0,06	1,84
Upp	Summer	158	0,42	0,66	0,03	0,47	194	0,12	0,23	0,03	0,58
Upp	Autumn	105	0,22	0,23	0,05	0,52	142	0,3	0,42	0,05	0,71
Upp	Winter	145	3,2	4,64	0,14	2,03	234	0,36	0,84	0,09	2,1
Upp	**Annual**	**608**	**1,29**	**8,17**	**0,07**	**4,02**	**877**	**0,24**	**2,1**	**0,06**	**5,23**
Low	Spring	94	9,17	8,62	0,92	8,65	202	1,14	2,3	0,05	1,01
Low	Summer	76	10,46	7,95	0,99	7,52	112	0,47	0,53	0,03	0,34
Low	Autumn	49	9,34	4,58	0,91	4,46	87	0,88	0,76	0,05	0,44
Low	Winter	68	9,81	6,67	1,07	7,28	158	1,62	2,56	0,05	0,79
Low	**Annual**	**287**	**9,7**	**27,8**	**0,97**	**27,91**	**559**	**1,09**	**6,15**	**0,05**	**2,58**

3. Eutrophication Status of the Sea of Marmara

Different tools/measures have been developed to classify eutrophication status of water masses impacted by human pressures, based on principal direct and indirect indicators of eutrophication classification (Vollenweider *et al.* 1998, HELCOM, 2009, MEDGIG, 2011, Andersen *et al.* 2010). TRIX index, developed by Vollenweider et al. (1998) for the western Mediterranean waters, have been widely used the other seas (EEA, 2001, UNEP, 2003, Moncheva *et al.* 2002, Alves *et al.* 2013). TRIX method is based on chlorophyll-a, oxygen saturation, total dissolved inorganic nitrogen and total phosphorus to characterize the trophic state of coastal marine waters. The index values vary from 0 to 10, ranging from oligotrophic to eutrophic conditions. TRIX values exceeding 6 indicate strong eutrophication due to human impact and <4 indicate low anthropogenic impact (Cloern, 2001). Giovanardi and Vollenweider (2004) indicates that only values higher than 6 units indicate strong eutrophication. The TRIX eutrophication index is an important tool that has been used in the management of coastal regions, in the analysis of the trophic state in the environment and water quality.

TRIX index estimates for the Marmara Sea ranged between from 2.09 in the open sea to 7 in the eutrophic coastal waters and bays (Tutak *et al.* 2012; Ediger *et al.* 2013; Polat-Beken *et al.* 2014, 2015) (Table 2 and Figure 3). Spatial distribution of TRIX values increases from Dardanelles to the enclosed bays and close to river and land based inputs (Figure 3). Detailed examination of the TRIX index values for the Marmara Sea indicate that generally a moderate to bad trophic conditions due to anthropogenic+ natural inputs appear in during wet winter period, and then these impact decreased in late summer, resulting in good trophic status in the open sea whereas bad trophic status lasts in the enclosed bays due to human impact (Table 2 and Figure 3).

Table 2. TRIX index values in the Sea of Marmara

Site	Time	TRIX	Ref
Marmara Sea	Summer 2011	2.8-6.54	Tutak *et al.* 2012
Marmara Sea	Autumn 2011	4.0-6.0	Tutak *et al.* 2012
Marmara Sea	Summer 2013	2.09-5.43	Ekozone 2013
Marmara Sea	Autumn 2013	2.82-5.3	Ekozone 2013
Marmara Sea	Summer 2014	3.85-6.21	Polat-Beken *et al,* 2014
Marmara Sea	Winter 2015	5.19-7.45	Polat-Beken *et al.* 2015
İzmit Bay	2008-2013	3.0-6.8	Ediger *et al.* 2013

Within the scope of the DEKOS (Marine and Coastal Waters Quality Status Determination and Classification) project, boundary values of the eutrophication indicator parameters were estimated in the surface layer of the Marmara Sea and given in Table 3 (Polat-Beken *et al.* 2014, 2015).

According to the Method of MEDGIG 2011, boundary values determined for the Marmara Sea indicate the transition of good/moderate quality status for each eutrophication indicator.

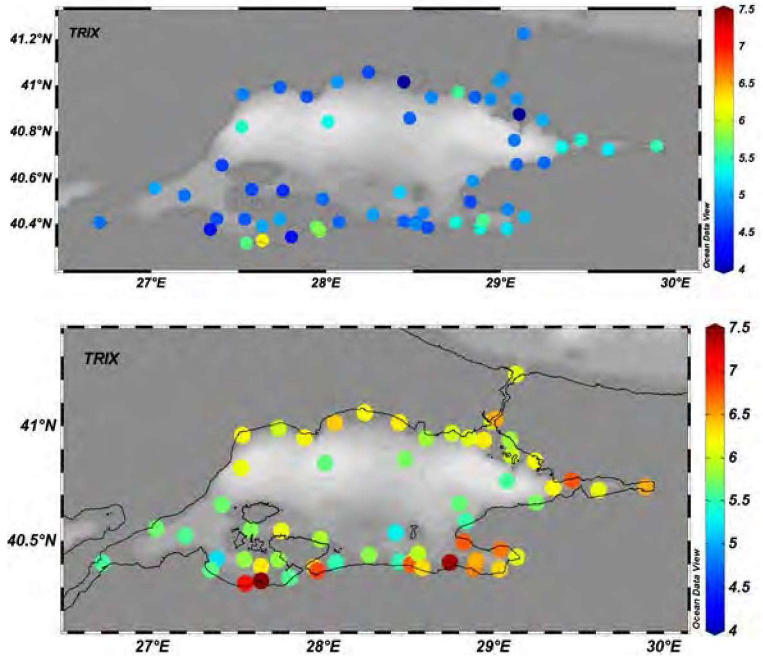

Figure 3. Spatial distribution of TRIX index in the Sea of Marmara a) Summer 2014 b) Winter 2015 (Polat-Beken *et al.* 2015, 2016)

Table 3. Recommendations of Boundary Values for the Surface Waters of the Central and Eastern Marmara Sea Regions (Polat-Beken *et al.* 2014)

PARAMETER	**PROPOSED BOUNDARY VALUES**
Phosphate (PO_4)	*<0.15 µM*
Total Phosphorus (TP)	
Nitrate (NO_3)	*< 0.5 µM*
Nitrite (NO_2)	*< 0,2 µM*
Ammonium (NH_4)	*< 0.4 µM*
Silicate (Si)	*> 1.0 µM*
Si/(NO_3)	*>3*
(NO_3)/PO_4	*> 2*
Chlorophyll-a	*< 1.5 µg/*
Secchi Disc Depth	*> 4.0 meters*
Oxygen Saturation %	*% > 20 (waters close to the seafloor; depth >30 m)*

4. Conclusion

The two-layer ecosystem of Marmara Sea has been drastically modified by the increasing chemical input from Black Sea, domestic and industrial discharges from the Marmara region. Until the 1990's the Black Sea input was the major source of organic+inorganic nutrients reaching the Marmara upper layer (Polat and Tuğrul 1995, 1998). Secondary input was partly treated waste waters of the Istanbul Metropolitan city (Polat and Tuğrul 1995; Okuş *et al.* 2008). The Black Sea inputs supply the majority of the nutrients and organic matter loads reaching the Marmara. However, the contribution of land-based has increased during the last two decades with highly increased coastal or basin population, new infrastructures and constructions (new bridges, airports, industrial areas etc.) and besides yet not completed advanced treatment systems for municipal and industrial wastes.

Istanbul is one of the most populated metropolises in the region with a population of over 13.5 million people (TUIK 2014). Today, more than 75% of domestic and industrial primary or secondary treated effluents are disposed directly into the Bosphorus lower layer and the strait-Marmara Sea junction via sewage outfalls with a daily capacity of 1,671,060 m^3 day^{-1} (Okuş *et al.* 2008).

In conclusion, development of eutrophication conditions in the Marmara Sea has not only altered the upper layer ecosystem but also the chemical properties of the sub halocline waters of Mediterranean origin. The Dardanelles under-current introduces the Aegean salty waters with almost saturated levels of dissolved oxygen but low values of nitrate and phosphate concentrations into the Marmara basin (Polat and Tuğrul 1995; 1998; Tuğrul *et al.* 2015). The enhanced eutrophication reduced the lighted zone in the upper layer and algal production has been limited to the upper layer and more POM exported into the halocline and sub halocline waters. Thus, the depths of nutricline and oxycline have shifted upward in the last 3 decades. These changes also highly influenced pelagic and demersal ecosystem over the basin. Enhanced nutrient inputs with the appropriate meteorological conditions has led to occur red-tides, mucilage formation and increased jelly organism blooms in the recent years. Anoxic conditions were also seen in the lower layer of polluted bay of İzmit (Balkıs 2012).

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