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Size-fractionated phytoplankton and nutrient dynamics in the inner part of İzmir Bay, eastern Aegean Sea

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Abstract: İzmir Bay has been one of most polluted bays of the Mediterranean for a long time. When the "Big Channel Project" was completed in 2000, sewage flow into the bay ended. Hence, the influence of creeks, which are the only source of water transportation to the inner bay, was investigated in the current study. Monthly samples of creek water and seawater were taken. Basic water quality variables and nutrients were measured. In addition, the phytoplankton community was arrayed into size fractions to assess the contribution of each size fraction to biomass and pigment concentrations. Analyses showed that the creek waters had very high nutrient concentrations. Although decreasing nutrient concentrations of the sea as compared to past years were detected, results of the analyses showed that the phytoplankton biomass was increased. Minimum and maximum values of nutrient concentrations and chlorophyll-*a* were 0.23–22.28 μ M for ammonium, 1.54–11.77 μ M for nitrate, 0.00–3.51 μ M for nitrite, 1.99–41.94 μ M for silicate, 0.00–5.96 μ M for phosphate, and 5.03–30.26 μ /L for chlorophyll-*a*. Nanoplankton was the dominant phytoplankton group in the inner bay. An increment in picoplankton was detected towards the outer part of the bay. The microplankton biomass was correlated with NH⁺₄-N, [Si(OH)₄-Si], and o.PO₄-P. [Si(OH)₄-Si], o.PO₄-P, and microplankton were the most important constituents in the inner bay. Consequently, controlling nutrient concentrations in the creeks might contribute to the cleaning process in İzmir Bay.

Key words: Aegean Sea, İzmir Bay, eutrophication, nutrient, phytoplankton size fractions

1. Introduction

One of the most important living organisms in the aquatic ecosystem is phytoplankton. Phytoplankton, the primary producer, plays an important role in the material circulation and energy flow in the aquatic ecosystem (Azari et al., 2011). The study of aquatic organisms is thus very useful to detect and assess human impacts (Solak et al., 2012). Most environmental studies focus on the bulk measurements of chlorophyll, suspended matter, and nutrients as a means of assessing the trophic state of an aquatic ecosystem. These measurements are important, but during the last decade it has been established that cell size distribution of primary producers plays a significant role within the community structure and in the trophic organisation of the pelagic ecosystem. Size is becoming an important ecological global variable of the structure and functioning of food webs by having a strong influence on the efficiency of transfer and the fate of carbon at higher trophic levels (Iriarte et al., 2000). Size structure of the phytoplankton community depends on the physicochemical characteristics of the environment. For this

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reason, water quality analysis of coastal ecosystems plays an important role in the environmental impact assessment of the marine environment.

İzmir Bay is one of the most naturally productive coastal areas in the Aegean Sea (Figure 1). The population numbers about 3,800,000 in İzmir. The main urban conurbation around the bay is the İzmir Metropolitan Municipality, covering 88,000 ha. İzmir is an important industrial and commercial centre and a cultural focal point. The bay has a total surface area of over 500 km², water capacity of 11.5 billion m³, and a total length of 64 km, and it opens in the Aegean Sea. The main industries in the region include food processing; beverage manufacturing and bottling; tanneries; oil, soap, and paint production; chemical industries; paper and pulp factories; textile industries; metal processing; and timber processing (Kontas et al., 2004). The bay is divided into an inner, middle, and outer bay with respect to the topographical and hydrographical characteristics. The inner part of the bay had received the majority of domestic and industrial wastewaters before the construction of wastewater treatment plants. Because

of the limited water exchange with the outer part of İzmir Bay and the Aegean Sea, the pollution of the inner bay had reached unacceptable levels. For this reason, construction of a wastewater treatment plant was completed in 2002. Although the sewerage system of the city is connected with the wastewater treatment plant, small creeks are still sources of nutrients, because there are several untreated discharge points along the creeks and domestic and industrial wastes are discharged into these creeks. The aims of the present study were to investigate the nutrient dynamics in both the inner bay and small creeks, and to determine the size-fractionated phytoplankton structure of İzmir Bay after the construction of the wastewater treatment plant.

2. Materials and methods

For the collection of marine water samples from the inner bay, 4 stations several hundred metres from the mouth of the creeks, and, for freshwater sampling, 7 creeks (old mouth of Gediz River, Bostanlı, Bayraklı, Bornova, Manda, Meles, and Balçova) were chosen (Figure 1). Seawater samples were collected from the surface and from the bottom of the water column at station 1 (ST 1) (7 m), ST 2 (7 m), and ST 3 (7 m) by Nansen bottle. In addition to these depth levels, samples were also gathered from the middle of the water column at ST 4 (15 m). Bottom water samples were collected from half a metre above the sediment.

The physico-chemical parameters and nutrients were measured monthly for 12 months (August 2007 to July 2008) for freshwater samples and for 10 months (September 2007 to August 2008) for seawater samples. The salinity and oxygen were calculated by the Harvey (Martin, 1972) and the Winkler methods, respectively. Furthermore, the temperature and pH values were measured using a Hanna HI 8314. A Hach DR/4000 spectrophotometer was used for nutrient analyses performed for ammonium, phosphate, silicate (Strickland & Parsons, 1972), nitrite, and nitrate (Wood, 1975). For the size-fractionated phytoplankton chlorophyll-*a* determination, 250–500 mL samples were fractionated with respect to phytoplankton densities into microplankton (>20 µm), nanoplankton (3–20 μ m), and picoplankton (<3 μ m) using 20 μ m mesh, and 3 and 0.2 µm Sartorius cellulose filters in the laboratory. Initially, the seawater samples were filtered using 20 µm mesh. Accumulated phytoplankton on the mesh was transferred to a Whatman GF/C filter with the help of a washing bottle. Then the seawater beneath the 20 µm mesh was filtered with a 3 µm filter. Finally, the samples beneath the 3 μ m filter were filtered with a 0.2 μ m filter. Thus, eventually, >20 μ m, 3–20 μ m, and <3 μ m size fractions were obtained. The pigments were extracted over 24 h in polyethylene tubes with 10 mL of 90% acetone at low temperature (4 °C) and in darkness (Thomas et al., 2005). Chlorophyll-a absorption was determined using a Hach DR/4000 spectrophotometer according to Strickland and Parsons (1972). A Kruskal-Wallis test was applied for comparing the nutrient concentrations, total chlorophyll-a, and phytoplankton size structure among the sampling stations. The test statistic was calculated from



Figure 1. Locations of sampling stations.

$$KW = \frac{12}{N \times (N+1)} \times \left(\sum_{i=1}^{k} \frac{R_i^2}{n_i}\right) - 3(N+1)$$

R: Sum of ranks

- N: The total number of samples
- N_i: The number of samples in each group
- k: The number of groups

Principal component analysis (PCA) was also utilised in order to explain which parameter(s) is/are the main source(s) of the variations among the defined parts of the bay.

3. Results

3.1. Seawater analyses

3.1.1. Physico-chemical and biological parameters

The ranges and average values of physico-chemical/ biological parameters and annual trends of these parameters are given in Table 1 and Figure 2, respectively. The temperature of the seawater varied between 11 °C (at ST 4 in January) and 27.6 °C (at ST 3 in June). Salinity ranged between 31.12‰ and 39.66‰. While the minimum salinity value was determined in July, at ST 3, the maximum value was measured in August, at ST 2. The salinity decreases in July were recorded at ST 1, ST 2, and ST 3, due to the freshwater input from creeks. Lower salinity values in Meles, Bayraklı, Bostanlı, and the old mouth of Gediz creeks sustained the same condition. Dissolved oxygen (DO) reached its minimum concentration (0.6 mg/L) in October, at ST 4's bottom layer, and its maximum (12.80 mg/L) in January, in ST 3's surface water. A similar trend in pH values was observed as well at all stations during the year and it ranged between 7.34 and 8.12. The Secchi depth varied between 0.6 m (at ST 1) and 8.0 m (at ST 4). Since ST 1, ST 2, and ST 3 are located in the shallow part of the bay, bottom material might be transported from the bottom to the water column by waves. These stations, especially ST 1 and ST 2, are located near the mouths of creeks transporting terrestrial solid material. As a consequence, the Secchi depth remained at lower values.

The ranges and mean concentrations of nutrient and chlorophyll-*a* are given in Table 1 for each station. The ranges of concentrations were 0.23–22.28, 1.54–11.77, below detection limit (BDL)–3.51, 1.99–41.94, and BDL–5.96 μ M for NH⁺₄-N, NO⁻₃-N, NO⁻₂-N, [Si(OH)₄-Si], and o.PO₄-P, respectively, and 5.03–30.26 μ g/L for chlorophyll-*a*. The average percentages of NO⁻₃-N, NH⁺₄-N, and NO⁻₂-N in total inorganic nitrogen were 53%, 39%, and 8% in the surface water and 50%, 42%, and 8% in the bottom water, respectively. Since high rainfalls were recorded in November, the highest NH⁺₄-N values were also measured during this month at all stations with

Table 1. The range and mean \pm standard error values of physicochemical parameters, nutrients (μ M), and size-fractionated phytoplankton biomass (μ g/L) 'Detection limit: 0.1 μ M for NO₃-N, 0.1 μ M for NO₂-N, 0.2 μ M for NH₄-N, 0.05 μ M for 0.PO₄-P, 0.26 μ M for Si, and 0.2 μ g/L for Chl-*a*.

	Station 1		Station 2		Stati	ion 3	Station 4	
	Range	Mean ± SE	Range	Mean ± SE	Range	Mean ± SE	Range	Mean ± SE
Temperature (°C)	14.00-27.20	21.10 ± 1.18	14.00-27.20	21.25 ± 1.13	11.40-27.60	20.83 ± 1.32	11.00-27.40	20.34 ± 1.03
Salinity (‰)	33.26-36.94	35.24 ± 0.24	31.5-39.66	35.33 ± 0.41	31.12-37.53	35.01 ± 0.46	31.32-38.88	35.68 ± 0.30
pН	7.34-8.10	7.86 ± 0.04	7.46-8.11	7.87 ± 0.04	7.38-8.12	7.84 ± 0.05	7.49-8.05	7.87 ± 0.03
DO (mg/L)	1.20-11.60	6.94 ± 0.68	1.20-12.40	6.87 ± 0.67	1.60-12.80	6.72 ± 0.78	0.60-12.60	6.61 ± 0.59
NH ₄ -N	0.27-15.14	3.97 ± 1.01	0.26-12.17	3.06 ± 0.81	0.29-11-51	3.17 ± 0.70	0.23-22.28	3.04 ± 0.77
NO ₃ -N	1.90-11.77	5.21 ± 0.63	1.54-8.49	4.12 ± 0.54	1.69-7.56	3.85 ± 0.45	1.61-8.73	4.02 ± 0.38
NO ₂ -N	0.00-3.51	0.80 ± 0.23	0.0-3.23	0.70 ± 0.22	0.00-2.25	0.62 ± 0.16	0.03-2.34	0.51 ± 0.12
o.PO ₄ -P	0.20-3.79	2.16 ± 0.29	0.17-3.98	2.19 ± 0.31	0.26-5.96	2.73 ± 0.45	0.00-4.10	1.79 ± 0.25
Si(OH) ₄ -Si	1.99-20.00	9.59 ± 1.12	2.61-25.48	9.41 ± 1.41	2.74-41.94	12.44 ± 2.49	2.42-33.51	11.45 ± 1.56
Chl-a	6.11-23.28	14.91 ± 1.11	4.93-16.80	12.10 ± 0.77	6.47-30.26	13.48 ± 1.57	5.03-19.79	10.34 ± 0.67
Microplankton Chl-a	0.22-11.56	3.23 ± 0.70	0.05-10.56	2.89 ± 0.67	0.34-13.58	3.22 ± 0.85	0.28-6.58	2.52 ± 0.35
Nanoplankton Chl-a	2.78-18.78	8.73 ± 1.03	3.64-13.63	7.03 ± 0.59	1.95-17.30	6.51 ± 0.81	0.67-7.83	4.39 ± 0.36
Picoplankton Chl-a	0.07-14.24	2.94 ± 0.74	0.33-5.88	2.18 ± 0.35	0.61-23.01	3.75 ± 1.09	0.42-12.82	3.43 ± 0.56



Figure 2. Spatio-temporal variations in nutrient and chlorophyll-a concentrations in İzmir Bay.

nutrient inputs from creeks. [Si(OH)₄-Si] concentrations were less than 15 µM during a large part of the sampling period. It had 2 important peaks that originated from remineralisation of silica from dead phytoplankton cells in June and August. During the phytoplankton bloom period (January-August), NH⁺₄-N, [Si(OH)₄-Si], and o.PO₄-P concentrations were lower than the values in autumn. While an inverse trend between NH⁺₄-N and chlorophyll-a showed consumption of ammonium by phytoplankton, a similar relationship was not observed between NO-3-N and chlorophyll-a. A similarity in the spatio-temporal distributions of NH⁺₄-N and NO⁻₂-N was observed at all stations. The annual variations in nutrient and chlorophyll-a concentrations are illustrated in Figure 2. The atomic ratio of dissolved inorganic nitrogen (DIN) to dissolved inorganic phosphate (DIP) ranged between 0.90 and 159.7. The observed mean N:P was lower than the assimilatory optimal (N:P = 15:1) in conformity with Redfield's ratio N:P = 16:1. A Kruskal-Wallis test was used to compare the nutrient and chlorophyll-a concentrations among the sampling stations. While the NO⁻₂-N, NO⁻₃-N, NH⁺₄-N, o.PO₄-P, and [Si(OH)₄-Si] concentrations did not vary among the stations (test statistics: 1.83, 4.20, 0.81, 4.35, and 0.95, respectively, P > 0.05), chlorophyll-*a* concentration diverged significantly. There were significant differences between ST1 and ST2, and ST1 and ST4 in terms of chlorophyll-*a* (test statistic: 11.28, P < 0.05).

NH⁺₄-N was correlated with NO⁻₂-N (r = 0.53, P < 0.05, n = 90), [Si(OH)₄-Si] (r = 0.48, P < 0.05, n = 90), and o.PO₄-P (r = 0.60, P < 0.05, n = 90). [Si(OH)₄-Si] was highly correlated with o.PO₄-P (r = 0.74, P < 0.05, n = 90). These results indicate that the origins of these nutrients are probably the same.

3.2. Size-fractionated phytoplankton structure

phytoplankton biomass The was 0.05 - 13.54, 0.67-18.78, and 0.07-23.01 µg/L for microplankton, nanoplankton, and picoplankton, respectively (Table 1). Two important peaks were recorded for the microplankton biomass in February and May. The nanoplankton biomass fluctuated over the sampling period. It reached its peak in January at all stations. After that, a decrease was observed in February but in March biomass started to increase. The picoplankton biomass showed a stable trend over a large part of the sampling period and only 2 remarkable increases were observed, in November and August (Figure 3). Although ST 1, ST 2, and ST 3 are in shallow areas, small differences were observed in the distribution of phytoplankton vertically. Generally the picoplankton biomass increased from the surface to the bottom layers. This situation emerged more clearly at ST 4, where the picoplankton biomass increased while the nanoplankton decreased and the microplankton did not change from surface to bottom. The nanoplankton dominated in the phytoplankton chlorophyll-*a* biomass in all stations and at all depths. The mean percentage contribution of the nanoplankton to total phytoplankton biomass was 55% at the surface and 51% at the bottom layer. While this was followed by the microplankton (23%) and picoplankton (22%) in the surface layer, the picoplankton (26%) and the microplankton (23%) followed at the bottom layer. The Kruskal–Wallis test showed that the nanoplankton biomass at ST 4 differed significantly from that at ST 1 and ST 2 (test statistic: 18.0, P < 0.05).

The microplankton biomass was correlated with NH⁺₄-N (r = -0.59, P < 0.05, n = 90), [Si(OH)₄-Si] (r = -0.48, P < 0.05, n = 90), and o.PO₄-P (r = -0.61, P < 0.05, n = 90). The strong correlations between the microplankton and the nutrients show that these nutrients were consumed by the microplankton. Every size fraction was correlated with the total chlorophyll-*a* (microplankton r = 0.42; nanoplankton r = 0.61; picoplankton r = 0.47, P < 0.05, n = 90).

3.3. Creek water analyses

3.3.1. Physico-chemical parameters

The minimum, maximum, and average values are given in Table 2. Each creek had different salinity and pH trends. This situation resulted from characteristics of the fresh water flowing into the creeks and its mixture with seawater at the mouth of the creek. Since the old mouth of Gediz River is a delta where a transposition process occurs between the river and the sea through the river floor, the salinity values reached 42.57‰. While DO concentration was below the detection limit in spring at some creeks, it reached 20 mg/L at the old mouth of Gediz River because of the exceptional phytoplankton bloom and the waves in the surface water.

The minimum, maximum, average, and median values are given in Table 3. NH_4^+ -N concentrations of the creeks were rather high compared to those of the sea. The highest NH_4^+ -N value was recorded at Meles Creek, followed by Bayraklı and Manda Creeks. Maximum NO- $_3^-$ N concentration was found at Balçova Creek due to the agricultural activities nearby. NO_2^- -N concentrations showed important increases over the sampling period. The highest concentrations were seen at Manda and Meles Creeks. [Si(OH)₄-Si] concentrations reached their exceptional values due to silicate originating from terrestrial sources.

While some $[Si(OH)_4$ -Si] increases were correlated with rainfall, some of them were uncorrelated. Averages and standard errors of $[Si(OH)_4$ -Si] were rather high because of $[Si(OH)_4$ -Si] inputs reaching high concentrations. Hence, the median might be more explanatory as a statistical parameter. Although $o.PO_4$ -P concentrations were determined below 10 μ M at Balçova and Bostanlı Creeks, they showed important increases at the others. Different



Figure 3. Spatio-temporal variations in phytoplankton biomass in İzmir Bay.

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	Temperature (°C)		Salinity (‰)		рН		DO (mg/L)	
-	Range	Mean ± SE	Range	Mean ± SE	Range	Mean ± SE	Range	Mean ± SE
Old mouth of Gediz	11.00-28.80	20.38 ± 1.7	11.32-42.57	29.89 ± 2.45	7.61-8.57	8.01 ± 0.07	3.60-20.00	7.55 ± 1.34
Bostanlı Creek	12.00-28.50	20.65 ± 1.45	1.95-37.91	24.24 ± 3.87	7.19-7.99	7.71 ± 0.07	0.00-8.80	4.77 ± 0.75
Bayraklı Creek	14.00-27.30	20.39 ± 1.38	12.49-35.39	30.81 ± 1.89	7.34-7.85	7.62 ± 0.04	0.00-6.00	2.83 ± 0.60
Bornova Creek	11.00-27.6	20.05 ± 1.50	2.98-37.52	23.71 ± 3.93	7.49-8.19	7.79 ± 0.06	0.00-8.80	4.07 ± 0.85
Manda Creek	11.00-29.50	20.40 ± 1.63	1.81-35.00	27.72 ± 2.60	7.56-8.04	7.82 ± 0.05	2.80-8.00	4.98 ± 0.44
Meles Creek	10.00-28.70	20.23 ± 1.69	1.81-35.00	23.66 ± 3.04	7.29-7.80	7.57 ± 0.05	0.00-7.40	3.87 ± 0.72
Balçova Creek	16.90-29.60	22.36 ± 1.41	6.86-22.38	11.38 ± 1.45	7.19-7.90	7.52 ± 0.08	1.40-16.00	7.58 ± 1.07

Table 2. The range and mean ± standard error values of physicochemical parameters.

Table 3. The range, mean \pm standard error, and median values of nutrients (μ M).

	$\rm NH_4$ -N		NO ₃ -N		NO ₂ -N		o.PO ₄ -P		Si	
	Range	Mean ± SE/Med.	Range	Mean ± SE/Med.	Range	Mean ± SE/Med.	Range	Mean ± SE/Med.	Range	Mean ± SE/Med.
Old mouth of Gediz	7.47-35.48	23.78 ± 2.49/ 25.74	1.96-28.70	7.10 ± 2.27/ 3.54	0.17-2.56	1.15 ± 0.21/ 0.97	1.16-23.71	9.34 ± 2.06/ 9.18	0.70-296.47	86.16 ± 27.34/47.2
Bostanlı Creek	1.91-90.39	22.81 ± 6.95/ 19.05	1.06-69.80	14.23 ± 6.09/ 6.42	0.43-5.60	2.19 ± 0.52/ 1.74	2.97-7.18	4.78 ± 0.40/ 4.72	1.62-302.38	103.38 ± 30.79/66.2
Bayraklı Creek	1.62-107.42	37.05 ± 9.83/ 27.74	1.81-36.83	9.26 ± 2.89/ 5.22	0.08-10.70	2.48 ± 0.85/ 1.41	2.19- 22.05	8.74 ± 1.74/ 6.28	0.33-159.01	30.20 ± 12.60/16.5
Bornova Creek	2.86-182.14	34.75 ± 14.47 /15.43	0.71-77.31	18.56 ± 7.52/ 7.33	0.07-7.10	2.08 ± 0.71/ 0.96	1.69-27.28	10.84 ± 3.02/4.98	1.98-449.66	109.78 ± 46.80/11.1
Manda Creek	1.62-88.39	31.42 ± 7.53/ 26.14	1.02-130.49	19.16 ± 10.57/ 6.50	0.07-22.64	5.47 ± 2.17/ 1.09	2.03-31.98	10.35 ± 2.76/6.51	0.80-189.75	35.69 ± 16.30/13.4
Meles Creek	32.55- 634.38	216.01 ± 53.39 /162.80	2.57-153.29	20.48 ± 12.20/ 5.70	0.25-17.78	5.89 ± 1.76/ 3.61	6.48-26.97	16.21 ± 1.89/16.24	2.42-195.24	59.30 ± 17.43/44.8
Balçova Creek	4.52-44.76	20.40 ± 4.88 /11.71	10.67– 374.12	127.53 ± 39.45 /79.12	1.35-4.84	2.66 ± 0.27 /2.6	0.09-8.02	1.75 ± 0.66 /1.01	73.78– 284.45	145.52 ± 23.3/125.4

 $o.PO_4$ -P inputs were observed in different periods of the year. The highest $o.PO_4$ -P concentration was found at Manda Creek.

3.4. PCA

The purpose of the analysis is to obtain a small number of linear combinations of the 11 variables that account for most of the variability in the data. In this case, 5 components were extracted, since 5 components had eigenvalues greater than or equal to 1.0. Together they account for 77.13% of the variability in the original data. Eigenvalues and eigenvectors for parameters are given in Table 4.

3.4.1. PCA for all stations shows that

- 26.61% of the variance in data was related to [Si(OH)₄-Si], o.PO₄-P, DO, and the microplankton biomass.
- 2. 16.20% was related to NO $_{3}^{-}$ -N, NH $_{4}^{+}$ -N, and NO $_{2}^{-}$ -N.
- 3. 12.87% was related to salinity and picoplankton.
- 4. 11.93% was strongly related to nanoplankton.
- 5. And 9.52% was related to pH.

Component 1 is essentially composed of $[Si(OH)_4$ -Si], which comes from rivers as the primary pollution parameter, and untreated o.PO₄-P. Microplankton is seen as a controlling factor on component 1 by reducing the component value, which increases with $[Si(OH)_4$ -Si] and

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Table 4. Eigenvalues (a) and eigenvectors (b) for parameters.

Component		Percent of	Cumulative
number	Eigenvalue	variance	percentage
1	2.92733	26.612	26.612
2	1.78185	16.199	42.811
3	1.41543	12.868	55.678
4	1.31186	11.926	67.604
5	1.04765	9.524	77.128

b

a

Eigenvectors	Component	Component	Component	Component	Component
	1	2	3	4	5
NH ₄ -N	0.275799	0.459449	-0.0632982	-0.310567	-0.144834
NO ₂ -N	0.0536674	0.603519	0.0897474	-0.252846	0.143351
NO ₃ -N	-0.210332	0.462421	-0.352083	0.179005	0.101839
[Si(OH) ₄ -Si]	0.402113	-0.0890745	0.315864	0.268705	-0.130402
o.PO ₄ -P	0.494531	0.00880958	0.0401834	0.246762	0.167885
Salinity	-0.145636	0.194374	0.521099	0.335305	-0.404256
DO	-0.449845	0.214537	-0.0223211	0.249596	-0.300676
рН	-0.108032	0.111901	0.542295	-0.151763	0.624959
Microplankton	-0.440245	-0.12674	0.320212	-0.1102	0.116902
Nanoplankton	-0.0116407	0.154118	-0.139699	0.679487	0.437615
Picoplankton	0.203389	0.258229	0.272788	0.0536121	-0.230948

o.PO₄-P. Oxygen concentration also changes depending on microplankton. Component 2 shows nitrogen compounds and picoplankton. All of them affect the component positively. The fact that all of them are positive indicates that nitrogen compounds control picoplankton growth (Liebig's minimum rule). Based on this fact, it can be expressed that treated nitrogen compounds control the picoplankton level. The nitrogen-limiting structure displayed by the bay throughout the year also supports this opinion. Component 3 is associated with salinity and [Si(OH)₄-Si]. This shows the contribution of the sediment and/or overlying-sediment water. The fact that bottom waters have lower NO⁻₃-N concentrations especially at ST 1 has a decreasing effect on the value of component 3. This is because of the fact that high $[Si(OH)_4$ -Si] and salinity show the effect of bottom water. Component 4 stands for the nanoplankton dynamics. It is the representative of the nanoplankton group living at relatively high salinity. Negative change of component 4 with NH⁺₄-N particularly expresses the NH⁺₄-N obtained from fresh waters. Component 5 represents the nanoplankton group living in relatively less salty waters (estuaries). Thus, it is a compound displaying the river's effect. With increasing proximity to the estuaries, while the nutrient limiting effect is eliminated, salinity and pH gain more importance.

The first component was more important than the others. It was seen clearly that $o.PO_4$ -P plays a key role in eutrophication. Plots of the first and second components are illustrated in Figure 4.



Figure 4. Plots of first and second components of PCA.

4. Discussion

When nutrients and chlorophyll-*a* concentrations were compared to those in studies carried out before the construction of the water treatment plant (WTP), significant decreases were observed for the nutrients but chlorophyll-*a* concentrations were higher than the values determined after the WTP by Kükrer and Aydın (2006) and Sunlu et al. (2012) (Table 5).

This indicates the role of primary production on reduction of nutrient concentration and thus it is thought that this reduction was transformed into phytoplankton biomass. During the phytoplankton bloom period (January–August) NH_4^+N , [Si(OH)₄-Si], and o.PO₄-P concentrations were lower than the values in autumn. The inverse relationships between the microplankton and the nutrients are particularly important in this period. Both high nutrient and chlorophyll-*a* values were observed in June (at ST 1) and August (at ST 3 and ST 4). This exception may be a result of the bloom of mixotrophic species (Bizsel et al., 2001). The opposite trend between NH₄-N and chlorophyll-*a* showed the consumption of

ammonium by phytoplankton but the expected negative correlation between NO_3^--N and chlorophyll-*a* was not found. The reason for this might that NH_4^+-N could block the uptake of NO_3^--N and/or NH_4^+-N might be preferred by phytoplankton (McCarthy, 1980).

The mixing processes that enable phytoplankton groups, which do not have movement organelles like diatoms, to stay in the water column explain the increase in microphytoplankton in February and May. The light intensities, which increase in May, might as well have an important effect on bloom species' staying in the water columns. Nanophytoplankton biomass shows increases in January, March, June, July, and September. Hence, the nitrogen forms decreased in the water column following stratification until the end of summer, limiting the growing of phytoplankton. Then the nanoplankton was replaced by picoplankton in August. As a result of the partial mixing of the water column by strong winds at the end of August, an increase was seen in nanophytoplankton in September again. Stratification provides an advantage for nano- and picophytoplankton. The fact that stratification takes a long time and nutrients (nitrogen compounds) are exhausted in the water column provides more advantages for the picoplankton. In winter and early spring conditions vertical mixing provides advantages for micro- and nanoplankton. Nitrate, which is a storable nitrogen type, provides advantages for micro- and nanoplankton (especially in September, January, February, March, May, and June) and ammonia provides an advantage for picoplankton (especially in November and August).

Similarities in the spatio-temporal distributions of NH_4^+-N and NO_2^--N were observed at all stations. Bizsel and Uslu (2000) explain this similarity by the nitrification process: NH_4^+-N rapidly transforms into NO_2^--N , but transformation of NO_2^--N to NO_3^--N is a slower process (Ozkan et al., 2008). Hence, NH_4^-N and NO_2^--N had similar trends in this study. NO_2^--N values were lower

Table 5. Comparison of the ranges of nutrients (μ M) and chlorophyll-*a* (μ g/L) values founded in this study with previous studies in İzmir Bay.

NH ₄ -N	NO ₃ -N	NO ₂ -N	o.PO ₄ -P	Si(OH) ₄ -Si	Chl-a	References
-	-	-	50.00 (max)	-	-	Bizsel et al., 2001
0.04-65.67	0.00-7.59	0.01-5.46	0.09-12.06	0.00-6.38	-	Kaymakçı et al., 2001
73.80 (max)	83.12 (max)	15.60 (max)	-	-	80.00 (max)	Gencay and Büyükışık, 2004
0.06-40.72	0.19-24.86	0.00-25.90	0.87-17.58	0.78-48.60	0.00-3 .93/1.31	Kükrer and Aydın, 2006
0.00-40.94/5.31	0.00-21.35/3.28	0.00-28.99/2.27	0.00-31.41/3.28	0.16-54.12/10.82	0.00-66.13/4.26	Sunlu et al., 2012
0.23-22.28/3.28	1.54–11.7 7/4.27	0.00-3.51/0.64	0.00-5.96/2.17	1.99-41.94/10.80	5.03-30.26/12.44	This study

Numbers written after "/" indicate average values.

than NO-3-N over the sampling period. McCarty (1980) reported that this situation was normal and NO-,-N accumulates noticeably under low DO condition. Koray et al. (1992) emphasised that a large part of total nitrogen in the polluted İzmir Bay was ammonium from industrial and domestic wastes. In contrast, in our study nitrate had the largest share of total nitrogen concentration due to the WTP, which reduces ammonium inputs. Additionally, ammonium concentration is kept under control by phytoplankton over a year. In spite of this progress, the ammonium enrichment continues owing to the creeks and sediment, which have high ammonium concentrations (Ozkan et al., 2008). The capacity of the wastewater plant has not been sufficient for phosphate reduction according to previous studies (Kontas et al., 2004; Kucuksezgin et al., 2006; Kükrer & Aydın, 2006). Although the phosphate concentration we found was lower than the values in those studies, it is thought that the decreases in phosphate concentration are a result of phytoplankton consumption. The observed mean N:P value was lower than the assimilatory optimal (N:P = 15:1) in conformity with Redfield's ratio N:P = 16:1 due to the reduction in nitrogen. The Eastern Mediterranean is one of the world's poorest seas as a concept based on the impoverished phytoplankton biomass and productivity levels mainly due to phosphorus deficiency (Ignatiades et al., 2002). However, in İzmir Bay, as a part of the Mediterranean basin, nitrogen is a limited nutrient. Nutrient levels found in this study in the inner bay were higher than those in the other parts of the Aegean Sea (Table 6).

Nutrients and light are probably more available to phytoplankton because of the smaller volume and the shallowness of the water column (Thomas et al., 2005). These structures of ST 1, ST 2, and ST 3 stimulate the increase in the phytoplankton biomass. The nanoplankton dominated the phytoplankton chlorophyll-*a* biomass at all stations and depths. Significant relationships were found between size fractionated phytoplankton and total chlorophyll-*a*. The contribution of size fractions to total chlorophyll-*a*

was statistically significant at all stations. Generally, the picoplankton biomass increased from the surface to the bottom layers. This situation occurred more clearly at ST 4. The predominance of the $<1 \mu m$ and $<3 \mu m$ phytoplankton populations in the "low-light/nutrient rich" deep layer suggests that pico- and ultraplankton are better adapted to these depths of the photic zone than nanoplankton (Raimbault et al., 1988). The vertical profile of the picoplankton biomass has been described in many studies with some conflicting data. Some investigators reported a decrease in picoplankton chlorophyll-a abundance with depth, whereas others observed an increase towards the base of the euphotic zone that was attributed to the thermocline or nitracline depth or to cell preference for dim light (Ignatiades et al., 2002). It can be supposed that eutrophication caused microplankton to increase in İzmir Bay, but nanoplankton was the dominant fraction. Microphytoplankton have a greater density and therefore a greater tendency to sink than nanophytoplankton; as a result, their growth may be limited by light (Thomas et al., 2005). While the predominance of small autotrophic organisms seems to be a distinguishing feature of warm oligotrophic oceans where the $<1 \mu m$ and $<3 \mu m$ fractions may represent more than 50% of the total phytoplankton biomass (Raimbault et al., 1988), in coastal estuarine areas they have been reported to account for about 24% of the total phytoplankton biomass, because small cells, due to their higher cell surface to volume ratios, are better competitors at low nutrient levels (Arin et al., 2005). All of these determinations explain the low picoplankton biomass in the polluted İzmir bay.

According the results of PCA, silicate, which comes from rivers, and untreated phosphate as primary pollutants are most important nutrients for eutrophication. Although nanoplankton is the dominant size fraction in the bay, microplankton have a larger contribution in the variations of the ecosystems. Nitrogen compounds control picoplankton growth (Liebig's minimum rule). With proximity to the estuaries, while the nutrient limiting effect is eliminated, salinity and pH gain more importance.

	o.PO ₄ -P	NH_4 -N	NO ₃ -N	NO ₂ -N	$NO_3 + NO_2$	N _{total}	Si(OH) ₄ -Si	References
Maliakos Gulf	0.00-0.68	0.00-0.20	0.00-0.88	-	-	-	-	Kormas et al., 2002
Aegean Sea (Northern and Southern)	0.01-0.05	-	-	-	0.29-0.89	-	1.18-2.40	Ignatiades et al., 2002
Saranikos Gulf	0.20-0.40	-	-	-	-	1.87-4.34	0.48-5.31	Moncheva et al., 2001
Thermaikos Gulf	0.44-0.70	-	-	-	-	0.60-4.63	0.10-4.47	Moncheva et al., 2001
İzmir Bay	0.00-5.96	0.23-22.28	1.54-11.77	0.00-3.51	-	-	1.91-41.94	This study

Table 6. Typical concentrations of essential nutrients (μM) in different parts of the Aegean Sea.

Consequently, although nutrient levels were reduced after construction of the WTP, high nutrient inputs continue from small creeks and $0.PO_4$ -P plays a key role in eutrophication. It is understood that the WTP is necessary but inadequate to control eutrophication for semi-closed bays compassed by creeks. This situation necessitates total monitoring and assessment studies.

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