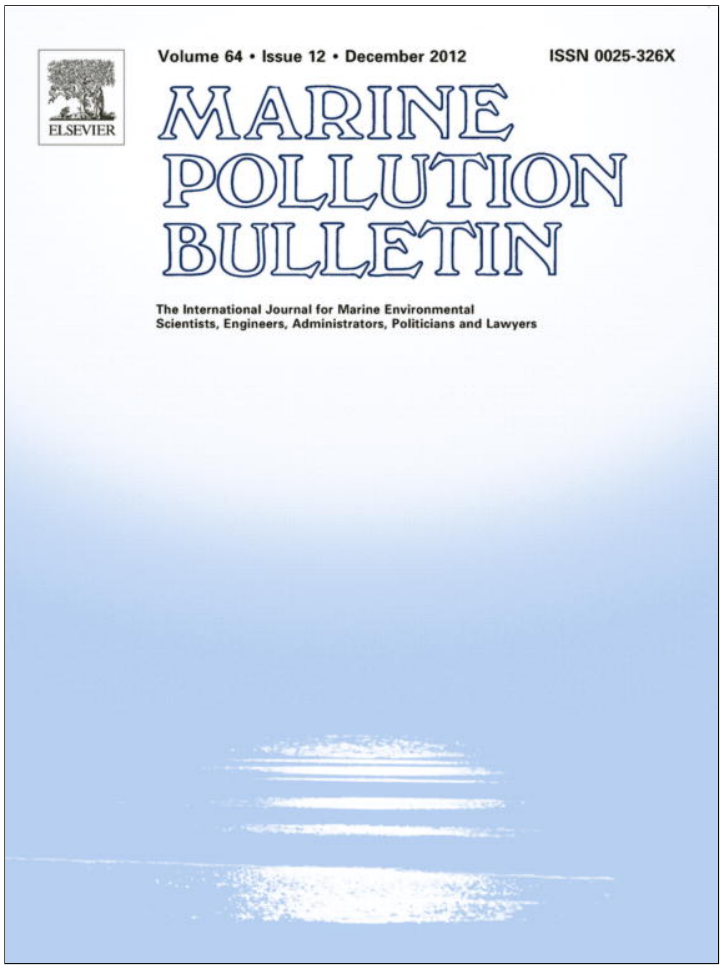
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Baseline

Evaluation of spatial and temporal variations of inorganic nutrient species in the eastern Aegean Sea waters

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ABSTRACT

In this study, the state of the five stations' quality was assessed on the basis of determination of temporal and spatial variability of nutrients with physicochemical variables. Besides this, organic matter of sediment, secchi disc depth and suspended solids were also determined. The samples were collected seasonally from different areas such as harbor and important touristic marinas along the eastern Aegean during June 2008–2009. As a result, the nutrients ranged between NH_4: 0.10–25.6, NO_2: 0.01–1.5, NO_3: 0.19–7.0, o.PO_4: 0.17–6.8, TPO_4: 0.32–9.6 and Si: 0.30–13.8 μM, respectively. Precipitation leads to large changes in temperature, salinity, dissolved oxygen and nutrients. The highest nutrient values in this study were observed during the rainy season except o.PO_4-P and TPO_4-P. However, the physico-chemical variables have exhibited considerable temporal variations while nutrients showed spatial differences. The relatively high nutrient increase in the sampling stations coupled with surface runoff events during rainy period and pollution arising from both point and non-point sources.

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The nutrient inputs (particularly nitrates and phosphates) as a consequence of major anthropogenic sources such as industrial, urban and agricultural activities to the coastal areas have increased greatly during the past two centuries. These anthropogenic influents as well as natural factors (changes in precipitation inputs, erosion, weathering of crustal materials) would be expected to have an effect on natural biogeochemical processes (Belias et al., 2007). Nutrients are essential chemical components of life in the marine environment phosphorus and nitrogen are incorporated into living tissues while silicon is necessary for the formation of the skeletons of diatoms and radiolaria (Basturk et al., 1986). Nitrogen and phosphorus are described as biolimiting elements because of the effects on biological growth. In the sea, most of the nutrients are present in sufficient concentration, and the lack of some of them limits the growth of phytoplankton (Pojed and Kveder, 1977).

The nutrient enrichment, or eutrophication, can lead to highly undesirable conditions in ecosystem structure and function. The recent researches indicated that the eutrophication had influences on transportation and transformation of contaminants in aquatic environment and causes outstanding environmental problems (Zhang et al., 1999). Nowadays pollution from the nutrients (N and P) and organic matter represents the largest source of degradation in coastal waters. The concentrations of biologically available nitrogen and phosphorus are well known to play a key role in determining the ecological status of aquatic systems (Jarvie et al., 1998). And in coastal ecosystem the sources of nutrients and organic matter can be classified into two groups, that is, the point and non point sources. Point sources, such as sewerage and industrial wastewater, flow out at discrete, identifiable locations and their impacts can be measured directly. However, the largest nutrient contribution for coastal marine environments is from non-point sources that are rather diffused and highly variable from year to year depending on climate and rainfall (Borum, 1996). The most important non point loads include the wet and dry deposition from the atmosphere, the erosion of land, the weathering of minerals and anthropogenic sources. The latter are directly related to human activities (Novotny and Chesters, 1981). Human disturbance has resulted from activities that mobilize the nutrients through land clearing, production and applications of fertilizer, discharge of human waste, animal production, accumulation of dust and litter, erosion of soil materials from agricultural farming and animal feedlots (Novotny and Chesters, 1981). As a result of these activities, the fluxes of N and P have been accelerated at coastal waters.

Although there have been a number of studies focused on the levels of nutrients and physicochemical variables of the water column in the eastern Aegean Sea (Turkey) (Kocak and Kucuksezgin, 2000; Kontas et al., 2004; Kucuksezgin et al., 2005, 2006; Kukrer and Aydın, 2006; Basaran et al., 2010; Kukrer and Buyukısık, 2010; Sunlu et al., 2012). There was limited information about the results obtained from harbor and marinas. The objective of this study was to determine the temporal and spatial variability of the main eutrophication parameters such as inorganic nutrients and physicochemical variables of the water column collected from

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important touristic marinas and harbor located from the eastern Aegean Sea.

Sampling was conducted during June 2008 to 2009 and stations were selected from different parts of the Aegean Sea; one of them in the northern part (Candarli), three of them inner part of Izmir Bay (Izmir harbour, Izmir-Pasaport, Izmir-Levent Marina) and the last one in the southern part (Kusadasi-Setur Marina) (Fig. 1). Stations were chosen from harbor and marinas which are important touristic, economical and transportation center for eastern Aegean Sea.

The sampling station located in the Candarli Gulf has been strongly affected by growing population and industrialization activities. The solid and liquid wastes come from great industrial settlements via Bakircay discharged into Candarli Gulf after limited treatment. Izmir Bay is one of the great natural inlets of the Mediterranean and it is divided conventionally into three zones: inner, middle and outer by virtue of topographical, hydrological and ecological features. Industrial activities cover a large range of industries including food processing, leather tanning, paint, chemicals, textile manufacture and petroleum refining. One of the selected stations was situated in the Izmir Harbor and influenced intensively by the harbor activities. Moreover, Levent Marina and Kusadasi-Setur Marina provide various services such as boat docking, boat repair and maintenance and the stations located in this region were affected by all kinds of painting activities.

Seawater samples collected seasonally using Nansen bottle between June 2008 and 2009 from five sampling sites and the physicochemical variables of seawater (temperature, conductivity, pH and salinity) were measured *in situ* by using a portable instrument (Wissenschaftlisch-Technische Werkstatten GmbH; WTW, Weilheim, Germany). Dissolved oxygen (DO) measurement using the Winkler titration method was performed immediately after collection. Additionally, transparency was measured by secchi disc and total suspended solid was determined according to reference methods (APHA-AWWA-WPCF, 1980).

Seawater samples obtained for the determination of nutrients were filtered through 0.45 μm Millipore membrane filters and then samples were transferred to 100 mL polyethylene bottles and were kept frozen in the refrigerator (+4 °C) until analysis. Nutrient analysis including nitrate (NO_3), nitrite (NO_2), ortho and total phosphate (PO_4), and reactive silicate (Si) was carried out within 1 week by means of Skalar (two-channel) Autoanalyzer using the standard colorimetric methods according to Strickland and Parsons (1972). Intercalibration seawater samples (from QUASIMEME, Plymouth Marine Laboratory, Round 22) were used as a control for the analytical methods of nutrients. The values obtained for the analyses of 10 replicates of this sample (certified; observed values in μM ± standard deviation) were as follows: TNO_x-N (8.68 ± 0.38; 8.78 ± 0.04), NO_2-N (0.50 ± 0.04; 0.50 ± 0.02), NH_4-N (0.84 ± 0.29; 0.74 ± 0.09), o.PO_4-P (0.76 ± 0.05; 0.78 ± 0.008), Total PO_4-P (0.88 ± 0.08; 1.0 ± 0.07).

Sediment samples were collected with a Van-Veen Grab (20 × 20 × 10 cm) and stored frozen at −20 °C for organic matter analysis. The amount of organic matter in sediment samples was determined spectrophotometrically following the sulphochromic oxidation method. The accuracy of this method is ±0.017% organic matter (Hach Publication, 1988).

The statistical analysis was performed using the STATISTICA v. 7.1 (STATSOFT) software package. Normal distribution of the data was tested using Kolmogorov–Smirnov test. Moreover, homogeneity of the variances was tested by Levene test. In order to find out significant relation between different parameters, the one-way analysis of variance (ANOVA) and the post hoc Tukey's HSD was used to analyze the effects of season and station on variations in chemical parameters. The nonparametric Kruskal–Wallis analysis and Mann–Whitney *U* tests were performed to detect differences

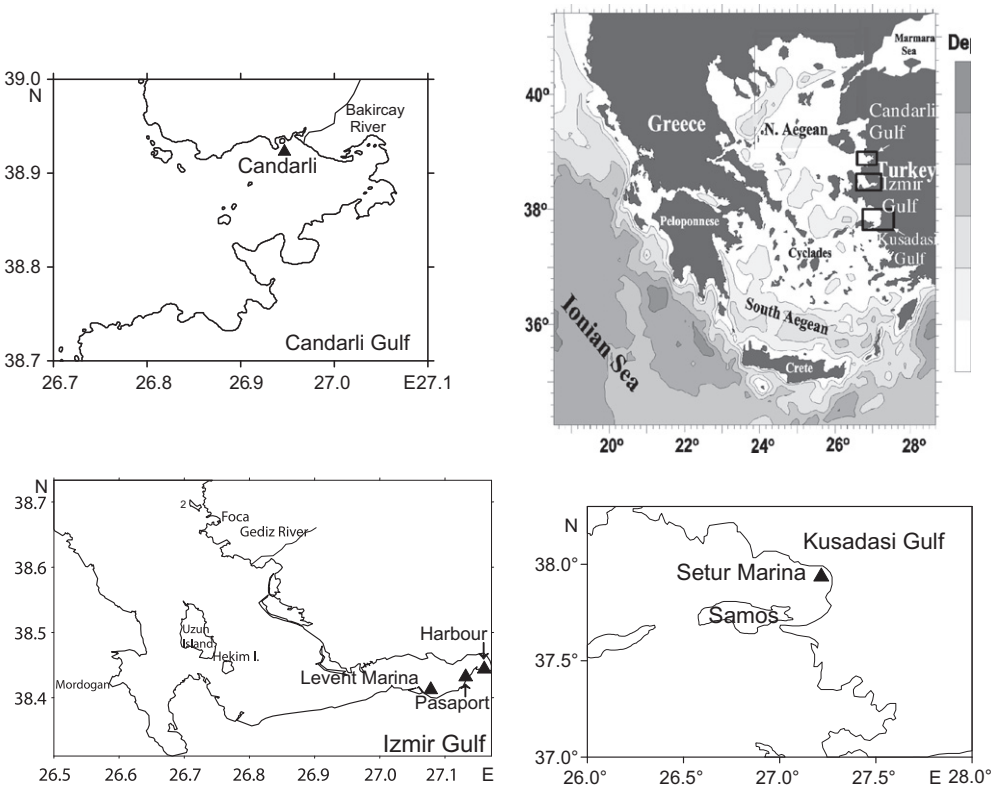


Fig. 1. The location of sampling points from the eastern Aegean Sea.

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among sampling stations and seasons. Spearman Rank Order correlation test was used to determine linear relationships between nutrients and physicochemical variables.

Principal Component Analysis (PCA) was carried out on 9 variables for different sampling stations in four seasons, in order to determine which variable contributes significantly to the variation in water quality of the coastal waters of the study area. Principal Components (PCs) are associated with eigenvalues; an eigenvalue greater than 1 suggests that the corresponding PC contributes to the variance in water quality. Eigenvalues of 1.0 or greater are considered significant (Shrestha and Kazama, 2007). Classification of factor loading is thus 'strong', 'moderate' and 'weak', corresponding to absolute loading values of >0.75, 0.75–0.50 and 0.50–0.30, respectively and loading values <0.30 are insignificant (Liu et al., 2003).

The quality of surface waters is a very sensitive issue and it is affected by various physicochemical factors such as temperature, pH, salinity, conductivity, dissolved oxygen, other dissolved gases, rainfall, turbidity, transparency and nutrients. In the present study, we explored temporal and spatial distributions of inorganic nutrient concentrations in relation to the other environmental variables. Table 1 presents the minimum, maximum, mean and standard error of some environmental variables of the five selected stations from the eastern Aegean Sea. According to the results, sea water temperature showed seasonal expected pattern and decreased from summer to winter and then increased towards spring. The highest temperature value (30.0 °C) was recorded in summer at Izmir Harbor while its lowest value (11.9 °C) was measured at Izmir-Levent Marina in winter (Table 1). Seasonal differences ($p < 0.001$) were observed in temperature during the study. Moreover, no significant difference was observed among stations (Table 2). According to Spearman Rank-Order correlation, the water temperature was positively correlated with TSS ($r = 0.4605$, $p < 0.05$).

According to the annual rainfall distributions of Izmir from July 2008 to June 2009, recorded rainfall values were changed between 0.0 and 204.1 mm with an average value of 72.6 ± 8.49 mm. Moreover, July–December 2008 was represented dry to moderately rainy season and January–June 2009 was showed heavily rainy to moderately rainy season (Onen, 2011).

Winter concentrations of dissolved oxygen were generally higher than other seasons at all sampling stations. The highest dissolved oxygen value was found at Izmir Harbor (9.8 mg l^{-1}) in winter while the lowest value was recorded at Izmir-Pasaport (3.2 mg l^{-1}) in summer, with an overall mean value of 6.81 ± 0.38 (Table 1). The significant differences were detected between seasons for DO concentrations (Kruskal–Wallis test, $p = 0.0027$) (Table 2). The levels of DO in the aquatic systems depend on the water temperature and salinity. According to the results, DO concentrations showed a positive significant correlation with pH ($r = 0.7435$, $p < 0.001$) and exhibited negative correlations with salinity ($r = -0.5028$, $p < 0.05$) and temperature ($r = -0.6525$, $p < 0.01$).

Table 2
Results of statistical comparisons between concentrations of physicochemical variables for all sampling stations during the study period.

	Season			*Station*		
	df	*F*	*p Level*	*df*	*F*	*p Level*
Temperature (C)	3	28.02	***	4	1.91	ns
Salinity (psu)	3	5.60	*	4	0.66	ns
pH	3	2.77	ns	4	0.71	ns
Conductivity (mSi/cm)	3	3.34	*	4	2.96	ns
DO (mg/l)	3	14.19	*	4	0.24	ns
TSS (mg/l)	3	0.51	ns	4	5.10	ns
Organic matter (%)	3	0.21	ns	4	15.31	***
Secchi disk (m)	3	1.59	ns	4	0.44	ns

ns, (non-significant).
* $p < 0.05$.
*** $p < 0.001$.

The pH values showed fluctuations throughout the sampling periods and winter values were higher than other seasons at all sampling stations. pH reaches its maximum value (8.52) during winter at Izmir Harbor and minimum pH value (7.00) was observed at the same station in summer (Table 1) with overall average value of 8.34 ± 0.06. Furthermore, no significant differences were detected between seasons and between stations for pH levels (Table 2).

Salinity decreased from summer–autumn towards winter–spring. The present data showed that all the sites revealed narrow variation in the level of salinity content. The annual mean value of salinity was varied from 38.3 ± 0.83 psu (Izmir Harbor) to 39.4 ± 0.25 psu (Candarli) and the highest salinity level (40.8 psu) was recorded at Izmir-Pasaport in summer (Table 1). Moreover, salinity levels differed significantly among seasons ($p < 0.05$) when all sites were considered together (Table 2). A strong positive relationship was observed between salinity and conductivity ($r = 0.8451$, $p < 0.001$), while negative correlation was found between salinity and pH ($r = -0.5541$, $p < 0.05$).

Concerning the conductivity, autumn and summer values were generally higher as compared to winter and spring values. Furthermore, conductivity levels varied within a range of 54.90 mSi/cm at Izmir Harbor in winter to 60.70 mSi/cm at Izmir-Pasaport in summer (Table 1) and the data showed significant temporal variation ($p < 0.05$) (Table 2). Based on the results of this study, conductivity showed a negative correlation with pH ($r = -0.6035$, $p < 0.05$) and no significant correlation was found with temperature.

TSS levels were generally higher during all seasons than autumn period for Izmir Harbor. However, no significant temporal and spatial variations were found among sampling periods (Table 2). Maximum TSS levels were obtained from Izmir Harbor (14.60 mg/l) in winter and spring (13.00 mg/l) period and from Kusadasi-Setur Marina (10.70 mg/l) in summer. However, the minimum value (1.50 mg/l) was recorded at Izmir-Levent Marina in winter (Table 1). Secchi disk levels varied from 0.70 m (Izmir Harbor in winter) to 4.00 m (Izmir Pasaport in winter) with an average value of

Table 1
The range and mean ± *SE* concentrations of the physicochemical variables in seawater.

	Candarli	Izmir-Harbour	Izmir-Pasaport	Izmir-Levent M.	Kusadasi-Setur M.
Temperature (°C)	16.7–25.1 21.18 ± 1.80	17.6–30.0 23.00 ± 3.19	0.04–25.1 13.84 ± 5.20	11.9–24.6 20.08 ± 2.93	16.8–25.2 21.38 ± 1.78
Salinity (psu)	38.07–39.8 39.43 ± 0.25	36.0–39.6 38.30 ± 0.83	38.1–40.8 39.15 ± 0.64	37.3–39.9 38.80 ± 0.55	38.1–39.6 38.53 ± 0.36
pH	8.19–8.47 8.34 ± 0.06	7.00–8.75 8.06 ± 0.38	7.98–8.52 8.29 ± 0.13	8.24–8.38 8.33 ± 0.03	8.09–8.39 8.24 ± 0.06
Conductivity (mSi/cm)	58.60–59.60 59.15 ± 0.22	54.90–59.60 57.66 ± 1.08	57.10–60.70 58.73 ± 0.92	58.10–60.00 59.03 ± 0.41	57.70–59.10 58.13 ± 60.00
DO (mg/l)	6.5–7.9 7.10 ± 0.29	3.7–9.8 6.35 ± 1.29	3.2–9.4 6.28 ± 1.29	4.7–8.1 7.05 ± 0.81	6.7–8.6 7.28 ± 0.45
TSS (mg/l)	2.30–5.30 3.58 ± 0.67	3.20–14.60 9.80 ± 2.56	2.70–6.75 4.64 ± 0.83	1.50–5.20 3.65 ± 0.82	2.90–10.70 5.82–1.69±
Secchi disk (m)	1.70–3.00 2.33 ± 0.28	0.70–3.50 1.73 ± 0.63	1.10–4.00 2.08 ± 0.65	1.60–2.50 2.28 ± 0.23	2.00–3.00 2.50±0.20

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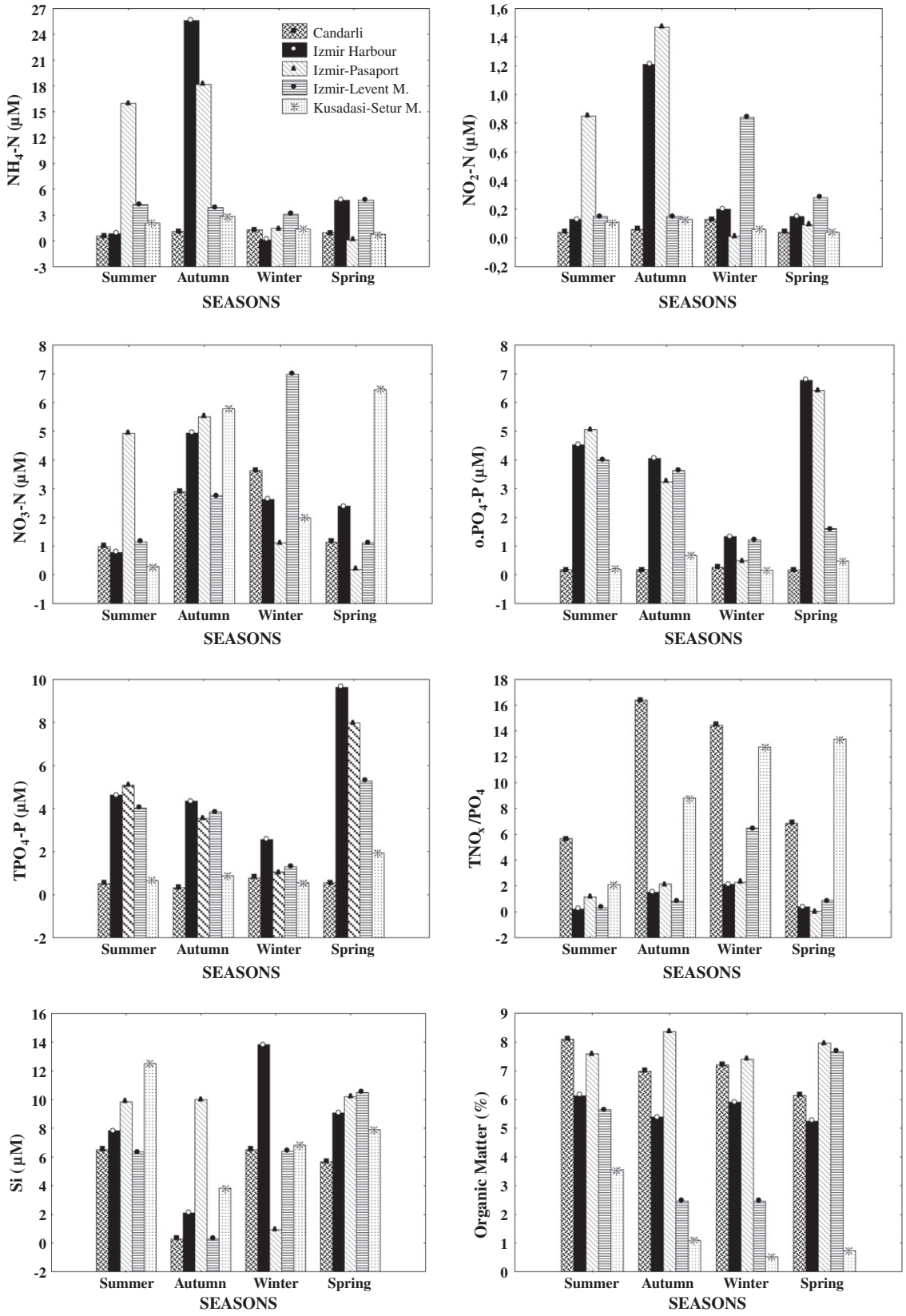


Fig. 2. Temporal variations of nutrient concentrations (in water column) and organic matter (in sediment) during the study period.

2.18 ± 0.19 m (Table 1). Furthermore, there were no statistically significant temporal and spatial variations observed (Table 2).

Temporal and spatial variations of nutrient concentrations in the study area are illustrated in Fig 2. Besides NH_4-N values did not show important differences among seasons and stations, 3 peaks throughout the sampling periods were observed. The maximum and minimum values were measured at stations located in the inner part of Izmir Bay (Izmir Harbor and Izmir-Pasaport,

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respectively) with a mean value of 4.69 ± 1.55 μM (Fig. 2). Spearman rank correlation analysis showed that no significant correlation was observed between NH_4-N and other parameters except NO_2-N.

NO_2-N values peaked in autumn period at Izmir Harbor (1.21 μM) and Izmir-Pasaport (1.47 μM) stations, the lowest NO_2-N level (0.01 μM) was recorded at Izmir-Pasaport in winter. However, NO_2-N values did not show significant temporal and spatial variations at all stations (Table 3). Based on the data, there were significantly positive correlations between NO_2-N with NH_4-N ($r = 0.7010$, $p < 0.01$), o.PO_4-P ($r = 0.6202$, $p < 0.05$), TPO_4-P ($r = 0.5516$, $p < 0.05$).

In terms of NO_3-N concentrations, the lowest value was recorded at Izmir-Pasaport (0.19 μM) in spring and the highest level was observed at Izmir-Levent Marina in winter (6.99 μM) (Fig. 2). Beside this, there were no clear temporal and spatial patterns were observed for NO_3-N levels (Table 3).

Higher o.PO_4-P concentrations were recorded at Izmir Harbor (6.78 μM) and at Izmir-Pasaport (6.43 μM) in spring period compared to other seasons. Moreover, the lowest value (0.17 μM) was determined at Candarli in spring (Fig. 2). On the other hand, o.PO_4-P concentration was not significantly different temporally. However, the non-parametric test Kruskal–Wallis indicated significant difference for stations ($p = 0.0075$) (Table 3). There was a highly significant correlation between o.PO_4-P and TPO_4-P ($r = 0.9244$, $p < 0.001$), while there was a negative correlation between o.PO_4-P and DO ($r = -0.4904$, $p < 0.05$).

TPO_4-P reached its maximum value (9.62 μM) at Izmir Harbor in spring with the mean level (5.29 ± 1.51 μM) at the same station as compared to other mean levels. According to stations, the lowest mean value of T.PO_4-P levels was obtained from Candarli (0.63 ± 0.13 μM). T.PO_4-P concentrations showed significant differences among stations ($p < 0.05$). Furthermore, no remarkable seasonal difference was observed (Table 3).

The reactive Si values changed between 0.30 (Candarli and Levent Marina in autumn) and 13.83 (Izmir Harbor in winter) with an average value of 6.87 ± 0.82 μM (Fig. 2). In addition to this, neither spatial nor temporal changes were observed for reactive Si levels (Table 3).

The NO_x/PO_4 ratio in seawater is an important index widely used by oceanographers in the world. In the present study, the lowest N:P ratios (0.04) were found at Izmir-Pasaport (Fig. 2). In addition, considering Redfield ratio, lower N/P was determined in all localities except Candarli (16.39). There was a significant spatial difference among stations (Kruskal–Wallis test, $p = 0.0228$), moreover, no significant temporal difference was determined among sampling periods (Table 3). NO_x/PO_4 showed a positive correlation with DO ($r = 0.4793$, $p < 0.05$) and also showed a negative correlation with temperature ($r = -0.5418$, $p < 0.05$).

Organic matter (%) concentrations ranged from 0.53 (Kusadasi Setur Marina) to 8.36 (Izmir Pasaport) (Fig 2). There was a remarkable spatial difference among stations ($p < 0.001$); moreover, seasonal sampling did not reveal any constant trend of organic matter distribution between the stations. However, a statistically significant difference were found among sampling stations ($p < 0.001$) (Table 3). Considering OM (%) levels, Kusadasi-Setur Marina station was different from other stations.

PCA analysis on the dataset during study period resulted in 3 principal component (eigenvalues >1) contributing a cumulative variance of the water quality (Fig. 3). PC1 contributed 66.5% of the total variance because of a strong positive loadings of o.PO_4-P (2.582), TPO_4-P (1.844), TNO_x (1.814) and compared to a strong negative loading of pH (−2.907), reactive silicate (−1.530) and DO (−1.459). The second PC is accounting for 16.2% of the total variance with a strong positive PC loading of NH_4-N (1.655). Furthermore, PC3 contributed the 13.3% of the total variance of the water quality resulting from a strong positive loading of TSS (1.511) compared to a strong negative loading of organic matter (−1.371) (Fig. 3).

The combined domestic and industrial effluents discharged into the harbors and marinas deteriorate the quality of water. Researching the spatial and temporal variability of nutrients in coastal areas is an essential first step towards clarifying this role and will provide indication of water quality.

Water temperature is probably the most important environmental variable, which affects the organisms as well as chemical and biological reactions in water (Soundarapandian et al., 2009). In the present study, water temperature values (11.0 to 30.0 °C) varied significantly throughout the study period ($p < 0.001$) and this could be attributed to seasonal changes in air temperature. Furthermore, the water temperature was negatively correlated with DO ($r = -0.6525$, $p < 0.01$). The inverse relationship between temperature and dissolved oxygen is a natural process because warmer water becomes more easily saturated with oxygen and it can hold less dissolved oxygen (Shrestha and Kazama, 2007). Temperature levels observed in this study is in agreement with results of previous studies conducted by Kukrer and Aydın (2006) (8.8–27.6 °C) and Kukrer and Buyukısık (2010) (11.0–27.6 °C) in various stations situated in inner Izmir Bay. Moreover, recorded temperature values were higher than the values obtained from Pagasitikos waters (the Western Aegean Sea): 11.60–27.80 °C (Neofitou and Klaoudatos, 2008); in middle and inner part of Izmir Bay waters: 8.90–28.20 °C (Sunlu et al., 2012).

Rainfall is an important factor in aquatic environment and greatly affects the dynamics of the environments, transports nutrients and allochthonous materials and alters the water's visual, physical and chemical characteristics (Lawson, 2011). While rainfall may dilute and weaken the effects of point source pollution, it also increases the contribution of non-point sources or diffuses pollution through land runoff from agricultural fields.

Table 3
Results of statistical comparisons between concentrations of nutrients for all sampling stations during the study period.

	Season			*Station*		
	df	*F*	*p Level*	*df*	*F*	*p Level*
NH_4-N	3	3.24	ns	4	4.83	ns
NO_2-N	3	2.03	ns	4	8.59	ns
NO_3-N	3	1.71	ns	4	0.20	ns
o.PO_4-P	3	2.14	ns	4	13.94	*
TPO_4-P	3	4.37	ns	4	4.13	*
Si	3	2.64	ns	4	0.53	ns
N/P	3	1.02	ns	4	11.35	*

ns, (non-significant).
* $p < 0.05$.

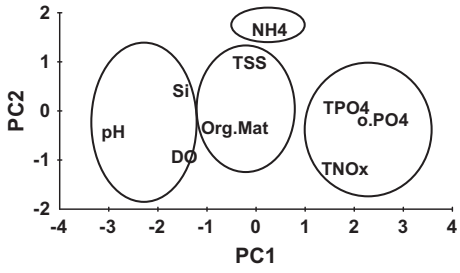


Fig. 3. Principal component analysis loading plots collected in sampling sites of the eastern Aegean Sea for nutrients and physicochemical variables.

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Monitoring dissolved oxygen will provide indication of water quality in coastal areas and used as a tool in ecosystem integrity (NLWRA, 2002). In the present study, DO levels varied within the range of 3.2–9.8 mg/l with the mean value of 6.81 ± 0.38 mg/l (Table 1). Coastal waters typically require a minimum of 4.0 mg/l and also do better with 5.0 mg/l of oxygen to provide for optimum ecosystem function and highest carrying capacity (UNESCO/WHO, 1978). According to our results, DO concentrations were generally upper the threshold value 4 mg/l during all seasons except Izmir-Pasaport (3.2 mg/l) and Izmir Harbor (3.7 mg/l) stations. DO concentrations indicated negative correlations with salinity and temperature. This may be due to the decrease in salinity increases the solubility of oxygen in the water column, which probably appears to be one of the main causes for the increase in the concentration of dissolved oxygen. Measured DO values in this study were within the range of reported in previous studies conducted in the inner part of Izmir Bay by Kukrer and Aydın (2006) (4.5 and 12.7 mg/l); Kukrer and Buyukısık (2010) (0.6 and 12.8 mg/l) and moreover, levels were higher than the values given by (Neofitou and Klaoudatos, 2008) (5.50 and 6.50 mg/l).

pH is one of the vital environmental characteristics for the survival, metabolism, physiology, growth of aquatic organisms and chemical processes (Ramanathan et al., 2005). According to Abowei (2010), pH values recorded (7.0–8.52) in this study were well within the preferred pH levels (7.0–8.5) for biological productivity. The higher pH values during summer period was due to the uptake of CO_2 by photosynthesizing organisms (Ananthan, 1994), conversely, the lower pH values were observed during winter period may be due to the influence of fresh water influx, dilution of sea water, low temperature and organic matter decomposition as suggested by Ganesan (1992). However, in this study, pH was negatively correlated with salinity and positively correlated with DO. Compared pH levels with other studies, observed pH levels were a bit higher than the values found in Pagasitikos waters: 7.74–8.13 (Neofitou and Klaoudatos, 2008); inner Izmir bay: 7.34–8.12 (Kukrer and Buyukısık, 2010); 7.40–8.60 (Sunlu et al., 2012).

Salinity is an important ecological variable and it is important in some chemical processes. In the present study, salinity levels were reduced sufficiently by winter rainfall because of high precipitation during rainy season. The highest salinity value was observed in summer period and this could be associated with higher temperature that leads to increasing the rate of evaporation. A nutrient-salinity relationship for a coastal area can provide information about processes involved in regulating nutrient concentrations (OSPAR, 1997). Compared with previous studies on salinity values, the measured levels in this study were higher than the mean values recorded Greece waters: 34.20–37.57 psu (Sylaios and Theocharis, 2002), Pagasitikos waters 36.50–38.00 psu (Neofitou and Klaoudatos, 2008) and in the inner part of Izmir Bay waters: 31.12–39.66 psu (Kukrer and Buyukısık, 2010). Furthermore, the recorded values in the present study were lower to those reported elsewhere (Sunlu et al., 2012) (31.93–44.85 psu) and similar trend in the salinity values were also observed from various stations situated in the inner part of Izmir Bay by Kukrer and Aydın (2006) (35.97–42.85 psu).

Electrical conductivity (EC) is a valuable indicator of the amount of material dissolved in water. The highest EC values at investigated stations are related to the increase in total dissolved solids and water temperature. EC values showed statistically significant temporal variation ($p < 0.05$). This can be due to rise in conductivity could result from concentration of ions by evaporation and increased mineralization of organic matter in summer period. The high conductivity values in autumn period could be due to the influx of materials from the surrounding area during rainfall. Boyd and Lichktoppler (1979) observed that conductivity significantly correlated with temperature, pH and salinity. In this study, conductivity showed a strong positive correlation with salinity and a negative correlation with pH.

Total suspended solids affect (TSS) metabolism and physiology of fish and other aquatic organisms. Source of total suspended solids include erosion from urban runoff and agricultural land, industrial wastes, wastewater discharges etc. They increase with increased rainfall and have adverse effects on dissolved oxygen and photosynthesis (Lawson, 2011). TSS level was peaked in winter and spring periods this can be due to floating materials carried by rainwater. High concentrations of total suspended solids can lower water quality by absorbing light (Lawson, 2011) and directly affected on the levels of transparency so that, TSS levels showed ($r = -0.4596$, $p < 0.05$) a moderate negative correlation with secchi disk levels. As expected, the transparency of seawater (secchi disk depth) decreases towards the inner bay depending on the productivity and the amount of terrestrial solid materials in the water. Our recorded secchi disk levels were below 10 m.

Variations in dissolved inorganic nutrients in marine waters can be ascribed to a number of factors including the extent of freshwater and groundwater input, degree of insolation, oxygen availability, standing stocks and productivity of phytoplankton and bacterioplankton (Boto and Wellington, 1988). According to our results, the observed increase in NH_4-N concentration in the water column during the rainy season was more remarkable. ANOVA result showed that, NH_4-N concentration did not show any significant differences (Table 3) among seasons and sampling stations ($p > 0.05$). Moreover, there was no significant correlation between this variable and other parameters except NO_2-N. Generally, a similarity in the spatio-temporal distributions of NH_4-N and NO_2-N were observed at all stations. This similarity can be explained by nitrification process. While NH_4-N rapidly transforms into NO_2-N, the oxidation process of NO_2-N is slower (Ozkan et al., 2008). The NH_4-N levels obtained from this study was similar with earlier reported results in Middle-Inner Bay of Izmir: 0.191–24.86 μM (Kukrer and Aydın 2006) and the results were lower than the values reported by Kucuksezgin (2011) (0.10–33 μM), Sunlu et al. (2012) (bdl-40.94 μM). Additionally, higher levels were found in Pagasitikos waters: 0.09–1.64 μM (Neofitou and Klaoudatos, 2008), in the inner part of Izmir Bay: 0.23–22.28 μM (Kukrer, 2009).

Although, higher NO_2-N values were obtained during autumn period there were no remarkable temporal and spatial variations. The nutrient level may be linked to rainfall events in the preceding months. This indicates that runoff and washout of lands brings to the area considerable loads of nutrients. Compared with previous studies on NO_2-N concentrations, the measured nitrite levels in the present study were lower than the values (0.00–3.51 μM) recorded in inner part of Izmir Bay (Kukrer and Buyukısık, 2010).

NO_3-N fluctuated throughout the sampling period at all stations. Moreover, NO_3-N showed a negative correlation with temperature ($r = -0.5147$, $p < 0.05$) which influencing NO_3-N indirectly. This can reveal that NO_3-N concentrations were higher in winter because of enhanced rainwater input as compared to summer period. The increase in summer period can be explained by the use of nitrate immediately by the phytoplankton (Kormas et al., 2001). The maximum NO_3-N value (6.99 μM) was recorded in the rainy season and this can be attributable to fresh water influx and predominantly the results of biologically activated reactions (Edokpayi et al., 2010). In surface waters of the Mediterranean Sea, in eutrophic waters, NO_3-N concentrations are usually increased at least by a factor of 2 (UNEP, 1988). In our study NO_3-N levels recorded in different periods and stations reflect eutrophic conditions. However, our results showed that NO3-N levels were lower than the measured values in waters of inner part of Izmir Bay: Kontas et al. (2004) (0.13–27 μM); 1.54–11.77 μM (Kukrer and Buyukısık, 2010), bdl-21.35 μM (Sunlu

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et al., 2012). Furthermore, NO3-N levels were higher than previously recorded levels in NE Greece waters: 0.009–0.21 μM (Sylaios and Theocharis, 2002); inner Izmir Bay waters: 0.91–4.1 μM Kukrer and Aydın, 2006) and the results found in Pagasitikos waters: 0.06–2.57 μM (Neofitou and Klaoudatos, 2008).

Generally, the stations located in Izmir inner bay showed higher o.PO_4-P values for all seasons as compared to other stations. This could be attributed to phosphorus in runoff from domestic, municipal and agricultural waste (non-point sources). Marchetti (1984) pointed out that, generally the concentration of PO_4 in the surface waters are extremely low (expressed as values for orthophosphate 0.03 μM or less), whereas in eutrophic coastal waters, typical concentrations are above 0.15 μM and in highly eutrophic system, it will be beyond 0.3 μM. In this study, except winter values, o.PO_4-P levels obtained from the stations located inner Izmir Bay were higher than this threshold level (0.3 μM) for all seasons. Comparison of the results found in the present study showed that o.PO_4-P levels were lower than the levels given by (Kontas et al. (2004) (0.01–10 μM), Kucuksezgin et al. (2005) (0.14–3.8 μM), Kucuksezgin (2011) (0.01–4.3 μM), Sunlu et al. (2012) (bdl-31.43 μM) in Middle-Inner Izmir Bay and the o.PO_4-P results were higher than Neofitou and Klaoudatos (2008) (0.01–0.28 μM).

TPO_4-P levels ranged between 0.32 and 9.62 μM with an overall mean of 2.97 ± 0.59 μM. Moreover, there were spatial ($p < 0.05$) differences for T.PO_4-P concentrations (Table 3). A remarkable increase in phosphate concentrations were recorded at Izmir Harbor, Izmir-Pasaport and Izmir Levent Marina. These stations are situated in Izmir Bay which affected directly with the relative increase in human activities. At the other locations such as Candarli and Kusadasi-Setur Marina, TPO_4 levels were very low and the N:P ratios were found high (16.39). As a consequence, phosphate could be the limiting nutrient for phytoplankton growth.

Giovanardi and Tromellini (1992) stated that the levels of TP and TN in oligotrophic waters are 0.27 and 47.2 μM whereas in mesotrophic waters these values reach 0.89 and 53.8 μM and in eutrophic seawaters 2.81 and 133.9 μM, respectively. These levels when compared with the results in the present study, the eastern Aegean Sea coastal waters are in the oligotrophic and mesotrophic conditions.

According to the results reported by Redfield et al. (1963), N/P ratio is indicating all year nitrogen importance for primary production (N/P < 16). On the other hand, the low values of N/P ratios may be related to the lower rate of consumption of reactive phosphate than inorganic nitrogen or allochthonous inputs. In addition, Buyukısık and Erbil (1987) reported that nitrogen compounds become much more limiting element based on their loss in Izmir inner bay to atmosphere.

The reactive Si values changed between 0.30 and 13.83 μM with an average value of 6.87 ± 0.82 μM (Fig. 2). Silicate is an important factor as a major nutrient for diatoms; the lowest content may be due to the phytoplanktonic uptake and slow regeneration rate from sediments. The higher concentrations of reactive silicate were indirectly proportional to the decomposition and death of diatom. Compared to previous studies, Si levels were lower than inner Izmir Bay: 1.99–41.94 μM (Kukrer, 2009), 0.16–54.12 μM (Sunlu et al., 2012).

Eutrophication is an increase in the rate of supply of organic matter in an ecosystem. Izmir-Pasaport and Candarli stations that are closer to significant pollution loadings were presented with higher percentages of organic matter and this can be attributed to the discharge of sewage wastes into the sampling stations. In this study, OM levels were within the range of obtained values (4.8–19.6%) from Engeceli Bay where fish farming activities began in 1990 (Kocak et al., 2011).

Considering PCA, in this study, most important water quality variables at sampling stations are the nutrients. (o.PO_4-P, TPO_4-P, TNO_x) accounting for 66.5% of the total variance in the whole dataset. They could be interpreted as representing influences from atmospheric and non point sources. In contrast, pH, reactive Si and DO with strong negative loadings are as another of the most significant variables thus suggesting a physicochemical source of variability.

The present study summarizes the spatial and temporal variability of the environmental characteristics of sampling points located in the eastern Aegean Sea which suffered different degrees of disturbance. The result showed that seasonal changes were generally observed for physicochemical variables while nutrient concentrations and organic matter have therefore been documented as having spatial patterns.

The physicochemical properties were significantly affected by fresh water influx during the rainy period. Furthermore, precipitation leads to large changes in temperature, salinity, flow pattern, dissolved oxygen and nutrients. The highest values of nutrients in this study were observed during the rainy season except o.PO_4-P and TPO_4-P. Conversely, salinity and conductivity were at their minimum level during the rainy period.

As a result, the high nutrient concentrations in water column are mainly associated with sources arising from various anthropogenic activities within the study area. Moreover, the spatial variability was due to increasing nutrient concentrations at the localities close to non-point sources. However, its temporal variability was related with increased rainfall especially in winter and autumn periods. In steady state, the results of Spearman rank correlation analysis between all variables in the dataset showed that a number of variables such as TPO_4-P with o.PO_4-P and NO_2-N with NH_4-N, TPO_4-P, o.PO_4-P were significantly inter-correlated. Our recorded nutrient levels were generally higher than the earlier reported results. The present information of the physicochemical properties of water would form a useful tool for further ecological assessment and monitoring of the eastern Aegean Sea coastal waters. These findings can contribute to the development of effective management strategies for the control of pollution arising from both point and non-point sources.

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