International Scholars Journals

African Journal of Ecology and Ecosystems ISSN: 9428-167X Vol. 6 (3), pp. 001-014, March, 2019. Available online at www.internationalscholarsjournals.org © International Scholars Journals

Full Length Research Paper

Physico-chemical characteristics of the open Mediterranean sea water far about 60 Km from Damietta harbor, Egypt

H. M. Faragallah[1], A. I. Askar[1], M. A. Okbah[1] and H. M. Moustafa[2]

[1]National Institute of Oceanography and Fisheries, Egypt.

[2]Department of Oceanography, Faculty of Science, Alexandria University, Egypt.

Accepted 105 January, 2019

The aim of the present study is to investigate the hydrographic characteristics, nutrient salts and some heavy metals (Fe, Cu, Zn, Pb and Ni) as well as chemical oxygen demand (COD), biological oxygen demand (BOD) and chlorophyll-a (Chl-a) in six vertical profiles in the open Mediterranean sea water far about 60 Km from Damietta harbor (Egypt). Water samples were collected during April 2007. The results revealed that most of nutrients and heavy metals are concentrated in the surface layer and decreased with increasing the depth. N/P ratio and abundance of the N-ions revealed that the area is mostly N-limiting. Enrichment factor (EF) of the metals gives low values, less than 1 indicating to the enrichment and advection of heavy metals counted each other. The results indicated that the impact of anthropogenic inputs was limited in the distribution of nutrient and heavy metals, the values of metals were similar or lower than that reported for water quality criteria (WQC) except that the Zn content was slightly higher. The relationships between the different heavy metal concentrations and the other parameters (salinity, chlorophyll-a and suspended particulate matter) were discussed. The values of BOD/ COD ratio indicated that the water of the study area has a biodegradable nature. Relatively high levels of Chl-a concentrations was recorded in the surface layer during the period of study and negative correlation was found between Chl-a and both NO_3-N, PO_4-P and SiO_4 (r= -0.58, -0.38 and -0.58, respectively).

Key words: Heavy metals, nutrient salts, hydrographic characteristics.

INTRODUCTION

Mostly Damietta is an industrial center known for its furniture, leathers, textile and sweets industries in addition to dairy products and rice mills and for its agricultural heritage. It is also a fishing industry town, with one of the largest fleets on the Mediterranean which accounts for fully half of the fishing boats of Egypt. Finally, it is well known for the port. Damietta Harbor is considered as semi closed water body affected mainly from loading /unloading operations, municipal and agricultural wastes resulting from Damietta governorate. It is generally agreed that, the pollution in near -shore waters of the Mediterranean sea has reached a critical level. This is chiefly due to the total absence of control on toxic components. River runoff (Damietta branch) has the direct effect of reducing the salinity of the surface layer of the Mediterranean sea, while tidal currents have a considerable influence on the vertical mixing of shallow water near the coast (Said and Hamed, 2001). Untreated domestic wastewater with agricultural and industrial wastes is still released through a number of drainages and outfalls along the coastal area of study (Said and Hamed, 2006).

Nutrient- type heavy elements such as Cd, Cu, Fe, Ni, are taken up by phytoplankton in surface waters and released back into the deep oceans through the oxidation of organic matter (e.g., Bruland, 1994; Wong et al., 1983). Metal availability to phytoplankton is proportional to the free ion concentration of the metal (Sunda, 1994). Marine organisms regulate available metals in response to changing environmental conditions by excreting orga-nic ligands that complex the metal and adjust the free metal ion concentration to levels optimal for the growth of

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*Corresponding author. E-mail: mohamed_okbah@yahoo.com.

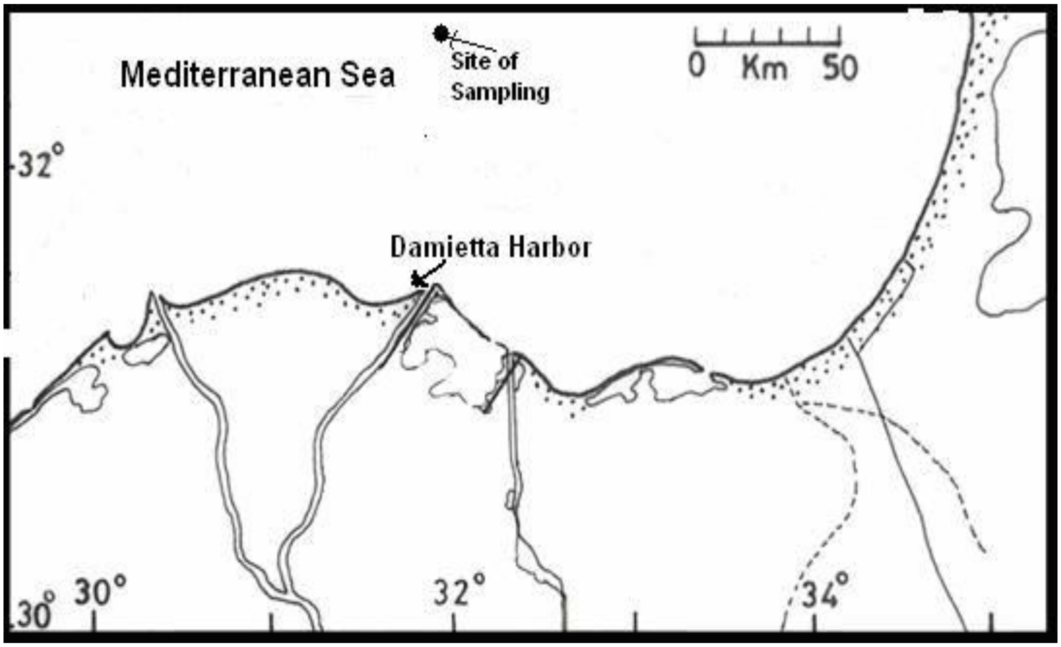

Figure 1. Sampling sites.

Table 1. Coordinates of the sampling sites of the study area.

Station No.	East	North
St. 1	397972.8	3540183.4
St. 2	398372.8	3539783.4
St. 3	398172.8	3539583.4
St. 4	398572.8	3539583.4
St. 5	398772.8	3539383.1
St. 6	399111.3	3539042.6

the organism (Morel and Price, 2003). There are important scientific and economic reasons to quantify the different forms of nitrogen and phosphorus (N and P) inputs and transformation in marine environment, excessive nutrient loading of seawater and consequently, eutrophication are important regional problems with potentially large economic impacts in terms of lost resources and reduced recreational value. Further consequences for human activities are: the decrease of water quality, aesthetic flow and navigation water problems and extinction in some water bodies of some oxygen depending organisms or animals.

Heavy metals playing a major role in the discussions on the state of pollution of the Mediterranean sea. Kremling and Petersen (1981) studied the levels of some trace metals to serve as useful background information for the open Mediterranean sea and at the same time to provide some additional insight into the geochemical cycles of the elements. The present work aimed to study hydrographic characteristics, nutrient salts and some heavy metals (Fe, Cu, Zn, Pb and Ni) as well as chemical oxygen demand (COD), biological oxygen demand (BOD) and chlorophyll-a (Chl-a) in six vertical profiles in the open Mediterranean sea water far about 60 Km from Damitta harbor (Egypt).

MATERIAL AND METHODS

Sample preparation

Seawater samples were collected from six profiles at four depths about (0.2, 10, 50 and 75 m depth) using Nisken bottles during April 2007 from the open Mediterranean sea water far about 60 Km from Damitta harbor, Egypt (Figure 1). The coordinates of the sampling sites for the study area were presented in Table 1.

Sample analysis

Hydrographic and some chemical parameters (Temperature, Salanity, pH, dissolved oxygen and ammonia fixation) were measured in-situ. Water temperature and pH were measured directly in the field using a standard Schmidt thermometer and a portable digital pH-meter (Orion Research, model 210), respectively. Salinity was determined using a Beckman Induction Salinometer (model RS-7C). The

Table 2. Concentrations (mean ± SD) for different metals in the reference material (NASS-5, national research of council of Canada).

Metals	Found (measured values)	Certified (true values)
Fe	0.199 ± 0.024	0.207 ± 0.035
Zn	0.099 ± 0.042	0.102 ± 0.039
Cu	0.301 ± 0.061	0.297 ± 0.046
Ni	0.265 ± 0.051	0.253 ± 0.028
Pb	0.009 ± 0.006	0.008 ± 0.005

classical Winkler method, modified by Grasshoff (1983) was used for determination of dissolved oxygen (DO). The method used for the determination of chemical oxygen demand (COD) was described by Fujlmori et al. (2001). The biological oxygen demand (BOD_5) determination was carried out in seawater samples following the procedure described by APHA (1985). The total nitrogen (TN) and total phosphorus (TP) were determined in unfiltered seawater samples (Valderrama, 1981), while it was filtered before analyzing PO_4-P, NO_2-N, NO_3-N and SiO_4 and kept under deep freeze until their analysis in the laboratory. PO_4-P was measured using the ascorbic acid method described by Murphy and Riley (1962). The determination of nitrite and nitrate described by Grasshff (1983), while ammonia (NH_4-N) and dissolved silicate compound is based on the method described by Koroleff (1983). Chlorophyll-a was measured according to the method described by Strickland and Parsons (1972). The measurements of dissolved nutrient salts (PO_4-P, NO_2-N, NO_3-N, NH_4-N, SiO_4) and Chlorophyll-a as well as total nitrogen and total phosphorus were performed using a Shimadzu double beam spectrophotometer UV-150-02. Ion exchange techniques have been the most commonly applied methods in determining the labiability of heavy metals in water samples (Chelex-100 ion exchange) (Van Veen et al., 2002; Gardner and Van Veen, 2004). The concentration of these metals in the final acidic extracts was measured using a GBC-932 Ver. 1.1 atomic absorption spectrophotometer in the flame mode.

Validation and quality control method

For heavy metals analysis; all reagents used were of analytical grade, Milli -Q water was used throughout the study, the glassware used were soaked in detergent, rinsed with water, soaked in 15% nitric acid for five days, rinsed with Milli-Q water and kept in the oven at 110°C till need. Seawater samples were collected in previously acid-washed polyethylene bottles. The method of validation and quality control samples were done by using a reference material (NASS-5, National Research of Council of Canada). The accuracy ranged from 90 to 110%, while precision agreed within 10%. The detection limits calculated by six determinations (in duplicate) in one batch of synthetic seawater. These limits (expressed in microgram metal per liter) 0.045 for Fe, 0.009 for Zn, 0.02 for Ni, 0.008 for Mn, 0.007 for Pb, 0.008 for Cd, 0.006 for Co and 0.03 for Cu. The results for the analyses of heavy metals in the reference material are shown in Table 2.

RESULTS

Physical characteristics

The highest temperatures occurred at the surface layer, where it ranged from 26.12 to 27.96°C, while the lowest one recorded at deep water, where it ranged from 17.57 to 18.32°C (Figure 2) . The vertical distribution of hydrogen ion concentration (pH) at the different stations of the study area is shown in Figure 2. The pH values revealed wide variations, ranged from 7.90 to 8.16 during the period of study. The minimum value was observed at station 5 at 75 m depth (pH = 7.90) and the maximum was observed at station 1 at 0.2 m depth (pH = 8.16). The highest level of the pH observed at the surface layer (its range is 8.05 – 8.16), while the lowest value was recorded at the deep layer (its range is 7.90 – 7.99).

Salinity (‰) of the water during the period of the present investigation is given in Figure 2. The present data showed that all the sites revealed narrow variation in the level of salinity content. High concentration of salinity was observed at the surface layer (0.2 m depth) comparing with that found in the bottom layer at 75 m depth. The minimum and the maximum absolute values of salinity was recorded at station 3 (38.44 and 39.44‰, respectively), the average values of salinity ranged between 38.94 ± 0.43‰ and 39.14 ± 0.20‰ (Table 3).

Dissolved oxygen in seawater for the study area (Figure 2) fluctuated between a minimum of 4.28 mgl^{-1} at station 3 and a maximum of 6.85 mgl^{-1} at station 2. The average values ranged between 5.43 ± 1.14 mgl^{-1} and 5.81 ± 1.15 mgl^{-1} (Table 3). The minimum concentration value of chemical oxygen demand (COD) was 2.71 mgl^{-1} recorded at station 1, while maximum value was 5.71 mgl^{-1} detected at station 6. Figure 2 explains the variation of COD concentrations at the investigated area; the results revealed slightly variation with depth. In the surface layer (0.2 m), the levels of COD was lower (ranged; 2.71 – 4.69 mgl^{-1}) than that detected in the deep water (75 m; 4.38 – 5.71 mgl^{-1}). The average values ranged between 3.43 ± 0.84 mgl^{-1} and 5.00 ± 0.60 mgl^{-1} (Table 3). The variation of the biological oxygen demand (BOD_5) revealed that the highest concentration (3.64 mgl^{-1}) was recorded at station 5 (75 m depth) and the lowest was (1.73 mgl^{-1}) observed at station 6 (Figure 3). The average values ranged between 1.78 ± 0.31 mgl^{-1}and 2.92 ± 0.66 mgl^{-1} (Table 3). As shown in Table 4, the ratio of BOD/ COD in the investigated area is less than one during the period of study, as follows: 0.7: 1 (St. 1), 0.7: 1(St. 2), 0.5: 1 (St. 3), 0.6: 1 (St. 4), 0.6:1 (St. 5) and 0.5:1 (St.6). The average value for all stations and depths

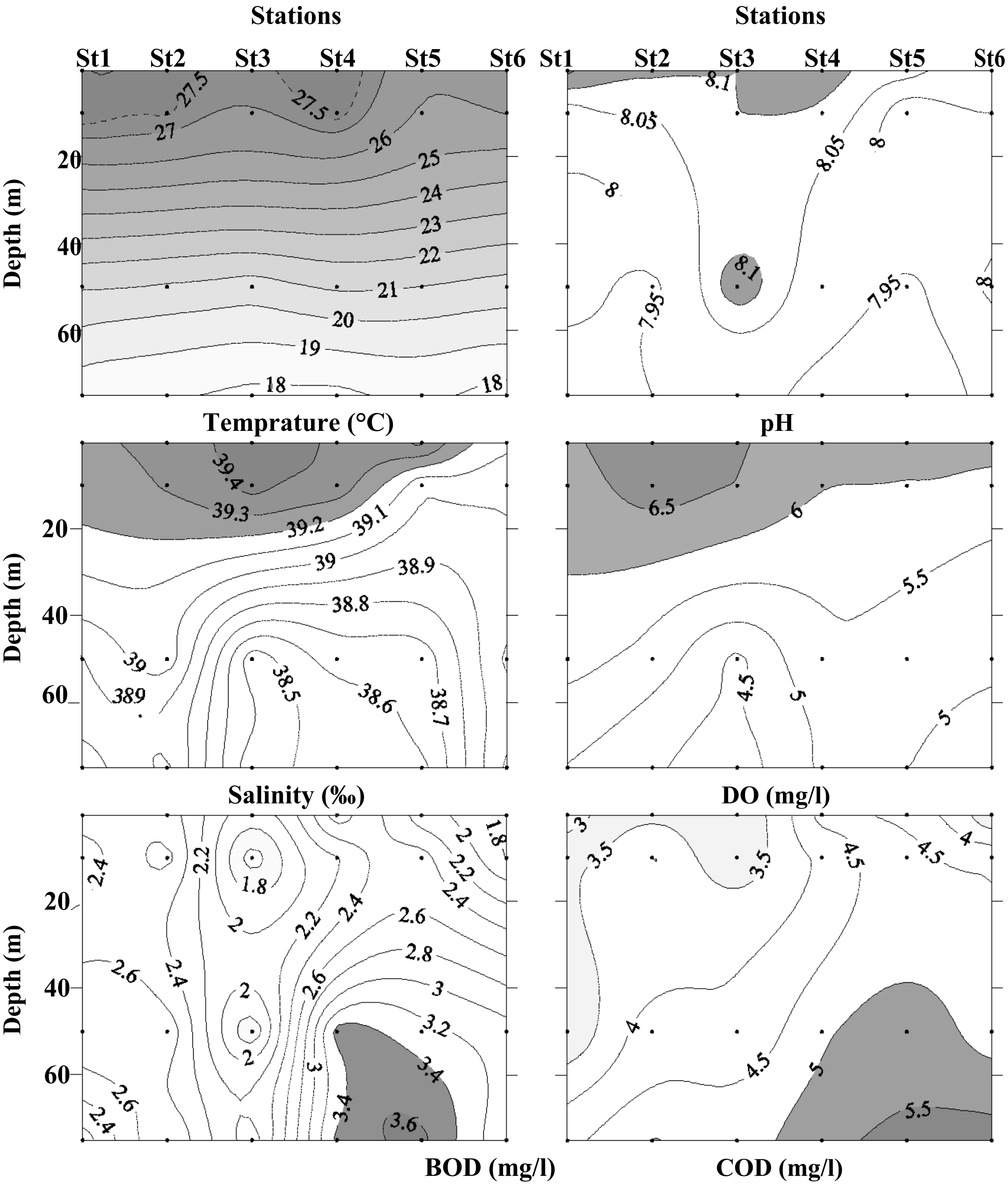

Figure 2. Vertical and horizontal distribution of physical characteristics, BOD and COD in the study area during April 2007.

of BOD/ COD is 0.6:1.

Nutrient salts, Chl-a and total suspended solid (TSS)

Dissolved inorganic nitrogen (DIN) represents the sum of NH_4-N, NO_2-N and NO_3-N content is relatively high in the different stations. The concentration of nitrite, nitrate and ammonia (Figure 3) was revealed wide variation. The average values of NH_4-N fluctuated between 0.60 ± 0.56 µM and 0.73 ± 0.60 µM. NO_2- N showed variations from 0.11 ± 0.02 µM to 0.15 ± 0.04 µM. The same trend was recorded for NO_3- N and the values are in the range of 3.40 ± 0.90 – 5.29 ±1.94 µM (Table 3). In all stations of

Table 3. Average (first line) and standard deviation (SD); second line of different parameters, April 2007.

Parameters	Stations					
	St. 1	St. 2	St. 3	St. 4	St. 5	St. 6
Temperature (°C)	22.59	23.39	23.34	22.90	22.46	23.59
	3.96	5.10	4.76	4.74	4.48	4.83
pH value	7.91-	7.93-	7.99-	7.91-	7.90-	7.97-
	8.16	8.11	8.14	8.13	8.07	8.05
Salinity (‰)	39.03	39.14	38.94	38.99	38.94	39.06
	0.27	0.20	0.50	0.39	0.43	0.05
DO (mgl^{-1})	5.79	5.81	5.43	5.65	5.68	5.47
	0.72	1.15	1.14	0.53	0.71	0.90
COD (mgl^{-1})	3.43	4.20	3.78	4.76	5.00	4.44
	0.84	0.83	0.83	0.67	0.60	1.33
BOD (mgl^{-1})	2.42	2.67	1.78	2.92	2.87	2.41
	0.35	0.16	0.31	0.66	0.78	0.68
NH_4-N (µM)	0.63	0.65	0.60	0.72	0.71	0.73
	0.47	0.41	0.56	0.60	0.60	0.60
NO_2-N (µM)	0.12	0.15	0.11	0.11	0.11	0.13
	0.05	0.04	0.03	0.04	0.02	0.07
NO_3-N (µM)	3.81	4.38	3.87	5.29	4.59	3.40
	0.99	2.58	2.21	1.94	0.87	0.90
TN (µM)	6.80	6.73	6.08	7.59	6.93	5.79
	0.91	2.38	1.46	2.46	1.32	0.62
PO4-P (µM)	0.18	0.23	0.25	0.19	0.21	0.17
	0.02	0.10	0.11	0.13	0.09	0.07
TP (µM)	0.42	0.48	0.42	0.34	0.37	0.33
	0.08	0.14	0.15	0.11	0.20	0.10
SiO_4 (µM)	2.29	1.96	1.58	1.74	1.69	0.68
	0.26	1.04	0.98	1.09	0.13	0.43
Chl-a (mgm^{-1})	1.14	1.22	1.20	1.27	1.55	1.92
	0.20	0.17	0.15	0.22	0.20	0.13
TSS (mgl^{-1})	28.32	28.83	28.61	28.47	26.72	27.82
	0.77	0.90	0.38	0.55	1.51	0.90
Iron, Fe (μgl^{-1})	32.38	34.07	43.31	28.66	43.73	30.64
	10.01	16.81	21.59	7.67	13.99	7.02
Copper, Cu (μgl^{-1})	5.70	6.74	5.37	2.81	2.00	2.66
	3.85	1.90	2.24	2.65	1.10	0.39
Zinc, Zn (μgl^{-1})	32.75	34.65	38.22	25.94	28.78	32.25
	27.78	24.02	7.58	17.33	26.02	12.66
Lead, Pb (μgl^{-1})	4.04	4.33	4.03	4.57	2.93	3.26
	2.60	2.44	2.50	1.59	2.38	2.54
Nickel, Ni (μgl^{-1})	0.20	0.17	0.12	0.12	0.10	0.15
	0.11	0.13	0.00	0.00	0.00	0.03

the study area, the highest values of DIN were recorded at stations 2, 4 and 5 with a concentration of 5.18, 6.12 and 5.41 µM, respectively.

Total nitrogen (TN) concentration in the investigated area showed narrow variation, ranging between 5.79 ± 0.62 µM at station 6 and 7.59 ± 2.46 µM at station 4 (Table 3). As shown in Figure 3, the greater values of TN exhibited in bottom layer at 75 m depth, while the lowest level was recorded in the surface layer (0 – 10 m). The high level of TN is attributed to the high content of DIN.

The distribution of reactive phosphate (PO_4-P) in the study area is shown in Figure 3. The average values ranged between 0.17 ± 0.07 µM at station 6 and 0.25 ± 0.11 µM at station 3 (Table 3 and Figure 3). The

Table 4. BOD/COD ratio in the study area.

Depth (m)	Stations					
	St. 1	St. 2	St. 3	St. 4	St. 5	St. 6
0.2	0.93	0.74	0.62	0.58	0.47	0.57
10	0.67	0.66	0.47	0.54	0.53	0.41
50	0.92	0.64	0.40	0.71	0.61	0.65
75	0.48	0.56	0.45	0.64	0.65	0.53
Min	0.48	0.56	0.40	0.54	0.47	0.41
Max	0.93	0.74	0.62	0.71	0.65	0.65
Average	0.73	0.65	0.49	0.62	0.57	0.54

concentration of PO_4-P was lower in the surface seawater (its range is 0.09 – 0.17 µM) comparing with relatively high levels in the deep water at 75 m depth (its range is 0.20 – 0.35 µM), relatively high values of PO $_4$-P were recorded at sites 2, 3 and 4 (around 0.33 µM at 75 m depth). In general slightly variations were observed in the content of PO_4-P at the surface layer (0.2 m depth). The total phosphorus concentrations were generally relatively high in the seawater of the study area (Figure 3). It ranges from 0.18 µM (station 5) at 0.2 m depth to 0.64 µM at station 2 at 75 m depth. The highest average concentration of total phosphorus was recorded at station 2 (0.48 ± 0.14 µM) compared with lower value (0.33 ± 0.10) for station 6 (Table 3). The reactive phosphate (PO_4-P) content was represented approximately 50% of the TP concentration (its range is 35 – 74% of TP) which only was in the form of inorganic PO_4-P (Table 5).

The results in Table 6 showed the spatial variations of N/ P ratios in the investigated area, ranged from 9 at station 2 and 64 at station 4. The average ratios of N/ P are 21:1, 20:1, 15:1, 39:1, 27:1 and 24:1 at stations 1, 2, 3, 4, 5, 6, respectively.

The lowest silicate values were recorded in the upper layer for all stations and increased gradually with increasing depth. The regional distribution of the reactive silicate in the study area is presented in Figure 3. It fluctuated between 0.23 and 3.26 µM at stations 6 and 2, respectively. The average value of SiO_4 varied between a minimum of 0.68 ± 0.43 µM and a maximum of 2.29 ± 0.26 µM (Table 3).

Chlorophyll-a (Chl-a)

Chlorophyll- a concentration is considered as a good indicator of the phytoplankton biomass. The absolute concentration of Chl- a was exhibited lower value at station 1 (0.92 mg m^{-3} at 0.2 m depth), while the highest value at station 6 (2.06 mg m^{-3} at 10 m depth) (Figure 4). The results as shown in Table 3 revealed relatively high average concentration of Chl-a. It ranged from 1.14 ± 0.20 to 1.92 ± 0.13 mg m^{-3}.

Total suspended solid (TSS)

Total suspended solid consists of lithogenic material and biogenic parts including of plankton and detritus, the absolute value of total suspended solid content was fluctuated between minimum value of 25.39 mg l^{-1} at station 5 at 50 m depth and maximum value of 29.70 mg l^{-1} at station 2 at 0.2 m depth. The average values in the study area ranged between 26.72 ± 1.51 and 28.83 ± 0.90 mg l^{-1} (Table 3).

Heavy metal distributions

The average values of Iron (Fe) concentration in the study area are shown in Figure 4 and Table 3, it ranged from 28.66 ± 7.67 to 43.73 ± 13.99 $µgl^{-1}$. The vertical distribution of Fe revealed high levels in the surface layers at stations 1, 2, 3 and 4 and decreased with depth at stations 5 and 6. It ranged from 22.23 to 67.89 $µgl^{-1}$. On the other hand, the deep layer (75 m depth) at stations 5 and 6 showed low concentration of Fe, ranged from 35.24 to 52.89 $µgl^{-1}$. In general, Fe profile concentration revealed irregular variation in its distribution (Figure 4). As shown in Figure 4, the copper profile concentration is remarkable in the surface water; the values tend to be higher at the surface water (2.23 – 10.75 $µgl^{-1}$) than deep water values (1.34 – 6.37 $µgl^{-1}$). In general, the average values of Cu ranged from 2.00 ±1.10 $µgl^{-1}µgl^{-1}$ at station 5 to 6.74 ± 1.90 $µgl^{-1}$ at station 2 (Table 3). The results revealed wide variation in the distribution of Zn concentrations (Figure 4). Surface Zn concentration varied between 10.32 and 63.40 $µgl^{-1}$, with the highest concentrations during the period of study. Although no clear spatial pattern could be established, maximum values were always found at the surface layer (0.2 - 10 m). The average Zn content ranged from 25.94 ± 17.33 $µgl^{-1}$ at station 4 and 38.22 ± 7.58 $µgl^{-1}$ at station 3 (Table 3). The lead (Pb) concentrations were generally increased at the surface layer and remained relatively low at intermediate at 50 m depth, but it decreased to six folds at deep waters, 75 m (Figure 4). Pb concentrations in the study area ranged from 0.85 to 6.76 $µgl^{-1}$ at stations 6 and

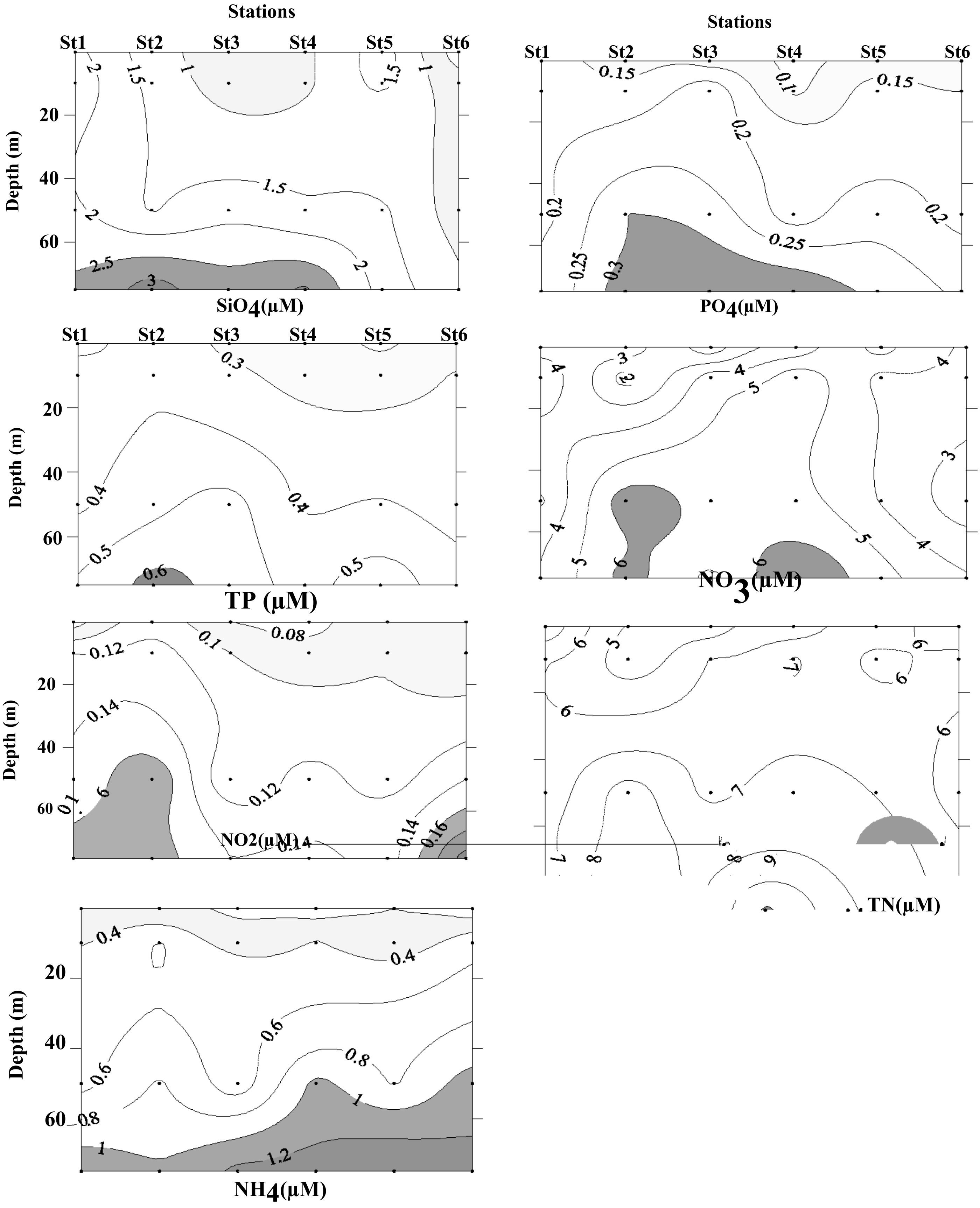

Figure 3. Vertical and horizontal distribution of nutrient salts in the study area during April 2007.

Table 5. Percentage of reactive phosphate (PO_4-P) from the TP concentration.

Depth (m)	Stations					
	St. 1	**St. 2**	**St. 3**	**St. 4**	**St. 5**	**St. 6**
0.2	40	35	48	36	67	43
10	51	40	73	35	69	48
50	47	64	52	45	59	51
75	39	52	63	74	50	56
Min	39	35	48	35	50	43
Max	51	64	73	74	69	56
Average	45	48	59	50	61	50

Table 6. N/P Ratios profile observed offshore for the study area.

Depth (m)	Stations					
	St. 1	**St. 2**	**St. 3**	**St. 4**	**St. 5**	**St. 6**
0.2	21	29	10	36	45	39
10	27	9	19	64	21	24
50	16	22	20	31	16	13
75	20	19	13	21	19	17
Min	16	9	10	21	16	13
Max	27	29	20	64	45	39
Average	21	20	15	39	27	24

6 and 2, respectively. The average values of Pb concentration in the study area are shown in Table 3, it ranged from 2.93 ± 2.38 μgl^{-1} at station 5 to 4.57 ± 1.59 μgl^{-1} at station 4. Figure 4 shows the concentration of nickel (Ni) during the study period, the concentration decreased to lower level at most of stations and it is not detected at surface layer at stations 3, 4 and 5.

DISCUSSION

Temperature is affected by several factors include weather, removal of shading stream bank vegetation and storm water. The highest level of the pH observed at the surface layer while the lowest value was recorded at the deep layer. The wide variety of aquatic animals prefers of pH ranged between 6.50 and 8.00. Outside this range the diversity may be reduced because it stresses the physiological systems of most organisms and can reduce reproduction. Low pH can also allow toxic elements to become more available for uptake by aquatic plants and animals. This can produce conditions that are toxic to aquatic life. The highest dissolved oxygen were recorded in the surface water and gradually decreased with increasing depth. It is obvious, from the distribution of dissolved oxygen profile that the decreasing levels reached to two units. This may be due to several factors, respiration of organisms and the increased rate of decomposition of organic matter.

The increasing of human population and industrial activity, organic contamination is the most serious problem for water quality. Heavy contamination causes an oxygen deficit due to decomposition of the organic matter. The amount of oxygen required oxidizing dissolved and particulate matter, called the chemical oxygen demand (COD), it is a practical measure of organic contamination, which is an environmental serious problem. Organic matter is mainly produced by photosynthesis of phytoplankton in the heavily eutrophied water body, COD is therefore well correlated with the concentration of chlorophyll-a ($r = 0.559$ $p < 0.05$), which is a measure of phytoplankton biomass (Ogawa and Ogura, 1990a). The photosynthesis of phytoplankton is mainly controlled by factors of solar radiation, water temperature and nutrients such as inorganic nitrogen and phosphate (Parsons et al., 1984). Generally, the present data comparing with that recorded by Okbah and Nasr (2006) at Damietta estuary region revealed lowest levels of BOD in the study area (the average ranged from 0.33 ± 0.10 to 0.48 ± 0.14 mgl^{-1}), while increased BOD concentrations fluctuated between 12.96 and 23.20 mgl^{-1} in Damietta estuary region. The type of wastewater discharge can be determined according to BOD/COM (ECPH, 1975). 1:1 ratio reveals well-purified water; the

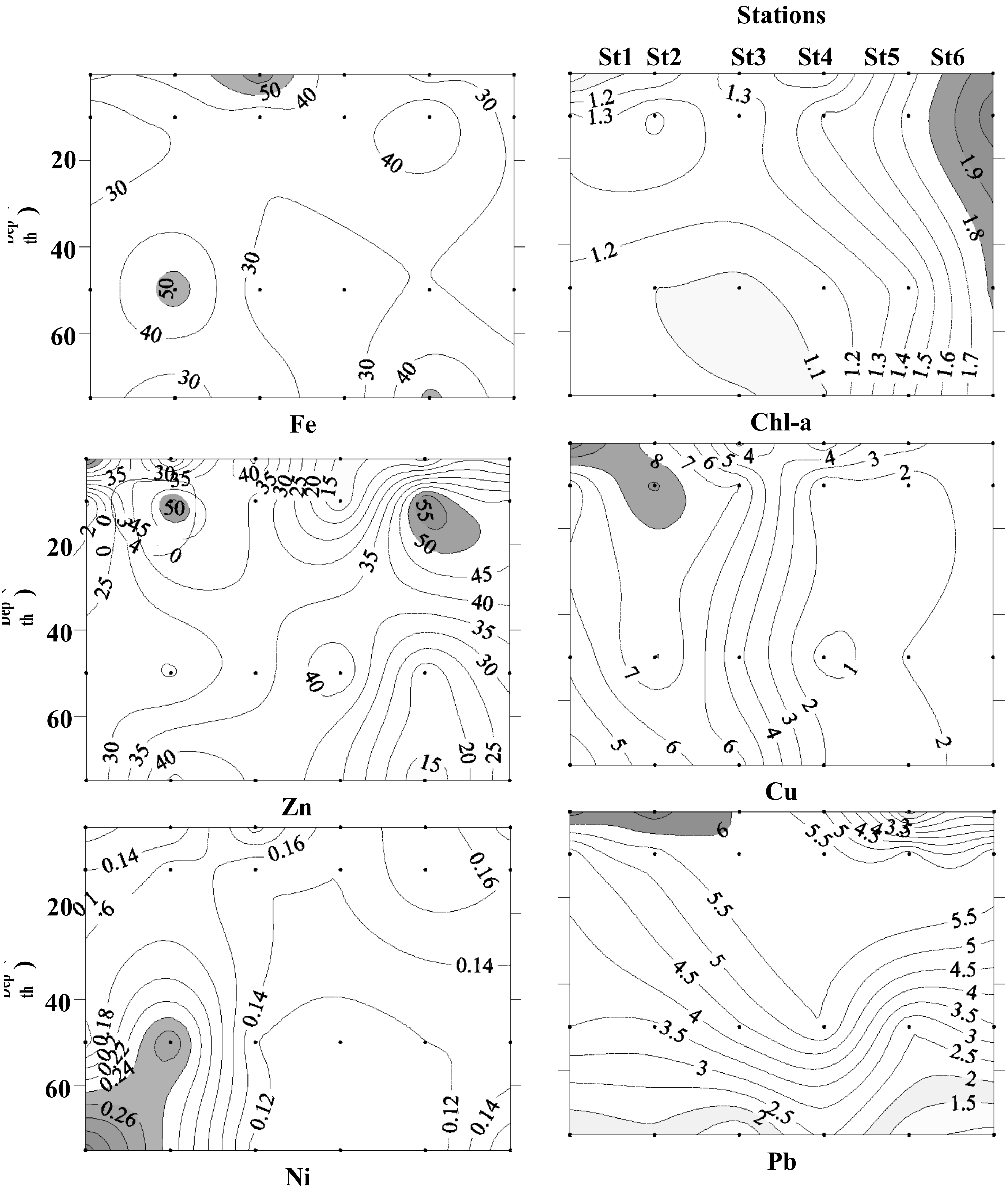

Figure 4. Vertical and horizontal distribution of Chl-a and heavy metals in the study area during April 2007.

Table 7. Correlation matrix between all parameters analyzed in the study area.

	T°C	pH	S‰	DO	COD	BOD	TP	PO_4-P	NO_2-N	NO_3-N	NH_4-N	TN	SiO_4	Chl-a	TSS	Cu	Fe	Zn	Ni	Pb
T°C	1.000																			
pH	0.712	1.000																		
S‰	0.822	0.578	1.000																	
DO	0.915	0.548	0.807	1.000																
COD	-0.646	-0.518	-0.519	-0.660	1.000															
BOD	-0.440	-0.371	-0.347	-0.303	0.676	1.000														
TP	-0.747	-0.486	-0.660	-0.733	0.349	0.268	1.000													
PO_4-P	-0.744	-0.544	-0.580	-0.728	0.447	0.264	0.827	1.000												
NO_2-N	-0.780	-0.692	-0.527	-0.641	0.496	0.403	0.618	0.574	1.000											
NO_3-N	-0.378	-0.416	-0.289	-0.379	0.590	-0.071	0.387	0.499	0.269	1.000										
NH_4-N	-0.897	-0.746	-0.747	-0.801	0.685	0.507	0.728	0.675	0.809	0.335	1.000									
TN	-0.553	-0.524	-0.447	-0.518	0.295	0.185	0.580	0.644	0.378	0.842	0.557	1.000								
SiO_4	-0.541	-0.474	-0.517	-0.486	0.174	0.104	0.678	0.595	0.468	0.536	0.524	0.717	1.000							
Chl-a	0.187	-0.485	0.215	0.131	0.559	-0.502	0.501	-0.382	-0.130	-0.581	-0.113	-0.383	-0.578	1.000						
TSS	0.651	0.614	0.619	0.576	-0.666	-0.575	-0.319	-0.370	-0.410	-0.089	-0.584	-0.205	-0.144	-0.155	1.000					
Cu	0.289	-0.426	0.384	0.295	-0.507	-0.272	0.195	0.079	-0.037	-0.061	-0.242	-0.008	0.171	-0.493	0.540	1.000				
Fe	0.098	-0.535	0.598	0.169	-0.150	-0.007	0.012	-0.011	-0.021	-0.161	-0.086	-0.083	-0.140	-0.521	0.481	0.580	1.000			
Zn	0.547	0.449	0.798	-0.015	-0.074	-0.069	-0.077	-0.585	-0.678	-0.059	-0.587	0.649	0.580	-0.422	0.436	0.487	0.461	1.000		
Ni	0.699	0.714	0.921	-0.019	-0.785	-0.658	-0.821	-0.542	-0.658	-0.711	-0.620	0.685	0.514	-0.146	0.372	-0.259	0.587	-0.452	1.000	
Pb	0.757	0.565	0.558	0.667	-0.575	-0.301	-0.427	-0.472	-0.629	-0.248	-0.648	-0.329	-0.395	-0.079	0.605	0.287	0.484	0.262	0.647	1.000

N = 24 $p < 0.05$ Significant at r > 0. 35.

biodegradable matter has a ratio 2:1. Finally the ratio that ranged between 2:1 and 4:1 is specific to crude domestic sewage. The ratio of BOD/ COD in the study area is < 1; these values indicate that the water of the study area has a biodegradable nature.

The relatively high concentration of inorganic nitrogen species may be attributed to the decomposition of organic matter in the area. This was also supported by the significant negative correlation between the contents of DIN and the COD (r = -0.41, 0.59 and 0.68, respectively) . Generally, high level of DIN was found in the present study compared with that reported by Kremling and Petersen (1981) for the open Mediter-ranean sea. The wind movement is an important factor, influencing the discharge of drainage water containing nitrogen compounds. The relative decrease of DIN in the surface seawater may be as a result of nutrients consumption by phytoplankton and aquatic plants which are more concentrated in the surface layer. This was confirmed by the relatively high levels of Chl-a concentrations recorded in the surface layer during this period (Figure 4) and negative correlation was found between Chl-a and NO3-N (r = -0.58). Generally, the present investigated area showed lower content of total nitrogen in comparison with the values reported in the other region of the Mediterranean sea (Fahmy et al., 1996).

The high level of reactive phosphate is mainly to the diffusion and migration of phosphorus from the sediment pore water to the overlying water. Also, the consumption rate is higher at the surface layer than the bottom. The concentrations of PO_4-P revealed a decreasing trend with depth, suggesting that at higher temperature and regeneration in the study area, the metabolic activity increases and affect PO_4-P content (Edmond et al., 1985). Significant negative correlation was observed between the dissolved phosphate concentrations and the amount of total suspended solid (TSS) in the water ($r = -0.37$; $p < 0.05$; $n = 24$). Sanders et al. (1997) showed that the removal of PO_4-P by total suspended solid ranged from 30 to 80% of phosphate input. Many studies have demonstrated that the interactions of DIP with total suspended solid represent one of the most important mechanisms affecting the behavior of phosphorus (Pratska et al., 1998). Also, indicating that large portion of TP was found in particulate and organic phosphorus. This pattern supports the idea that a large fraction of TP is transported in suspension bound to sediment particles (Perez et al., 2003). In general, the water movement and re-suspension of the sediments of the study area led to relatively high content of phosphorus and nitrogen compound especially in the bottom water at 75 m depth.

According to the results reported by Redfield et al. (1963), N/ P ratio is 16:1, indicating that the N/ P ratio of the present study is higher in most stations than that of Redfield ratio and reflecting higher nitrogen content in comparison with phosphorus in the present study. On the other hand, the low values of N/P ratios may be related to the higher rate of consumption of reactive phosphate than inorganic nitrogen, also the low values of the N/P ratio may be as a result of an allochthonous condition from wastewater drainage. This could suggest that nitrogen is the most limiting factor for the growth of phytoplankton.

Silicate is an important factor as a major nutrient for diatoms; the lowest content may be due to the uptake of silicate by phytoplankton as well as to the slow rate of regeneration of silicate from the sediments. The higher concentrations of reactive silicate were indirectly proportional to the decomposition and death of diatom, in addition to the increase of generation rate from underlying sediments. This may be the major's factors influencing silicate variability in the present study. It is interesting to observe that the higher concentrations of reactive silicate are controlled by the content of dissolved oxygen. This can be explained by the fact that in very badly oxygenated area, the decomposition of siliceous compounds increases under the effect of aerobic bacteria (Okbah and El-Gohary, 2002).

The simple regression analysis between Chl-a and both PO_4-P and NO_3- N indicated a poor linear relationship (r = -0.38 for PO_4- P and r = -0.58 for NO_3-N). This may be related to the rapid utilization of NO_3-N and PO_4-P by phytoplankton. On the other hand, there is a significant positive relationship between ammonia and Chl-a content; (r = 0.5). This may reflect the role of ammonia content in the growth of phytoplankton and the biological processes.

The highest values of total suspended Solid (TSS) were directly affected on the levels of transparency. In general, the values of TSS in the open seawater revealed low levels of organic and inorganic matter produced by living organisms as well as terrigenous particles transported by land run off.

The level of Iron concentration increased around 100 folds than that recoded by Kremling and Petersen (1981) (0.18 - 0.83 $\mu g l^{-1}$). Also, their results revealed that the samples from the Egyptian coast which were taken between about 5 and 50 km off the African continent (20 m depth) showed a slight tendency for higher Cu value (0.21 - 0.36 $\mu g l^{-1}$), they showed that the higher concentrations may, therefore, be transported from earlier deposits the near shore side.

For comparison, Okbah and Nasr, 2006 reported an average Cu concentration (0.93 ± 0.35 $\mu g l^{-1}$) along the Mediterranean in front of Nile Delta region, Egypt. In the Gulf of Lions, the average Cu concentration was found to be 2.80 nM (Morley et al., 1990), whereas in the Western Mediterranean it fluctuated around 1.50 nM (Morley et al., 1997). Copper is known to have both a deep remineralization cycle and an affinity to sinking particles. This process is most likely the cause of the removal of dissolved forms of copper, from the water column. Thus, a permanent gradient in Zn concentrations, between high salinity surface and saline subsurface layers, were established throughout the profile. This feature, expected from the scavenging character of Fe, may also be enhanced by the presence of distinctive water masses. Furthermore, it has been demonstrated by many authors (Sunda and Huntsman, 1988; Sholkovitz et al., 1994) that sunlight favors photo reduction of particulate Fe oxides in the euphotic zone, causing dissolved forms of Fe to increase.

This pattern is in accordance with what has been stated by many authors (Laumond et al., 1984; Copin-Montegut et al., 1986; Tankere and Statham, 1996; Achterberg and Van den Berg, 1997; Morley et al., 1997), that is, that surface depletion of trace metals is not obvious in the Mediterranean, due to the proximity of local sources and the oligotrophic character of the area. Consequently, it appears from the present data set, that mechanisms other than biogenic activity play a more important role in the distribution of heavy metals in the seawater.

As with the other metals, maximum values were always encountered at the surface layers. Pb concentrations in the study area were found to be similar to those reported by Okbah and Nasr (2006). The results for Pb concentration reported in the literature shows that the concentrations observed here are higher than those recorded in the Eastern Harbor, El-Max Bay, Arabian Gulf, and the Red Sea (Shriadah and Emara, 1991; Shriadah et al., 2004) and are similar to those of the south Agean, Greece (Voutsinou-Talladour et al., 1997). In general, the data for dissolved Pb concentration in this study were increased 100-fold in comparison with those reported by Martin and Whitfield (1983) in the coastal waters (0.03 μgl^{-1}). On the other hand, dissolved Pb in the coastal zone of the Mediterranean Sea of Egypt is lower than the minimal risk concentration (10 μgl^{-1}) reported by WQC (1972). In the present study, the concentrations of copper (Cu) and Lead (Pb) were increased at the surface layer of the whole of the study area. From the pattern described in Figure 4, it is clear that any involvement of this element in the biological processes of the euphotic zone is masked by the strong inputs existing in the area.

In order to identify the relative importance of dissolved heavy metals on the study area, the present study compared the concentrations on the surface layer of each station, with those in the deep layer of the area, during the period of study. It was considered that the minimal risk concentration of heavy metals reported for water–quality criteria (WQC, 1972) are 50 µg/l for Fe; 20 µg/l for Zn; 10 µg/l for Cu; 2 µg/l for Ni and 10 µg/l for Pb, the enrichment factors (E_f) had been calculated based upon these concentrations of heavy metals. E_f values greater than 1 indicate the enrichment of the waters with heavy metals, relative to the water–quality criteria. From the results of the presented study, it is clear that the average of all the metals have low E_f values; in most cases this falls below 1, indicating that enrichment and advection of heavy metals counteract each other.

Correlation matrix (Table 7) was carried out on the data set of nutrient salts, heavy metals and hydrographic condition, to describe the behavior and the association of the heavy metals with all parameters. The variability of dissolved heavy metals (Cu, Fe, Zn, Ni and Pb) revealed elevated values comparing with those reported in the other related studies. This may be explained as a result of the effect of the agitation of the bottom sediments, which have relatively high metal concentrations. This could be confirmed by the relationship between the concentration of dissolved heavy metals with the values of total suspended solid (r = 0.540, 0.481, 0.436, 0.372 and 0.605, respectively. at $P < 0.05$). The decomposition of organic matter and release of metals might explain the high content of heavy metals in the aquatic system (Swift, 1996). The relationship between the concentrations of dissolved heavy metals with the values of Chl-a concentration revealed significant negative correlations with Cu, Fe and Zn content (r = -0.493 and -0.422 at $P < 0.05$). This may suggest that Cu, Fe and Zn are important elements in the biogeochemical cycle of phytoplankton growth (Tada et al., 2001). Generally, the biological factors seem to have a strong influence on bioaccumulation of the metals. The present work suggested that the biological uptake may the main factor controlling the removal mechanisms of dissolved heavy metals. In the study area, phytoplankton play an important role in the distribution of the dissolved metals; directly, through the uptake them (negative correlations between Ch1-*a* and these metals (Cu, Fe and Zn) and indirectly by increasing the pH, followed by a transition of the dissolved heavy metals to the particulate form (Turner and Millward, 2002; Che et al., 2003), this can be confirmed by the negative correlation between the pH values and dissolved trace metals concentrations (r = -0.426 for Cu; -0.535 for Fe; -0.449 for Zn; -0.714 for Ni and -0.565 for Pb at $P < 0.05$).

The correlation matrix for the different heavy metals in the present work showed that there were significant correlations for some pairs of heavy metals (Table 7). The correlation of Pb with both Zn and Cu was poor ($r < 0.30$), thus indicating that a local high concentration for one metal as a result of possible contamination does not necessarily indicate high values for other metals. This also reflects different sources and different biogeochemical behaviors (Fahmy et al., 1997; Shriadah, 1999). On the other hand, a significant positive correlations ($P < 0.05$) were found between several pairs of heavy metals; Fe with Cu, Zn, Ni and Pb concentrations (r = 0.580, 0.461, 0.587 and 0.484, respectively.). This reflects the role of Fe in scavenging other metals and the solubility's of Cu, Zn, Ni and Pb are affected strongly by the solubility of Fe (Turner et al., 2004a). The relationship between salinity (S ‰) and heavy metals (Cu, Fe, Zn, Ni and Pb showed significant positive correlations (r = 0.384, 0.598, 0.798, 0.921 and 0.558, respectively at $P < 0.05$). This appears that the increasing in dissolved heavy metals with increasing salinity and may be indicated that these metals discharged from the same sources. The interpretation of the relationship between any two metals may be related to several main factors which are the stability constants of trace metal complexation reactions, the input of trace metals into water bodies; the quantities of ligand which refer to the binding sites (Tessier et al., 1985; Yu et al., 2001). In general the correlation matrix in the present work gives an indication that the dissolved metals are not mainly related to the anthropogenic materials, but they are associated with the original material in this area and reflect the complexing nature of the organic matter. The significant positive correlation between TP and Chl- a ($r = 0.501$ at $P < 0.05$) revealed that relatively a great amount of phosphate may be due to decomposition of living organisms. The important role of PO_4-P and NO_3- N for increasing of phytoplankton were observed from the correlation between Chlorophyll-a and both reactive phosphate and nitrate ($r = -0.382$ and -0.581, respectively), the negative correlation related to the consumption of these nutrients in the growth of phytoplankton. The relationship between Chl- a and reactive silicate revealed significant correlation ($r = -0.578$ $p < 0.05$). In general, the decrease in silicate concentrations is due principally to uptake by diatoms.

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