Nutrient Salts and Chlorophyll-a During Short Term Scale in the Eastern Harbor, Alexandria (Egypt).

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ABSTRACT The present study aims to follow the changes of NH_4-N, NO_2 -N, NO_3-N, PO_4-P, SiO4, chlorophyll-a (Chl-a), OOM and pH-values in a rapid short-term variation. During the period from August 2004 - 2005, 136 surface water samples were collected three times every week from the Eastern Harbor, Alexandria (Egypt). The study revealed that the pH values lie in alkaline side, with a range of (7.53-8.70), Chl-a showed a wide range (0.41–78.68µg/l) with an average value of 13.60 µg/l. The range and the average obtained values of nutrients (µmole/l) were; 0.47-10.40(2.23) for NO_3-N, 0.12–1.48 (4.06) for NO_2 -N, 0.35–6.19(2.23) for NH_4-N, 0.04-8.58(1.03) for PO_4-P, and 0.37-11.90(3.45) for SiO4. The values of OOM ranged from 0.42 to 17.50 mg O_2/l with an average value of 4.73mg/L. The distribution of both NO_3-N and NH_4-N were referred to that the rate of nitrification and denitrification is mostly similar. The N/P ratio (4.76) in the present study is lower than Redfield's ratio , indicated that nitrogen is the limiting factor. The levels of nutriens and chlorophyll-a indicated that the harbor is in eutrophic condition.

(**Keywords***:* Eastern Harbor, N/P ratio, nutrients, chlorophyll-a, Alexandria)

INTRODUCTION

The continuous release of untreated domestic ,industrial and agricultural wastewater in the Eastern, Western and El-Dekhaila Harbors of Alexandria (Egypt) has turned them highly eutrophic basins, the three harbors are characterized by abnormally heavy phytoplankton blooms, high chlorophyll-a and low diversity index [1]. The increasing of population has been associated with the The harbour was affected by the direct sewage from eleven outlets distributed along its south and southwest coastline (about 15,000 m^3/d and 10,000 m^3/d in winter and summer, respectively,[3]. After 1993, all sewers of the harbor were closed, except those of Kayet Bay and EL-Silsilla, due to the diversion of sewage discharge into Lake Mariot [4]. Recently, numerous studies have been carried out on the physical, chemical and biological characteristics of the Eastern Harbor. Faragallah [3] studied seasonally the distribution of nutrients through the sediment-water interface in EH. Awad [5] pointed out that, the effect of variable environmental factors, causing eutrophication condition and abnormal flourishing of phytoplankton and consequently play a crucial role in changing water quality of the harbor. Phytoplankton intensive development of human activities, which directly or indirectly have led to the increase in nutrient enrichment in the harbor[2] and the consequent increase in the level of eutrophication during the past three decades. Eutrophication has become a persistent problem in the Eastern Harbor of Alexandria and was recorded since 30 years ago. These problems came about as a result of the continuous enrichment of nutrients from different sources.
species and fish mortality relationships in the harbor were studied by Mikhail et al., [6]. EL-Geziry and Maiyza [7] studied seasonally the hydrographic structure of the Harbor. Madkour et al [4] studied weekly the surface salinity, nutrients and dynamics of phytoplankton community. The potential impact of some a biotic parameters on a phytoplankton community in a confined bay of the eastern Mediterranean Sea (Eastern Harbor of Alexandria) studied by[8]. Mikhail et al., [9] studied the blooming of toxic microalgae and co-occurring ciliates, heterotrophic and mixotrophic dianoflagellates in the harbor.
The present study aims to follow the changes of nutrient salts and chlorophyll-a in a rapid short-term variation which were not recognizable through the monthly or seasonally records.

MATERIALS AND METHODS

Area of Study

Eastern Harbor (EH) is a shallow semicircular bay (area 2.53 km^2), situated between longitudes 29° 53' and 29° 54' E and latitudes 31° 12' and 31° 13' N (Fig. 1). The harbor is communicated with the Mediterranean Sea through two openings called EL-Boughaz (main opening) and EL-Silsilla. The bottom slops gradually from coastline towards the center of the harbor behind the main opening. The overall average depth of the harbor is about 6m. Nutrient salts and organic matter in the Eastern Harbor may be related to the investigated area was subjected to additional amount of waste water from different land sources, mainly from the sewer of Alexandria at kayet Bey.

Samples collection and measurements

Surface water samples (136 samples) were collected from three stations of the Eastern Harbor during the period from August 2004 to August 2005 (Fig. 1). The samples were chosen to represent the sites which the red tide phenomenon is occurred. Water samples were taken three times every week by attaching a cleaned two liters polyethylene bottle immersing to a depth 20-cm below the surface water. Samples for nutrient salts were immediately filtered through Whatman GF/C filters and kept frozen until analysis, except the samples of ammonia were fixed in the field with out filtration. The pH value was measured using a pocket pH meter (model 201/digital pH meter). Oxidizable organic matter (OOM) was determined using permanganate values test [11]. Dissolved inorganic nitrogen compounds DIN (NH_4-N, NO_2-N and NO_3-N), reactive phosphate (PO_4-P) and reactive silicate (SiO_4) were determined according to Grasshoff [12]. Chlorophyll-*a* in the surface water was extracted with 90% acetone and measured spectrophotometrically using the SCORE UNESCO equation given in Strickland & Parsons [13]. The measurements of dissolved Nutrient salts (PO_4-P, NH_4-N, NO_2-N, NO_3-N and SiO_4) and Chlorophyll-*a* were performed using a Shimadzu double beam spectrophotometer UV-150-02.

Statistical analysis

Matrix correlation, Eutrophication Index, Nitrogen / Phosphorus ratio (N/P ratio) were calculated. Also, simple regression equations at p =0.05 were estimated to reveal the relationship between the Chl-a and nutrient salts concentrations was performed. These analyses were applied to interpret the data and influence from many sources before the period 2001; eleven outfalls located along the region of Eastern Harbor basin originally designed to discharge the Corniche street surge waters during the winter rainy season. These sewage effluents have led to a considerable increase in the level of most of the nutrients and heavy metals in the harbor's water compared with their counterparts outside in the waters of the Mediterranean Sea [10], Eastern Harbor of Alexandria is used as a dock for fishing-ships and as a recreational area for peoples of Alexandria and also as a place for all kinds of water sports including, fishing, swimming, sailing [3]. The to get better information about the water types of the studied system.

Results and Discussion

pH

Hydrogen ion concentration plays an important role in many of the life processes. Living organisms are very dependent on, and sensitive to pH. Not only is the hydrogen ion a potential pollution in itself, but it is also related intimately to the concentration of many other substances, particularly the weakly dissociated acids and bases. The concentrations of pH (Fig. 3) ranged from 7.53 to 8.70. The distribution of pH shows that most reading was > 8 with few picks during August 2004 (< 8). Generally, the values of pH measured in E.H are still lying on the alkaline side reflecting the high buffer capacity in sea water of E.H. The present data was in agreement with that reported by Abdel- Halim and Khairy [8]; they showed that the changes of pH in the area mainly related to photosynthesis activities of phytoplankton, aquatic plants, respiration and variation in temperature.

Oxidizable organic matter (OOM)

Oxidizable organic matter ranged from 0.42 to 17.5mg/l with average 4.73mg/l. As shown in Fig. 3, the distribution of OOM indicates that the concentration during the days of 2005 is higher than that during 2004. Also show that there are two periods characterized by high levels of OOM, the first from 11/8 to 29/11/2004 (ranged; 0.42-12.25mg/l) and the second period from 14/4 to 30/8/2005 (ranged; 1.28-16.10mg/l). But from 29/11/2004 to 14/4/2005 was characterized by low levels of OOM (>1.88<3.14mg/l). The main values of the oxidizable organic matter in the study area were approximately similar to those recorded for El-Mex Bay and El-Dekhaila Harbor; around 5.8 mgO_2/l [14].On the other hand, the values of OOM was increased two folds than that recorded by Aboul Kassim [15].

Dissolved inorganic nitrogen (DIN)

Ammonia (NH_4-N), Nitrite (NO_2-N) and Nitrate (NO_3-N)

Ammonia is the major nitrogenous product of the bacterial decomposition of organic matter containing nitrogen, and is an important excretory product of invertebrates and vertebrates. As for the utilization of nitrogenous materials, ammonia is the preferred inorganic source because of its ease of uptake and incorporation into amino acids (N-assimilation). The present study show that, most days of winter 2004 except January has low levels of NH_4 (<2.52µmole/l). Faragallah [3] observed low concentration of NH_4 during winter (3.37µM/L) and respect this to promotion of nitrification due to violation of the water as a result of wave and wind action prevailing in this season. Also, Madkour et al [4] pointed out that March has the lowest value of NH_4 during 2002. Most days of August, September and October has high concentration of NH_4 (ranged; 1.04 - 6.50 µmole/l). Madkour et al [4] respect this to the stratification and the effect of the rise in water temperature which may induce the mineralization from the sediment, decomposition rate of sewage and other organic wastes. Also, Faragallah [3] pointed out that summer was characterized by the high level of NH_4 (4.07µmole/l). The level of NH_4 during most days of spring is relatively low, this attributed to the increase in consumption rate by phytoplankton. Generally, the concentrations of NH_4 during days of 2004 are mostly higher than that of 2005.

Nitrite concentration ranged from 0.47 to 1.48 µmole/l with an average value 0.37 µmole/l. The distribution of NO_2-N indicate that most days during October month characterized by the high level (ranged; 0.4 - 0.93 µmole/l). This mostly due to the high rate of denitrification processes where the level of NH_4 concentration was high during this month. The other days during the year are mostly < 0.4 µmole/l. The mean values of NO_2-N were slightly lower comparing with those recoded in the previous studies; it was 0.95 µmole/l [15] and 0.48 µmole/l [3].

The nitrate form is generally considered as the most stable and predominant inorganic nitrogen compound in oxygenated sea water. Nitrate concentration ranged between 0.47 and 10.25 µmole/l. October days (2004) has the highest levels of NO_3-N (ranged; 1.2 - 10.26 µmole/l), also during March days observed relatively high values (ranged; 2.1-3.48 µmole/l), with some exception the other days has relatively low values (ranged; 0.5-2.5 µmole/l). The distribution of NO_3-N (Fig. 2) showed that the concentration during 2004 is higher than that of 2005. From the same figure, the concentration of NH_4 during 2004 was less than that of NO_3-N and this reverse to that observed in 2005, also the distribution of NO_3-N through the study period is mostly similar to that of NH_4-N (r= 0.46, table 1), This refers to that the rate of nitrification is mostly similar to that of denitrification. EL-Geziry and Maiyza [7] pointed out that the E.H is an ideal system for self recovery against domestic sewage and waste materials from tourism and fisheries activities. The average percentage values of different N ions relative to DIN indicated that NH_4-N (45.5%) and NO_3-N (46.9%) are the abundant forms, while NO_2-N is the least constituent (7.6%). This observation may be reflecting similarity between the rate of nitrification and denitrification processes. The average value of NO_3-N concentration (2.35 µmole/l) were slightly increased than the average content of NH_4-N (2.24 µmole/l), while the concentration of NO_2-N decreased seven folds than those recorded for NO_3-N and NH_4-N. Based on this results, the abundance of nitrogen species in the study area is principally in the order NO_3-N> NH_4-N> NO_2-N. This reflects the uptake preferable of the inorganic nitrogen species by phytoplankton organisms in their N-assimilation. This could be confirmed by the relationship between the concentration of both NO3-N and NH4-N with the values of Chl-a, respectively.

Chl-a =20.15 - 2.847 NO_3-N r=0.26 at *P*, 0.05 n=136

Chl-a =8.63 + 2.232 NH_4-N r=0.25 at *P*, 0.05 n=136

In general, dissolved inorganic nitrogen (NO_3-N+ NO_2-N+NH_4-N) were fluctuated between 1.24 and 16.76 with average 4.95 µmole/l. Fahmy, et al., [16] found wide difference between the concentrations of total nitrogen and dissolved inorganic nitrogen, they suggested that nitrogen is found in the Mediterranean coastal waters off Egypt principally in organic forms, since the organic nitrogen is assimilated by aquatic organisms in a much slower rate than those of the inorganic species.

Reactive phosphate (PO_4-P)

Phosphorus plays a major role in biological metabolism; it is an essential nutrient element, which plays an important role in photosynthesis and other processes in plants. Reactive phosphate fluctuated between not detectable on three days during March 2005 and 8.58µmole/l during August with average 1.03 µmole/l. March days has the lowest levels of PO_4-P (ranged; LOD - 0.17 µmole/l), while August has the highest levels (ranged; 0.12-8.59 µmole/l). Also May days has high concentration (ranged; 0.63-2.28 µmole/l). The other days through the year has mostly values < 1 µmole/l (Fig.4). Faragallah [3] pointed out that summer has the maximum values of PO_4-P (1.5 µmole/l) and the minimum concentration was in spring (0.29 µmole/l) and referred that to the accumulation of the sewage effluent in the harbor during summer season, and the high rate of consumption of PO_4-P during spring. Generally, the days of 2005 have PO_4-P levels higher than that of 2004 (Fig.4). The highest level of PO_4-P reflects the influence of wastewater discharge which is loaded with high phosphate content introduced to the harbor. The theoretical half saturation constant (Ks) is 0.2 µmole/l for the uptake of dissolved inorganic phosphorus [17]. Throughout the period of study in the investigated area, it was found levels higher or close to 0.2 µmole/l. Towfic [18] and Madkour [4] found that the mean value of PO_4-P in the same area was around 0.60 µmole/l. positive correlation was recorded between Chl-a and reactive phosphate (r = 0.27 at p 0.05 n=136)

Reactive silicate (SiO_4)
Silicate is one of the major constituents in the sea water. It is a good indicator of fresh water dispersion and of the potential for diatom [16]. The concentration of SiO_4 in the present study varied from 0.37 to11.90 µmole/l (Fig. 4) with average 3.45 µmole/l. The concentration of SiO_4 during November days and most days of winter (2004) and summer (2005) revealed low levels (<3.0 µmole/l), while the other days especially during August, September and October (2004), April and May (2005) have high levels of SiO_4 (mainly >4 µmole/l). This means that, summer and spring has values of SiO_4 higher than that in autumn and winter (Fig.4), probably a chemical precipitation of silicate occurred which was retained to the sediment and did not diffuse to the water column. But during summer and spring, the dissolution of diatom skeletons by increasing temperature is responsible for the high level of silicate content. The average concentration of SiO_4 (3.45 µmole/l) was higher than that of the other nutrient salts. This means that SiO_4 is not a limiting factor of phytoplankton growth in the Harbor. The present level of silicate (average; 3.45µmole/l) was similar to that recorded by Abdel-Halim and Khairy [8] at the same area. On the other hand, the data was markedly lower than those recorded by Dorgham et al., [2] ,Abdel Aziz et al.,[19] and Abdel Aziz et al.,[20] (western Harbor, Abu Qir bay and El-Dekhaila harbor; 9.03, 16.74, 49.52 µmole/l, respectively.) . Although the drainage waters have been reported as the principal source of silicate in the harbor and play a significant part in its spatial and temporal distribution, it was phytoplankton growth that was actually regulating the silicate level [2].The results showed relationship between phytoplankton and silicate content, this is confirmed with the negative correlation between silicate and Chl-a concentration(r = -0.3, table1) (Chl-a =20.88 - 2.108 SiO_4 r=-0.3 at *P*, 0.05 n=136). The same observation was found by Abdel-Halim and Khairy (2007).

Chlorophyll-a (Chl-a)
Chl-a is considered the main pigment that can be used for the determination of phytoplankton biomass [21], and it is used as a trophic state indicator. The concentration of Chl-a varies between 0.41µg/l and 78.68µg/l with average 13.60µg/l. The results as shown in Fig.3 revealed that the days during November and December (2004) and January and February (2005) has the lowest concentrations of Chl-a (ranged; 0.41-1.26 µg/l). But the days during March, April, May, July and August (2005) has the highest levels of Chl-a (ranged; 2.8-78.8 µg/l). This means that most days during autumn and winter mainly has levels of Chl-a lower than that recoded during spring and summer. The results of Chl-a concentration during 2005 was higher than those recorded during 2004. The present data of Chl-a was in agreement with that of phytoplankton biomass collected from the same sites and during the same period [9]. This can be confirmed by the relationship between Chl-a and oxidizable organic matter (r = 0.24 at p, 0.05 n=136 as shown in table 1) Also, it was observed higher Chl-a concentration in the Harbor comparing with that reported in the north and eastern Mediterranean sea (0.01-0.15µg/l) [22] and higher than that recorded in Aegean Sea; 0.10-0.80 µg/l [23]. In general, the high values of chlorophyll-a in the investigated area is undoubtedly due to the rich supply of DIN, reactive silicate and reactive phosphate, these nutrient salts contribute for the growth of phytoplankton expressed in high levels of Chl-a which lead to eutrophication process in the harbor the levels of DIN, PO_4 and chlorophyll-a indicated that, the harbor is in eutrophic condition.

Statistical analysis
Nitrogen / Phosphorus ratio (N/P ratio):

Dissolved inorganic nitrogen (DIN) and PO_4-P are the main forms of N and P that are readily bioavailable for the growth of phytoplankton. The N/P ratio in the present study is significantly and lower than the assimilatory optimal N/P=15/1 and the Redfield's ratio N/P=16/1. According to the previous works, extremely variability of N/P ratio is common along the Mediterranean Sea coast of Egypt, particularly in areas exposed to land based runoff [2]. The results recorded by Chraudani & Vighi [24] found that marine algae are P-limited at N:P ratio > 6 and N – limited at ratio < 4.5; in range of 4.5 – 6, the two nutrients are near their optimal assimilative proportion. In the present study, N/P ratio ranged between low value > 1 and very high value 326. Very low values of N/P ratio was recorded at most period of study (Fig.4), this consideration shows that phosphorus was limiting factor in the harbor. Also, if we considered the results recorded by Chraudani & Vighi [24] for marine algae, nitrogen and phosphorus are removed from water at almost constant proportions. This observation was true by the studies which carried out by Aboul-Kassim [15] and Faragallah [3] in the same region. On the other hand, the period from 2/3 – 30/3/2005 was characterized by high values of N/P ratio, increased than that report at Redfield's ratio; 61:1(Fig. 4). This reflect the high content of nitrogen and low concentration of phosphorus which uptake by phytoplankton in March 2005. In general, nitrogen is the limiting factor in the Eastern Harbor, and phosphorus is an important source for eutrophic condition in the harbor, which originates from domestic and industrial waste water.

Eutrophication Index:

The trophic state index (TSI) is a valuable tool in determining the condition of marine water or in comparing the present condition to the past. Several studies considered that the concentration of nitrate, reactive phosphate, chemical oxygen demand, chlorophyll-a and primary production are important factors to calculate the main indices of eutrophication in marine water [1&25]. The water quality criteria for marine fisheries of China were 0.015, 0.100 and 3.00 mg/l for PO4-P, NO3-N and COD, respectively [25]. In the present study, these parameters values revealed wide variations than those reported by Tomotoshi Okaichi [25], the range and average value in mg/l were ; 0.01-0.27 (0.03) for PO4-P; 0.01-0.15(0.03) for NO3-N and 0.42-17.50(4.79) for COD. In general, the values of eutrophication index were higher more than 1 during four periods at the years of study. These periods were characterized among the eutrophic condition. Two periods recorded during 2004; 9/8-12/8/2004, 19/10-24/10/2004). In the year 2005, the period of eutrophied condition increased more than two months (two periods during 2005; 15/4-31/5 and 1/8-30/8/2005). The present data of eutrophication index showed higher values comparing with that reported by Zaghloul [1].

CONCLUSION

1- The concentration of NO_3-N during 2004 is higher than that of 2005, the concentration of NH_4-N during 2004 was less than that of NO_3-N, also the distribution of NO_3-N through the study period is mostly similar to that of NH_4-N (r= 0.46). This observation may be reflecting similarity between the rate of nitrification and denitrification processes.

2-Based on the results, the abundance of nitrogen species in the study area is principally in the order; NO_3-N> NH_4-N> NO_2-N. This reflects the uptake preferable of the inorganic nitrogen species by phytoplankton organisms in their N-assimilation.

3-The period of summer and spring revealed high values of SiO_4 than that in autumn and winter, probably due to the precipitation of silicate occurred which was retained to the sediment and did not diffuse to the water column. But during summer and spring, the dissolution of diatom skeletons by increasing temperature is responsible for the high level of silicate content.

4-The concentration of Chl-a showed wide variations (0.41- 78.68µg/l) with average 13.60µg/l, the days during autumn and winter mainly has levels of Chl-a lower than that recoded during spring and summer. The results of Chl-a concentration during 2005 was higher than those recorded during 2004. Also, it was observed higher Chl-a concentration in the Eastern Harbor comparing with that reported in the north and eastern Mediterranean sea (0.01-0.15µg/l)

5-According to the trophic state index (TSI)**,** The E H was characterized by eutrophic condition. Two periods recorded during 2004; 9/8-12/8, 19/10-24/10). In the year 2005, the period of eutrophied condition increased during three months (the period from 2/3 – 30/3, 15/4-31/5 and 1/8-30/8/2005).

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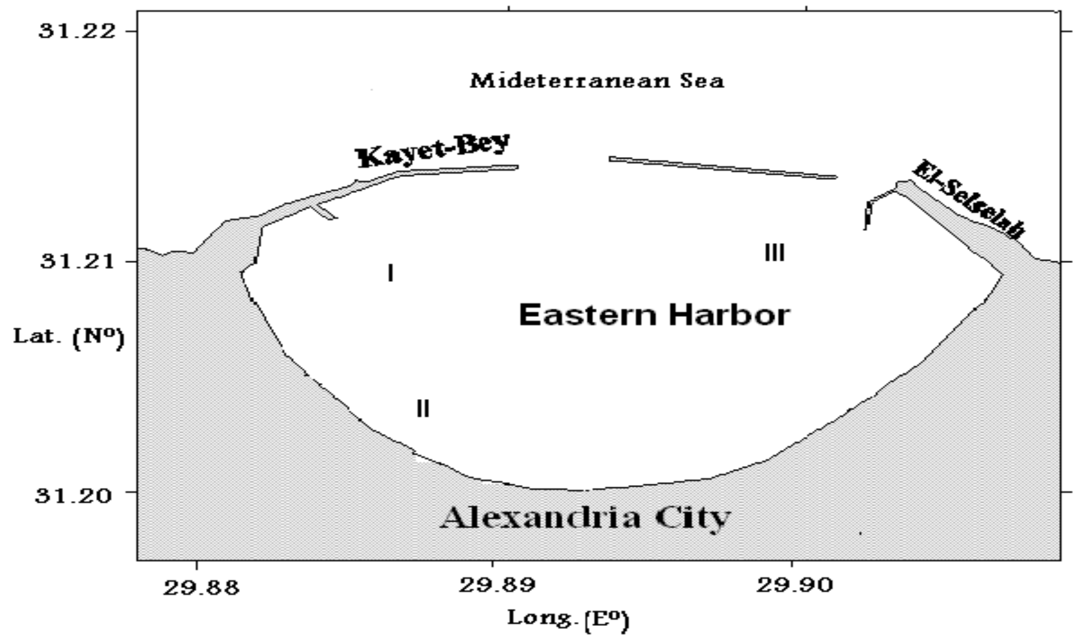

Figure 1: Location of Water Sampling in the Eastern Harbor

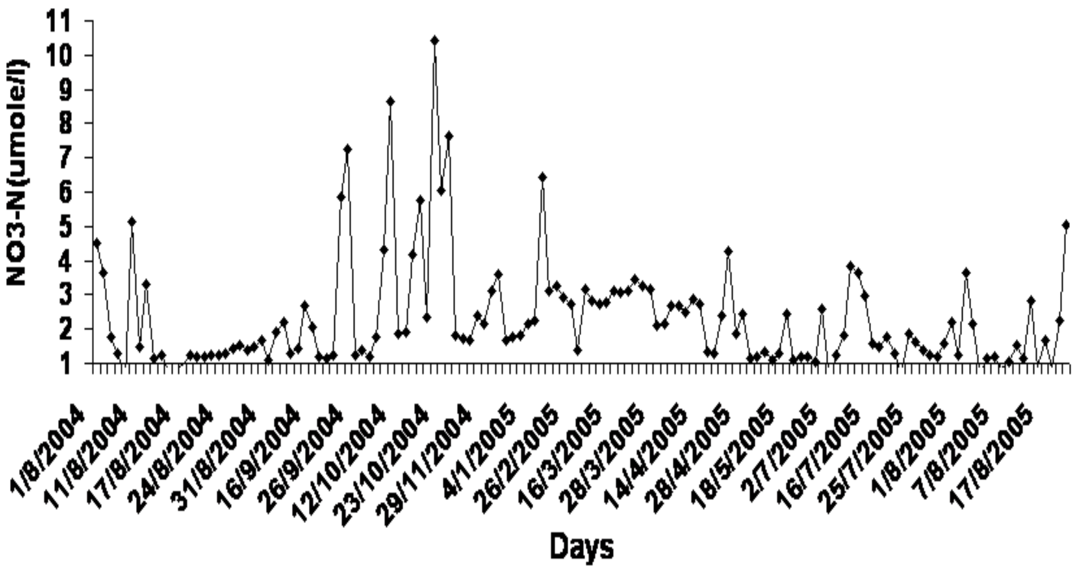

Figure 2: The distribution of NH4-N, NO2-N and NO3-N in the Eastern harbor (2004-2005)

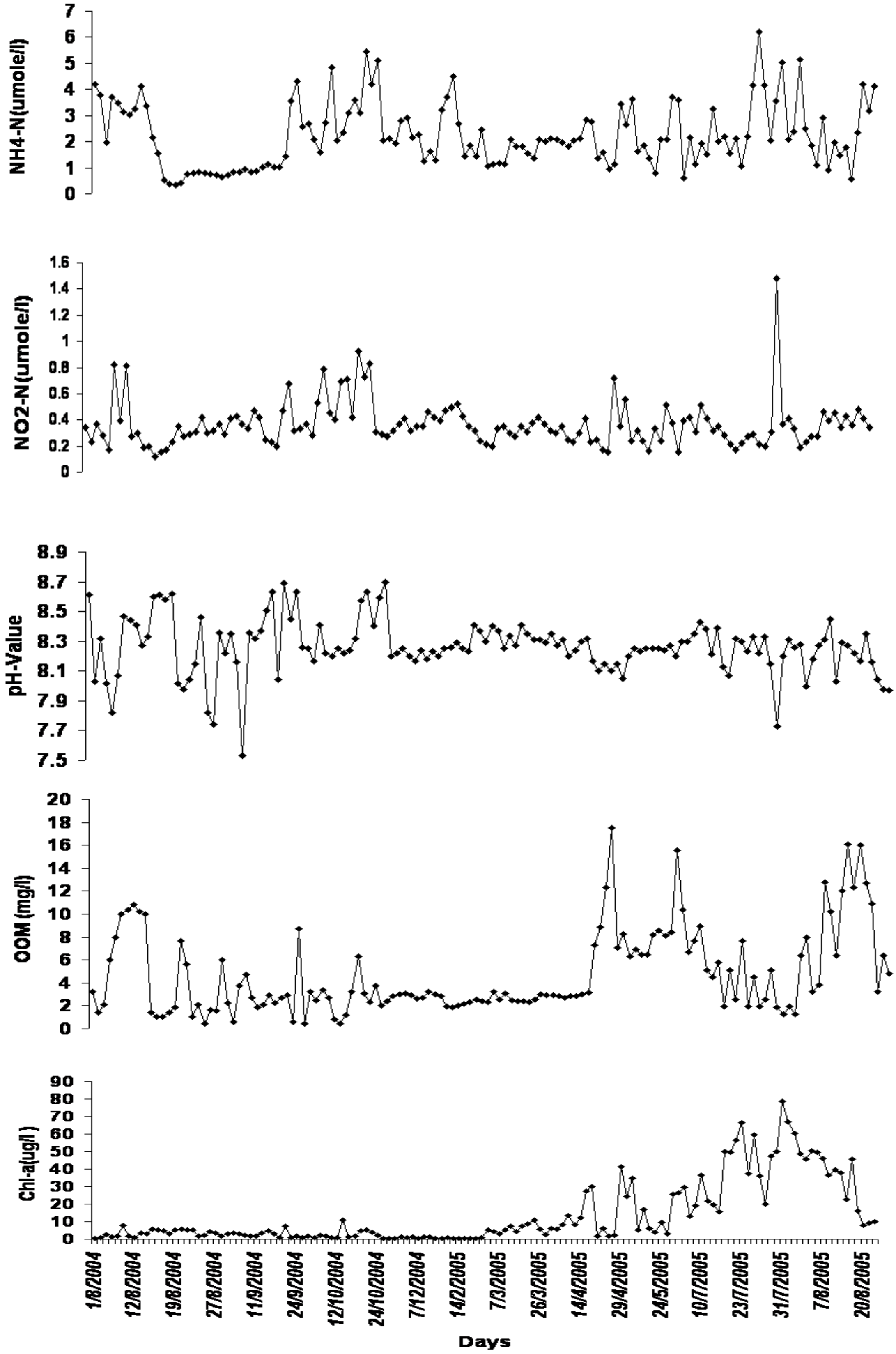

Figure 3: The distribution of pH-values, OOM and Chl-a in the Eastern harbor (2004-2005)

Table 1: Correlation Matrix

	pH	***Chl-a***	***OOM***	***NO3-N***	***NH4-N***	***NO2-N***	***SiO4***	***PO4-P***
pH	1.000							
Chl-a	-0.063	1.000						
OOM	-0.106	**0.235**	1.000					
NO3-N	0.180	**-0.252**	-0.151	1.000				
NH4-N	-0.017	0.151	0.052	**0.461**	1.000			
NO2-N	0.081	0.073	0.043	**0.548**	**0.497**	1.000		
SiO4	0.142	**-0.297**	-0.066	**0.398**	0.200	**0.276**	1.000	
PO4-P	-0.126	**0.266**	**0.415**	0.029	0.114	0.110	-0.188	1.000