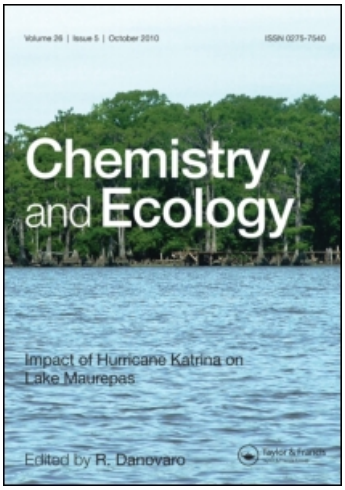

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

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Online publication date: 12 May 2010

To cite this Article Okbah, Mohamed Abd Elaziz(2004) 'Seasonal changes in inorganic nutrient concentration in the alexandria western harbour (Egypt)', Chemistry and Ecology, 20: 2, 97 — 105
To link to this Article: DOI: 10.1080/02757540410001664576
URL: http://dx.doi.org/10.1080/02757540410001664576

Chemistry and Ecology, April 2004, Vol. 20(2), pp. 97–105

SEASONAL CHANGES IN INORGANIC NUTRIENT CONCENTRATION IN THE ALEXANDRIA WESTERN HARBOUR (EGYPT)

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(Received 21 January 2003; In final form 16 December 2003)

Surface and bottom water samples were collected on a monthly basis from six locations in the Alexandria Western Harbour between April 2002 and March 2003. Total nitrogen, ammonia, nitrite, nitrate, total phosphorus, reactive phosphate and silicate were analysed. The average content of total nitrogen ranged from 81.1 to 65.7 $\mu mol\,l^{-1}$ in the surface and bottom waters, respectively, while ammonia ranged from 13.77 to 15.79 $\mu mol\,l^{-1}$ in surface and bottom waters, respectively. Also, the average concentration of nitrite was relatively higher in surface waters than in bottom waters (0.89 and 0.61 $\mu mol\,l^{-1}$, respectively). The results of this study also indicated a considerable temporal variation in nitrate concentrations which ranged from 1.12 to 13.83 $\mu mol\,l^{-1}$. Total phosphorus displayed an irregular pattern throughout the year, ranging from 1.9 to 11.8 $\mu mol\,l^{-1}$ in surface waters and from 1.7 to 9.1 $\mu mol\,l^{-1}$ in bottom waters. The results of PO_4-P analysis showed higher values in surface waters (0.28–2.75 $\mu mol\,l^{-1}$) than in bottom waters (0.10–1.70 $\mu mol\,l^{-1}$). The average concentration of silicates was relatively lower in the surface than in the bottom waters (8.97 and 10.1 $\mu mol\,l^{-1}$, respectively). The analysis of variance (ANOVA) among seasons and sites revealed significant differences for ammonia, total nitrogen and phosphate, while nitrate showed no significant differences among stations. Finally, silicate did not show any significant variance among sites and seasons (ANOVA, $P > 0.05$).

Keywords: Nutrient; Western Harbour Alexandria; Drainage waters; Mediterranean Sea

1 INTRODUCTION

Anthropogenic waste such as dredged spoils, sewage, industrial and municipal discharges in marine environments containing several contaminants, besides overpopulation, overexploitation and limited coastal resource management are considered the main causes of coastal pollution.

Alexandria Western Harbour is subjected to several sources of waste water loaded with nutrient salts from the neighbouring area (Nessim, 1995). The increasing input of nutrients into the harbour has effects on the growth of phytoplankton and, consequently, on the low dissolved oxygen concentration. Nessim and Tadros (1986) found that the P:N:Si ratios were 1:23:27 in the water and 1:129:49 in the pore water of the sediment. They also reported that the pollutants disposed of into the harbour caused eutrophic condition. Nessim (1995)

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ISSN 0275-7540 print; ISSN 1029-0370 online
DOI: 10.1080/02757540410001664576

reported that the most abundant fractions of nitrogen and phosphorus were found in the dissolved form, and the N:P ratio for the different forms was close to 50:1, thus indicating that phosphorus was the most limiting nutrient for phytoplankton biomass in the harbour water.

Water quality and general hydrographical conditions of the harbour water have been reported in previous studies. Dargham *et al.* (2001) showed that the aeration of the harbour water was relatively poor, with a dissolved oxygen content of 3.4 and 2.3 $mg\,l^{-1}$ in the surface and near bottom waters, respectively. The pH values ranged from 7.71 to 8.68 at the surface and from 7.48 to 8.29 near the bottom. The surface salinity (35.3 PSU) was lower than that reported for the eastern Mediterranean Sea, and the surface water temperature followed the seasonal pattern reported in the southern Mediterranean Sea (11–29 °C).

The objective of the present study was to evaluate the temporal changes of inorganic nutrient concentration as well as the total nitrogen and total phosphorus (TP) in Alexandria Western Harbour.

2 MATERIALS AND METHODS

2.1 Study Area

Alexandria Western Harbour is the most important harbour in Egypt facing the Mediterranean coast (29°50′ to 29°53′ E and 31°9′ to 31°12′ N). It is a semi-enclosed basin, 5.5–16.0 m deep, and is connected to the sea by a narrow opening (El-Boughaz, 750 m). The harbour receives huge amounts of wastewater from different sources. El-Noubaria canal discharges about 90,000 m^3 of waters daily, and Misr Chemical Industries releases about 35,000 m^3 of industrial wastes daily. The harbour is also affected indirectly by industrial and domestic wastewaters discharged to El-Mex bay from the Umum drain.

Farag (1982) and Hassan and Saad (1996) reported two non-coherent ideas about the main current directions in the harbour. One exited from the harbour at the uppermost 5 m depth, and the other entered the harbour at a depth of 10 m. The surface currents were south-easterly and south-westerly in the summer and autumn, and westerly to southerly in the winter and spring. At a depth of 10 m, the current directions fluctuated between northerly and north-easterly in the winter and summer, and between south-westerly and northerly in the autumn and spring.

2.2 Sampling and Analysis

Surface and bottom water samples were collected monthly (April 2002 to March 2003) at six stations (Fig. 1). The samples were taken using Niskin bottles from the surface (0.5 m depth) and the bottom (10 m depth) waters, and were kept in clean polyethylene bottles. Dissolved nutrient salts in the water samples were analysed immediately. Nitrites, nitrates, ammonia, reactive phosphates and silicates in the water samples were measured in a colorimeter (Grasshoff, 1976). Absorbance was measured using a double-beam spectrophotometer (Shimadzu UV-150–02). Analyses of total nitrogen and TP were carried out following the method described by Valderrama (1981).

An ANOVA statistical analysis was carried out to test the significant differences of nutrients concentrations among seasons and stations.

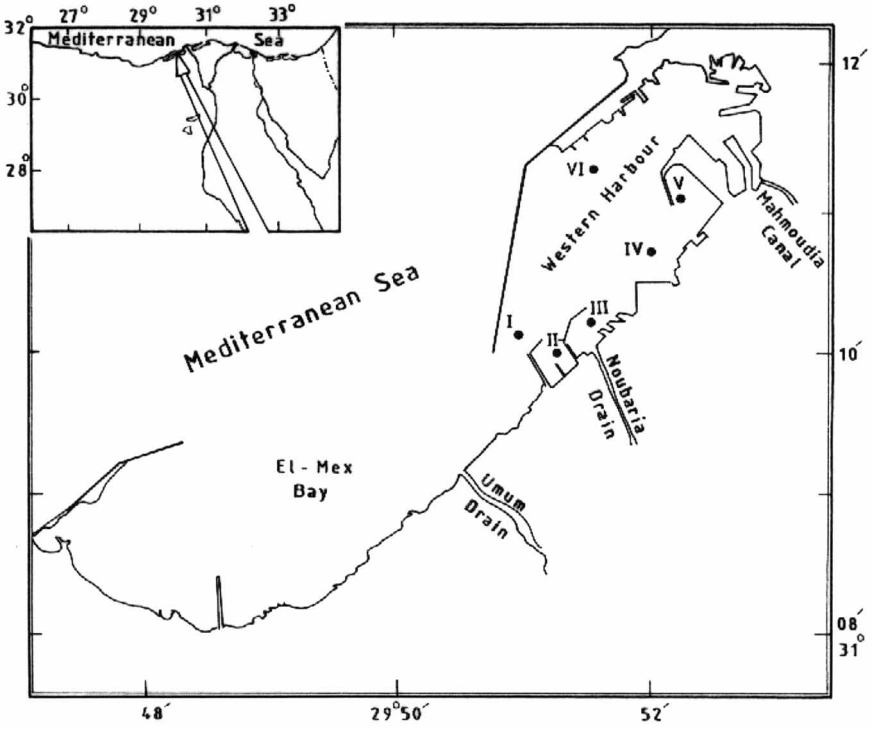

FIGURE 1 Map of the sampling locations in the Western Harbour.

3 RESULTS AND DISCUSSION

3.1 Ammonia

With regard to regional variations, ammonia concentrations were relatively high in the surface and bottom waters (Tab. I) and ranged from $9.82 \pm 6.46\,\mu mol\,l^{-1}$ at station VI to $23.54 \pm 18.15\,\mu mol\,l^{-1}$ at station I in surface water and from 9.43 ± 8.75 to $19.14 \pm 12.80\,\mu mol\,l^{-1}$ in the bottom water.

TABLE I NO_2, NO_3, NH_3, and TN concentrations ($\mu mol\,l^{-1}$) in the surface and bottom waters for each month.

	NO_2		*NO_3*		*NH_3*		*TN*	
	Surface	*Bottom*	*Surface*	*Bottom*	*Surface*	*Bottom*	*Surface*	*Bottom*
Apr.	1.69	0.21	7.53	0.4	5.67	0.56	64.3	23.4
May	1.29	0.42	1.75	0.88	18.73	27.36	93.8	53.7
Jun.	0.55	0.41	1.96	1	17.41	16.79	96.2	59.4
Jul.	0.95	0.98	2.62	1.92	8.97	5.87	116.4	74.5
Aug.	0.7	0.64	2.8	3.25	12.49	25.18	62.3	78.7
Sep.	0.59	0.5	1.12	1.33	4	6.09	64.3	40.1
Oct.	0.7	0.49	2.69	2.12	12.67	13.2	85.2	61.6
Nov.	0.9	0.54	5.14	2.16	15.93	23.5	174.4	154.7
Dec.	0.6	0.49	9.4	5.6	11.2	15.75	44	45.5
Jan.	0.69	0.43	14.33	13.83	24.46	14.75	75.7	64.2
Feb.	1.07	1.2	12.73	8	23.83	18.82	68.6	68
Mar.	0.92	0.56	6.75	5.87	9.83	6.41	28.1	22.1

Seasonal changes in ammonia concentrations in the Western Harbour are illustrated in Figure 2A. Both the lowest ($0.56 \pm 5.40\,\mu mol\,l^{-1}$) and the highest ($27.36 \pm 10.72\,\mu mol\,l^{-1}$) ammonia concentrations were recorded in the bottom water in April and May, respectively.

The bottom water contained high levels of ammonia concentrations in May, August and November, while the surface water was richer in the other months (January, February, June and July). These differences were significant ($P < 0.05$) according to the two-way ANOVAs among seasons and stations (Tab. II).

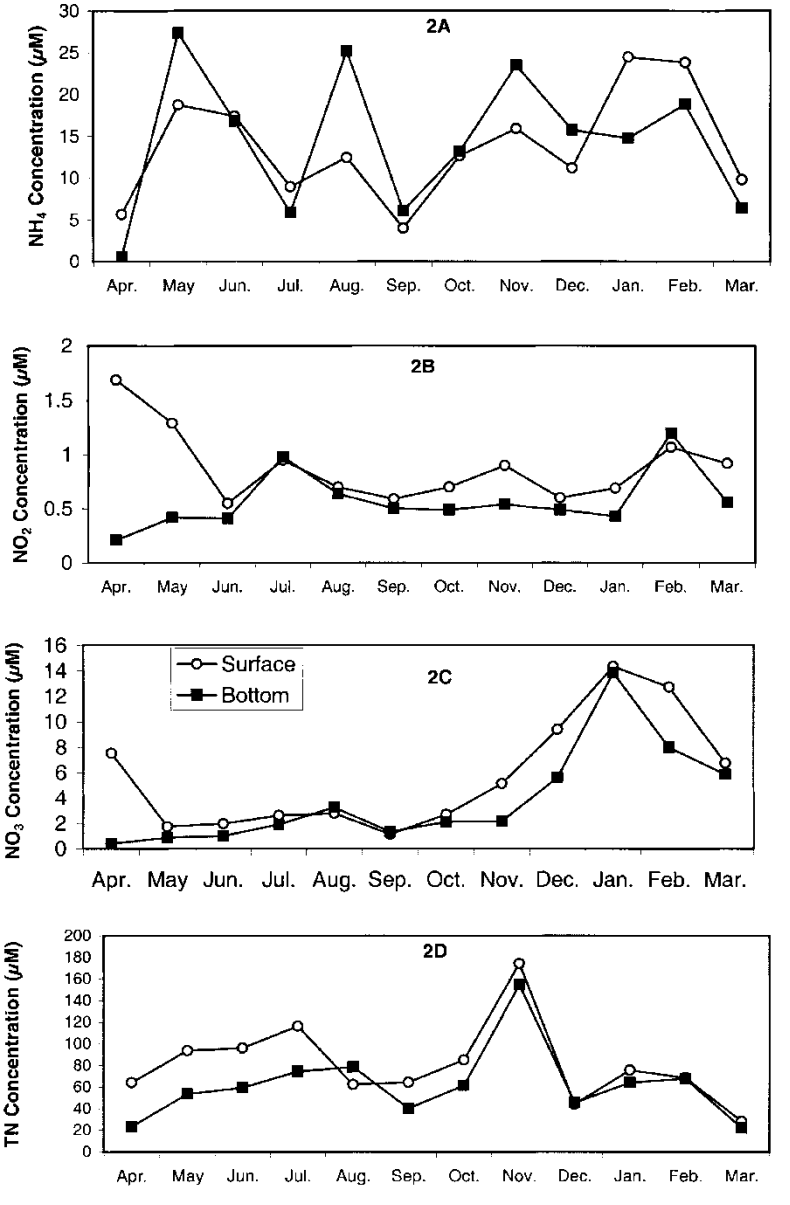

FIGURE 2 Seasonal variations (April 2002 to March 2003) in (A) NH_4, (B) NO_2, (C) NO_3, and (D) total nitrogen concentrations (mmol l^{-1}) in the surface and bottom waters of the Western Harbour of Alexandria.

TABLE II Results of two-way ANOVA for all the parameters studied.

Variables source		*df*	*F*	*P*	
PO_4-P	month	11	2.978	0.106	Significant difference
	site	5	32.828	0.000	
Total phosphorus	month	11	2.848	0.112	Significant difference
	site	5	31.071	0.000	
Ammonia	month	11	0.890	0.575	Significant difference
	site	5	30.845	0.000	
NO_2-N	month	11	12.137	0.000	Significant difference
	site	5	9.520	0.000	
NO_3-N	month	11	13.331	0.000	Significant difference
	site	5	2.765	0.144	No significant difference
Total nitrogen	month	11	13.065	0.000	Significant difference
	site	5	8.470	0.016	
Silicate	month	11	3.313	0.036	No significant difference
	site	5	1.735	0.280	

The decreasing ammonia concentrations in the surface water during spring and summer may reflect intensive consumption of ammonia by phytoplankton or possibly the abnormally high concentrations of chlorophyll *a*, particularly during the same period of low ammonia availability.

Ammonia is known to be the preferable form of inorganic nitrogen for phytoplankton. Wafar *et al.* (1986) stated that ammonia is an important nitrogen source for aquatic plants, and a complete exhaustion of ammonia by phytoplankton could occur during the spring blooms. Finally, our data were markedly higher, both in the surface ($13.77\,\mu mol\,l^{-1}$) and in the bottom ($15.79\,\mu mol\,l^{-1}$) waters, than concentrations reported in previous studies in the Western Harbour of Alexandria ($5.38\,\mu mol\,l^{-1}$; Nessim, 1995).

3.2 Nitrite and Nitrate

The temporal pattern of nitrite indicated relatively wide seasonal variations in both surface and bottom waters with the highest values all over the year, except July and February (Fig. 2B). This was mainly due to the continuous supply of nitrite from discharged wastewaters. In the surface water, the average NO_2-N values fluctuated between 0.55 ± 2.40 and $1.69 \pm 4.62\,\mu mol\,l^{-1}$ in June and in April, respectively, whereas in the bottom waters, the average NO_2-N values ranged between 0.41 ± 0.85 and $1.2 \pm 2.60\,\mu mol\,l^{-1}$ in June and in February, respectively.

The annual average of NO_2-N in the surface waters ($0.89 \pm 0.71\,\mu mol\,l^{-1}$) was relatively higher than in the bottom ($0.61 \pm 0.52\,\mu mol\,l^{-1}$). These values were twice as high as those given by Nessim and Tadros (1986) and slightly higher than those recorded by Nessim (1995) in the surface water ($0.71\,\mu mol\,l^{-1}$).

Most of the stations investigated showed moderate concentrations with a narrow range in the surface waters (from 0.71 ± 0.32 to $0.87 \pm 0.50\,\mu mol\,l^{-1}$ for nitrite and from 4.07 ± 4.46 to $6.4 \pm 5.71\,\mu mol\,l^{-1}$ for nitrate, respectively; Tab. I).

Nitrate content in the surface as well as in the bottom water showed different temporal patterns ranging from 0.4 ± 5.2 to $13.83 \pm 7.4\,\mu mol\,l^{-1}$ for the bottom waters and from 1.12 ± 4.30 to $14.33 \pm 9.72\,\mu mol\,l^{-1}$ for the surface waters (Fig. 2C). Nitrate concentrations revealed significant differences among seasons (ANOVA, $P < 0.05$) and no significant variations among stations (Tab. II). Nitrate showed a relative narrow variation from May to October, with a close value in both layers followed by a sharp increase to the maximum in January. The nitrate concentration decreased again in surface and bottom waters.

Throughout most of the year, nitrate was more abundant at the surface than in bottom waters (Fig. 2C). The average abundance of nitrate was related to the seasonal concentration of chlorophyll *a*, and both reached the maximum concentration in January. Labib (1997) also found the maximum nitrate concentration to occur in January and the minimum concentration to occur in July. Dargham *et al.* (2001) observed that the period during which nitrate was low was characterized by remarkably high chlorophyll *a* levels. This suggested that phytoplankton played a significant role in seasonal nitrate variations in the Western Harbour.

3.3 Total Nitrogen (TN)

The temporal patterns of total nitrogen content in the waters of the Western Harbour of Alexandria are reported in Figure 2D.

Total nitrogen concentrations were higher in the surface than in the bottom waters throughout most of the year. The opposite pattern was observed during August, whereas no differences were reported between surface and bottom waters during December and February. The annual mean of total nitrogen in the harbour revealed a wide variation between the surface ($81.1 \pm 48.4\,\mu mol\,l^{-1}$) and bottom ($65.7 \pm 47.4\,\mu mol\,l^{-1}$) waters. ANOVA for the total nitrogen concentrations showed significant differences among seasons and stations ($P < 0.05$). The total nitrogen content was significantly higher at station I ($107.31 \pm 50.31\,\mu mol\,l^{-1}$) than at station VI ($72.57 \pm 42.96\,\mu mol\,l^{-1}$) in surface waters, whereas it was significantly higher at station IV ($84.34 \pm 61.22\,\mu mol\,l^{-1}$) than at station I ($51.26 \pm 17.85\,\mu mol\,l^{-1}$; Tab. II) in bottom waters. These values were relatively higher than those previously reported by Nessim (1995), and this increase might be due to an increase in land-based outfalls in the Western Harbour in recent years.

3.4 Reactive Phosphate

Figure 3A shows the temporal changes of reactive phosphate concentrations in the Western Harbour. Throughout most of the year, the surface waters were characterized by higher values (0.28 ± 3.1 to $2.75 \pm 7.52\,\mu mol\,l^{-1}$) than the bottom water (0.10 ± 8.40 to $1.70 \pm 5.3\,\mu mol\,l^{-1}$). However, in August 2002 and January 2003, PO_4 concentrations were slightly higher in the bottom than in the surface waters. Spring and summer were characterized by a higher concentration of reactive phosphate than winter and autumn, reflecting the seasonal variation in the amounts of phosphorus. Moreover, reactive phosphate showed significant differences among seasons and stations (ANOVA, $P < 0.05$; Tab. II). Reactive phosphate showed relatively high levels at stations I, II and III (Tab. I), which were influenced by waste water discharged from El-Noubaria Canal and El-Max Bay region. On the contrary, the lowest content was found at station VI both in the surface ($0.77 \pm 0.57\,\mu mol\,l^{-1}$) and in the bottom ($0.68 \pm 0.44\,\mu mol\,l^{-1}$) waters.

The chemistry of phosphates is extremely complicated in the natural environment, and interpretation of the results was very difficult. The phosphorus content in the water was mainly affected by anthropogenic nutrient inputs. The PO_4-P values in this study were slightly higher than those reported by Nessim and Tadros (1986) and Okbah and Tayel (1999). Labib (1997) found the concentrations of phosphates to be 4.4 and $3.5\,\mu mol\,l^{-1}$ in April and July, respectively, in the surface water at the entrance of the Western Harbour during a red-tide bloom mainly caused by dinoflagellates. Generally, the high PO_4-P concentrations reflected the eutrophic condition of the basin in the harbour.

The theoretical half saturation constant (K_s) for uptake of PO_4-P is $0.2\,\mu m$ (Gallegos and Jordon, 1997). Throughout the study area, the data revealed that the concentrations of

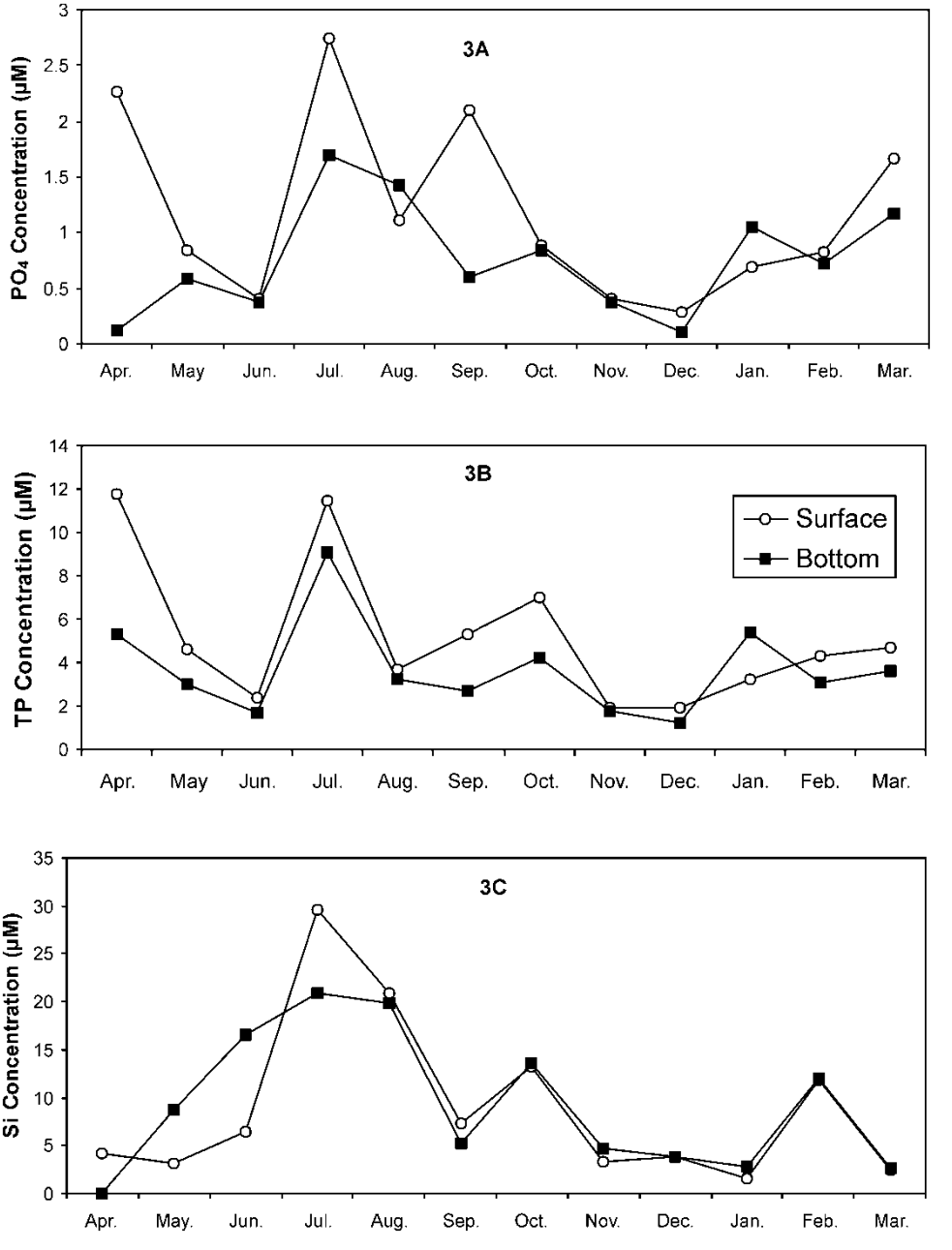

FIGURE 3

reactive phosphate were higher than 0.2 µm during March, April, July, August and September, and could increase the risk of eutrophication.

3.5 Total Phosphorus (TP)

Figure 3B shows the temporal pattern of TP concentrations in the Western Harbour waters and indicates widely fluctuating TP concentrations throughout the year. TP concentrations

ranged between 1.90 ± 8.20 and $11.8 \pm 9.13\,\mu mol\,l^{-1}$ in the surface waters and between 1.2 ± 4.62 and $9.1 \pm 10.2\,\mu mol\,l^{-1}$ in the bottom waters.

The two highest mean values of TP concentration in the surface waters were found in April and July (11.8 and $9.1\,\mu mol\,l^{-1}$, respectively) and may be attributed to the high values of organic phosphorus concentrations (Nessim, 1995), which is ecologically important in this area. TP concentrations were higher in the surface than in the bottom waters. In June, November and December, a clear decrease was observed in TP concentrations in both surface and bottom waters (1.7, 1.9 and $1.2\,\mu mol\,l^{-1}$, respectively). Generally, the annual average of TP concentrations in the Western Harbour at the surface and bottom waters were 5.19 ± 15.3 and $3.55 \pm 21.47\,\mu mol\,l^{-1}$, respectively. The concentrations found in this study were lower than those reported by Nessim (1995) but higher than the annual mean value reported in El Mex Bay (Okbah and Tayel, 1999).

3.6 Silicate

Temporal variations of silicate concentration in the Western Harbour (Fig. 3C) showed little difference between the surface and bottom waters, except during April, May, June and July. The highest values of silicate concentrations were recorded during July and August (ranging from 29.66 ± 20.4 to $20.89 \pm 18.25\,\mu mol\,l^{-1}$ in the surface water) and were *ca.* $20\,\mu mol\,l^{-1}$ in the bottom waters. The lowest silicate concentration in surface water occurred during January ($1.63\,\mu mol\,l^{-1}$), whereas that in bottom waters occurred during March ($2.5\,\mu mol\,l^{-1}$).

Table I shows the regional distribution of silicate concentrations in the investigated area. Silicates showed limited variations in the surface waters ranging from $8.47 \pm 6.86\,\mu mol\,l^{-1}$ at station VI to $10.23 \pm 8.43\,\mu mol\,l^{-1}$ at station II, while in the bottom waters, the variations ranged from $8.30 \pm 5.68\,\mu mol\,l^{-1}$ at station I to $14.45 \pm 11.29\,\mu mol\,l^{-1}$ at station III. Nevertheless, no significant differences were detected for silicates among stations and sites (Tab. II; ANOVA, $P < 0.05$). Moreover, the highest values of silicate concentrations appeared during summer and autumn due to the impact of the wastewater discharged, which increased during the warm period after irrigation of the adjacent cultivated lands. Moreover, the regeneration processes, microheterotrophic excretion and the dissolution of sedimentary biogenic silica could be considered as possible reasons for the increase in silicate concentrations.

The lowest silicate concentrations were found during winter and spring, as previously reported by Zaghloul and Nessim (1991). The annual mean value of silicate was relatively lower in the surface than in the bottom waters (8.97 and $10.1\,\mu mol\,l^{-1}$, respectively). Moreover, the concentrations of silicate in the Western Harbour were relatively higher than those recorded in the Eastern Harbour ($0.88–15.6\,\mu mol\,l^{-1}$; Alsayes and Shakweer, 1997).

4 CONCLUSION

During most of the year, the nitrate content was found to be higher in the surface than in the bottom waters, and there was a gradual increase to the maximum concentration in January. In contrast, the distribution of ammonia showed an irregular temporal variation reaching the highest concentration at station I. The highest concentrations of total nitrogen were found at stations I and II, especially during November. The highest content of reactive phosphate was recorded during spring and summer, especially at stations I, II and III. The distribution of TP and reactive phosphate showed a significant difference throughout the seasons and

sites. The seasonal distribution of silicate content showed a slight variation between the surface and bottom water except during April, May, June and July. However, the regional distribution revealed that inorganic nutrient concentrations showed wide variations in the bottom waters and limited variations in the surface waters.

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