International Journal of Oceans and Oceanography
ISSN 0973-2667 Vol.1 No.1 (2006), pp. 1-19

http://www.ripublication.com/ijoo.htm

Role of phosphorus and nitrogenous species in water quality of a coastal Egyptian heavily polluted Mediterranean basin

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Abstract

Abu-Qir Bay, a semi-enclosed heavily polluted Mediterranean basin in Egypt, is receiving huge amounts of untreated sewage and industrial wastewaters via Tabia Pumping Station (TPS). The distribution of phosphorus and nitrogenous species in this bay and in its effluents was investigated, to illustrate the role played by these nutrients in its water quality. The maximum and minimum temperature averages in July (summer) and January (winter) indicate that temperature is a season dependant. Low pH values coincided with intensive industrial wastewater discharges via TPS. Salinity decreased near discharges regions. The annual mean surface salinity value was lower than the bottom annual mean, reflecting the influence of freshwater discharges. The annual mean total suspended matter (TSM) in the surface water was lower than that for the bottom water. The increase in TSM values in TPS discharges confirms that TPS was the main contributor of TSM.

The extraordinary high bottom dissolved inorganic phosphorus (DIP) values might be resulted from extensive production of effluents from the phosphate fertilizers factory. The high average surface DIP value in front of TPS confirms the external input of domestic and industrial discharges. The effluents of land-based sources showed higher dissolved organic phosphorus (DOP) values compared with the marine region. The DIP/DOP ratios indicate that DOP was predominant in the surface water, while the reverse occurred in the bottom water. Both water layers near TPS showed the maximum regional average particulate phosphorus (PP) values and the maximum seasonal average PP values in October. The latter was statistically correlated with TSM content. The regression equation of nitrate against salinity confirmed that land based sources seemed to be not the main source of nitrate in the bay. The annual surface and bottom nitrate means were nearly similar, due to shallowness of the bay water column. The increase in nitrite content with depth coincided with nitrate reduction in the relatively oxygen-poor bottom water. A significant positive correlation was found between nitrite and nitrate in the surface water. However, the correlation with ammonium was not significant, indicating that nitrate reduction rather than ammonium oxidation was the major internal source of nitrite. Ammonium was the predominant species of dissolved inorganic nitrogen (DIN) fraction. The increase in ammonium concentrations with depth coincided with decomposition of organic matter in the deposited discharged wastes. Nitrite and ammonium decreased away from land-based sources. Dissolved organic nitrogen (DON) constituted most of total dissolved nitrogen (TDN) in both water layers. Statistical correlations indicate that DON might be associated with biological activities. The significantly negative correlation between DON and particulate nitrogen (PN) in both water layers in addition to the regression equation against TSM indicate that PN levels were mainly derived from TPS.

Key words: phosphorus, nitrogen, suspended matter, land-based sources, Abu-Qir Bay, Mediterranean Sea.

Introduction

During the last four decades the coastal waters of Alexandria have been subjected to extensive discharges of untreated industrial, agricultural and sewage wastewaters. The industrial activities in Alexandria constitute about 40% of the total industries of Egypt. About $183x10^6m^3$ of untreated domestic sewage and wastewaters are discharged annually from land-based sources into the coastal waters of Alexandria. Anthropogenic nutrient inputs play an important role in the high productivity and biomass of the coastal zone of Alexandria relative to its continental shelf [1]. Dowidar et al. [2] reported the importance of land-based sources on the phosphorus species and budget in a heavily polluted basin of the Alexandria coast. The data obtained from previous studies showed that these waters were suffering from risks of deterioration as a result of the increase in degradation of the coastal water quality [3,4,5,6]. In 1999, a study was carried out to make a comparison between the influences of the Rhone River (France) and the Nile River (Egypt) upon their adjacent coastal waters (Gulf of Marseilles and Abu-Qir Bay). During this study, several missions were performed in the Egyptian waters of Abu-Qir Bay and in front of the River Nile; following the French time-series strategy named SORCOM [7]. Studying the composition of these waters is very important to discriminate the respective contributions of the different freshwater inflows upon these endangered coastal ecosystems. The influences of the exceptional or accidental meteorological, climatic and/or ecological events are to be integrated to spot the modifications in the vertical structure of such water masses. Continental water inflows and assessment of their influence on coastal marine ecosystem represent a great deal not only for environmental protection purposes, because they are often charged with toxic compounds [8], but also for fundamental water studies on dynamic processes, matter budget and temporal evolution of ecosystems [9]. A long-term follow-up for the physico-chemical and biological evolution in the coastal water at daily, monthly, seasonally and annual levels is urgently needed to identify changes occurring in a particular coastal area [6,7].

This work, as a part of the MED-POL Program (Phase II), was designed to investigate beside the environmental characteristics the dissolved and particulate fractions of phosphorus and nitrogen in the marine coastal waters of Abu-Qir Bay in addition to the effluents discharging into this bay. A part of the work was focused on identifying the alterations in such phases across the freshwater-seawater interface during passing to the marine environment. The estimation of the present load of both nutrient species delivered to the sea via industrial, domestic and agricultural inputs is a tool to evaluate the role of land-based sources as a major contributor of pollutants to the coastal waters of the bay. Comparison between the values obtained from the present study with the corresponding ones previously recorded in other studies was carried out for illustrating the present pollution status in the study area.

Study area

Abu-Qir Bay is a semi-enclosed basin located about 36 km east of Alexandria (Fig. 1). It is bordered in the western side by Abu-Qir Peninsula and in the east by the Rosetta Nile branch. It lies between 30°05'- 30°22' E and 31°16'- 31°21' N. The bay has an area of 360 km^2, an average depth of 12 m and a volume of 4.32 km^3 [10]. The maximum depth of the investigated area was 9 m and the average depth was 3.8 m. This western inshore area of the bay is a shallow region interrupted with several rocky islets; the most important of which is Nelson Island located 2-3 km to the north of Abu-Qir Headland. The seaward limit of the bay is considered as the line adjoining the Nile River mouth and Abu-Qir Headland. The exchange of water between Abu-Qir Bay and Lake Edku (Fig.1), occurring through El-Maadia Channel (about 200 m long and 2 m deep), is controlled by the prevailing wind and the difference in water levels between the bay and the lake.

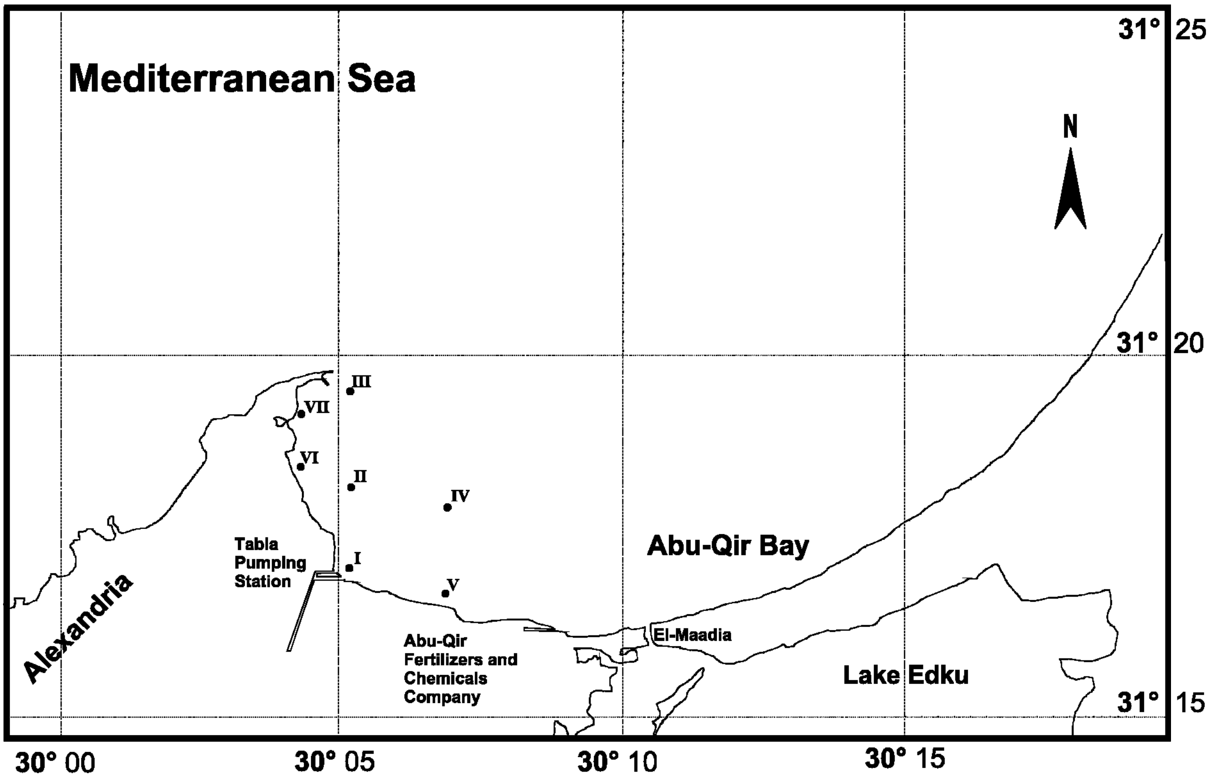

Figure 1: Sampling stations in the southwestern part of Abu-Qir Bay.

In the southwestern area of the bay, about 1.5 to 2.0 $x10^6 m^3.d^{-1}$ of untreated sewage and industrial wastewaters were pumped via TPS. The industrial wastes include mainly fertilizers, textile, dyes and weaving, food processing, paper and cement industries. The annual rainfall in the area is 200 mm (rainy season from November to May), while the annual evaporation rate is 1.5 mm^{-2} [11]. The water circulation in the bay is mainly wind dependent. Current measurements in the bay, carried out by El-Sharkawy & Sharaf El-Din [12] during March, indicated a NW current with a speed of 50 $cm.s^{-1}$ at the inner bay and 5 $cm.s^{-1}$ in the outer bay. Mohamed [13] illustrated that the monthly current measurements in the mid channel, connecting the lake with the bay showed, a predominant lake-bay flow all the year round, with a maximum speed between 60 and 100 $cm.s^{-1}$ along the axis. The surface salinity distribution in the bay during the high flood period (summer) showed low salinity values reaching less than 4 at the lake-bay connection. However, during the low flow period (winter), the salinity values were more than 22 [10]. This author also reported that at the line adjoining the headlands, salinity in both periods ranged between 35 and 38. The water exchange between the bay and the open sea is summarized in a surface bay-sea current of salinity 36 encountered by a bottom sea-bay current of salinity 39.1. In the region surrounding Abu-Qir Bay, there are many industries discharging their wastes into Abu-Qir Drain which subsequently discharges into Abu-Qir Bay via TPS.

Material and Methods

Water samples were collected seasonally from April 1991 to January 1992 in Abu-Qir Bay and from July 1991 to April 1992 in TPS. In the bay, sample stations were positioned along transects oriented perpendicular to the land-based sources. Surface and bottom water samples were collected at each station according to the maximum depth, from two to three stations were sampled from each transect (Fig. 1). However, surface water samples were only collected at the very shallow water of station VI. Sampling of seawater was carried out using an out-board motor boat at 30 cm below the water surface and 30 cm above the bottom using 5 liters PVC Niskin water sampler. The water samples from TPS have been collected by means of a plastic bucket sampler attached with a nylon robe. Samples for salinity determination were collected using hard glass salinity bottles provided with air-tight closures. For determination of TSM and nutrient salts, the water samples were kept in 2 liters acid-cleaned PET bottles [Coke bottles] as described by Pai et al. [14]. Immediately before sampling, the bottles were rinsed with a portion of the seawater samples. The bottles were then tightly closed and the samples were frozen at -20°C until analyses could be performed. Surface water temperatures were measured by a bucket thermometer, while bottom water temperatures were recorded using the standard reversing protected thermometer attached to the reversing frame of the Niskin bottle. Samples for pH measurements were recorded at the site of sampling, using a pre-standardized portable digital pH meter.

Immediately after transporting the water samples to the laboratory, a number of procedures were performed, including filtration, storage and pre-concentration. All water sample determinations were clean bench-processed in an acrylic cupboard, provided with all-plastic ventilations. Salinity was determined on pre-weighed seawater samples using Mohr's method. Millipore membrane filter papers (0.45 µm porosity - 47 mm diameter) were used to separate the dissolved from the particulate nutrient fractions. For TSM determination (expressed in $mg.l^{-1}$), one liter of water was filtered through the Millipore filters using all-plastic filtration system (Sartorius model) under reduced pressure. The residue on the filter papers was then dried and weighed until constant weight. Nutrient salts were determined colorimetrically using Bauch & Lomb Spectronic 2000 double beam spectrophotometer using 1 cm cell. DIP, nitrate, nitrite and ammonium were determined according to Strickland & Parsons [15]. TDN, total nitrogen (TN), total dissolved phosphorus (TDP) and total phosphorus (TP) were determined according to the method described by Valderrama [16]. DON, DIN, PN, DOP and PP were determined by calculations. The values of salinity (S) were determined as practical salinity unit (psu). Those for nutrients were expressed in µM. In case the analyses could not be performed immediately, the filtrates were stored at -20°C in previously cleaned 1 liter PET bottles.

Results

Environmental parameters

In the surface water layer, three stations (I, VI and VII) exhibited the lowest absolute temperature values in January (16.0°C). However, the maximum absolute surface temperature was recorded at station I in July (29.3°C). For the bottom water layer, station I also recorded the highest absolute value (28.7°C) in July. The minimum bottom absolute value (16.1°C) was recorded at station II in

January. The seasonal averages for both surface and bottom water layers appeared as minimum in January; 16.3 ± 0.4°C (surface) and 20.1 ± 4.3°C (bottom) and maximum in July; 28.5±0.5°C (surface) and 27.9 ± 0.5°C (bottom) as shown in Table 1.

Table 1: Seasonal average values of temperature, pH, salinity and TSM in the surface and bottom water layers of Abu-Qir Bay.

Seasons		Temp (°C)	pH	Salinity	TSM ($mg.l^{-1}$)
April	S	20.5 *±0.9*	8.09 *±0.15*	35.00 *±5.62*	30.0 *±10.0*
	B	22.4 *±2.3*	8.03 *±0.22*	37.31 *±3.91*	31.8 *±19.3*
July	S	28.5 ±0.5	7.55 *±0.18*	37.62 *±2.68*	32.6 *±10.7*
	B	27.9 *±0.5*	7.54 *±0.26*	38.64 *±1.73*	72.0 *±106.3*
October	S	20.6 *±0.7*	7.62 *±0.34*	24.97 *±11.29*	15.7 *±5.9*
	B	21.9 *±0.9*	7.91 *±0.26*	32.09 *±9.06*	21.2 *±7.3*
January	S	16.3 *±0.4*	7.67 *±0.32*	15.97 *±5.65*	17.9 *±2.6*
	B	20.1 *±4.3*	7.57 *±0.11*	19.19 *±3.51*	17.2 *±1.0*

The surface water at station I showed the minimum absolute pH value of 7.13 in October. The maximum absolute surface pH value of 8.38 was recorded in January at station V. For the bottom water, stations I in July and V in October exhibited the lowest and highest absolute pH value of 7.05 and 8.21, respectively. Subsequently, the surface and bottom water layers at station I showed the calculated minimum regional average pH values of 7.40 ± 0.31 (surface) and 7.48±0.35 (bottom). However, the maximum average value for the surface water (8.04 ± 0.40) was found at station V, while that for the bottom water (7.86 ± 0.35) was obtained at station III (Fig. 2). The seasonal average pH values for the surface water ranged from 7.55 ± 0.18 in July to 8.09 ± 0.15 in April. The bottom seasonal averages varied from 7.54 ± 0.26 to 8.03 ± 0.22 also in July and April, respectively (Table 1). The annual mean pH value for the surface water (7.73 ± 0.19) was close to that of 7.76 ± 0.14 calculated for the bottom water.

Station I exhibited an extraordinary low surface absolute salinity value in January (5.25), resulting from the extreme freshwater discharges at this station. This gave rise to the lowest regional average value of 20.70 ± 15.39 in the surface water layer of station I (Fig. 2). Accordingly, the minimum surface seasonal average value of 15.97 ± 5.65 appeared in January (Table 1). However, the absolute minimum salinity value for the bottom water layer (13.13) appeared in January at station V. From the lowest absolute salinity values recorded for the surface and bottom waters of Abu-Qir Bay, it is clear that salinity levels were dependant on the amount of the discharged freshwater derived from the effluents of land-based sources. Surface and bottom salinity values followed the trend of the increase towards the offshore stations, due to mixing with the Mediterranean coastal waters; the status of prevailing winds and currents. In July, the surface and bottom water layers exhibited the peaks of seasonal averages (37.62 ± 2.68 and 38.64 ± 1.73), respectively (Table 1).

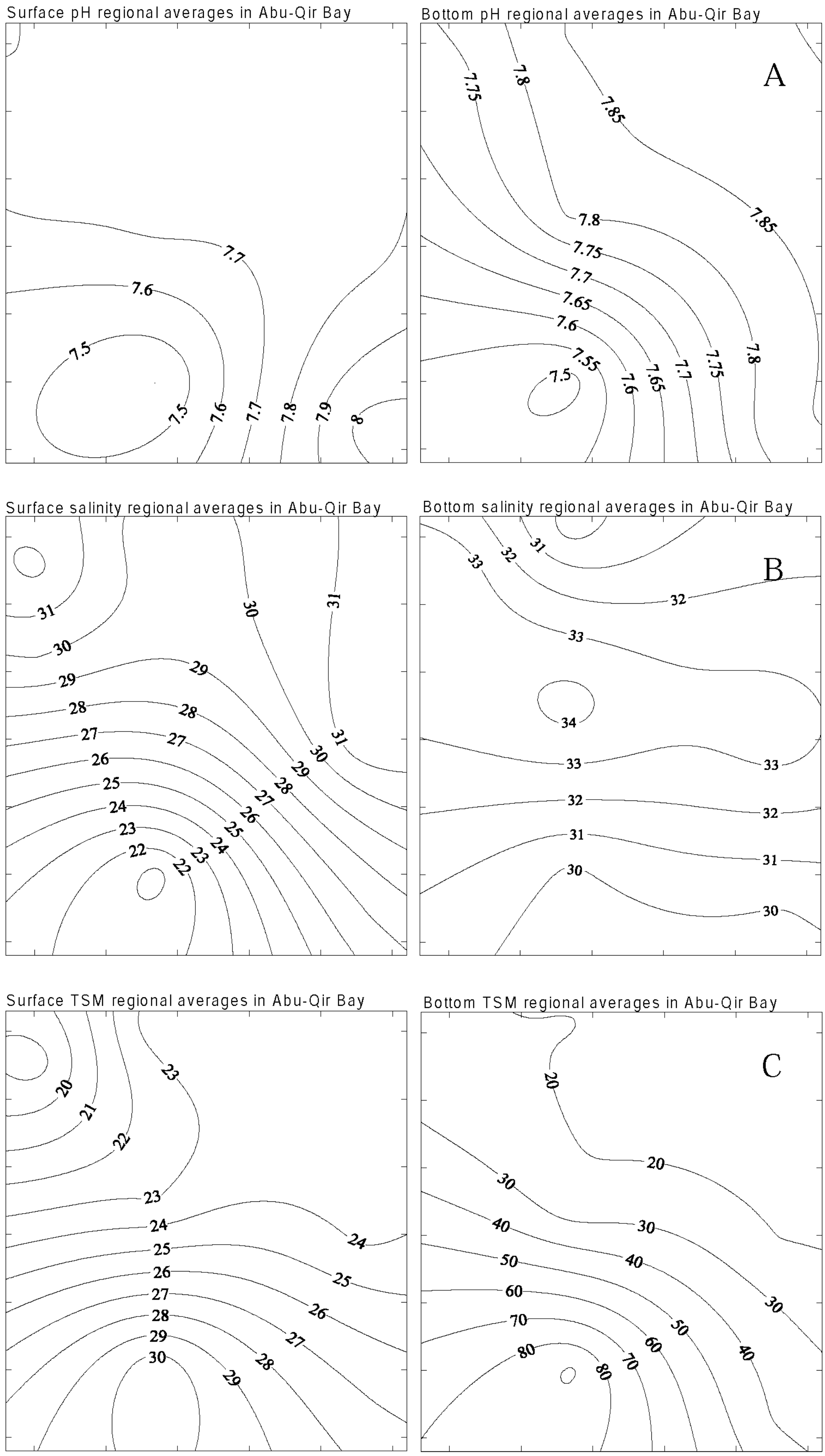

Figure 2. Regional average values of pH (A), salinity (B) and TSM (C) in the surface and bottom waters of Abu-Qir Bay.

The surface water layer exhibited absolute TSM values ranging widely between 9 $mg.l^{-1}$ at stations I and II in October and 49 $mg.l^{-1}$ in July also at station I. Again in July, the bottom water of station I showed an extraordinary high absolute TSM value of 289 $mg.l^{-1}$ lowered to a minimum of 14 $mg.l^{-1}$ in October at station III. Station I showed the maximum regional average values of 30.8 ± 19.8 $mg.l^{-1}$ (surface) and 91.3 ± 132.4 $mg.l^{-1}$ (bottom). The surface water of station VII gave the minimum average TSM value of 18.5 ± 4.2 $mg.l^{-1}$, while the bottom water of station IV showed the minimum average of 19.5 ± 3.3 $mg.l^{-1}$ (Fig. 2). The seasonal average TSM values for the surface water layer ranged widely from 15.7±5.9 $mg.l^{-1}$ in October to 32.6 ± 10.7 $mg.l^{-1}$ in July. The bottom averages varied significantly between 17.2 ± 1.0 $mg.l^{-1}$ in January and 72.0 ±106.3 $mg.l^{-1}$ in July (Table 1). Although the bottom water exhibited an extraordinary high value in July, the annual mean TSM value for the bottom water (35.5 ± 28.1 $mg.l^{-1}$) was not so noticeably higher than that calculated for the surface water (24.0 ± 4.0 $mg.l^{-1}$).

Phosphorus species

For the bottom water, a considerably high absolute value of DIP (15.10 µM) was recorded in April at station V. This was responsible for the highest seasonal average DIP value of 2.98 ± 5.94 µM in April (Table 2). The maximum regional average DIP value of 4.40 ± 7.20 µM was also obtained in the bottom water of station V (Fig. 3) from the alternating appearance in DIP values during the study period. The minimum absolute DIP value (0.05 µM) was recorded at station III in October and stations III and IV in January. In the surface water layer, the minimum absolute DIP value of 0.05 µM was recorded at station II in April and stations IV and VII in July, while the maximum of 3.61 µM was recorded at station I in April. The regional average DIP values for the surface water ranged from 2.79 ± 1.05 µM at station I to 0.36 ± 0.42 µM at station IV. The bottom water minimum regional average appeared at station III (0.11 ± 0.09 µM), as shown in Fig. 3. The annual mean DIP values in the surface and bottom water layers were nearly equal (1.11 ± 0.82 and 1.14 ± 1.62 µM, respectively). The contribution of DIP to TDP was 48% for the surface water and 49% for the bottom water.

Table 2. Seasonal average concentrations of DIP, DOP and PP (µM) in the surface and bottom water layers of Abu-Qir Bay.

Seasons		DIP	DOP	PP
April	S	1.51 *±1.22*	0.20 *±0.23*	1.00 *±1.44*
	B	2.98 *±5.94*	0.27 *±0.39*	1.99 *±1.57*
July	S	0.76 *±1.05*	0.61 *±0.40*	1.46 *±1.04*
	B	0.43 *±0.37*	0.53 *±1.14*	2.07 *±0.98*
October	S	1.24 *±0.66*	1.51 *±0.71*	7.43 *±2.69*
	B	0.58 *±0.72*	1.46 *±0.53*	3.10 *±2.56*
January	S	0.94 *±1.13*	2.82 *±2.90*	2.41 *±2.84*
	B	0.56 *±0.84*	1.96 *±0.74*	1.22 *±0.80*

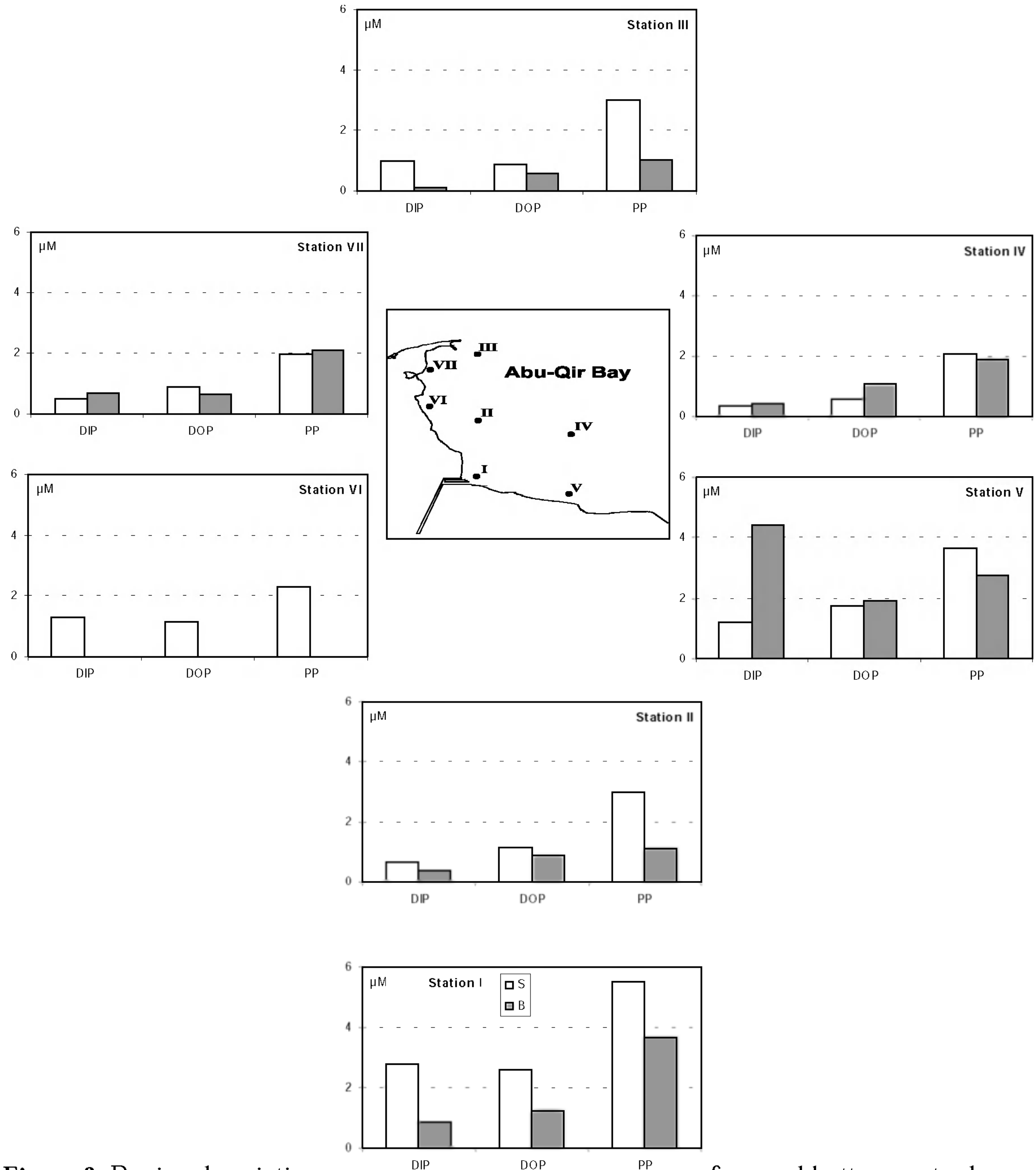

Figure 3. Regional variations of DIP, DOP and PP (µM) in surface and bottom water layers of Abu-Qir Bay.

In January, station I showed the maximum absolute DOP values for both surface (9.15 µM) and bottom (3.05 µM) water samples. The high absolute DOP value for the surface water led to the highest regional average of 2.61±4.36 µM at station I. The bottom maximum regional average of 1.91±1.15 µM appeared at station V (Fig. 3). In January, two maximum peaks of seasonal DOP averages were represented with values of 2.82 ± 2.90 and 1.96 ± 0.74 µM for the surface and bottom water samples, respectively, while surface and bottom minimum averages were detected in April (Table 2). The annual mean DOP value for the surface water was higher than that for the bottom water (1.28 and 1.05 µM, respectively), contrary to those of DIP annual means.

In April, station VII exhibited the lowest value of the absolute PP in the surface water layer (0.02 µM) and its bottom water was depleted from PP. In October, station I showed the maximum absolute bottom PP value (6.20 µM), while the highest surface value of 10.50 µM was observed at station III.

The surface regional average PP values varied between 1.98 ± 2.48 and 5.53 ± 4.13 µM at stations VII and I, respectively. Meanwhile, the same averages for the bottom water varied between 1.03±0.26 µM at station III to 3.66±2.13 µM at station I (Fig. 3). The annual mean value of PP in the bottom water (2.09 µM) was approximately two thirds of that for the surface water (3.07 µM). Markedly high seasonal averages of PP appeared in October for surface and bottom water layers, 7.43 ± 2.69 and 3.10 ± 2.56 µM, respectively (Table 2).

Nitrogenous species

The surface and bottom water layers showed extreme differences in the absolute nitrate values during the study period. Station V, located opposite to Abu-Qir fertilizers and chemical company (Fig. 1), exhibited two approximately nitrate maxima in January in the surface and bottom waters (40.26 and 37.48 µM, respectively). The appearance of these maxima was reflected on the highest regional averages of 15.26±18.40 µM (surface) and 14.74 ± 17.36 µM (bottom) at this station (Fig. 4). In addition, the maximum seasonal average nitrate values were obtained in January (10.78 ± 13.62 and 10.83 ± 13.64 µM) for the surface and bottom water layer, respectively (Table 3). The absolute bottom minimum value was 0.04 µM in April at station IV and the absolute surface minimum was 0.37 µM at station III in July. The nitrate minimum regional averages were recorded in the surface of station IV (1.44 ± 0.94 µM) and the bottom of station VII (1.13 ± 0.89 µM), as shown in Fig. 4. In July, two minimum nitrate seasonal averages were distinct, giving 1.36±0.86 µM for the surface and 1.03±0.40 µM for the bottom waters (Table 3). The annual mean nitrate values for the bottom water (5.80±5.38 µM) and the surface water (5.87±5.61 µM) were mostly identical.

Table 3. Seasonal average concentrations of nitrate, nitrite, ammonium, DON and PN (µM) in the surface and bottom water layers of Abu-Qir Bay.

Seasons		NO_3	NO_2	NH_4	DON	PN
April	S	1.57 *±1.10*	0.12 *±0.18*	14.01 *±8.55*	285.1 *±52.1*	33.0 *±31.6*
	B	1.06 *±0.82*	0.07 *±0.05*	14.41 *±17.09*	301.3 *±44.1*	42.3 *±36.6*
July	S	1.36 *±0.86*	0.22 *±0.13*	7.79 *±13.83*	208.9 *±101.9*	68.5 *±71.5*
	B	1.03 *±0.40*	0.64 *±1.21*	38.53 *±84.40*	229.1 *±83.1*	43.8 *±36.4*
October	S	9.76 *±10.80*	0.89 *±0.95*	7.57 *±5.86*	277.1 *±38.9*	39.0 *±45.7*
	B	10.30 *±8.87*	1.32 *±2.19*	5.01 *±6.08*	212.3 *±61.7*	97.8 *±83.0*
January	S	10.78 *±13.62*	0.97 *±1.16*	2.62 *±6.64*	190.9 *±76.3*	94.0 *±35.4*
	B	10.83 *±13.64*	0.63 *±0.42*	0.94 *±1.95*	180.0 *±53.1*	121.2 *±25.9*

Abu-Qir fertilizers and chemical company contributed considerably large amounts of nitrite to Abu-Qir Bay. Station V, selected in the vicinity of their discharges (Fig. 1), showed a significantly high absolute nitrite value in January, reaching 3.58 µM for the surface layer. Also, the maximum absolute nitrite bottom value of 5.76 µM was recorded in October at this station. These two maxima have led to the highest regional averages of 1.67 ± 1.81 and 2.60 ± 2.44 µM for the surface and bottom water layers of station V. The lowest regional averages were 0.22 ± 0.18 µM (surface) and 0.15 ± 0.22 µM (bottom) at station III (Fig. 4). The minimum detected absolute value of nitrite was 0.02 µM at stations I and III in April and station II in July for the bottom water samples, while the same absolute value of 0.02 µM was recorded also at stations III and VII in April for the surface water layer. The maximum and the minimum seasonal averages for the surface water were 0.97 ± 1.16 and 0.12±0.18 µM in January and April, respectively (Table 3). Meanwhile, the maximum average value for the bottom water was recorded in October (1.32 ± 2.19 µM), while the minimum of 0.07 ± 0.05 µM was found in April.

The highest absolute ammonium value for the surface water (38.9 µM) was recorded in July at station V. An extraordinary ammonium concentration for the bottom water appeared also at station V in July (210.60 µM). In January, the minimum detected ammonium values were 0.01 µM recorded in the surface water of station II and 0.02 µM in the bottom water of station IV. In the bottom water layer, the peak of the maximum regional average concentration of ammonium (70.19 ± 95.47 µM) was obtained at station V. This was approximately triple that maximum regional surface value found also at station V (26.34 ± 9.48 µM). The minimum regional average value calculated for the surface water was 3.18 ± 3.41 µM at station VII and that for the bottom water was 2.34 ± 4.12 µM at station III (Fig. 4). In July and January, the maximum and minimum seasonal averages for the bottom water were 38.53 ± 84.40 and 0.94 ± 1.95 µM, respectively. For the surface water, these averages fluctuated between 2.62 ± 6.64 µM in January and 14.01 ± 8.55 µM in April (Table 3).

The bottom water at station I showed the absolute maximum DON value in April (363.4 µM). However, the bottom water at station V showed the absolute minimum value of 76.1 µM in January. The absolute DON values in the surface water varied very significantly from 3.2 µM at station II in July to 351.5 µM at station IV in April. The surface regional average DON values ranged widely from 165.5 ± 115.2 µM at station II to 315.9 ± 35.5 µM at station IV. The maximum regional average of DON for the bottom water (271.9 ± 74.0 µM) was calculated at station I, lowered to 146.4±81.4 µM at station V (Fig. 4). The peak of seasonal average DON concentration for the surface water layer appeared in April (285.1 ± 52.1 µM), while the minimum seasonal average of 190.9 ± 76.3 µM was found in January. For the bottom water, the seasonal average DON values ranged from 180.0 ± 53.1 µM in January to 301.3 ± 44.1 µM in April (Table 3).

The absolute PN values in the surface water ranged from 2.9 µM at station VI in April to 214.8 µM at station II in July. The bottom water at station I in July showed the minimum absolute PN value of 0.9 µM, while the maximum absolute PN value appeared in October at station VII (205.4 µM). The regional average PN values for the surface water ranged from 42.0 ± 44.8 µM at station VI to 107.4 ± 80.0 µM at station II. The peak of regional average PN value for the bottom water appeared at station VII (110.3 ± 65.4 µM) and the minimum bottom average PN value (43.0 ± 48.3 µM) was found at station II (Fig. 4). In the bottom water layer, an alternating appearance of different seasonal average PN values ranged from 42.3 ± 36.6 µM in April to 121.2 ± 25.9 µM in January. The appearance of low and high seasonal average PN values for the surface water was also noticeable in the same seasons, ranging from 33.0 ± 31.6 µM in April to 94.0 ± 35.4 µM in January (Table 3). The PN in the surface water gave an annual mean of 58.6 µM and increased to 76.2 µM in the bottom water. These two values contributed on the average 20 and 23% of TN, respectively.

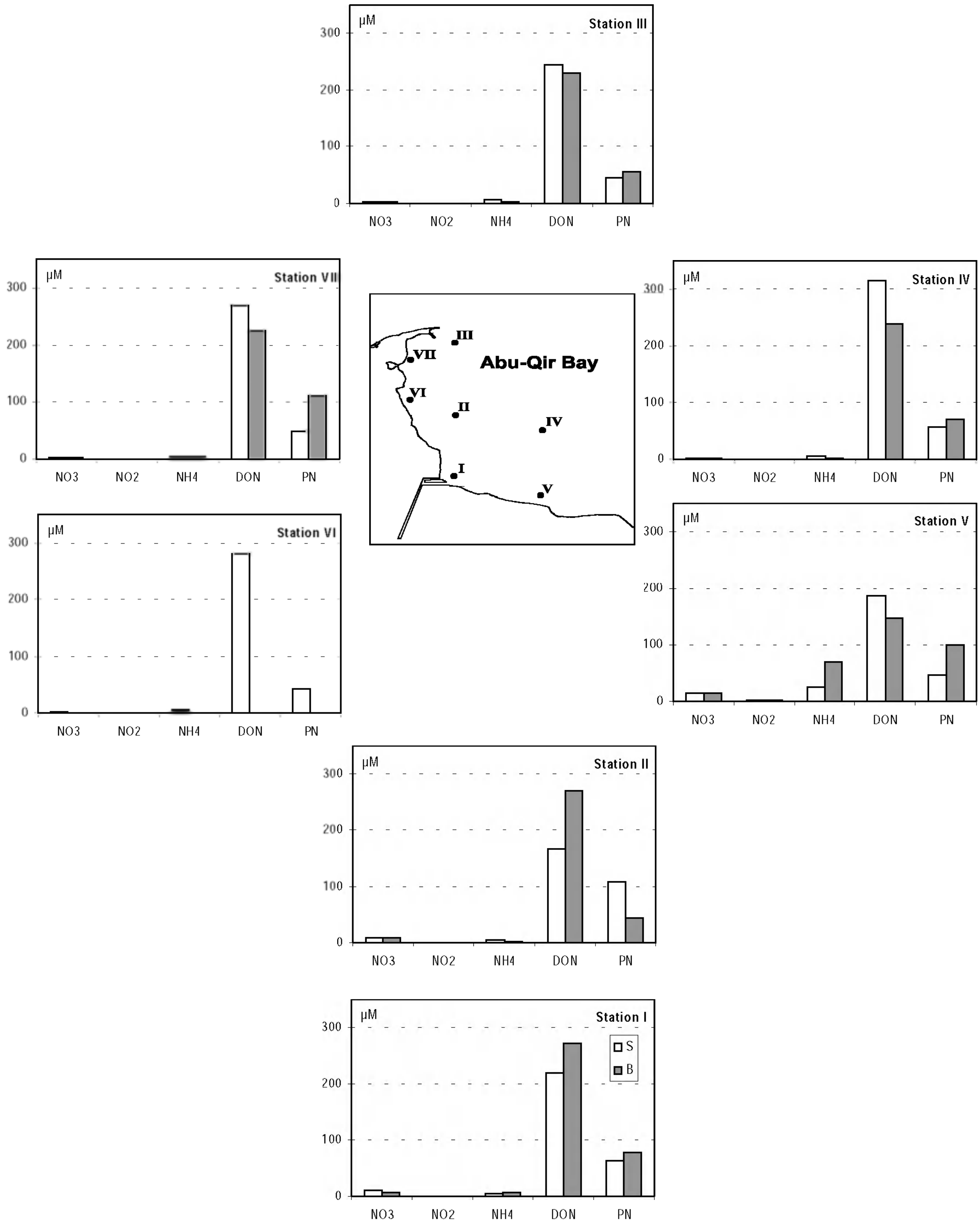

Figure 4. Regional variations of NO_3, NO_2, NH_4, DON and PN (µM) in surface and bottom water layers of Abu-Qir Bay.

Discussion

Environmental parameters

The maximum and minimum seasonal average temperature values for the surface and bottom water layers appeared in July (summer) and January (winter) confirmed the role of seasonal variations, as the main factor controlling the temperature readings in the study area. Due to shallowness of the investigated marine region, thermal stratification was rarely detected, except at locations directly subjected to thermal pollution from industrial warm water discharges. In periods of calm weather, thermal stratification might occur to a limited extent. The area of study, as a part of the southeastern Mediterranean, represents a warm subtropical region. The temperature ranges recorded in the present investigation were comparable to previous records from the same and other coastal Mediterranean waters in front of Alexandria (Table 4).

Table 4. Ranges of water temperature values (°C) in the present study compared with previous investigations.

Marine areas	Depth	Ranges	Reference
Abu-Qir Bay	S	16.0-29.3	This study
	B	16.1-28.7	
Abu-Qir Bay		15.4-29.5	[24]
Eastern Harbor	S	16.9-29.2	[1]
	B	17.0-28.5	
Western Harbor	S	15.1-27.8	[25]

Table 5. Absolute values and their regional average concentrations of pH, TSM, DIP, DOP, PP, nitrate, nitrite, ammonium, DON and PN in the water of Tabia Pumping Station (TPS).

Parameters	July	October	January	April	Regional averages	SD
pH	7.60	7.46	8.55	7.99	7.90	*±0.49*
TSM ($mg.l^{-1}$)	153	16	29	196	98.5	*±89.7*
DIP (µM)	6.69	4.60	2.20	9.80	5.82	*±3.22*
DOP (µM)	0.21	1.00	7.50	14.00	5.68	*±6.44*
PP (µM)	7.36	15.70	14.90	18.40	14.09	*±4.70*
NO_3 (µM)	0.37	40.94	30.04	12.70	21.01	*±18.00*
NO_2 (µM)	1.29	30.46	0.66	0.40	8.20	*±14.84*
NH_4 (µM)	94.30	15.24	2.62	6.27	29.61	*±43.45*
DON (µM)	119.3	131.3	64.9	192.4	126.9	*±52.3*
PN (µM)	2.4	100.1	51.0	61.1	53.7	*±40.2*

The low pH values resulted most probably from the intensive industrial wastewater discharged into the bay through TPS. The regional average pH in TPS was 7.90±0.49 (Table 5). On the contrary, the high pH values for both surface and bottom water layers possibly resulted from the effect of the wastewater discharged from the fertilizer industries, which comprised high pH values. The regional averages indicate that pH values showed a trend of the increase away from the points of freshwater discharges, as a result of dilution, in addition to the corresponding decrease in organic matter load. Badr [17] reported that the bottom sediments in front of TPS were dominated by silty sandy type, while sediments from other areas of the bay were almost sand. This author also concluded that the enrichment of organic matter was observed in the sediments covering the area of the Tabia section, whereas, El-Maadia region showed low organic matter content. The maximum seasonal average pH value appeared in April and the minimum in July for both surface and bottom water layers (Table 1). This might be due to the introduction of low-pH water into the bay in July, as confirmed from the low pH value (7.60) in TPS that month. However, the highest value of 8.55

in TPS was recorded in January (Table 5). Table 6 illustrates the comparison of the pH values of this study with other previous investigations.

Table 6. Means and ranges of pH values in the present study compared with previous investigations.

Marine areas	Depth	Means	Ranges	Reference
Abu-Qir Bay	S	7.73	7.13-8.38	This study
	B	7.76	7.05-8.21	
Abu-Qir Bay	S	8.11	7.20-8.72	[24]
	B	8.15	7.10-8.90	
Eastern Harbor	S	8.20	7.80-8.58	[1]
	B	8.08	7.65-8.43	
Western Harbor	S	7.64	7.00-8.81	[25]
Egyptian Mediterranean water	S		7.80-8.00	[26]

Table 7. Means and ranges of salinity values in the present study compared with previous investigations.

Marine areas	Depth	Means	Ranges	Reference
Abu-Qir Bay	S	28.39	5.25-40-22	This study
	B	31.81	13.13-40-22	
Eastern Harbor	S	33.17	34.78-38.77	[1]
	B	37.92	35.47-39.21	
Western Harbor	S	36.97	26.23-39.36	[25]

Abu-Qir Bay is subjected to huge freshwater invasion through either domestic sewage outfalls, industrial and agricultural effluents. Accordingly, the salinity values near the points of discharges were lower compared to those normally present. This is confirmed from the lower regional average salinity values at the stations located opposite to the outfalls or the effluent discharges. The peaks of seasonal surface and bottom salinity averages in July (Table 1) might be resulted from the high solar energy in the shallow water bay and/or from the low freshwater discharges in summer season compared with winter season. The annual surface mean salinity value (28.39 ± 3.91) was lower than that for the bottom water (31.81 ± 2.32), reflecting the influence of freshwater discharges from the land-based sources. Table 7 shows the means and ranges of salinity values recorded during this study compared to the previous investigation values in the Eastern and Western Harbors of Alexandria.

Changes in the signal output induced in coastal waters by the Nile's influence appear to be considerably weaker than the impact of the continental waters introduced into the marine environment by the human activity developed along the southwestern area of Abu-Qir Bay (TPS, fertilizer factory, channel between Lake Edku and the bay). Romano et al. [6] indicated that if the values of different parameters recorded along the eastern part of the bay are considered in comparison with those in the southwestern part, it can be concluded that under the prevailing meteorological conditions the discharge influence remains confined in the western and southern parts of the bay.

The regulation which had been introduced by the Aswan High Dam (1968) and the downstream capture of the river waters for human needs (agriculture and industry) have strongly reduced the Nile's influence upon its delta bordering the coastal marine waters. Most of the freshwater rejects to seawater passes through canals which drain from 1 to 1.4 x 10^9 $m^3.y^{-1}$ [18]. In our opinion, the case of direct anthropogenic water discharge from factories and agricultural drains to seawater is not in fact so different than the rivers when we consider that in practice most of the Mediterranean rivers discharge the untreated residues of the human activities [19,20].

Table 8. Means and ranges of TSM values (mg.l^{-1}) in the present study compared with previous investigations.

Marine areas	Depth	Means	Ranges	Reference
Abu-Qir Bay	S	24.0	9-49	This study
	B	35.5	14-289	
Eastern Harbor	S	38.45	8-188	[1]
	B	30.52	9-96	
Western Harbor	S	154	22-414	[25]

Table 9. Correlation coefficients between the different measured parameters in the surface water of Abu-Qir Bay.

	Temp	pH	Salin.	TSM	DIP	DOP	PP	NO_3	NO_2	NH_4	DON
Temp	1										
pH	-0.194	1									
Salinity	0.657	0.341	1								
TSM	0.538	0.046	0.480	1							
DIP	-0.082	-0.060	-0.267	0.337	1						
DOP	-0.384	-0.165	-0.619	-0.287	0.358	1					
PP	-0.172	-0.360	-0.557	-0.372	0.410	0.413	1				
NO_3	-0.316	0.106	-0.557	-0.387	0.107	0.351	0.463	1			
NO_2	-0.253	0.313	-0.291	-0.272	-0.036	0.267	0.240	0.816	1		
NH_4	0.182	0.449	0.187	0.254	0.113	-0.128	-0.004	0.091	0.200	1	
DON	-0.049	0.065	0.215	-0.151	0.053	-0.271	0.062	-0.442	-0.344	0.026	1
PN	-0.081	-0.330	-0.258	-0.109	-0.374	0.036	-0.193	0.114	-0.056	-0.271	-0.585

Table 10: Correlation coefficients between the different measured parameters in the bottom water of Abu-Qir Bay.

	Temp	pH	Salin.	TSM	DIP	DOP	PP	NO_3	NO_2	NH_4	DON
Temp	1										
pH	-0.218	1									
Salinity	0.433	0.233	1								
TSM	0.382	-0.505	0.237	1							
DIP	0.053	-0.112	-0.002	0.119	1						
DOP	-0.240	-0.056	-0.565	-0.250	-0.170	1					
PP	0.259	-0.112	0.185	0.246	0.048	0.008	1				
NO_3	-0.126	0.055	-0.415	-0.123	-0.019	0.501	0.200	1			
NO_2	0.048	0.222	0.005	-0.059	-0.105	0.553	0.307	0.415	1		
NH_4	0.310	0.001	0.138	0.052	0.145	0.326	0.054	-0.117	0.428	1	
DON	0.007	0.212	0.364	0.185	-0.003	-0.643	-0.146	-0.440	-0.477	-0.390	1
PN	-0.229	-0.306	-0.390	-0.288	0.187	0.424	0.364	0.384	0.215	-0.138	-0.611

A comparison between TSM values recorded in this study with other previous investigations is shown in Table 8. Due to the maximum absolute TSM values recorded in July, the surface and bottom waters exhibited the maximum seasonal averages that month; 32.6 ± 10.7 and 72.00 ± 106.3 $mg.l^{-1}$, respectively, as shown in Table 1. These results indicate that the main contributor of TSM into Abu-Qir Bay was the TPS, exhibiting a direct effect on the surface and also on the bottom water layers at station I, selected close to its discharges (Figs. 1 and 2). This is confirmed from the higher values of TPS compared to the TSM values recorded in Abu-Qir Bay (Tables 1 and 5). However, the significant positive correlation (Table 9) observed between surface TSM and salinity ($r= 0.480$, $p<0.01$) suggests the presence of another source for TSM loading into the bay rather than the freshwater discharges through TPS, probably from the extensive biological activities taking place during the study period. Harris [21] attributed the high TSM in the Gulf of Mexico partially to phytoplankton. In the bottom water, TSM showed a significant negative correlation with pH ($r=-0.505$, $P<0.001$), indicating the association of TSM with low-pH water discharged from TPS (Table 10). The annual mean of TSM in the surface water in Abu-Qir Bay was lower than that obtained for the bottom waters.

Phosphorus species

The maximum regional average DIP values for both surface and bottom water layers appeared at stations I (2.79 ± 1.05 µM) and V (4.40 ± 7.20 µM), respectively as shown in Fig. 3. These high marine values might be probably resulted from the extensive production of the effluents from the phosphate fertilizers discharging into the bay and from TPS. This is confirmed from the high DIP regional average value of 5.82 ± 3.22 µM calculated for TPS (Table 5) compared to the marine values. Another assumption is the release of DIP from the bottom sediments and/or detritus fraction which might probably enhanced the DIP levels in the bay. This is confirmed from the annual mean DIP values which were nearly similar for the surface and bottom water layers (1.11 and 1.14 µM, respectively). Generally speaking, the average DIP values showed a marked decrease with increasing distance from the shore. In a study carried out in Abu-Qir Bay in April and May 1999, the DIP surface values in southwestern part of the bay in front of TPS ranged between 0.20 and 1.75 µM [7]. The surface water of Abu-Qir Bay showed DIP/DOP ratio of 0.9, while that for the bottom waters was 1.1. This indicates that DOP was predominant than DIP in the surface water, reflecting preference of DIP utilization by phytoplankton in the euphotic zone.

Similar to DIP local variations, the maximum regional average surface DOP value (2.61 ± 4.36 µM) at station I and that for the bottom water of 1.91 ± 1.15 µM at station V (Fig. 3) reflect the direct effects of the phosphate fertilizer factory and TPS effluents, as confirmed from the obviously high regional average DOP concentration of 5.68 ± 6.44 µM in TPS (Table 5). In January, both water layers exhibited the maximum seasonal average DOP values of 2.82 ± 2.90 µM (surface) and 1.96 ± 0.74 µM (bottom). The DOP value in TPS was also markedly high in January (7.50 µM). This again indicates the role of TPS in introducing large amounts of DOP through the intensive discharges of freshwater during the rainy season. The DOP values showed statistically significant negative correlation with salinity $r= -0.619$, $P< 0.001$ for the surface water and $r= -0.565$, $P= 0.01$ for the bottom water (Tables 9 and 10). These correlations indicate that DOP levels declined seaward, which may be due to the decrease in the effect of anthropogenic wastewaters and the uptake by organisms. The increase in the annual surface DOP mean (1.28 µM) compared to that of 1.05 µM for the bottom water reflects the direct effect of man's impacts first on the surface bay water.

The markedly high average PP value in TPS (14.09 ± 4.7 µM) caused the maximum regional surface (5.53 ± 4.13 µM) and bottom averages (3.66 ± 2.13 µM) at station I, selected in the vicinity of the TPS discharges (Figs.1, 3 and Table 5). The Maximum surface and bottom seasonal PP averages in Abu-Qir Bay (Table 2) coincided with the October high PP value in TPS (15.70 µM), as shown in Table 5. Surface PP gave a statistically significant negative correlation with salinity ($r = -0.577$, $P<0.001$) as shown in Table 9, indicating its association with low-saline water discharged from TPS.

Nitrogenous species

Nitrate in the surface water layer contributed to an average of 42% of DIN and about 2% of TDN, while in the bottom water layer it contributed 46% of DIN and 2% of TDN. Generally, TPS showed a great effect on the nitrate content in the water of Abu-Qir Bay. For the surface and bottom water layers, station V showed the highest regional average nitrate values (Fig. 4), indicating that this station was subjected to extreme nitrate input. In addition, station I exhibited also high nitrate regional averages. Accordingly, nitrate might be associated with industrial discharges and production of fertilizers. As shown in Table 9, nitrate values for the surface water showed negative correlation with salinity ($r = -0.557$, $P< 0.01$) confirming the influence of freshwater discharges on elevation of nitrate content. The minimum seasonal nitrate averages appeared in July in both water layers are ascribed probably by the increase in nutrient utilization by phytoplankton blooms during the summer season. This is supplemented with the lowest nitrate level (0.37 µM) in TPS water in July (Table 5), with a regional average of 21.01 ± 18.0 µM. Younes [7] reported nitrate values in the southwestern area of Abu-Qir Bay, ranging between undetected value and 13.29 µM, during April-May 1999. Due to lack of stratification and/or probably due to shallowness of the water column of the bay, the annual surface and bottom means of nitrate were nearly similar.

The annual mean surface nitrite value (0.55±0.51 µM) and bottom value (0.66±0.95 µM) contributed about 5% of DIN in both water layers. The nitrite contribution to TDN was almost negligible in the surface and bottom layers. The increase in nitrite content with depth can be attributed to nitrate reduction in the relatively oxygen-poor bottom water [22] and the extra cellular release of nitrite, accompanying the assimilation of nitrite-nitrogen by marine phytoplankton. The nitrite values in Abu-Qir Bay showed a marked tendency to decrease towards the offshore stations. The surface and bottom water layers exhibited the maximum regional average nitrite values (Fig. 4) at station V, located opposite to Abu-Qir fertilizers and chemicals company effluents (Fig. 1). Younes [7] reported nitrite values in the southwestern area of Abu-Qir Bay, ranging between 0.03 µM in April and an extraordinary high value of 7.87 µM in May 1999. It might be concluded that the maximum seasonal average bottom nitrite value (1.32 ± 2.19 µM) in October coincided with the markedly high absolute nitrite concentration of 30.46 µM that month in TPS (Table 5). Riley & Chester [23] found that during the earlier part of regeneration, nitrite increased progressively to a maximum in autumn and then decreased to lower values in winter. A statistically significant positive correlation was found between nitrite and nitrate in the surface water ($r = 0.816$, $P< 0.001$). However, the correlation with ammonium was not significant (Table 9), indicating that nitrate reduction, rather than ammonium oxidation, was the major internal source of nitrite.

The bottom waters gave an annual mean ammonium value of 14.72±27.21 µM, which was nearly double that for the surface water (8.00 ± 8.22 µM). The increase in ammonium values with depth was mostly due to decomposition processes of the high organic matter contained in the wastes sedimented on the bottom of Abu-Qir Bay. However, ammonium concentrations showed a marked tendency to decrease away from land-based sources (Fig. 4), as confirmed from the influence of the comparatively high regional average ammonium value in TPS water of 29.61 ± 43.45 µM (Table 5). Surface water layer showed that on the average ammonium constituted annually 52% of DIN and 3% of TDN. On the other hand, NH_4/DIN% for the bottom water was 49, while NH_4/TDN% was 6. It constituted on the average about half of DIN fraction in the surface and bottom water layer of Abu-Qir Bay during the study period. The positive correlation between ammonium and pH in the surface water (Table 9) giving $r = 0.449$, $P <0.1$ confirms that ammonium was also derived from an external source (fertilizers company).

The annual mean DON value of 240.5 ± 53.2 µM for the surface water was slightly higher than that for the bottom water (230.7 ± 45.9 µM). The contribution of DON to TDN in the surface and bottom water layers was the same (91%). In spite of this, the percentage of DON/TN for the surface water was higher than that for the bottom water (77 and 70%, respectively). The maximum regional average DON value for the bottom water appeared at station I, located opposite to TPS (Fig. 1), whereas that for the surface water was found at station IV (Fig. 4). The TPS regional average was only 126.9 ± 52.3 µM, indicating the poverty of DON in TPS compared to the level present in the bay. Table 9 shows that surface DON gave a negative correlation with nitrate ($r = -0.442$, $P < 0.1$). In the bottom water, DON showed significantly negative correlation with DOP ($r = -0.643$, $P < 0.001$) and was correlated negatively with nitrite ($r = -0.477$, $P < 0.1$) as shown in Table 10. This indicates that DON might be associated with biological activities, which have probably played an important role in introducing large amount of DON through extra cellular metabolites of phytoplankton and/or resulted from protein decomposition during the decay of organic tissue.

In Abu Qir Bay, the maximum regional average PN values were observed in the surface water of station II (107.4 ± 80.0 µM) and in the bottom water of station VII (110.3 ± 65.4 µM), as shown in Fig. 4. The significantly negative correlation with DON ($P < 0.001$) for both water layers in addition to the regression equation between PN with TSM: [TSM (mg.l^{-1})=38.074-0.139 PN (µM)], indicate that PN levels were mainly derived from the TPS discharges, which introduced huge amounts of untreated industrial wastes from several factories. The TPS gave PN values ranged widely between 2.4 and 100.1 µM in July and October, respectively, giving a regional PN average of 53.7 ± 40.2 µM (Table 5).

Conclusion

The hydrographic data obtained during the present study were compared with previous investigations for illustrating the present pollution status in the study area. The present temperature ranges were comparable to previous records. The low pH values in the bay might resulted from the intensive industrial wastewater discharged into the bay through TPS, while the high surface and bottom pH values could be attributed to the wastewater discharged from the fertilizer industries. The salinity values near the points of discharges were lower compared to those normally present. TPS was considered as the main contributor of TSM into Abu-Qir Bay, giving higher TSM when compared to those obtained in this bay. The estimation of the present load of nutrients delivered to the sea via industrial, domestic and agricultural inputs is a tool to evaluate the role of land-based sources as a major contributor of pollutants to Abu-Qir Bay. The budget of nutrient salts in Abu-Qir Bay is controlled by several processes including; 1) inputs by industrial, agricultural and domestic discharges; 2) precipitation; 3) release from the bottom sediments and the detritus of living organisms; 4) uptake by organisms and 5) exchange with the open seawater. The volume of Abu-Qir Bay is 4.32 km^3 and the exchange of water between the bay and Lake Edku through El-Maadia channel occurs in the southern area. On the southwestern area, the bay received about 730 x10^6.m^3 y^{-1} of untreated sewage and industrial wastewaters via TPS. According to Abdel-Moati [10], the annual input from the Mediterranean neritic waters was 19.43 km^3 y^{-1} and thus the mean residence time for Abu-Qir Bay water was 2.5 months. In the present study, since the results are based only on the input from TPS, the freshwater residence time in the bay was 5.9 y. The bay exhibited high standing stock for the different elements compared to the input from TPS. This major difference resulted from the accumulation of elements in the bay after being discharged from TPS, accompanied by long residence times almost exceeding one year. The residence times ranged from 1.1 y for DIP, DOP and PP to 10.9 y for DON. Only nitrite showed a short residence time (83.7 days) in the bay. The standing stocks of phosphorus species in Abu-Qir Bay were 149.9, 156.8 and 345.2 tons for DIP, DOP and PP, respectively. For nitrogenous forms, they were 353.0, 36.7, 686.9, $14.2x10^3$ and $4.1x10^3$ tons for nitrate, nitrite, ammonium, DON and PN, respectively. Regarding the present situation in Abu-Qir Bay, the accumulation of elements will increase proportionally with increasing industrial operations, which of course would increase the residence time of some elements. Also, due to the limited exchange between Abu-Qir Bay and the open Mediterranean seawater, it will become a recipient of excessive quantities of pollutants exceeding its natural assimilative capacity leading to serious environmental problems.

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