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Long-Term Water Quality Monitoring at an Industrial Site on the Northern Gulf of Aqaba, Red Sea

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Abstract

The present study focuses on seawater samples collected monthly, for 12 years (June 1998 to December 2010), within the framework of the sustainable monitoring program in front of the Industrial Complex (IC) Aqaba Jordan. In situ measurements of temperature, salinity, pH and dissolved oxygen have been recorded, for three different depths, at six different stations. Also, samples have been collected and analyzed for inorganic nutrients, fluoride and sulfate. The data collected, when compared with the offshore waters, showed the dominance of natural Aqaba seawater conditions for most variables throughout the year. Phosphate concentrations were slightly higher in some sampling events. This, however, did not exert any considerable effect on the environmental quality of the seawater, mainly because anthropogenic phosphate reaching the sea does with the help of the wind in very limited amounts and insoluble form. Also, phosphate is not the primary productivity limiting nutrient in the waters of the Gulf of Aqaba.

Keywords: Aqaba, environment, water quality, monitoring, industrial site.

Introduction

Coastal zones represent the interface between the land proper and sea proper. They offer several attractions for investment, prompting the hosting of intense and diverse human activities, from recreation to heavy industry. The nearshore marine ecosystem is a dynamic environment that could be impacted by such activities. Coastal waters and sediments adjacent to the major urban areas, in particular, can be heavily influenced (Daby, 2006). A high-resolution long-term time series of studies offers a reliable approach to study the impact of human activities on coastal water (Badran, 2001).

The characteristics of seawater are distinguishable into two main categories; conservative and non-conservative. Conservative characteristics are those which are unaffected by the biological productivity of the system, such as temperature and salinity. Non-conservative characteristics are those produced by the biological productivity of the system such as nutrients, dissolved oxygen and chlorophyll *a* (Badran & Al-Zibdeh, 2005; Giordani *et al.,* 2005). Modifications in the water temperature caused by the run-off of cooling water or fresh water, which can be easily detected using self-recording sensitive and reliable equipment, are extremely significant because they directly affect biological productivity. Modifications of non-conservative characteristics can be either natural or anthropogenic. These are usually more difficult to detect, particularly in the oligotrophic waters. They are, however, essential determinants in a monitoring program because they shape the biological productivity of the system and consequently the ecosystem biodiversity.

The Gulf of Aqaba is a semi-enclosed water body located at the northern end of the Red Sea (Fig. 1). The mean depth of the Gulf is about 800 m, with a maximum of about 1800 m, close to that of the Red Sea. The annual variation in the current is attributed to variations in the production and propagation associated with changes in the strength and structure of the thermocline throughout the year (Monisnith & Genin, 2004). The seasonal variation range in the sea surface temperature in the northern part of the Gulf of Aqaba is about 6-7°C (Al-Rousan *et al*., 2002; Manasrah *et al*., 2004). The upper 200 m segment of the water column in the northern Gulf displays characteristics during summer quite different from winter. During summer, a strong thermocline is noted with a temperature range of 21 to 27° C in the upper 300 m. During winter, the water column gets thoroughly mixed

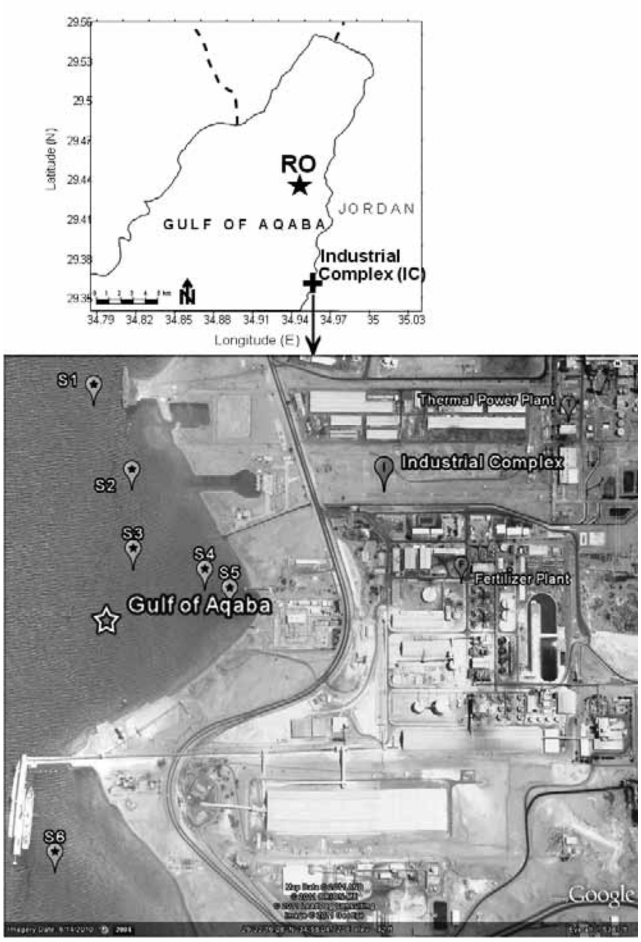

Fig. 1: Map of the northern Gulf of Aqaba showing the location of the study sites.

with a temperature range of ~20.5-21.0°C, in the upper 300 m. Below 500 m, the water column is more or less homogenous during summer and winter, with a temperature range between 500 m and the bottom similar to that in the upper 300 m during winter (Manasrah *et al*., 2006). Nutrient concentrations, particularly nitrates, phosphates and silicates in the offshore waters of the Gulf of Aqaba exhibit similar profiles to those of the temperature, but with an inverse relationship (Klinker *et al*.,1978; Badran, 2001). Both studies reported strong nutriclines of nitrate, silicate and phosphate during the summer and complete mixing in the entire water column during winter.

Aqaba, the southernmost city of Jordan, at the northeastern part of the Gulf of Aqaba (Fig. 1), is especially important as it is Jordan's only sea gate. The extremely limited Jordanian coast of Aqaba of less than 30 km must serve all the multifarious uses of the coastal area: tourism, ports, industry, military, education and marine conservation. The present investigation focuses on an industrial site that extends for about 2 km at the southern most part of the Jordanian coast (Fig. 1). The Industrial Complex site (IC) harbors a Timber Plant, a Thermal Power Station, a Phosphate Fertilizer Complex, a Potash Export Terminal and a Mixed Fertilizers plant. It also comprises the main platform in which a mega investment project of moving the Ports is being implemented. These industrial activities, could if not properly managed, pose a potential threat to the adjacent coastal ecosystem.

The present study includes 12 years of records (1998-2010) of the basic physico-chemical properties of seawater collected from six locations along the Industrial Complex (IC) coast. All the records were then compared with results collected from a reference offshore site (RO). This serves as an indicator of the modification of these coastal waters relative to the far-from-human-impact offshore surface water.

Material and Methods

Sampling

Water samples were collected from six stations (Fig. 1) at three different depths in front of the industrial complex; and one reference offshore station 3 km off the coast, at approximately 400 m depth. The sampling sites were chosen to cover most of the industrial activities on the IC coast. S1 is located north of the IC, S2 and S3 are the cooling water inlet and outlet, respectively, for Aqaba Thermal Power Plant, S4 and S5 are the Cooling Water inlet and outlet, respectively, for the Fertilizer Industry, and S6 is located south of the IC.

A 10-liter PVC Niskin seawater sampler was used to collect samples at 10, 20 and 30 m depths, at each station. Offshore samples were collected from 1 m depth. Collected samples were immediately stored in a dark ice-box with an internal temperature of around 0^o C. Back at the laboratory (2 – 3 hours from the collection site) the seawater samples were filtered under vacuum using 45 μm cellulose acetate membrane filters and stored in a deep freezer at -20^o C for later analysis.

In Situ Measurements

Water temperature and dissolved oxygen were measured by a CTD and a pre-calibrated dissolved oxygen meter, model YS1 58 equipped with 200 ft cable, YSI Model 5739 probe. Seawater pH was measured with using a HANNA Instrument portable microcomputer pH meter Model HI 8424 equipped with a combined electrode following the guidelines delineated in Strickland and Parsons (Strickland & Parsons, 1972). Transparency was estimated by employing a white, 30 cm diameter, Secchi disc as described in MOOPAM (1989).

Analytical methods

For reactive nutrients analyses, frozen filtered seawater was thawed at room temperature or by using a shaking water bath set at 30^oC. All nutrients were measured with a spectrophotometer. The nitrite concentration was deter-

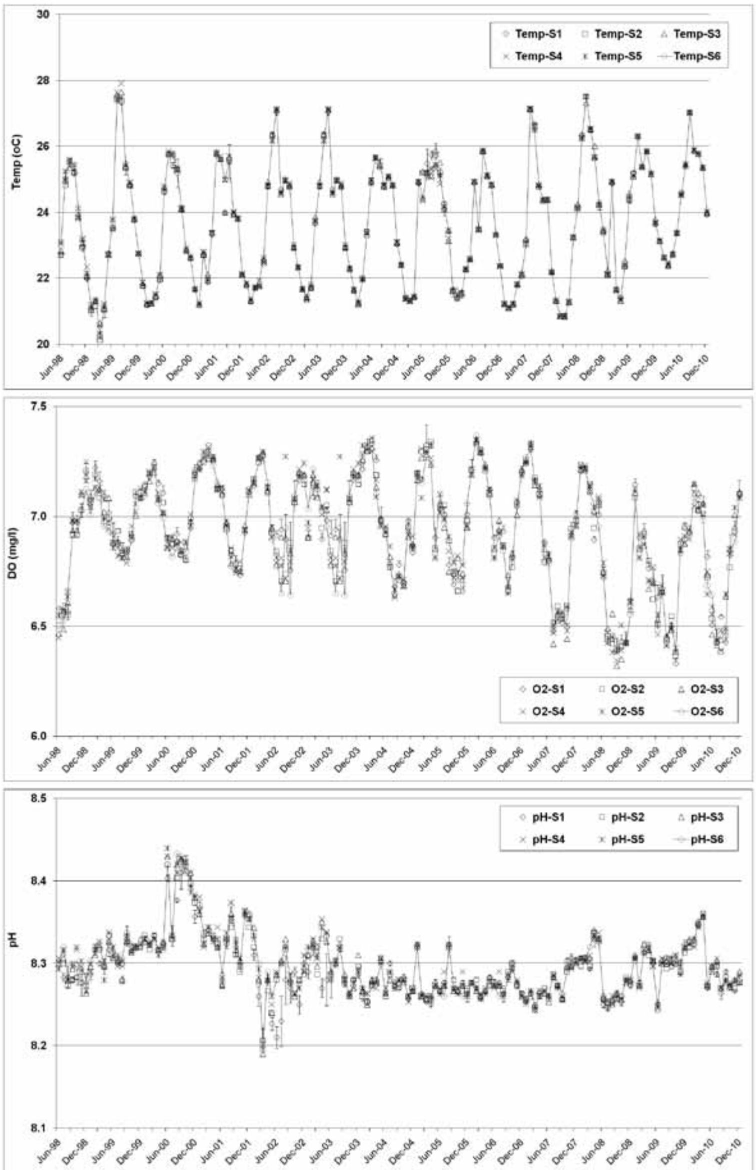

Fig. 2: Time series of temperature (°C), dissolved oxygen (mg/l), pH measurements from the coastal water in front of the six IC sites (Fig. 1). The line represents the time series data of S6 as an example to clarify the trend with time. Error bars represent the standard deviations of the three depths at the S1 site, as an example to show the differences between the different depths at one site.

mined with the help of azo dye formation, colorimetric method as described by GRASSHOFF *et al*. (1999). The nitrate was measured after reduction to nitrite using a copper-coated cadmium reduction column (Wood *et al.*, 1967) as modified by Grasshoff *et al.* (1999) and recommended by MOOPAM (1989). The phosphate was measured by the colorimetric method of Murphy and Riley (1962) as suggested by Parsons *et al*. (1984). Samples were analyzed for ammonium by the indophenol blue colorimetric method developed by Solarzano (1969) and described by Parsons *et al*. (1984)

Statistical analysis

To evaluate the significance of the difference in the recordings of the different variables between the different sites and depths in the IC, as well as between IC and RO waters, ANOVA analysis (5% significance level) was performed. For comparison between IC and RO, summer months (June-October) and winter months (December-April) are analyzed separately because the Gulf of Aqaba exhibits mainly two seasonal patterns that can be distinguished, as reflected in the physical and chemical characteristics of the water column (Badran, 2001).

Results and Discussion

The results of all the measured parameters at all six sampling sites at the IC are shown in Figures 2 and 3. No significant differences were found among the different sites and depths for all parameters (p values were always more than 0.05). Thus, for the sake of comparison,

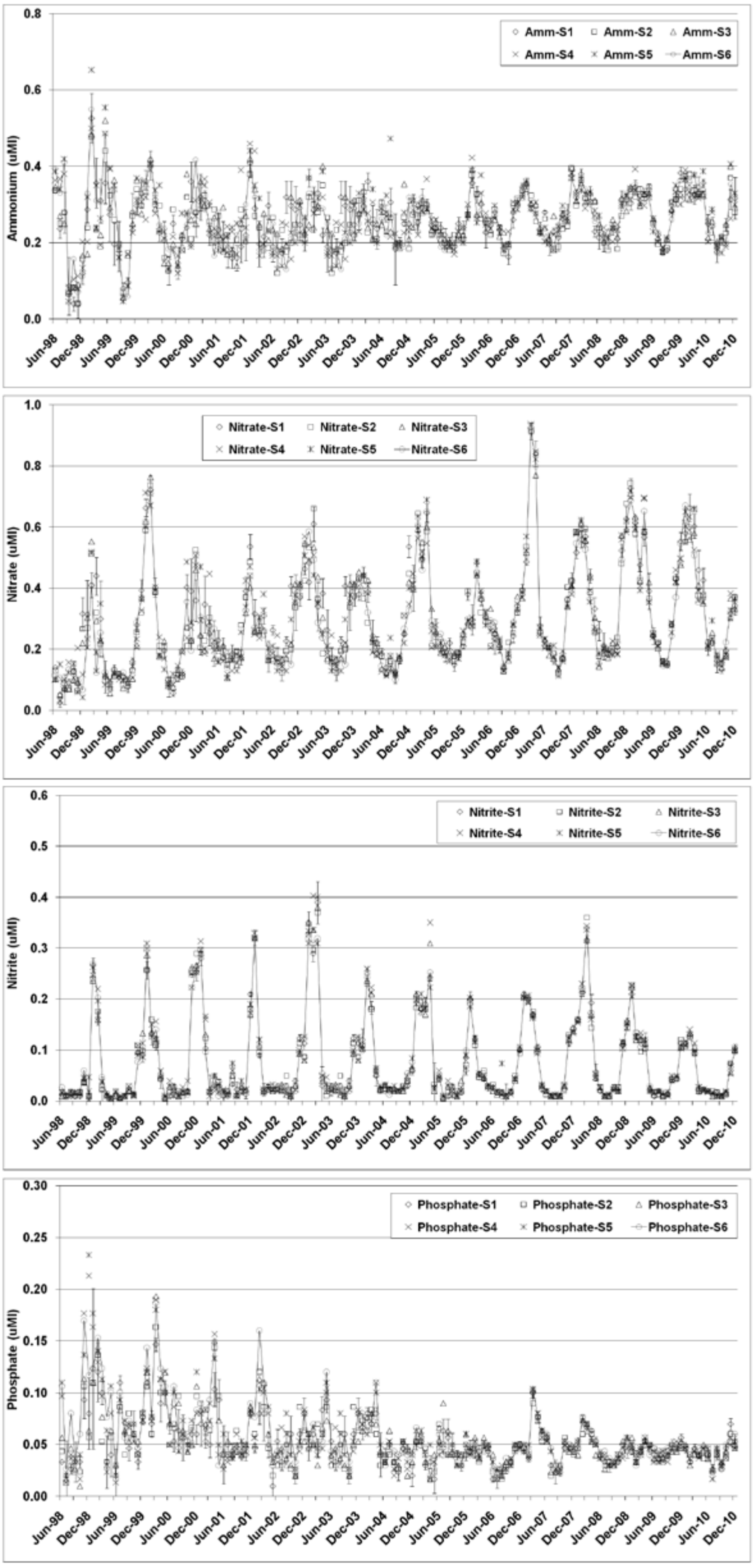

Fig. 3: Time series of ammonium, nitrate, nitrite and phosphate (μM) measurements from the coastal waters in front of six IC sites (Fig. 1). The line represents the time series data of S6 as an example to clarify the trend. Error bars represent the standard deviations of the three depths at the S1 site as an example to show the differences between the different depths at one site.

between the results recorded at the IC and at the RO, the averages of the six sampling stations in the IC were compared with the concurrently measured values at the RO. Significantly, an important basic feature of the Gulf of Aqaba, is that is its steepness and active density near-shore currents act as a conveyor built in the near-shore waters (Nieman *et al.*, 2004).

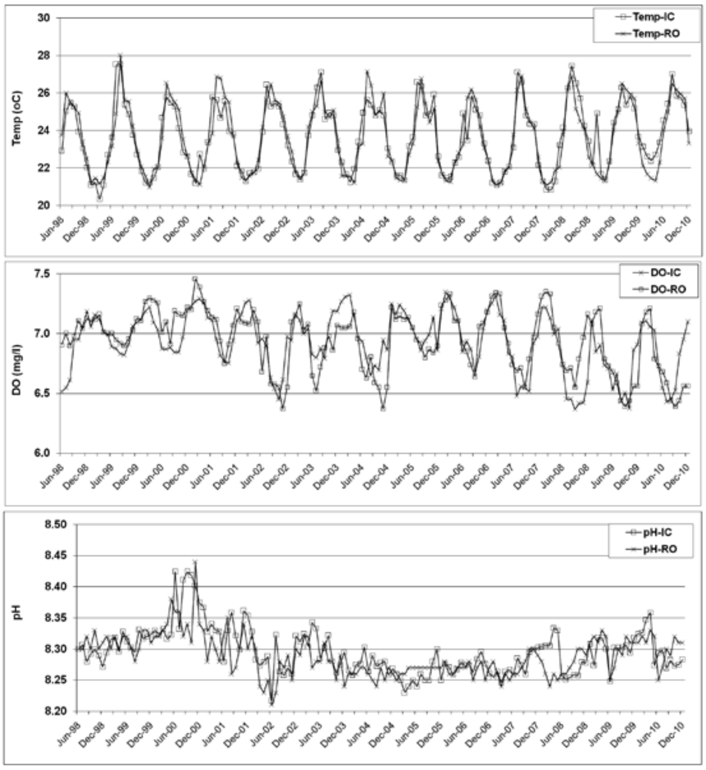

Fig. 4: Time series of temperature (^oC), dissolved oxygen (mg/l), pH measurements from the coastal water in front of the IC site and RO waters 3 km off the coast.

Temperature

Water temperature records at the IC and the RO (Fig. 4) show a gradual increase from April to September, reaching up to 27.5^{o}C, and then decrease, attaining a minimum in February, March or April, varying in different years with the variation of the mixing depth. The lowest values recorded in all the stations were around 21.0^o C. No significant variations between the water temperatures at the RO and IC could be observed either in summer or in winter (P= 0.77 and 0.20, respectively, Table 1). The temporal variations in the water temperature at both the coastal and offshore stations were obviously significantly different, where high temperature values were recorded in summer and low values were recorded in winter (Fig. 4). No incidence of abnormal temperatures has been recorded even at stations S5 or S3, which represent the outlets of the cooling waters. This may indicate that the cooling water exerts no considerable effect on the temperature field in front of the IC. Jordanian regulations for cooling seawater, permit the returning water to be of 3^{o}C higher ambient at the source. The length of the cooling water pipes and the depth at which the cooling water is returned to the sea appear to be effective in restoring the seawater temperature back to normal, once mixed with the surrounding waters at the outlet.

An increase in the seawater temperature may impact the flora and fauna of the ecosystem. Long-term records of the surface water temperature may serve as an important indicator of global climate change (Sanchez-Arcilla *et*

Table 1. Abundances (% mean ± se) of the food items in the gut content of the sea urchin over the study period. Ha, *Halopteris scoparia*; Di, *Dictyota* spp.; Br, unidentified brown pieces; Ce, *Ceramium* spp.; Ge, *Gelidium* spp.; Pl, *Plocamium cartilagineum*; As, *Asparagopsis armata* and *Falkenbergia rufolanosa*; Ca, crust and articulated calcified Rhodophyta; Ch, *Chaetomorpha* sp.; Cl, *Cladophora* spp.; Ul, *Ulva* spp. and other non-identified remains of Chlorophyta; and Ui, remaining unidentified items.

		Temp	**DO**	**pH**	**Ammonium**	**Nitrate**	**Nitrite**	**Phosphate**
summer	P value	0.7699	0.1021	0.1065	0.0624	0.6009	0.1207	0.2345
	Mean Diff	0.03	-0.031	0.005	0.012	0.004	-0.005	0.001
winter	P value	0.1962	0.5864	0.105	0.2314	0.0001	0.0001	0.1076
	Mean Diff	0.103	0.001	0.008	0.008	-0.065	-0.034	0.004

al., 2011). The rise in temperatures may decrease the oxygen solubility impacting the physiological process of the coral reef. It may also result in localized bleaching of the coral colonies (Pilcher, 2000). Besides, it could lead to a depressed feeding response of the coral, reduce the reproductive rates, increase the zooxanthellae and mucous extrusion and decrease the photosynthetic/respiration rate as well as the coral growth rates (Johannes, 1975; Lesser, 1997; Al-Horani, 2005).

Dissolve oxygen

Dissolved oxygen concentration in the marine ecosystems is controlled by photosynthesis, respiration, decomposition, ventilation, temperature, and salinity. The dissolved oxygen concentration at the IC and the RO sites showed a regular pattern inversely proportional to that of temperature with a range of 6.4 to 7.4 mgl^{-1} (Fig. 4), indicating that the effect of the other ecosystem variables was masked by that of the temperature. There were also no significant differences between the IC and the RO sites, neither in summer nor in winter (P=0.10 and 0.59, respectively, Table 1). The concentrations recorded most of the time were in fact 100% saturation concentrations. Waters of the Gulf of Aqaba are very well balanced in terms of respiration and photosynthesis and well ventilated due to the annual deep mixing (Badran 2001; Rasheed *et al.,* 2006; Manasrah *et al.,* 2006). This highlights temperature and salinity as the two main factors controlling the dissolved oxygen concentration, because of the strong dependence of the oxygen solubility on these two variables.

pH

Records of pH, at both the IC and the RO sites, fluctuated around 8.3 with very minor temporal and spatial variations (Fig. 4) showing no difference between the two sites in summer and winter (Table 1). This is typical not only for the waters of the Gulf of Aqaba, but for all coral reef waters (Sorkin, 1995). This is because these waters are always saturated with calcium carbonate, which acts as a buffer and resists any change in the pH. This coral reef water specific property can also be seen in the very small year-to-year variations; (Pelejero *et al.,* 2005) studying pH in coral reefs detected changes only over decadal cycles of 50 years.

Ammonium

Ammonium concentration is an important ecosystem variable in water monitoring because of its high reactivity in the biogeochemical processes and the relatively high uncertainty in its analysis when compared with other environmental variables (Badran & Foster, 1998; Richter *et al.,* 2001). Ammonium concentrations in the present study fluctuated irregularly around 0.25 μM (Fig. 5) at both the near-shore and offshore sites, with a tendency to higher concentrations during the winter months, especially in January and February, which can be attributed to the mixing conditions in the water column (Badran 2001). No significant difference was noted between the ammonia concentrations at the IC and RO (P= 0.058, Table 1).

Nitrate and nitrite

Both nitrate and nitrite concentrations during the annual cycle (Fig. 5) showed a regular shift from a summer low (0.10 and 0.01 μM, respectively) to relatively high early winter values (0.6 and 0.3 μM, respectively). They were the only variables that exhibited significant differences between the IC and RO sites during the winter months (P= 0.0001 for nitrate and nitrite). Contrary to expectations, higher concentrations for both nutrients in the winter were found at the RO when compared with the IC (Mean Differences are -0.065 and -0.034 for nitrate and nitrite, respectively). Winter mixing in the Gulf of Aqaba dominates during the period between January and April (Klinker *et al.,* 1978; Badran, 2001; Rasheed *et al.,* 2002; Badran *et al.,* 2005; Manasrah *et al.,* 2006). Deep winter mixing introduces new nutrients into the surface water. Nitrate concentrations in deep water were recorded to be more than 2 μM (Badran *et al.,* 2005; Manasrah *et al.,* 2006). This could have a higher impact on the nitrate and nitrite concentrations at the RO, when compared with the coastal water.

The typical behavior of these two nutrient species is that they almost vanish during the summer and grow abundantly in the winter (Badran & Foster, 1998; Al-qutob *et al.,* 2002; Rasheed *et al.,* 2006). This is due to their rapid consumption by the primary productivity during the summer and the thermal stratification in the water column that prevents new inputs to reach the euphotic zone from the deeper waters. Nutrient concentrations build up in deep water during summer due to the efficient decomposition of organic matter and the lack of primary productivity (Levanon-Spanier *et al.,* 1979; Klinker *et al.,* 1978). In winter, the water column is well mixed and whatever is consumed by the primary productivity is substituted for or even exceeded by entrainment from deep waters (Levanon-Spanier *et al.,* 1979; Klinker *et al.,* 1978; Rasheed *et al.,* 2006).

Phosphate

Typical of the oligotrophic waters, phosphate concentrations were generally low and higher during the winter when compared with the summer values (Badran & Foster, 1998; Rasheed *et al.,* 2002). Records of phos-

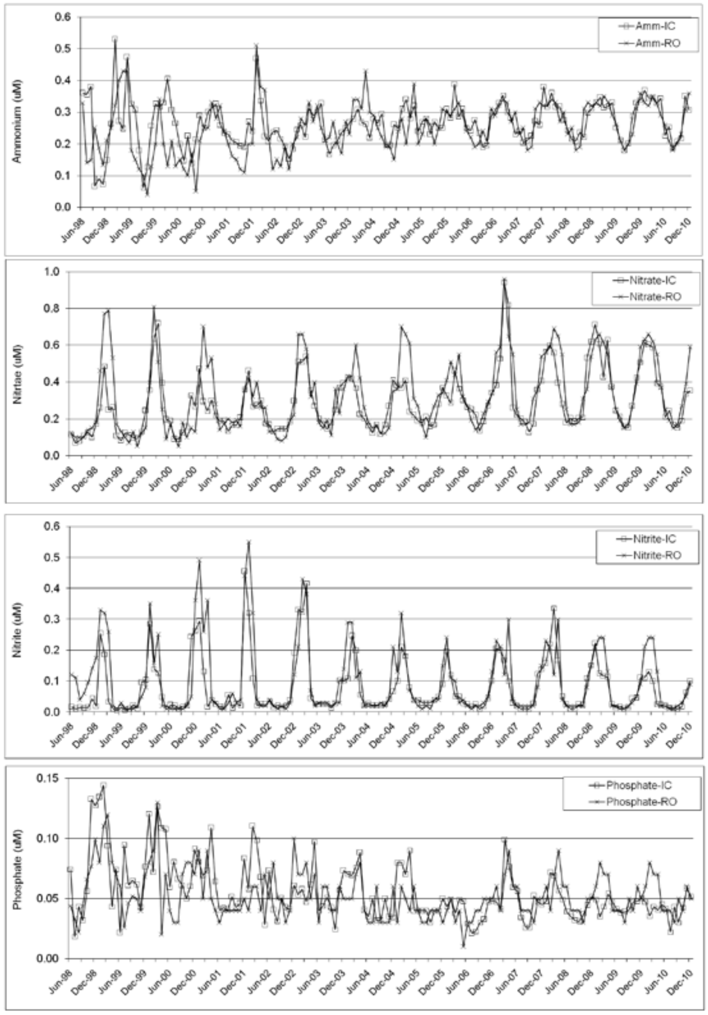

Fig. 5: Time series of ammonium, nitrate, nitrite and phosphate (µM) measurements from the coastal waters in front of the IC and RO waters 3 km off the coast.

phate at the IC and the RO sites showed a higher concentration during the winter (~ 0.10 µM) and lower values during summer (0.03 µM). Interestingly, no significant difference was evident between the IC and RO records, either in summer or in winter (Table 1). However, in several sampling events, higher concentrations could be observed at the IC (Fig. 5). Seasonality in phosphate concentrations in the IC was not as clear as they were for nitrates and nitrites. In the RO, the phosphate annual concentration pattern was close, in seasonality, to that of the nitrates and nitrites. The irregularity in pattern at the IC site could be attributed to the intrusion of the phosphate from the land sources. In fact, it would be unrealistic to expect 100% prevention of land-based phosphate entering the seawater here. It can reach the seawater by wind, during shipment and during rare out-of-control incidences when limited amounts of the IC wastewater may reach the sea. However, a small amount of raw phosphate reaching the Aqaba seawater in a localized area could be sequestered by the ecosystem. Phosphate rock is insoluble in seawater (Abu-Hilal, 1985; Rasheed *et al.,* 2005). Besides, localized small amounts of soluble phosphate can be of minor significance, because it has been almost established that nitrogen rather than phosphorus is the primary productivity limiting nutrient (Badran & Foster, 1998; Badran, 2001; Rasheed *et al.,* 2005). This implies that anthropogenic phosphorus can be assimilated only if surplus nitrogen is available (Rasheed *et al.,* 2005).

Water from the IC coast, in general, compared with the RO waters exhibits dominance of the normal Aqaba seawater conditions for most variables, throughout the year. Slightly higher phosphate concentrations appear to have no significant effect on the environmental quality of the seawater. The nitrogen-phosphorus ratio (Fig. 6) shows that the ratio was less than 16 in 80% of the samples (average = 12.67: 1, standard deviation = 5.85). This concurs with Hulings and Abu-Hilal (1983) and Badran (2001) who found average ratios of 11.8:1 and less than 16, respectively. This supported the concept that nitrogen rather than phosphate is the primary productivity limiting nutrient in the waters of the Gulf of Aqaba.

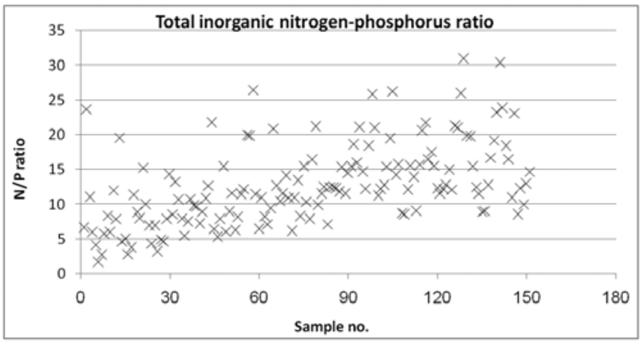

Fig. 6: Nitrogen-phosphorus molar ratios for the measurements from all the sites at IC and RO.

Conclusion

The results of the seawater temperature, dissolved oxygen concentrations, pH and nutrient concentrations recorded in the seawater, regularly, over 12 years, at the IC site compared with the results recorded offshore, show the dominance of the normal Aqaba seawater conditions throughout the year. This includes phosphate concentrations, which at some sampling events, exhibited higher concentrations than offshore. Strong seasonality of the basic characteristics of the waters of the Gulf of Aqaba associated with its steep slopes, great depth-to-width ratio, and the conveyer built effect that enhances dissipation in the near-shore water are natural factors that can play a significant role in keeping the coastal water in front of the industrial complex unaffected. In addition, the industry at the IC applies high care measures concerning the environmental factors and maintains regular training programs for their employees, accordingly. The governing authority in Aqaba also enforces strict environmental regulations to maintain zero discharge policy.

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