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Spatio-temporal variations in conservative and non-conservative properties of the surface seawater along the Red Sea coast, Egypt

Ahmed Salah-Tantawy[1,2*], Aldoushy Mahdy[2], Mahmoud A. Dar[3], Shuh-Sen Young[1], Abdelbaset M.A Abdelreheem[4]

1. Institute of Analytical and Environmental Sciences, College of Nuclear Science, National Tsing Hua University, Hsinchu, Taiwan.
2. Department of Zoology, Marine Science division, College of Science, Al-Azhar University, Assiut Branch, Egypt.
3. Division of Marine Environment, National Institute of Oceanography and Fisheries (NIOF), Egypt.
4. Zoology Department, Faculty of Science, Al-Azhar University, Assiut, Egypt.

*__Corresponding Author: asalah90@azhar.edu.eg__

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ABSTRACT

This study investigated the Spatio-temporal variations in the physico-chemical properties of the surface seawater along the northern Red sea. 41 seawater samples were gathered from Ras Gharieb, Hurghada, Safaga, and Qusier cities to measure conservative (temperature, DO, salinity, pH) parameters. In parallel, non-conservative parameters (ammonia, phosphorous, nitrite, nitrate) were analyzed via a colorimetric-spectrophotometer instrument. Our findings revealed that physical parameters fluctuated between 19.01 ± 0.75 - 35.01 ± 0.47 ºC, 5.05 ± 0.54 - 11.70 ± 1.06 mg/l, 39.81 ± 0.35 - 42.31 ± 0.50 ‰, and 8.10 ± 0.14 - 8.50 ± 0.44 for temperature, DO, salinity, and pH, respectively. While chemical parameters ranged from 0.12 ± 0.06 to 1.53 ± 0.20 mg/l for ammonia, BDL to 1.71 ± 0.23 mg/l for phosphorous, BDL to 1.38 ± 0.05 mg/l for nitrite, and 0.09 ± 0.06 to 4.50 ± 1.22 mg/l for nitrate. Statistically, no discernible variation was detected among different seasons for all measurements except temperature, DO, and phosphorous ($P < 0.05$). In addition, Pearson's correlation analysis showed some positive or negative relationships between temperature and salinity (r = 0.75), salinity and pH (r = 0.50), temperature and phosphate (r = 0.70), salinity and phosphate (r = 0.73), nitrite and nitrate (r = 0.71), temperature and DO (r = - 0.73), DO and phosphate (r = **-** 0.50), pH and ammonia (r = **-** 0.71), as well as phosphate and nitrate (r = **-** 0.55). These results indicate that physico-chemical properties should be taken into account during the development of management strategies to protect the Egyptian marine environment, especially in the Red sea areas.

INTRODUCTION

The Red Sea is semi-closed and distinctive between basins, occupying a unique place owing to its seclusion from the world's oceans and geographical location **(Halim, 1984)**. It is the warmest and saltiest body of water among the open seas, and it has a distinctive ecosystem with coral reefs **(Alraddadi, 2013)**. By definition, the conservative characteristics including seawater temperature, and salinity are unaltered by the nutrient enrichment of the system **(Manasrah *et al.*, 2019)**. Several factors, including air temperature, seasonal fluctuations, winds, depth, waves, and the loss or acquisition of heat in an intertidal area close to the coast lead to a wide variation of seawater temperatures. Alterations in seawater temperature potentially impede the normal growth and evolution of certain marine creatures. When the rise is above the specific range, the balance of the whole ecosystem is disrupted. High mortalities of living organisms are associated with sudden discharges of hot water in the sea **(Hassan, 2002; Salem, 2006)**. However, dissolved oxygen is regarded as one of the most essential and realistic indicators of various water bodies, determining the pollution level, particularly the organic contaminants that harm marine life by depleting oxygen concentrations **(Australia, 2002)**. In addition, salinity is a crucial conservative factor that responds to precipitation, freshwater inflow, evaporation, and water mass mixing, and it plays a role in several chemical reactions **(Skogen *et al.*, 2014)**. pH value is a reflection of numerous biological and chemical processes occurring in natural water. pH values of seawater are controlled by dissolved oxygen, water temperature, eutrophication rate, and photosynthetic activities **(Nassar & Hamed, 2003)**.

Additionally, the non-conservative characteristics, viz. ammonium, phosphate, nitrite, and nitrate, respond to biogeochemical activities. Ammonium is a biologically active molecule abundant in most water as typical biodegradation of organic nitrogen and can be directly used by a variety of algae and macrophytes **(Guerrero & Jones, 1997)**. Neurological and cytological failure as well as the destruction of the gill epithelium ultimately lead to asphyxia, a result of the toxic effects of ammonia. Phosphate is the only form of phosphorus that autotrophs can assimilate. Generally, phosphate concentrations decline during the peak of primary output **(Guerrero & Jones, 1997)**. Nitrite has not only a profound effect on marine organisms **(Al-Qutob *et al.*, 2002)** but also has the greatest toxicological concern for human health if found in diets at a detectable concentration **(Abdelmongy & El-Moselhy, 2015)**. Nitrate is regarded as the most stable and prevalent inorganic nitrogen form in seawater and was the most stable oxidized form of nitrogen, accounting for 42.6% of dissolved inorganic nitrogen and 12.4% of the total dissolved nitrogen **(Elrefaey *et al.*, 2017)**. Modern society faces many challenges, but environmental pollution is one of the worst **(Salah-Tantawy *et al.*, 2022)**. Hence, the results from regular monitoring are important for comprehending and studying seasonal or spatial physical and chemical properties in marine environments.

In our study, we collected seawater samples from the north of the Egyptian Red sea including Ras Gharieb, Hurghada, Safaga, and Qusier in winter and summer. Conservative or physical parameters (temperature, DO, salinity, and pH) were analyzed. In parallel, non-conservative or chemical parameters (ammonium, phosphate, nitrite, and nitrate) of seawater were investigated using the spectrophotometric method to determine the interactions in the northern Red Sea. The specific objectives of this study were to: (i) quantify the seasonal and geographic fluctuations in the physical and chemical characteristics of seawater, (ii) evaluate the seawater quality by comparing the results with those of previous studies, and (iii) assess the statistical association between conservative (temperature, DO, salinity, pH) and non-conservative (ammonia, phosphorous, nitrite, nitrates) factors. As a result, this study would provide useful data for future management and serve as a reference guide for the Egyptian researchers to jointly protect the coastal environments of the northern Red Sea.

MATERIALS AND METHODS

1- Study stations & sampling process

The study stations extend for about 290 km along the Red Sea coastline from Ras Gharieb (150 Km northern of Hurghada city) to Qusier (140 Km southern of Hurghada city). The selected stations are located at the tidal flat zones off the main cities; Ras Gharieb (n = 8), Hurghada (n = 11), Safaga (n = 10), and Qusier (n = 10) (Fig. 1). These cities have been exposed to over-populations and severe land-based activities involving; oil exploration and production, maritime activities, tourist activities, marine wharves, marinas, shipyards, desalination plants, sewage treatment stations, fishing operations and harbors, land reclamation, mining and shipment operations, subsurface untreated sewage runoff and the human waste dumping in the tidal flats as well as the temporary flash floods and non-point sources.

A total of 41 seawater samples were collected from four main cities along the northern Red Sea, Egypt. Each city was divided into different stations (Figs. 1B, C, D, E). From each station, three samples of surface seawater were collected during winter and summer in 300 ml BOD bottles; air bubbles generation were avoided for dissolved oxygen analysis. The samples were put in one liter of previously acid-washed polyethylene bottles for chemical parameters (except for phosphate samples which were kept in glass bottles) and immediately transported to the laboratory in the icebox. Thereafter, samples were filtered through a 0.45 µm membrane and directly kept deeply frozen till carrying out the analyses, except the dissolved ammonia which was fixed in the field **(Grasshoff *et al.*, 2009)**. Each station was GPS-located. High-purity reagents were utilized in the investigations, and each sample was measured in triplicate.

2- Physical oceanography parameters

2.1. Seawater temperature, salinity & pH

Physical oceanographic parameters including surface water temperature (ºC), salinity (‰), and pH were measured *in situ* during winter and summer using Water Quality Checker Type U-10 of the Egyptian Environmental Affairs Agency (EEAA).

2.2. Dissolved oxygen (DO)

Dissolved oxygen (DO) was measured by Winkler's method **(Strickland, 1972)**. DO was fixed in the field by adding 1ml of manganese sulfate (364 g/l $MnSO_4.H_2O$) and 1ml of iodide azide mixture (700 g/l potassium hydroxide + 150 g/l potassium iodide +10 g/l sodium azide) to each sample. The bottles were sealed, agitated, and left until the precipitate sank to the bottom, and then 1ml of H_2SO_4 conc. was added to each sample and shaken for the complete dissolution of the precipitate. Titration was accomplished utilizing 200ml of the sample against sodium thiosulfate solution (0.025 N). Then the thiosulfate solution was normalized against potassium bi-iodate solution (0.025 N) until the blue hue vanished. The dissolved oxygen concentrations were expressed in mg/l and calculated by eq. 1:

$$DO_{\,(mg/l)} = (V_{\,titrant} \times N_{\,titrant} \times 8000) \,/\, V \text{ sample} \qquad (1)$$

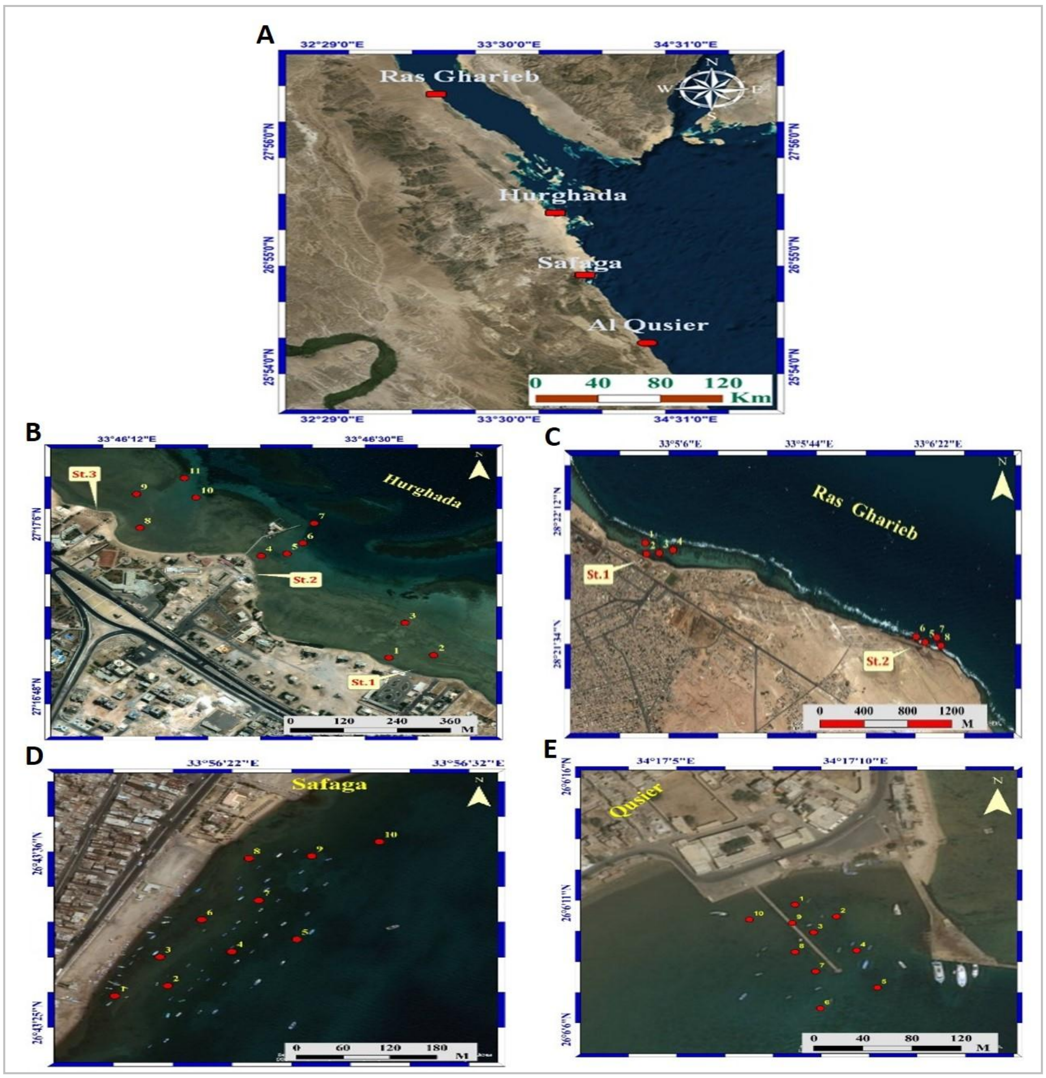

Fig. 1. Satellite maps showing the location of the studied stations along the northern Red Sea. (**A**) Northern Red Sea, (**B**) Ras Gharieb, (**C**) Hurghada, (**D**) Safaga and (**E**) Qusier (*Google Earth program*).

3- Chemical oceanographic parameters

3.1. Ammonia (NH_4^+)

Dissolved ammonia (NH_4^+) was determined according to the method of **Koroleff (1969)**. About 50ml of seawater samples were collected in dark-brown vials and fixed in the field by a mixture of the followings: 1ml of trisodium citrate solution (480 g/l), 1ml of phenol reagent (38 g/l), and 1ml of hypochlorite reagent (5%). After allowing the mixture to stand overnight (10-12 hours), the blue color of the indophenols produced was assessed using a spectrophotometer (GENWAY 6800 UV/Vs) at 630nm, and the results were expressed as mg/l.

3.2. Dissolved phosphate (PO_4)

Dissolved phosphate was determined according to **Grasshoff *et al.* (2009)** dependent on the molybdate-ascorbic method; 9 N sulfuric acid, ascorbic acid solution (70 g/l), ammonium molybdate (95 g/l), and potassium antimony tartrate (32.5 g/l). The mixture was well blended into 35ml of each sample. Within a few minutes, the absorbance of the blue phosphorus complex reached its maximum, and then it remained steady for numerous hours. Nevertheless, the absorbance was detected within 20 to 30 minutes and the developed color was determined by the spectrophotometer (GENWAY 6800 UV/Vs) at the wavelength of 880nm. Based on the standard curve, the phosphate concentrations were computed and reported in mg/l.

3.3. Dissolved nitrite (NO_2)

Dissolved nitrite was measured following the procedures of **Grasshoff *et al.* (2009)**. A volume of 50ml of seawater samples was mixed with 1ml of the sulfanilamide reagent (100 g/l), agitated, and allowed to react for 1 minute before 1ml of the N-l-naphthylethylene diamine reagent was added (NED) (1 g/l). The azo dye color was entirely produced in 20-30 minutes, and the intensity was analyzed with a spectrophotometer at 540 nm. The results were represented in mg/l.

3.4. Dissolved nitrate (NO_3)

Dissolved nitrate was measured according to the method of **Grasshoff *et al.* (2009)**. The cadmium column was used to convert nitrate (NO_3) to nitrite (NO_2). 100 ml of each sample was combined with 2 ml of ammonium chloride solution and passed through the cadmium reduction column. Consequently, the concentrations of nitrate were determined by subtracting the previously observed nitrite concentration from the overall concentration of nitrite; the intensity was evaluated with a spectrophotometer at 540 nm (GENWAY 6800 UV/Vs). The results were recorded in mg/l.

4- Statistical analysis

The data were statistically analyzed using R programming version 4.1.3. The spatio-temporal variations of physical and chemical parameters were visualized using (*ggplot2*) package version 3.3.6. Analysis of variance (*ANOVA*) was used to analyze the seasonal and regional differences in physical and chemical factors among the studied sites. In addition, Pearson's correlation analysis was achieved using the (*cor.test*) function in the R script to detect any relevance among all conservative and non-conservative factors. Variances were recorded significant when $P < 0.05$.

RESULTS AND DISCUSSION

Seawater temperature is one of the most critical factors affecting the living organisms and their biological activities **(Ghanem, 2006; 2011; Mahdy *et al.*, 2015)**. During winter, it fluctuated between 19.0ºC in Ras Gharieb and 22.63ºC in Safaga, while during summer, it ranged from 31.32ºC in Qusier to 35.01ºC in Hurghada (Fig. 2A). Seasonal variations of seawater temperature in the studied cities recorded nearly the same range for summer and winter alike, with variations reaching 13ºC in Ras Gharieb and Hurghada, declining to about 10ºC in Safaga and Qusier. Shifts in seawater temperature may suppress the normal growth and development of certain marine organisms.

Dissolved oxygen (DO) refers to the gaseous oxygen that is dissolved in the water and made accessible to aquatic organisms. It is required for the respiration of the majority of aquatic species. The values of DO ranged from 8.08 ± 1.33 mg/l at Ras Gharieb to 11.70 ± 1.06 mg/l at Safaga during winter, while during summer ranged from 5.05 ± 0.54 mg/l at Hurghada to 7.11 ± 0.83 mg/l at Ras Gharieb (Fig. 2B). The maximum averages of DO were recorded during winter; indicating adequate mixing in the water column **(Girgis, 1980)**, while the minimal averages were recorded during summer affected by the high rates of evaporation and the high humidity in the Red Sea. With decreasing water temperature, oxygen becomes more soluble **(Singh *et al.*, 1990)**. Additionally, the highest dissolved oxygen was recorded in Safaga due to the flourishing of seagrasses as meadows that release a large amount of oxygen in seawater. The concentration of dissolved oxygen is affected by four main factors: temperature, salinity, winds, and the distribution of green plants **(El-Enany, 2004)**. Based on our findings, DO concentrations were generally higher than the threshold value (4 mg/l) during all seasons **(Gilbrich *et al.*, 1978)**.

Salinity is a critical ecological parameter and important in some physicochemical activity, and it has a strong effect on nutrient levels and dissolved oxygen contents in coastal areas **(Skogen *et al.*, 2014)**. It is one of the most crucial constituents affecting the species dynamics, faunal composition, distribution, and diversity of the bottom population in many aquatic ecosystems **(El-Enany, 2004)**. In this study, the maximum average of salinity was recorded with a value of 40.98 ± 0.87 ‰ in Qusier while the minimum average was 39.81 ± 0.35 ‰ in Ras Gharieb during winter. During summer, the averages of salinity fluctuated between 41.05 ± 1.17 ‰ in Hurghada and 42.31 ± 0.50 ‰ in Ras Gharieb (Fig. 2C). Due to the increase in the rate of evaporation during summer, the highest values of salinity were reported in summer, while the lowest values were in winter.

pH is an important environmental factor for aquatic creatures' survival, physiology, metabolism, and growth, as well as chemical activities **(Ramanathan *et al.*, 2005)**. In our work, the highest pH averages were reported in summer, while the lowest values were in winter (Fig. 2D); this may be ascribed to the increase in temperature and salinity, and the increasing level of organic matter degradation **(Ganesan, 1992)**, in addition to the uptake of CO_2 by photosynthetic organisms **(Ananthan, 1994)**. The pH of seawater is influenced by temperature, dissolved oxygen, the pace of eutrophication, and biomass production **(Nassar and Hamed, 2003)**.

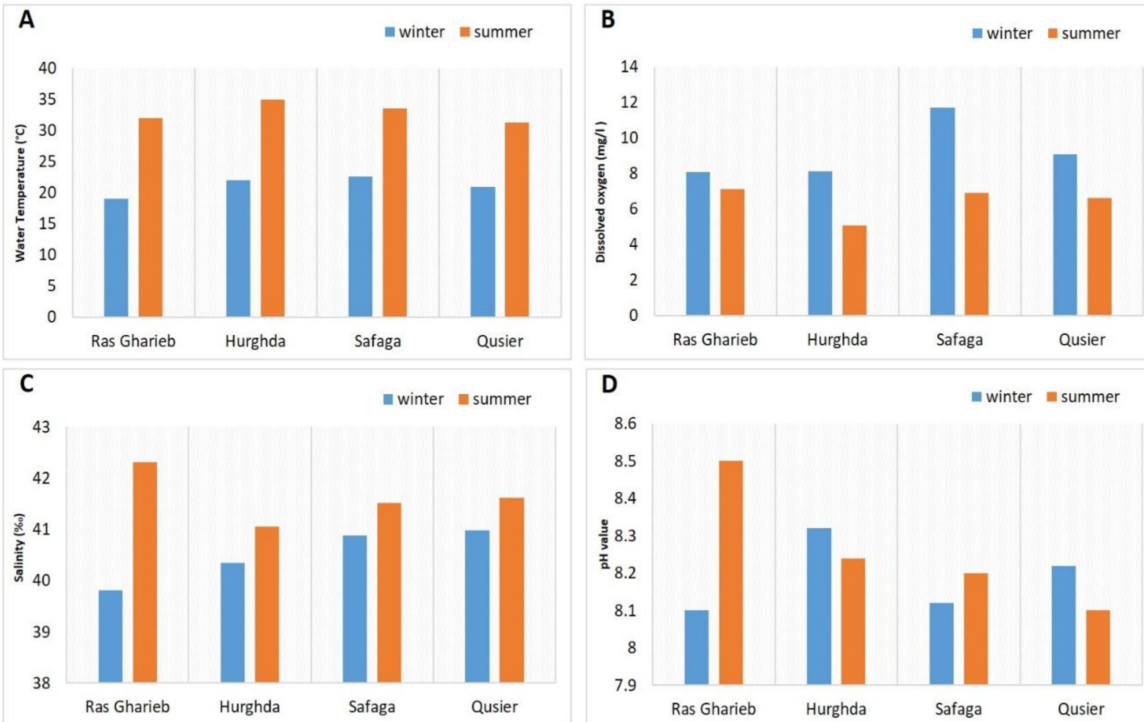

Fig. 2. Bar plot depicting the averages of physical parameters in the studied cities along the northern Red Sea during winter and summer

Besides, the chemical or nutrient characteristics were investigated including ammonia, phosphorus, nitrite, and nitrate since they play an important role in marine primary production, and excessive nutrient inputs leading to eutrophication and aquatic system degradation and globally serious environmental problems **(Howarth *et al.*, 2000)**. In addition, all living organisms require the nutrients of nitrogen and phosphorus for their growth, reproduction, and metabolism.

Dissolved ammonia (NH_4^+) is the most abundant form of inorganic nitrogen. It can be directly used as a nutrient by many algal species and aquatic plants **(Romagna, 1988)**. Light hurts ammonium oxidation by nitrifying bacteria **(Guerrero & Jones, 1997)**. The highest permissible concentration of ammonia is 0.10 mg/l of NH_3-N which is equal to 0.823 mg/l of ammonia **(Meade, 1985)**. In this investigation, ammonia varied between 0.12 mg/l in Ras Gharieb to 1.53 mg/l in Qusier during summer (Fig. 3A). The highest averages of ammonia were recorded in Hurghada and Qusier during summer. These values were higher than the maximum acceptable concentrations for the living organisms that may affect the occurrence of the benthos communities in tidal flat zones of these cities. This elevation may be attributed to the domestic sub-surface sewage due to the population zones near the collection areas depending on the sub-surface sewage drainage.

Phosphate (PO_4) is the only form of phosphorus that autotrophs can assimilate. Generally, phosphate concentrations are depressed during the time of the highest primary production **(Conkright *et al.*, 2000)**. In our study, Qusier city showed the highest average of PO_4 (0.32 mg/l) in winter to 1.71 mg/l in summer (Fig. 3B) due to the subsurface sewage and wastewater runoff; meanwhile, it wasn't detected in winter in Ras Gharieb due to the continuous water mixing. In general, most of the recorded values in all cities are much higher than the acceptable range of phosphate (0.01 to 0.03 mg/l) in the uncontaminated seawater recorded by the **USEPA (1986)**.

Nitrite (NO_2) is an intermediate oxidation state between ammonia and nitrate. It is essential to plants and microorganisms as a nutrient or bio-stimulate **(El-Enany, 2004)**. In this study, Qusier city recorded the highest value (1.38 mg/l) in winter affected by the sub-surface drainage of the city (Fig. 3C). In general, the different measurements in all cities are much higher than the range of nitrites in the marine water (00.0 to 0.059 mg/l) as computed in the study of **Sverdrup *et al.* (1942)**.

Nitrate (NO_3) is an essential nutrient for many synthetic autotrophs and can be considered as a nutrient limiting growth in some cases. As in the nitrite case, the nitrate in the studied cities ranged from 0.09 mg/l in Qusier to 4.50 mg/l in Hurghada (Fig. 3D). The highest averages of nitrates were recorded in winter due to water mixing which converts most of the nitrite to nitrate form.

Based on the statistical analysis utilizing ANOVA. no discernible spatial differences were recorded among conservative and non-conservative parameters ($P > 0.05$). Contrarily, seasonal variations were recorded in seawater temperature, DO, and dissolved phosphorous values ($P < 0.05$) and lacked significance in other parameters (Table 1).

Seawater quality assessment

In comparison with the previous studies (Table 2), the recorded levels of the seawater temperature are in the same range as those recorded in the work of **Dar *et al.* (2012)**. While, they are higher than levels recorded in the study of **Madkour (2005)** in the Red Sea. Notably, the present findings are lower those of **Abdelmongy and El-Moselhy (2015)** and **El-Metwally (2015)** along the northern Red Sea. While, DO levels are higher than those of **Dar and Abd El Wahab (2005)**, **Mohammed *et al.* (2010)**, and **Dar *et al.* (2012)**, though close to the findings of **Abdelmongy and El-Moselhy (2015)** at the inshore zones of the Red Sea. Additionally, salinity was similar to those **Abdelmongy and El- Moselhy, 2015)** at the inshore zones of the Red Sea. Additionally, salinity was similar to those **(Abdelmongy and El-Moselhy, 2015), (Madkour, 2005)**, and **(Dar *et al.*, 2012)**. Finally, pH findings were similar to those measured by **(Madkour, 2005)**, **(Mohammed *et al.*, 2010)**, **(Dar *et al.*, 2012)**, **(Abdelmongy and El-Moselhy, 2015)**, and **(El-Metwally, 2015)**. Also, ammonia and phosphorous values are higher than those measured by **(Abdelmongy and El-Moselhy, 2015)** but, nitrite and nitrate are close to those **(Abdelmongy and El-Moselhy, 2015)**.

Correlation relationship between physical and chemical properties

Table 3 depicted the association between the physical and chemical parameters in seawater using a correlation function that showed some correlations, both positive and negative. There was positive correlation between temperature and salinity (r = 0.75), salinity and pH (r = 0.50), temperature and phosphate (r = 0.70), salinity and phosphate (r = 0.73), nitrite and nitrate (r = 0.71). Inversely, negative correlation was noticed between temperature and DO (r = - 0.73), DO and phosphate (r = - 0.50), pH and ammonia (r = - 0.71), phosphate and nitrate (r = - 0.55).

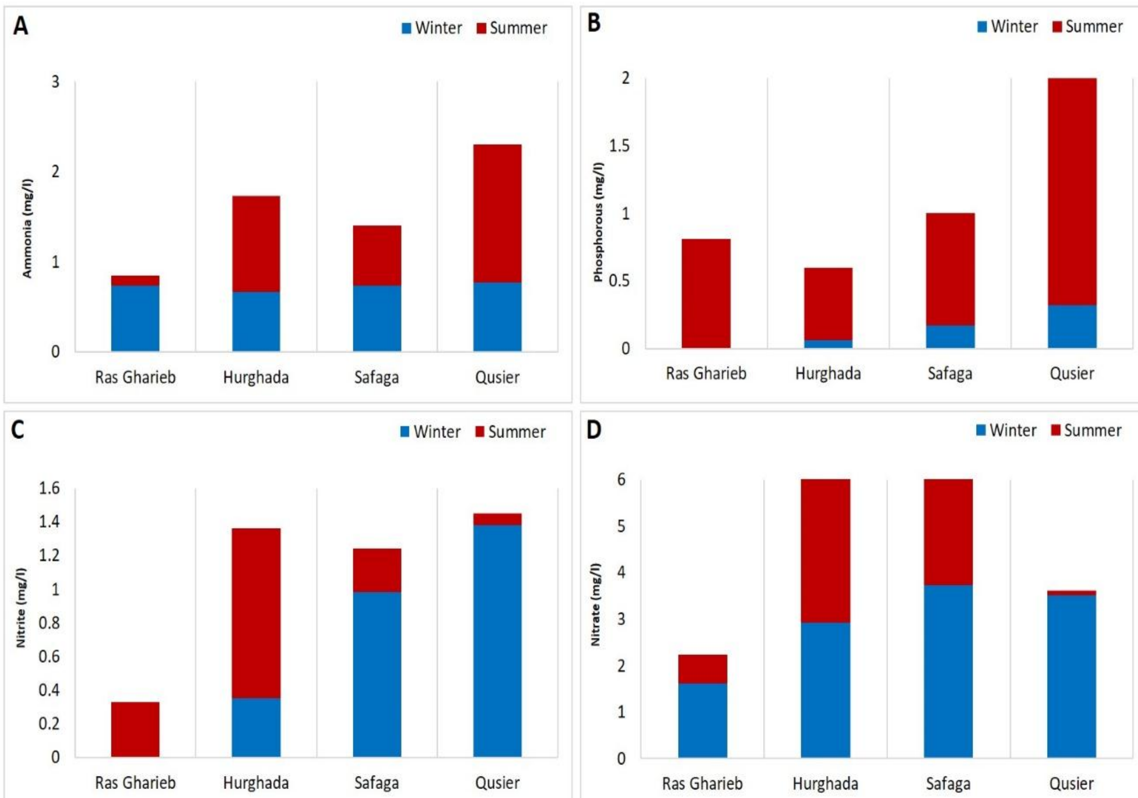

Fig. 3. Stacked bar illustrates the averages of spatial and temporal variations of chemical parameters in seawater at the studied cities along the northern Red Sea.

Table 1: Spatio-temporal variation utilizing *ANOVA* test performed on the values of conservative and non-conservative parameters recorded from different sites.

Physic-chemical factors	Variance	P-value	F-value
Temperature	Sites	0.13	4.35
	Seasons	0.00*	288.99
DO	Sites	0.29	2
	Seasons	0.04*	12.71
Salinity	Sites	0.81	0.33
	Seasons	0.09	5.97
pH	Sites	0.76	0.41
	Seasons	0.60	0.35
Ammonia	Sites	0.49	1.04
	Seasons	0.70	0.18
Phosphorous	Sites	0.23	2.60
	Seasons	0.02*	17.98
Nitrite	Sites	0.36	1.58
	Seasons	0.51	0.55
Nitrate	Sites	0.81	0.32
	Seasons	0.61	0.32

(*) imply significant value.

Table 2: The averages of physical factors in seawater at the studied cities in comparison with the other studies in Egypt and worldwide.

Site	Parameters (range)				Reference
	Temperature °C	DO mg/l	Salinity ‰	pH	
Northern Red Sea	**19.01 - 35.01**	**5.05 - 11.7**	**39.81 - 42.31**	**8.10 - 8.50**	**Current study**
Red Sea coast	22 - 29.74	5.8 - 8.62	40.60 - 42.30	8.29 - 8.70	(Madkour, 2005)
Artificial lagoon, Red Sea	---	5.12 - 5.52	41.25 - 41.66	8.45 - 8.66	(Dar and Abd El Wahab, 2005)
Red Sea coast	24.95 - 30.47	4.57 - 5.90	41.23 - 41.84	7.91 - 8.60	(Mohammed *et al.*, 2010)
Inshore zone of Red Sea	22.86 - 33.78	4.36 - 5.90	40.50 - 42.55	7.91 - 8.60	(Dar *et al.*, 2012)
Northern Red Sea	17.96 - 32.56	6.05 - 8.05	40.02 - 42.32	7.78 - 8.21	(Abdelmongy and El-Moselhy, 2015)
Red Sea coast	19.30 - 34.28	---	39.70 - 43.27	7.5 - 8.44	(El-Metwally, 2015)
Gorgan bay (Southeastern Caspian Sea), Iran	30.60 - 31.10	5.6 - 6.8	12.80 - 13.20	6.20 - 6.90	(Raeisi *et al.*, 2014)
Al-Kumrah and Al- Shoaibah (Red Sea), KSA	27.80 - 32.41	2.58 - 7.47	38.60 - 39.56	6.99 - 8.31	(Al-Wesabi *et al.*, 2015)

Table 3: The association relationship among conservative and non-conservative factors in seawater recorded from different sites during different seasons.

	Temperature	DO	Salinity	pH	NH_3	PO_4	NO_2	NO_3
Temperature	1							
DO	**-0.73**	1						
Salinity	**0.75**	-0.31	1					
pH	0.29	-0.26	**0.50**	1				
NH_3	0.15	-0.25	-0.14	**-0.71**	1			
PO_4	**0.70**	**-0.50**	**0.73**	-0.03	0.49	1		
NO_2	-0.13	0.32	0.00	0.03	-0.02	-0.33	1	
NO_3	-0.05	0.17	-0.32	-0.13	-0.04	**-0.55**	**0.71**	1

Orange color refers to the correlation that is present

CONCLUSION

Physico-chemical properties should be taken into account during the development of management strategies to protect the Egyptian marine environment. Since, this study revealed there were seasonal variations in seawater temperature, DO, and dissolved phosphorous, but lacked the regional differences among studied cities ($p < 0.05$). This research will provide useful data for future management and serve as a reference guide for Egyptian researchers to jointly protect the coastal environments of the northern Red sea.

AUTHOR CONTRIBUTIONS

Salah-Tantawy conceptualized the project, gathered samples, performed methodology, statistical analyses, and manuscript writing. ***Dar and Mahdy*** conceptualization, participated in the fieldwork, and revision. ***Young*** reviewed and revised the manuscript. ***Abdelreheem*** reviewed, and revised. All the authors contributed to the manuscript and approved the submitted version.

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