

Spatial and Seasonal Distribution of Total Dissolved Copper and Nickel in the Surface Coastal Waters of Rabigh, Eastern Red Sea, Saudi Arabia

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Abstract. Copper (Cu) and nickel (Ni) were determined in the coastal waters of Rabigh, Saudi Arabia, eastern Red Sea during 2007. The data revealed spatial and seasonal variability along the study area. The concentrations of both metals were the highest during winter in comparison to their values in spring and summer. This behaviour could be attributed to the biological activities. On the other hand, the spatial distribution of both metals was irregular. However, high values of both of these coincided with particular locations. In the absence of river runoff, it is suggested that the atmospheric input and diffusion from sediments could be considered as a potential source of both metals to the coastal waters of Rabigh. In the view of the present studies, it is desirable that similar studies be carried out on the other coastal waters of Saudi Arabia.

Keywords: Copper, Nickel, Trace metals, Red Sea, Rabigh, Saudi Arabia, Dissolved.

Introduction

In the Kingdom of Saudi Arabia, numerous developments have been initiated on the eastern coast of Red Sea. A number of projects of economical importance were planned to be established with long term sustainable development of Saudi Arabia.

Rabigh City is located at 140 km north of Jeddah City. Its geographical coordinates are 22° 47' 55" North, 39° 1' 56" East. The city is relatively small with a population of 100,000 according to latest statistics carried out by the government. Along the coast of Rabigh, there are many factories and plants; *e.g.* Arabian Cement Factory (ACF), Electric Power Plant (EPP), Water Supply Plant (WSP) and, on a large area, Aramco Company (AC) which consists of Aramco Refinery (AR) and Aramco Residential Area (ARA) (Fig. 1).

Further to the south, at about 40km from Rabigh, a new economical city is under construction; King Abdullah Economic City (KAEC). The city will accommodate approximately two million inhabitants. The new development will include the biggest port on the western coast, an industrial district, central business district, sea-shore resort, educational zone and residential area. The city will be completed over a period of 20 years, starting from 2006 to a projected completion date in 2025 (<http://www.kingabdullahcity.com/>).

It is unusual that the data of the environmental conditions of the coastal waters of Rabigh are not sufficiently up-to-date. Such data are very important for coastal zone management since the area is expected to be under pressure of human activities in the next few decades. Our aim was to provide insight on the distribution pattern of total dissolved Cu and Ni in the surface coastal waters of Rabigh during various seasons in order to understand their biogeochemical accumulation.

Materials and Methods

Instrumentation

Voltammetric instrumentation consisted of Metrohm polarograph (Metrohm, Switzerland), controlled by an industry standard personal computer. Solutions in the voltammetric cell were stirred using a rotating teflon rod. Potentials were set with respect to an Ag/AgCl saturated AgCl in 3M KCl (SSCE) reference electrode. Glass voltammetric cells were used for the voltammetric analyses. These cells were soaked in 0.1 M HCl (Aristar grade) prior to use, and rinsed with purified water after each analyses.

Sample Collection and Treatment

Water used for rinsing and reagent preparations was deionised using a Milli-Ro and further treated by using a Milli-Q ion-exchanger system. Seawater samples were collected at about 40 cm from the surface in high density polyethylene (HDPE) bottles. The HDPE were cleaned according to the following procedure. The bottles were filled with 6M HCl (Analar grade, BDH) and left for one week; filled with 2M HNO₃ (Aristar grade) for another week, and subsequently stored partially filled with pure water acidified to pH 2 with HCl (Aristar grade). The samples were filtered using acid-cleaned cellulose nitrate filters (0.45 μm) under clean conditions (laminar flow hood in a clean room) using a vacuum pump. Samples were stored at temperature of -18 °C without acidification and were analyzed within three months. Seawater samples for chlorophyll-*a* (Chl-*a*) were collected in preconditioned appropriate bottles (Aminot and Chaussepied, 1983). The samples were filtrated with GF/C filter, 0.45 μm pore size. The particles on the filters were used for the determination of Chl-*a* after the extraction with 90% acetone according to Lorenzen, (1967).

Voltammetric Procedure

The determination of dissolved Cu and Ni was carried out using cathodic stripping voltammetry (CSV) (van den Berg, 1986; van den Berg and Nimmo, 1987). Acidified seawater was UV-irradiated prior to the total dissolved Cu and Ni determination, followed by neutralization with NH₃ solution. An aliquot of 10 ml seawater was pipetted into the voltammetric cell; 100 μl borate pH buffer (final concentration 0.01 M). For determination of Cu and Ni a complexing agent was added. For Ni a 25 μl Dimethylglyoxime (DMG; final concentration 25 μM) whereas for Cu a 25 μl 8-hydroxyquinoline (Oxine; final concentration 25 μM). The solution was deaerated by purging for 5 minutes with high purity nitrogen gas. The deposition potential was set to -1.1 V; four mercury drops were discarded before a new mercury drop was extruded, the solution was stirred for a preset period of 1-2 minutes. Then the stirrer was stopped and a quiescent period of 10 seconds was allowed before switching the potential to -0.15 V to re-oxidize the deposited and plated metal. Then the potential scan was initiated from -0.2 and terminated at -1.1 V.



Fig. 1. Satellite image for Rabigh City reproduced using Google Earth program showing major activities along the coast; ARA (Aramco Residential Area), WSP (Water Supply Plant), AR (Aramco Refinery), EPP (Electric Power Plant) and ACF (Arabian Cement Factory).

Area of study

The area of study is located northern of Rabigh City. It lies between longitudes 38.65° & 39.00° E and latitudes 22.80° & 23.30° N (Fig. 2). The area was marked as a sensitive area due to the presence of mangrove and seagrass beds as well as large stands of dense halophyte (IUCN 1987). It is a shallow area, has a width ranging from 150 to 250 m followed by steep slope seaward. The sea floor is blanketed with a thin layer of unconsolidated sediments overlying consolidated reefal limestone. Calcium carbonate is the dominant component of the sediments; originating from skeletal and non-skeletal remains with small portions of subordinate quartz sand grains (Gheith and Abou Ouf, 1994). Al-Karrar

Lagoon (named in some references by Sharm Al-Karrar or Khawr Al-Karrar) is connected to the coastal waters of Rabigh through a narrow channel where the water from the lagoon and the Red Sea is exchanging during tidal cycles. A total of 13 stations were selected parallel and perpendicular to the coast. The sampling was carried out during 2007 to cover various seasons; winter (Januray 2007), spring (April 2007) and summer (August 2007).

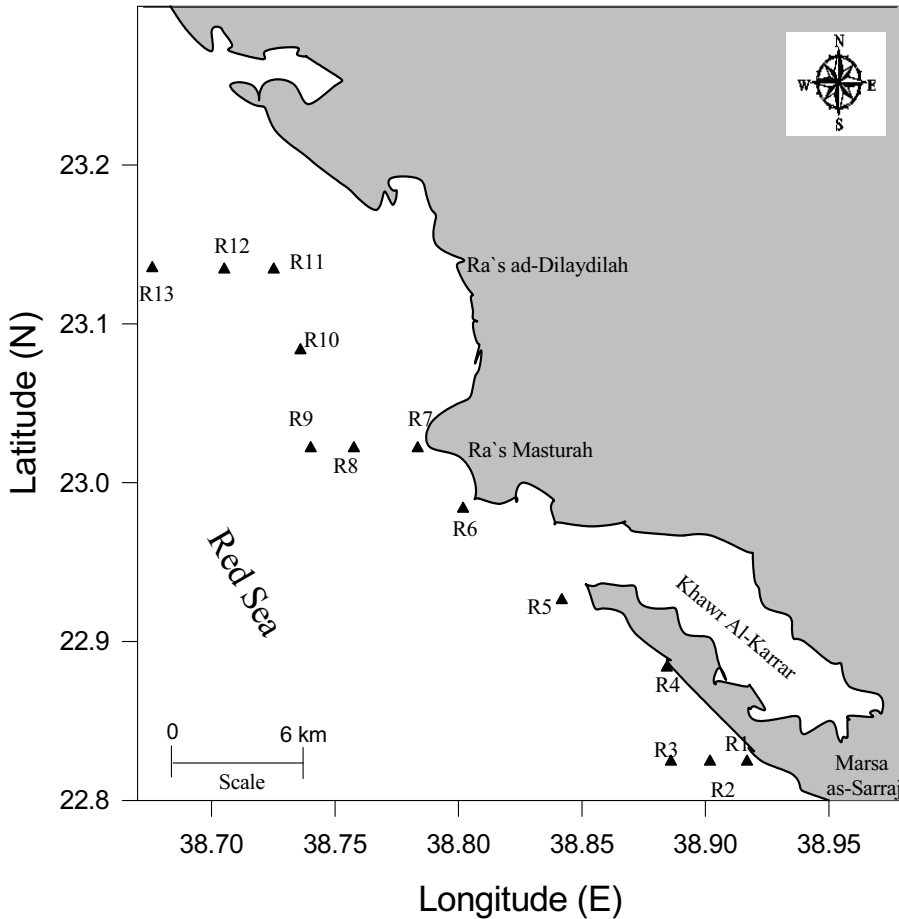


Fig. 2. Map showing the sampling stations along the surface coastal waters of Rabigh.

Results and Discussion

Hydrographic Properties

In comparison to the other oceans and seas, the data of temperature and salinity of the Red Sea is relatively limited. However, in the northern Red Sea, at about 20° N, the decrease of temperature and increase of salinity with increasing latitude is fairly regular and well marked (Edwards, 1987). Furthermore, the temperatures, at the same latitude, on the eastern coast (coast of the Arabian Peninsula) are higher than on the western coast (the African coast) whereas the behavior of salinity is opposite to the temperature behavior.

The values of temperature and salinity of the surface coastal waters of Rabigh for various seasons are shown in Table 1. The temperature ranged between 25.20 and 31.84 °C, whereas salinity ranged between 39.46 ‰ and 40.24 ‰. These values are in good agreement with the values reported at the same latitude of the Red Sea (Edwards 1987). The average temperature increased from 25.42 °C in winter to 27.78 °C in spring and finally approached 31.54 °C in summer. In contrast to the seasonal distribution of temperature, the average salinity in spring (39.64 ‰) and summer (40.10 ‰) was lower than its average in winter (40.18 ‰). Although salinity values are significantly controlled by temperature, the evaporation rate in the Red Sea during winter is higher than summer due to high wind speeds (Edwards 1987).

In all seasons, there is a general increase of salinity toward the northern part of the area whereas temperature exhibited irregular distribution pattern.

Total Dissolved Cu, Ni and Chl-a

The distribution pattern and concentrations of Cu, Ni and Chl-*a* in the surface coastal waters of Rabigh for various seasons are shown in Table 2 and Fig. 3. For all seasons, surface Ni concentrations ranged between 1.8 and 10.3 nM whereas surface Cu concentrations ranged between 1.4 and 14.4 nM. During winter and summer, the highest concentrations of both metals were measured at a particular station (St. R1 for winter; St. R6 for summer).

At St.11, the lowest concentrations of Ni during spring were accompanied with the highest concentrations of Cu. The average winter concentrations of Ni and Cu were almost double of its concentrations in spring and summer (Table 2). High levels of Ni and Cu during winter at St. R1 can be attributed to human activities at Marsa as-Sarraaj. Furthermore, the former assumption can be applied during summer for St.R6. This station is located at the the entrance of Al-Karrar Lagoon; therefore, the activities of fishermen in the area may lead to the elevated levels of both metals. The spatial distribution of both metals did not

show any distinct pattern; but in general, the concentrations of Ni decreased northward during winter.

Table 1. The levels of temperature (T) and salinity (S) in the surface coastal waters of Rabigh during 2007.

STATION NO.	JAN 2007		APR 2007		AUG 2007	
	T (°C)	S (‰)	T (°C)	S (‰)	T (°C)	S (‰)
R1	25.42	40.14	28.84	39.74	31.84	40.06
R2	25.37	40.12	27.90	39.46	31.79	40.09
R3	25.34	40.12	27.94	39.47	31.77	40.10
R4	NA	NA	NA	NA	NA	NA
R5	NA	NA	NA	NA	NA	NA
R6	NA	NA	NA	NA	NA	NA
R7	25.43	40.17	27.38	39.65	31.43	40.09
R8	25.49	40.17	27.36	39.63	31.28	40.10
R9	25.52	40.21	27.70	39.66	31.32	40.11
R10	NA	NA	NA	NA	NA	NA
R11	25.20	40.22	27.66	39.72	31.45	40.13
R12	25.24	40.22	27.80	39.70	31.46	40.13
R13	25.35	40.24	27.48	39.70	31.48	40.12
Average	25.37	40.18	27.78	39.64	31.54	40.10
SD	0.11	0.05	0.45	0.10	0.21	0.02

NA= not available

Table 2. Concentrations of total dissolved Ni, Cu and Chl-*a* in the surface coastal waters of Rabigh during 2007.

STATION NO.	JAN 2007			APR 2007			AUG 2007		
	Ni (nM)	Cu (nM)	Chl- <i>a</i> ($\mu\text{g L}^{-1}$)	Ni (nM)	Cu (nM)	Chl- <i>a</i> ($\mu\text{g L}^{-1}$)	Ni (nM)	Cu (nM)	Chl- <i>a</i> ($\mu\text{g L}^{-1}$)
R1	10.0	11.6	ND	3.5	3.3	0.040	2.8	2.1	0.006
R2	9.1	5.3	ND	2.9	2.6	0.010	3.3	2.2	0.002
R3	5.7	5.2	ND	2.9	9.1	0.007	2.2	2.3	0.002
R4	4.4	5.9	ND	2.8	4.1	0.050	2.3	7.3	0.002
R5	4.4	5.7	ND	3.6	1.5	0.020	4.0	2.6	0.002
R6	1.5	4.1	0.037	2.4	1.9	0.010	10.3	11.0	0.003
R7	8.6	7.0	ND	4.2	3.1	0.020	3.5	6.0	0.003
R8	9.3	6.1	0.042	2.3	2.2	0.007	3.6	4.6	ND
R9	8.3	6.9	ND	2.1	1.6	0.010	2.4	1.9	0.008
R10	4.9	4.5	0.047	2.7	1.4	0.040	2.4	2.54	0.007
R11	3.4	5.5	0.026	1.8	14.4	0.030	5.2	4.8	0.001
R12	4.7	6.0	0.017	2.3	2.8	ND	5.2	6.7	0.001
R13	4.6	7.1	0.037	2.4	2.1	0.003	1.9	2.2	0.005
Average	6.2	6.2	0.016	2.8	3.8	0.019	3.8	4.3	0.003
SD	1.8	1.8	0.019	0.7	3.8	0.016	2.2	2.8	0.002

ND= not detected.

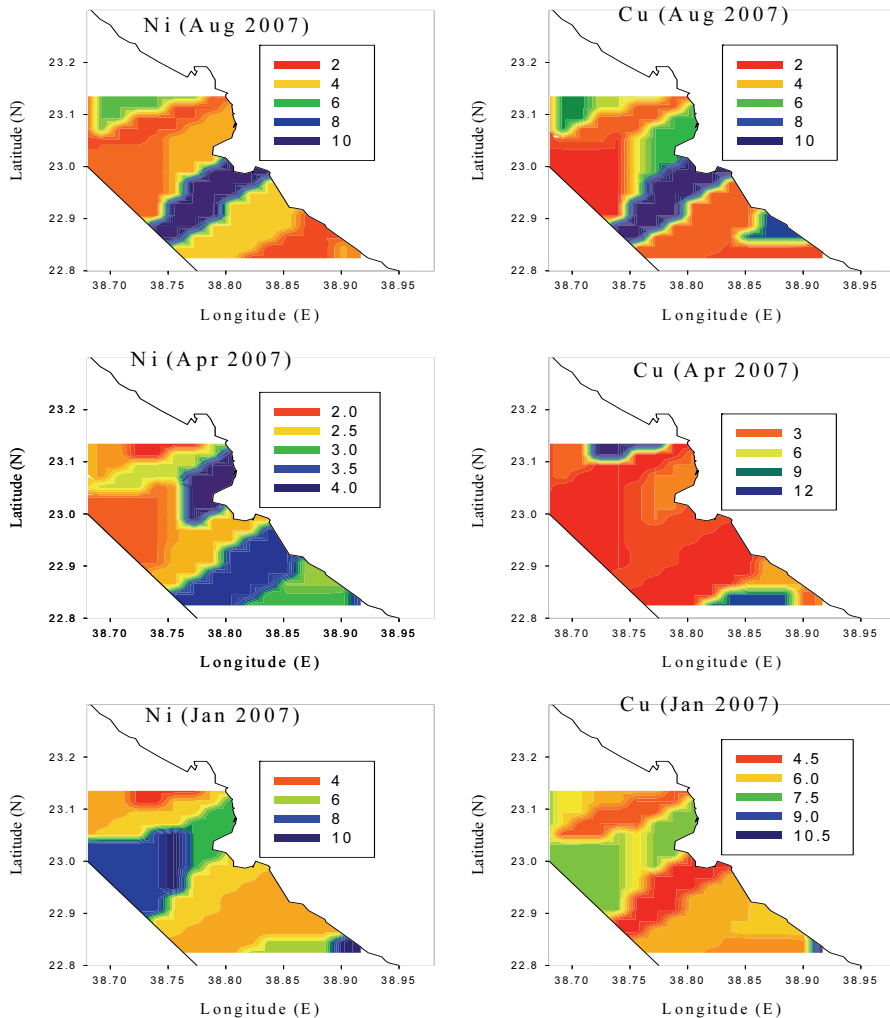


Fig. 3. The surface distribution of Ni (nM) and Cu (nM) in the coastal waters of Rabigh during 2007.

Chl-*a* values varied between undetectable to $0.050 \mu\text{g L}^{-1}$ (Table 2). The average Chl-*a* concentration calculated during spring ($0.019 \mu\text{g L}^{-1}$) was higher than that of summer ($0.003 \mu\text{g L}^{-1}$); and almost similar to that of winter ($0.016 \mu\text{g L}^{-1}$). Chl-*a* was undetectable during winter at the southern part of the area. However, the concentrations of Chl-*a* in the northern part were high and comparable to the values of spring. It is surprising to notice that the concentrations of Chl-*a* in winter is higher than summer although the activities

of marine organisms are expected to be at the lowest level during winter. The Chl-*a* distribution in the Red Sea was shown to exhibit seasonal variations with concentrations in the northern Red Sea lower than the southern Red Sea (Acker *et al.*, 2008). Furthermore, the seasonal variations at the northern part are different than that at the southern part. At the northern part, high levels of Chl-*a* have been reported during February, March and April whereas at the southern part high levels were found during August (Acker *et al.*, 2008). It is worthwhile to mention that the highest levels of Chl-*a* during winter at the northern part are comparable with relatively low concentrations of Ni. This behavior could be attributed to the biological consumption of Ni simultaneously with other micronutrients during the process of photosynthesis leading to high concentrations of Chl-*a* (Ellwood, 2008; and Whitfield, 2001). In contrast, high concentrations of Ni and low concentrations of Chl-*a* at the southern part is assumed to be the result of regeneration process in this area. Unfortunately, this assumption is based on the fact that the only factor affecting dissolved Ni is biological activities. Ni is known to be a nutritional requirement for many marine organisms and is a component of the proteinaceous metalloenzyme urease (Thomson, 1982). If the content of dissolved Ni is assumed to be in steady state, the average Chl-*a* in winter and spring as well as for Ni should be similar; but the data of Ni did not support such hypothesis. Therefore, other processes have to be taken into account to explain the behavior of dissolved Ni.

The spatial and temporal distribution of Cu was irregular and no clear pattern was observed. Ni and Cu were shown to behave as a conservative element under condition of mixing river water with seawater (Achterberg *et al.*, 1999; and Tankéré *et al.*, 2001). The fluctuations of salinity in the study area were not sufficient to correlate its values with Ni and Cu, although it was expected to observe significant variations of salinity due to some local discharges. However, inverse and weak correlation was obtained between salinity and Ni during winter and spring (Fig. 4).

The impact of Cu on some marine organisms has been reported by many workers. For example, the growth of the dinoflagellate *Gonyaulax tamarensis* was shown to be limited at cupric ion activities less than 10^{-13} M (Schenck, 1984). The distribution of Cu and Ni in seawater has recently (post-1975) been determined reliably, with profiles intermediate between that of a nutrient-type element (surface depletion, deep water enrichment) and an element that show a strong surface water source and scavenging throughout the water column (such as lead and manganese) (Bruland, 1983). On the other hand, Cu forms strong complexes with natural organic ligands in seawater (Coale and Bruland, 1990; Hanson *et al.*, 1988; Leal *et al.*, 1999; and van den Berg, 1984) and as a result lowers the free Cu concentrations. This strong complexation controls the

concentrations of Cu and causes the conservative behavior throughout the water column.

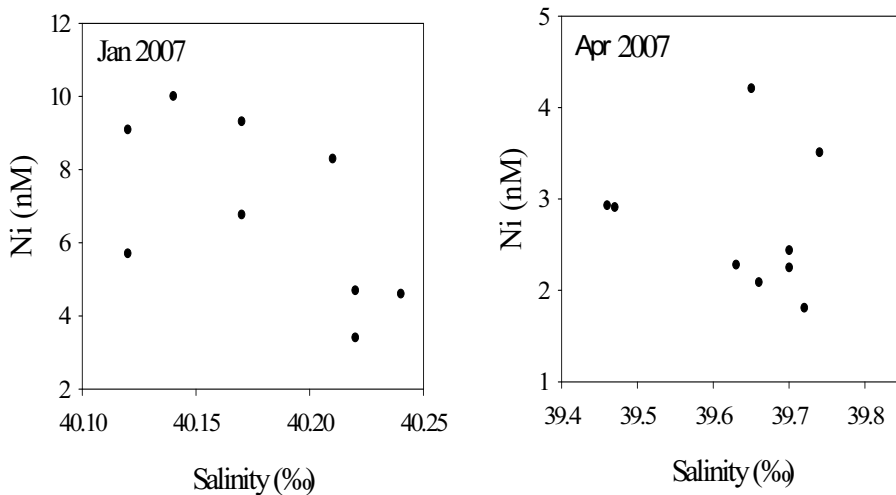


Fig. 4. Correlations between salinity and total dissolved Ni (nM) in the surface coastal of Rabigh during 2007.

The concentrations of trace metals are known to be higher in coastal waters as compared to those from open waters. River inputs are considered as an important factor that caused the high concentrations of trace metals in the coastal areas; but their influences on the coastal waters of Red Sea are negligible. In the arid region like the Red Sea environment, the runoff can play a role in providing trace metals to the coastal waters *via* wadies. Unfortunately, this factor is linked to the occasional rains that are very rare in this area.

Beside the biological factors, it seems that the concentrations of Ni and Cu in the study area are controlled by many processes; atmospheric input, benthic input during re-suspension of the sediments and/or diffusion from interstitial waters.

The atmospheric input to the coastal area of eastern Red Sea should be considered to understand its role in the study area. The importance of atmospheric input of trace metals to the marine environment has been recognized widely. For example, the atmospheric input is accounted for more than 50% of the trace metals to the open waters of NW Mediterranean (Guieu *et al.*, 1997; and Martin *et al.*, 1989). The concentration of elements were determined in the Red Sea Marine Aerosol, and it was shown that the concentrations of crustal derived elements (*e.g.* Al, Mn and Fe) were higher

than those from the eastern Mediterranean and Arabian Sea (Orif, 2007). Furthermore, the enrichment factor (EF_{crust}) of aerosol in Jeddah revealed that trace metals such as Cu and Ni has crustal origin (Orif, 2007; and Refaat *et al.*, 2009). These high concentrations were attributed to dust re-suspension and transport in the Nubian Desert and local sources. It is worthwhile to mention that the contribution of anthropogenic sources such as Rabigh Electric Power Plant should be taken into account since its input of trace metals to the atmosphere is well documented (Abu-Rizaiza 2004).

Cu and Ni levels measured in the present study were compared with values reported for the other Red Sea and oceanic regions (Table 3). Most of the studies on the trace metal levels in the off shore areas of the Red Sea were concentrated on hot brines that are deeps spread along the axial part of the Red Sea (Garbe-Schönberg *et al.*, 1998).

Apart of the water body of the hot brines, few studies dealt with the distribution of trace metals in the waters column (Brooks *et al.*, 1969; Karbe *et al.*, 1981). Most studies concerning trace metals in seawater in the eastern Red Sea were concentrated on the coastal waters of Jeddah (Behairy *et al.*, 1983; El-Rayis *et al.*, 1984; Fahmy & Saad, 1994; and Saad & Fahmy, 1994). Our data for Cu are lower than those reported for the coastal waters of Jeddah by an order of magnitude. The data of the Arabian Gulf were in the range of our data (Fowler *et al.*, 1984). The values of dissolved Cu and Ni at the northern Red Sea and Gulf of Aqaba were lower than our data (Shriadah *et al.*, 2004). It is worth to mention that their data were obtained from off shore waters, therefore their values were expected to be lower than our data. Also, dissolved Cu and Ni values for the coastal waters of Yemen were lower than our data (Al-Shiwafi *et al.*, 2005). This finding may be related to the differences in the environmental conditions of the coastal area of Saudi Arabia and Yemen. We suggest that, the atmospheric input could have more impact on the coastal waters of Saudi Arabia especially at Jeddah City in comparison to Yemen coast. This is because the coastal area of Yemen is bordered by high mountains that limit the input of trace metals to the coastal area. The coastal area of Jeddah is bordered by a plain surface from the east. Therefore, during dust events the dust contributes in the load of trace metals to the coast of Jeddah. These aerosols find their way to the sediments, and therefore re-suspended and contribute the concentrations of Cu and Ni in the overlaying waters (Al-Shiwafi *et al.*, 2005).

There is a Rabigh Cable Factory (built by Nesma Partners & Co.) towards the north of Jeddah; apart from civil construction, their scope of work includes electrical and telecommunication infrastructure using electric copper wires. In addition, there is a desalination plant near Rabigh using reverse osmosis. It is a joint venture of Sumitomo Chemical Company of Japan and ARAMCO of Saudi Arabia. This reverse osmosis is based on less high alloy metals such as, nickel, chromium and copper. It is conceivable that the waste effluent of these two industries is dumped into the seawater either treated or partially treated. Further if Ni exceeds more than 0.05 mg/cm^3 , it may cause undesirable effects in the body of marine animals. Nickel sulfide is believed to be a carcinogenic. If it's intake through sea food is more than the permissible limits, it may show allergic manifestation on the skin of human. Cu on the other hand is present in traceable amounts in liver, muscles and bones of man and animals, however it's excessive quantity may cause liver cirrhosis, therefore it is necessary that its presence particularly in sea food animals should be periodically monitored carefully.

Table 3. Comparison between the measured total dissolved Cu and Ni in the present study with those of previous studies. Data between brackets is for mean value.

Area	Area type	Cu (nM)	Ni (nM)	Reference
Red Sea, Saudi Arabia, Jeddah	Coastal	15.28-23.94	---	(El-Rayis et al. 1984)
Red Sea, Saudi Arabia, Jeddah	Coastal	(18.43)	---	(Behairy et al. 1983)
W. Arabian Sea, Oman	Coastal	3.46-6.61 (4.57)	---	(Fowler et al. 1984)
Arabian Gulf, UAE and Bahrain	Coastal	3.31-18.90 (8.03)	---	(Fowler et al. 1984)
Red Sea, Yemen	Coastal	0.55-0.94 (0.74)	0.55-1.28 (0.90)	(Al-Shiwafi et al. 2005)
North Red Sea	Open	1.42-2.20 (1.73)	1.70-2.56 (2.04)	(Shriadah et al. 2004)
Gulf of Aqaba	Open	1.26-2.83 (1.73)	2.56-4.09 (3.24)	(Shriadah et al. 2004)
Red Sea, Saudi Arabia, Jeddah	Coastal	(25.83)	----	(Saad and Fahmy 1994)
Red Sea, Saudi Arabia, Jeddah	Coastal	(25.83)	---	(Fahmy and Saad 1994)
Red Sea, Saudi Arabia, Rabigh	Coastal	1.42-14.43 (4.80)	1.81-10.32 (4.25)	Present study

Conclusion

Measurements of total dissolved Cu and Ni were carried out in seawater samples collected from the surface coastal waters of Rabigh, Saudi Arabia, eastern Red Sea. The distribution patterns were obtained for both metals during winter, spring and summer 2007. The spatial and seasonal distributions of dissolved Cu and Ni were evident. Attempt to correlate the distribution of Cu and Ni with salinity and Chl-*a* was hampered probably due to complexity nature of the coastal environment. However, the present data indicated that the biological activities could be important factor in controlling Cu and Ni concentrations. More research works are needed to understand the role of the other factors such as atmospheric input and diffusion from sediment in controlling the concentrations and behavior of dissolved Cu and Ni in the coastal waters of Rabigh.

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التوزيع المكاني والموسمي للنحاس والنيكل الكلي الذائب في المياه السطحية للمياه الساحلية لمدينة رابغ، المملكة العربية السعودية، شرق البحر الأحمر

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المستخلص. تم تعيين التغيرات المكانية والموسمية للنحاس والنيكل الكلي الذائب في المياه السطحية لمدينة رابغ، المملكة العربية السعودية، شرق البحر الأحمر. تعطي النتائج المتحصل عليها دلالة على وجود التغيرات المكانية والموسمية على طول منطقة الدراسة. ووجد أن أعلى تراكيزات للعنصرين خلال موسم الشتاء، بالمقارنة مع موسم الربيع والصيف. وهذا السلوك ربما يرجع إلى نشاطات الكائنات الحية. وعلى الجانب الآخر، لوحظ عدم انتظام في التوزيع المكاني للعنصرين. وعلى العموم، وجدت تراكيزات عالية متلازمة لكلا العنصرين في بعض المواقع. وفي غياب صب الأنهار، فإنه من الضروري إجراء دراسات مستقبلية عن الترسيب الجوي، والانتشار من الرواسب كمصادر مهمة لكلا العنصرين في المياه الساحلية لرابغ. وعلى ضوء هذه الدراسة فإنه من المستحسن إجراء دراسات مشابهة على المناطق الأخرى للمياه الساحلية للمملكة العربية السعودية.