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Spatial, seasonal distribution and ecological risk assessment of Zn, Cr, and Ni in Red Sea surface sediments, Egypt

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ABSTRACT

Recently, the marine ecology in the Red Sea coast has been altered due to various anthropogenic activities that led to an accumulation of heavy metals (HMs) in its sediments. To evaluate the spatial and temporal distribution and the ecological risk assessment along the study area of the Egyptian Red Sea coast, fourteen samples of sediments were collected during spring and autumn in 2015. The present study aimed to address chromium, zinc, nickel, total carbonate and organic matter in the sampled sediments to assess the risk. In both seasons, the descending order of metal concentrations was Zn > Cr > Ni. The level of studied metals was compared to the background and sediment quality guideline (SQG) values. Results revealed that an adverse biological effect in some sites was possible. Zinc, for instance, recorded higher averages than those of the background and those detected along worldwide coasts. Additionally, to evaluate pollution, methodologies such as the enrichment factor (EF), contamination factor (CF), pollution index (PI) and modified pollution index (MPI) were calculated and interpreted.

INTRODUCTION

Heavy metals (HMs) are extremely poisonous, non-biodegradable, and readily accumulated in the aquatic life. Surface runoff, especially with the development of industry, agriculture, and urbanization, discharged them into the marine environment **(Diagomanolin *et al.*, 2004; Zhang & Gao, 2015; Ranjbar Jafarabadi *et al.*, 2017; Liu *et al.*, 2018; Younis *et al.*, 2019; Soliman *et al.*, 2020)**. Metals are scavenged by particulate matter and deposited to coastal sediments after entering coastal waters, and hence, sediments are considered a major component of metal storage in marine ecosystems **(Pan & Wang, 2012)**. The build-up of heavy metals (HMs) in sediments and seawater poses a substantial hazard to the aquatic animals and the human health as well as an end-user.

Because certain pollutants may be recycled through biological and chemical processes within the water column, sediments are the primary accumulation sites and transporters of toxins in aquatic settings **(Vink, 2009; Nemati *et al.*, 2011; Bartoli *et al.*, 2012; Younis *et al.*, 2014a; Younis, 2018; Younis *et al.*, 2018; Younis *et al.*, 2020)**. Furthermore, numerous factors influence the levels of HMs in sediments, including the pH and the availability of organic matter **(Chakraborty *et al.*, 2014)**.

The Red Sea has long served as a vital transportation route connecting Europe and Asia **(Hanna & Muir, 1990; Younis, 2020)**. Various anthropogenic activities, such as oil spills, desalination plant effluents, wastewater discharge, marine traffic, and building activities along the coastline, have altered the marine ecology of the Red Sea coast in the recent decades **(Al-Taani *et al.*, 2014; El Nemr *et al.*, 2016; El-Metwally *et al.*, 2017; Ibrahim *et al.*, 2019; Soliman *et al.*, 2019a; Youssef *et al.*, 2020)**. Therefore, the current study was conducted to assess the accumulation of Ni, Cr and Zn in the study area of the Red Sea coast in Egypt using several contamination indices paralleled with the sediment quality guidelines. In addition, this work aimed to document the HMs spatial and seasonal distribution and address their sources.

MATERIALS AND METHODS

2.1. Sampling and analyses

Fourteen samplings were collected along, approximately 450 km of the Egyptian Red Sea coast, from Ras Gharieb to Marsa Alam (Table 1 & Fig. 1). The surface sediment samples were collected during two seasons (spring and autumn) in 2015 with a Van Veen grab from the upper five cm; layers were carefully taken to avoid disturbance. The upper five cm layer was chosen because it is more chemically and biologically active than the deeper layers, where substances exchange between sediment. The sediment samples in plastic bags were immediately kept in an icebox at 4°C to reduce biochemical reactions. After being transferred to the laboratory, they were reserved in a freezer at -20°C for further analysis. In an oven, sediments were dried to a consistent weight at 105°C.

The total carbonate content was determined following the method of **Black (1965)**. The organic carbon of the investigated sediments was determined using acid/dichromate titration method described in the study of **Gaudette *et al.* (1974)**.

Determination of trace metals in sediments was obtained using the method of **Oregioni and Aston (1984)**.A weight of 0.2 g of dry sediment sample was digested in Teflon vessels containing a mixture of HNO_3: HF: $HClO_4$ (3:2:1 v/v, 10 ml) at 70°C. The obtained solution was diluted in 25 ml with deionized water and analyzed by using an Atomic Absorption Spectrophotometer (FAAS, Shimadzu Model AA- 6800). The AAS results were obtained in mg/kg dry weight.

Reagent blanks were made using the same procedures of sample preparation and were used to rectify the analytical results. Calibration standards were performed using

appropriate dilutions of the metals' stock solutions (1000 mg/l; Merck Grade). Precision was checked against standard reference material and set within the range of certified values with 95-103% recovery for all metals studied.

2.2. Statistical and data analysis

Descriptive statistics such as and Multivariate statistical analyses, and Pearson correlation inferential statistics were performed using SPSS 25 for windows version. Several methodologies were used to analyze and evaluate pollution, including enrichment factor (EF), contamination factor (Cf), Pollution index (PI) and Modified pollution index (MPI).

Table 1: Location of sampling stations

Region	Location	Station	Lat	Long
Ras Ghareb		1	28.367697	33.079566
Hurghada	El Gona	2	27.377533	33.682500
	Magawish	3	27.155732	33.832323
	Marine Sport Club	4	27.177252	33.827352
	Hurghada shipyard	5	27.229625	33.843496
	Hurghada Tourist Harbour	6	27.234217	33.847896
Safaga	Safaga shipyard	7	26.685864	33.935216
	Post Abu Tartour harbour	8	26.705540	33.937291
	Fishermen harbour	9	26.725473	33.938653
El-Hamraween	Pre-Hamraween harbour	10	26.251890	34.201657
	Post-Hamraween harbour	11	26.267222	34.197569
Marsa Alam	Marsa Egla	12	25.172442	34.840708
	Marina Marsa	13	25.078822	34.891744
	Marsa Sefeen	14	25.105628	34.878447

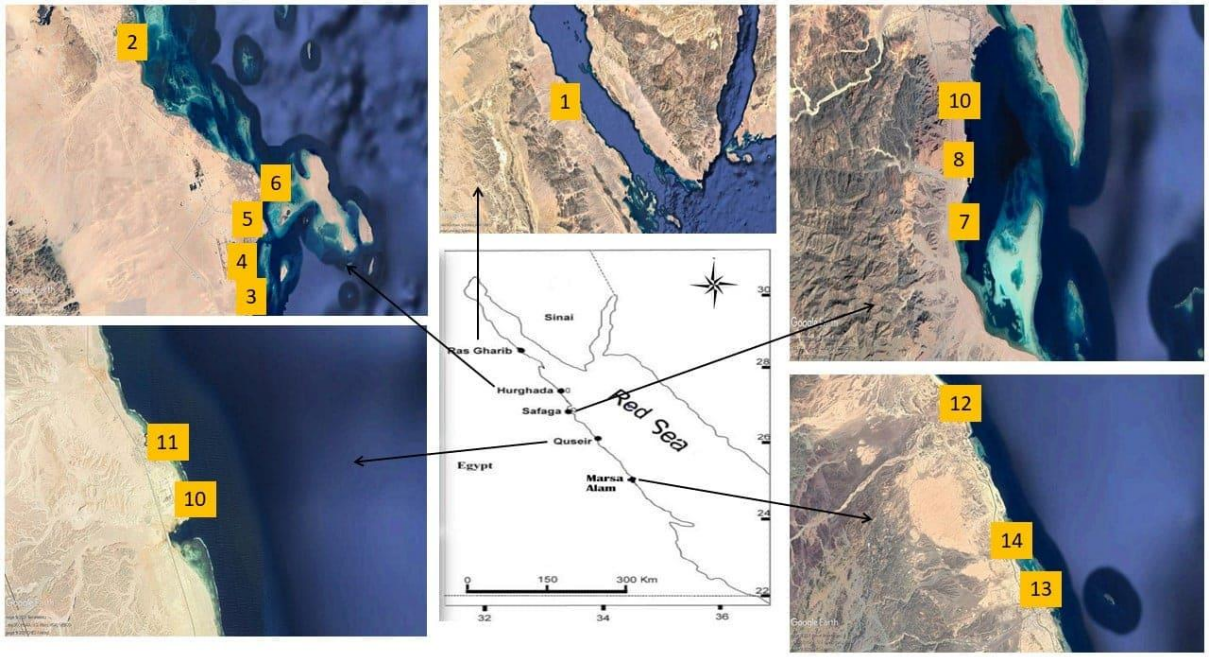

Fig.1: Location of sampling sites along the Red Sea coast

RESULTS AND DISCUSSION

3.1. Total Carbonates and total organic matter in sediments

The determined total carbonate content in the sediments of the study area was highly variable ranging from 4.43% at station 3 (Magawish) to 72.00% at station 12 (Marsa Egla) with an average of 32.89% in the spring season. In autumn, the values ranged from 2.33% at station 3 (Magawish) to 68.10% at station 12(Marsa Egla) with an average of 33.52% (Table 2).

Maxwell (1968) divided sediments into four categories depending on carbonate content: high carbonate (>80%), impure carbonate (60– 80%), transitional (40–60%), terrigenous (20–40%) and high terrigenous (<20%). Accordingly, sediment samples from stations 3 and 13 in spring and stations 3, 5, 9 and 13 in autumn were classified as high terrigenous with a carbonate < 20%. Additionally, the terrigenous materials with carbonate range of 20–40% were shown in sediments from stations 1, 5, 9, 10 and 11 in spring and stations 1, 2, 4, 7, 10 and 11 in autumn. Meanwhile, stations 2, 4, 6, 7, 8 and 14 in spring and stations 6, 8 and 14 in autumn were of a transitional type (40–60%) (Table 2& Fig. 2) indicating the influx of terrigenous materials. The highest value of $CaCO_3$ content was observed at station 12 in Marsa Egla in both seasons and was classified impure carbonate (60–80%). The high value of carbonate may be due to the presence of an appreciable amount of tubiform skeletons of some calcareous organisms, (gastropod and pelecypod) and shell fragments **(Draz, 1983)**.

For the Pearson correlations, results revealed that in both seasons the low correlation mostly observed among Ni, Cr and Zn and carbonates indicates that these metals are poorly linked to carbonates.

The distribution of organic matter content in the study area is presented in both Table (2) and Fig. (3). The range of TOM% in the surface sediments of the study area varied from 0.97 to 12.69 % with an average of 4.53% in spring while in the autumn, it ranged from 0.38 to 14.4 % with an average of 4.93%. The highest value of TOM% was observed at stations 4, 5, 6, 7, and 9 in marine sport club, Hurghada shipyard, Hurghada tourist Harbour, Safaga shipyard and fishermen harbour, respectively in both seasons. The detected high values of TOM% are attributed to the contamination caused by hydrocarbons from boats, domestic wastes and sewage, repairing and maintenance in a shipyard, petroleum spilt from tanks and boats, in addition to shipping activities.

Results of Pearson's correlation (Fig. 4) reveal that, Zn in the spring season showed a high positive correlation with TOM% ($r=0.8$, $P < 0.01$), and Zn in the autumn season showed a positive correlation with TOM% ($r= 0.64$, $0.P < 0.05$). These results indicate that the distribution of Zn was controlled by the organic matter content in this area **(Soliman *et al.*, 2019b)**.

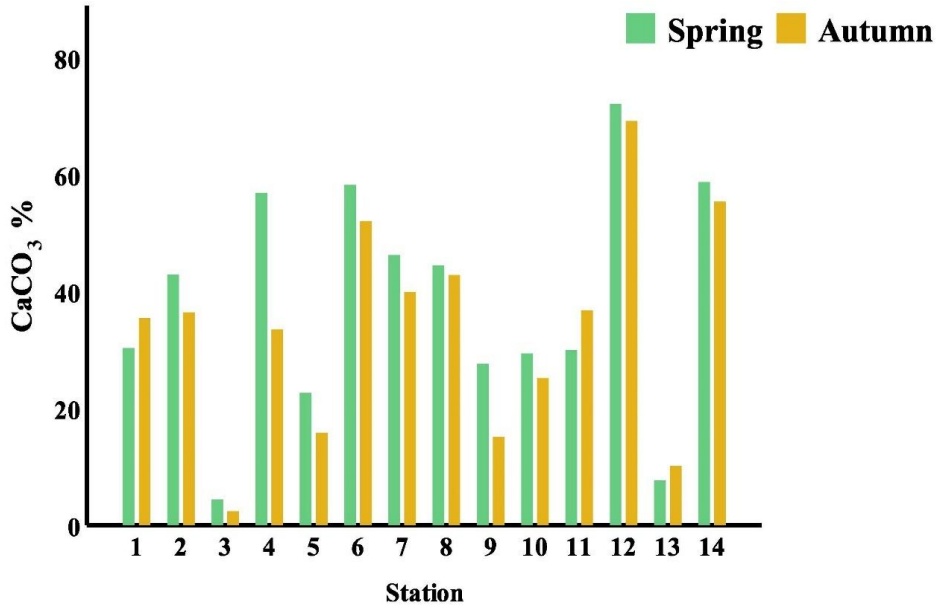

Fig. 2: Distribution of $CaCO_3$ % in surface sediments along the Egyptian Red Sea coast study area in the spring & autumn seasons

Table 2: Distribution of selected metals concentration (Cr, Ni, and Zn; mg/kg) and (TCO_3 and TOM; %) for sediments collected from the Red Sea coast, Egypt

Station	Cr		Ni		Zn		TCO_3%		TOM%	
	Spring	Autumn	Spring	Autumn	Spring	Autumn	Spring	Autumn	Spring	Autumn
1	60.22	52.33	12.22	5.45	123.22	56.12	30.25	35.39	3.22	2.50
2	26.15	62.74	12.02	6.14	89.32	94.54	42.8	36.37	2.46	1.48
3	16.02	111.13	1.63	7.15	68.24	80.22	4.34	2.33	0.97	0.38
4	28.74	134.21	16.11	11.76	77.38	154.49	56.8	33.43	7.16	12.01
5	23.16	109.34	1.15	31.69	651.92	179.32	22.54	15.76	12.69	14.41
6	82.85	101.42	1.15	0.88	111.43	99.54	58.18	51.95	6.32	4.43
7	32.94	28.42	1.95	0.85	135.65	79.23	46.13	39.82	6.65	7.91
8	36.96	85.17	3.39	0.73	110.55	69.59	44.4	42.77	3.35	3.44
9	63.53	123.2	7.74	9.02	380.21	230.23	27.58	15.04	9.35	9.58
10	86.91	90.23	10.01	6.31	124.22	96.23	29.3	25.16	1.83	1.23
11	61.66	34.47	4.89	1.27	69.84	50.79	29.9	36.7	3.66	3.32
12	44.37	32.17	5.27	16.19	67.49	128.98	72	69.1	2.00	2.63
13	31.05	54.39	74.23	66.38	216.21	170.54	7.57	10.11	2.02	3.22
14	18.45	4.46	9.09	6.01	70.86	88.56	58.69	55.3	1.71	2.50
Min	16.02	4.46	1.15	0.73	67.49	50.79	4.34	2.33	0.97	0.38
Max	86.91	134.21	74.23	66.38	651.92	230.23	72.00	69.10	12.69	14.41
Mean	43.79	73.12	11.49	12.13	164.04	112.74	37.89	33.52	4.53	4.93
Median	34.95	73.96	6.51	6.23	110.99	95.39	36.53	35.88	3.29	3.27
Background										
[1]Average shale	90		68		95		-		-	
[2]Crustal average	100		75		70		-		-	
[3]Upper crust	35		20		71		-		-	
[4]Mean crust	100		75		75		-		-	
[5]Mean sediment	72		52		95		-		-	
[6]Continental crust	126		56		65		-		-	
Sediment Quality guidelines										
[7](ERL)	81		20.9		150		-		-	
[7](ERM)	370		51.6		410		-		-	
[8]USEPA guidelines: **Not polluted**	<25		<20		<90		-		-	
[8]USEPA guidelines: **Moderately polluted**	25-75		20-50		90-200		-		-	
[8]USEPA guidelines: **Heavily polluted**	>75		>50		>200		-		-	

[1]Average shale **(Turekian & Wedepohl, 1961)**
[2]Crustal average **(Taylor, 1964)**
[3]Upper crust **(Taylor & McLennan, 1995)**
[4]Mean crust **(Bowen, 1979)**
[5]Mean sediment **(Salomons & Förstner, 1984)**
[6]Average Continental crust **(Hans Wedepohl, 1995)**
[7]Effects range low (ERL) **(Long *et al.*, 1995)**
[7]Effects range median (ERM) **(Long *et al.*, 1995)**
[8]USEPA guidelines **(USEPA, 1977)**

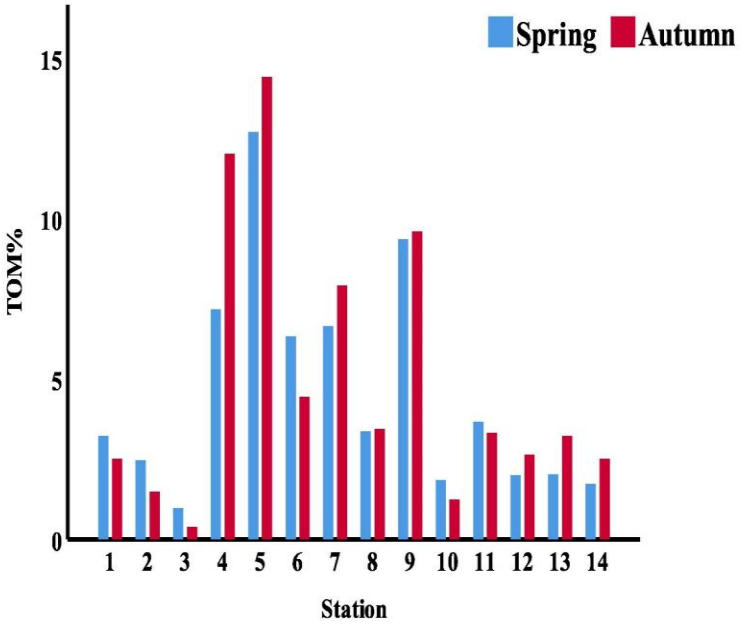

Fig. 3: Distribution of TOM% in surface sediments along the Egyptian Red Sea coast study area in spring & autumn seasons

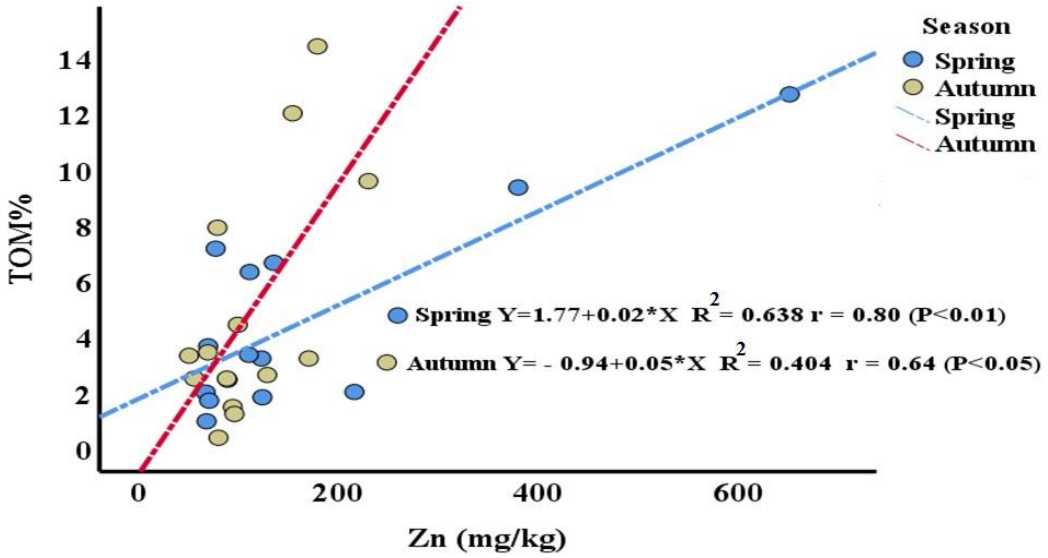

Fig. 4: Regressions of Zn(mg/kg) with %TOM at study area of the Red sea coast in different seasons

3.2. Spatial and seasonal distribution of trace metals in sediments

The range and average of concentration (mg/ kg) of trace metals (Ni, Cr, and Zn) varied from narrow to wide-scaled as follows: 1.15 − 74.23 (11.49) for Ni, 16.02 − 86.91(34.79) for Cr and 67.49−651.92 (164.04) for Zn in the spring season. In the autumn season, the ranges of studied trace metals (mg/kg) were: 0.73-66.38 with an average (12.13) for Ni, 4.46-134.21 with average (73.12) for Cr, and 50.79 – 230.23 with an average (112.74) for Zn (Table 2). The average of trace metals in the surface sediments compared to that in other studies in the Red Sea and worldwide sites are tabulated in Table (3).

A large variability was detected in the level of Ni among sites. The highest concentration of Ni (74.22 and 66.38 mg/kg) was observed at station 13 (Marsa Marine) in the spring and autumn seasons, respectively. Whereas, the lowest concentrations (1.15 and 0.73 mg/kg) were found at station 6 (Hurghada Tourist Harbour) and station 8 (Post Abu Tartour harbour) in the spring and autumn seasons, respectively. The highest concentrations (86.91 and 134.21 mg/kg) of Cr were found at station 10 (Pre-Hamraween harbour) and station 4 (Marine Sport Club) in the spring and autumn seasons, respectively, while the lowest concentrations (16.02 and 4.46 mg/kg) were at stations 3 (Magawish) and 14 (Marsa Sefeen) in spring and autumn, respectively. Moreover, the highest concentration of Zn (651.91 mg/kg) was observed at station 5 (Hurghada shipyard) and the lowest (67.49 mg/kg) was at station 12(Marsa Egla) in spring while in the autumn season, the highest concentration of Zn (230.23 mg/kg) was recorded at station 9 (fishermen harbour in Safaga) and the lowest (50.79 mg/kg) was found at station 11(Post-Hamraween harbour) (Table 2 & Fig. 5).

It is worthy to mention that, the high concentration of trace metals' (Ni, Cr and Zn) contaminations in the surface sediments of stations 5, 7 and 9 are derived from different navigation activities (boat moorage and repair, dockyards and shipping repair and maintenance).

Based on Pearson's correlation, results spotted that Zn in the autumn season showed a high positive correlation with Ni ($r=0.54$, $P < 0.05$). Notably, the high correlations between two heavy metals most likely indicate that they come from similar pollution sources or undergo a similar transformation and migration processes under certain conditions **(Wang *et al.*, 2012)**.

3.3. Sediment Quality Guideline (SQGs)

To protect aquatic biota from the damaging and toxic impacts of sediment-bound pollutants, a variety of sediment quality guidelines (SQGs) have been applied **(McCready *et al.*, 2006)**. These guidelines aid to assess the extent to which sediment-associated chemical status may harm aquatic life and are intended for sediment quality interpretation. They are also used to rank and prioritize contaminated areas for further investigation **(Díaz-de Alba *et al.*, 2011)**.

Based on the SQGs proposed by **USEPA (1977)**, sediments were categorized into three classes; nonpolluted, moderately polluted and heavily polluted. The chemical contamination in the sediments was assessed using the USEPA's proposed sediment quality guidelines, which are listed in Table (2) and Fig. (6). The data considered show that the concentration of Ni at all stations and in both seasons belonged to unpolluted sediments with the exception of station (5) in Hurghada shipyard in autumn. It was moderately polluted, whereas in both seasons, station (13) in Marsa Alam was classified as heavily polluted. The concentration of Cr at stations (3, 5 in spring season and 14 in both seasons) in Magawish, Hurghada shipyard, Marsa safeen in Marsa Alam, respectively was not polluted, while at stations (1, 2, 7, 11, 12 and 13) in both seasons and (8, 9) in spring season in Ras gharieb, El-Gona, Safaga shipyard, Post-Hamraween harbour, Marsa Egla, Marsa marina, post-Abu Tartour Harbour and fishermen Harbour, respectively were moderately polluted. Furthermore, stations (3, 4, 5, 8 and 9) in autumn and (6& 10) in both seasons in Magawish, marine sport club, Hurghada shipyard, Post Abu Tartour harbour, fishermen harbour, Hurghada tourist Harbour and Pre-Hamraween harbour, respectively were heavily polluted.

In Fig. (6), the presented data reveal that the sediment at all stations was classified as nontoxic with Zn at stations (1, 7, 8 and 12) in the autumn season, stations (2, 3 and 14) in both seasons and station (4) in autumn season, while stations (1, 7, 8 and 10) in spring season and stations (4, 5, 12 and 13) in autumn season and station (6) in both seasons were moderately polluted. Stations (5 and 13) in the spring season and station (9) in both seasons were heavily polluted.

The Effects-rang-low (ERL) and Effects-range-median (ERM) chemical doses were named after the 10^{th} and 50^{th} percentiles of adverse biological effects, respectively. The NOAA recommendations assign two values to each chemical, categorizing the sediment as rarely (<ERL), occasionally (**>**ERL and <ERM), or frequently (> ERM) related with deleterious biological consequences **(MacDonald *et al.*, 2000)**.

When comparing the results of the current study's with ERL and ERM values (Fig. 6), it was observed that the concentration of Ni at stations (13 in both seasons) and Zn at a station (5 in spring season) had a concentration > ERM. This reflects that the adverse effects on the benthic organisms at these stations frequently occur. While the concentration of Ni at a station (5 at autumn season), the concentration of Zn at (a station 5 in the autumn season and stations 9 and 13 in both seasons) and the concentration of Cr at stations (3, 4, 5, 6, 8 and 9 in the autumn season and stations 10 in both season) had a concentration >ERL and < ERM. This reflects that the adverse effects on the benthic organisms at these stations occasionally occur. On the other hand, all the rest of the studied stations in both seasons had a concentration of these metals below the ERL value which indicates that Ni, Cr and Zn in the study area is no threat to the benthic organisms.

3.4. Comparison with the background value

The average shale background concentration of global sediments **(Turekian and Wedepohl, 1961)** is selected as the reference baselines in this study, which are shown in Table (2). Station 13 in both seasons (Marsa Marine; Marsa Alam region) are considered polluted with Ni when compared to that of the mean sediment (52 mg/kg) reported by **Salomons and Förstner (1984)** and the average continental crust (56 mg/kg) reported by **Hans Wedepohl (1995)**. On the other hand, all sediments samples in both seasons were considered unpolluted with Ni when compared with the crustal average (75mg/kg) **(Taylor, 1964)** and the average shale (68 mg/kg) **(Turekian and Wedepohl, 1961)**.

The concentration of Cr at stations (1, 6, 8, 9, 10, 11 and 12) in the spring season and stations (1, 2 and 13) in the autumn season were higher than the upper crust background (35 mg/kg) **(Taylor and McLennan, 1995)** and the average continental crust background (35 mg/kg) **(Hans Wedepohl, 1995)**, which explained a new input of toxic Cr to those stations. On the other hand, according to **Taylor (1964) and Bowen (1979)** the concentration of Cr at stations (3, 4, 5, 6, 9 and 10) exceeds the background concentration of the crustal average, mean crust and average shale. Cr concentrations at stations (2, 3, 4, 5, 7, 13 and 14) in the spring seasons and stations (11, 12 and 14) in the autumn season which is considered unpolluted with Cr according to background concentration of metals (Table 2).

Table (2) shows that stations 1, 5, 6, 7, 8, 9, 10 and 13 in the spring season and stations 4, 5, 6, 9, 10, 12 and 13 in the autumn season considered as polluted with Zn when compared to the crustal average (70 mg/kg) **(Taylor, 1964)**, upper-crust (71 mg/kg) **(Taylor and McLennan, 1995)**, mean crust (75 mg/kg) **(Bowen, 1979)**, Average shale (95 mg/kg) **(Turekian and Wedepohl, 1961)**, mean sediment concentration (95 mg/kg) **(Salomons and Förstner, 1984)** and the average continental crust (65 mg/kg) **(Hans Wedepohl, 1995)**. On the other hand, station 2 in the spring season as well as stations 2, 3 and 14 in the autumn season are considered as polluted with Zn when compared to the crustal average (70 mg/kg) **(Taylor, 1964)**, upper-crust (71 mg/kg) **(Taylor and McLennan, 1995)** and the average continental crust (65 mg/kg) **(Hans Wedepohl, 1995)**. The levels of Zn in the sediments for these stations are higher than the permissible levels which indicate its high concentration according to the background value in sediments.

Table 3 Comparison between the metal concentrations (mg/kg) in the studied sediments and those in other worldwide sites.

Location	Ni	Cr	Zn	References
Egyptian Red Sea in the spring season	11.49	43.79	164.04	Present study
Egyptian Red Sea in the autumn season	12.13	73.12	230.23	Present study
Russia, Caspian Sea	14	-	17.1	**(de Mora *et al.*, 2004)**
Aden Port, Yemen, Red sea	34.54	82.19	128.58	**(Nasr *et al.*, 2006)**
Hurghada area	1.91	-	4.66	**(Mansour *et al.*, 2007)**
Red Sea coast, Egypt	11.4	18.47	22.64	**(Salem *et al.*, 2014)**
Red Sea coast, Egypt	22.5	30.44	62.44	**(Younis *et al.*, 2014b)**
Mediterranean Sea, Egypt	30.85	-	32.03	**(Okbah *et al.*, 2014)**
Red Sea, Saudi Arabia	8.69	20.62	39.71	**(Youssef and El-Sorogy, 2016)**
Mediterranean Sea, Libya	23	-	26.6	**(Nour and El-Sorogy, 2017)**
Arabian Gulf, Saudi Arabia	77	48.3	64	**(El-Sorogy *et al.*, 2018)**
Hurghada area, Red Sea coast, Egypt	1.73	-	7.47	**(Nour *et al.*, 2018)**
Hurghada area	23	-	73	**(Zakaly *et al.*, 2019)**
Gulf of Suez, Egypt	46.47	26.42	47.59	**(Ibrahim *et al.*, 2019)**
Red Sea-Gulf of Aqaba, Saudi Arabia	14	39	24	**(El-Sorogy *et al.*, 2020)**
Yanbu coastline, Saudi Arabia	23.5	27.21	80.4	**(El-Sorogy *et al.*, 2021)**

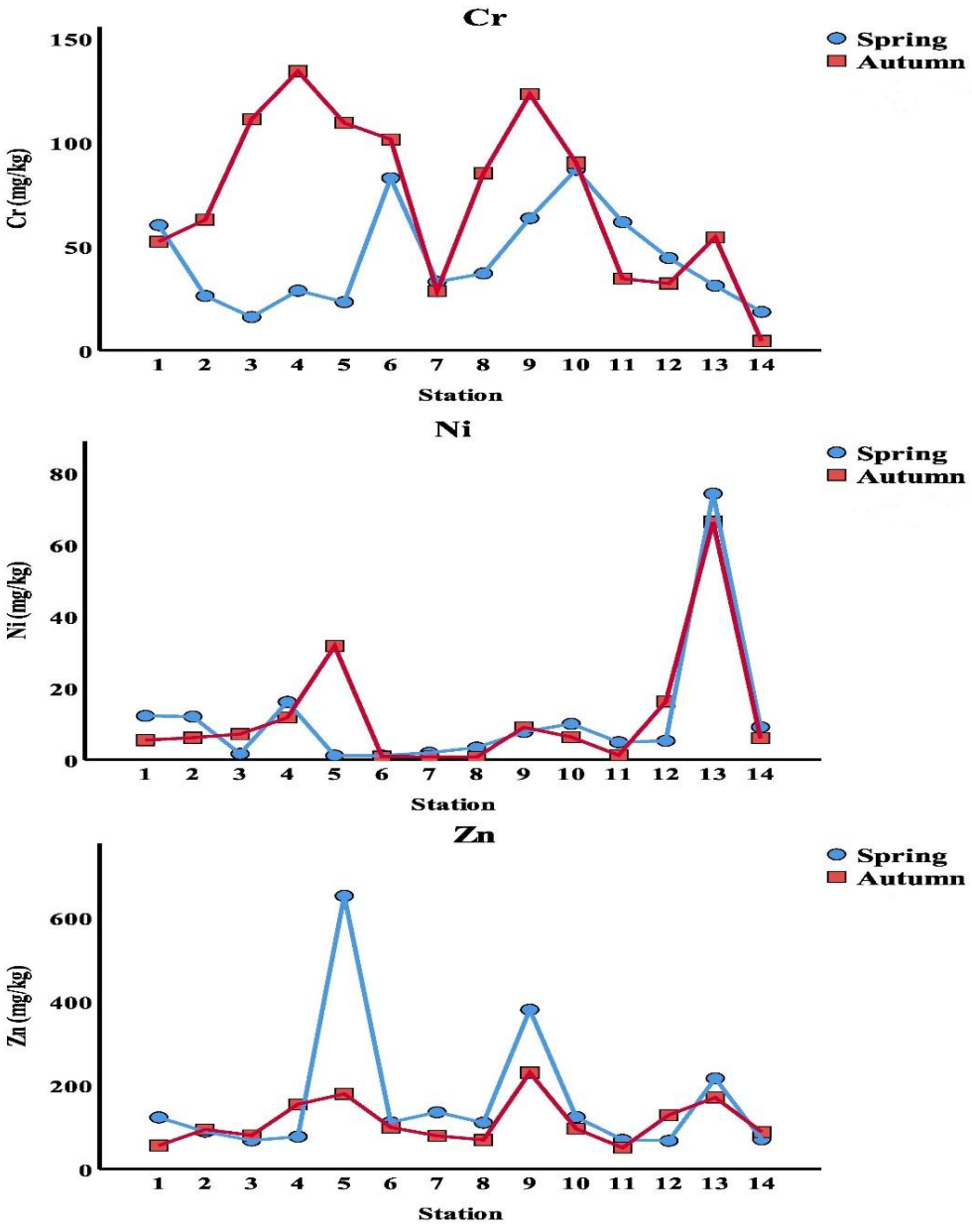

Fig. 5 Spatial and seasonal distribution of Cr, Ni and Zn (mg/kg dry weight) within the study area of the Red Sea coastline.

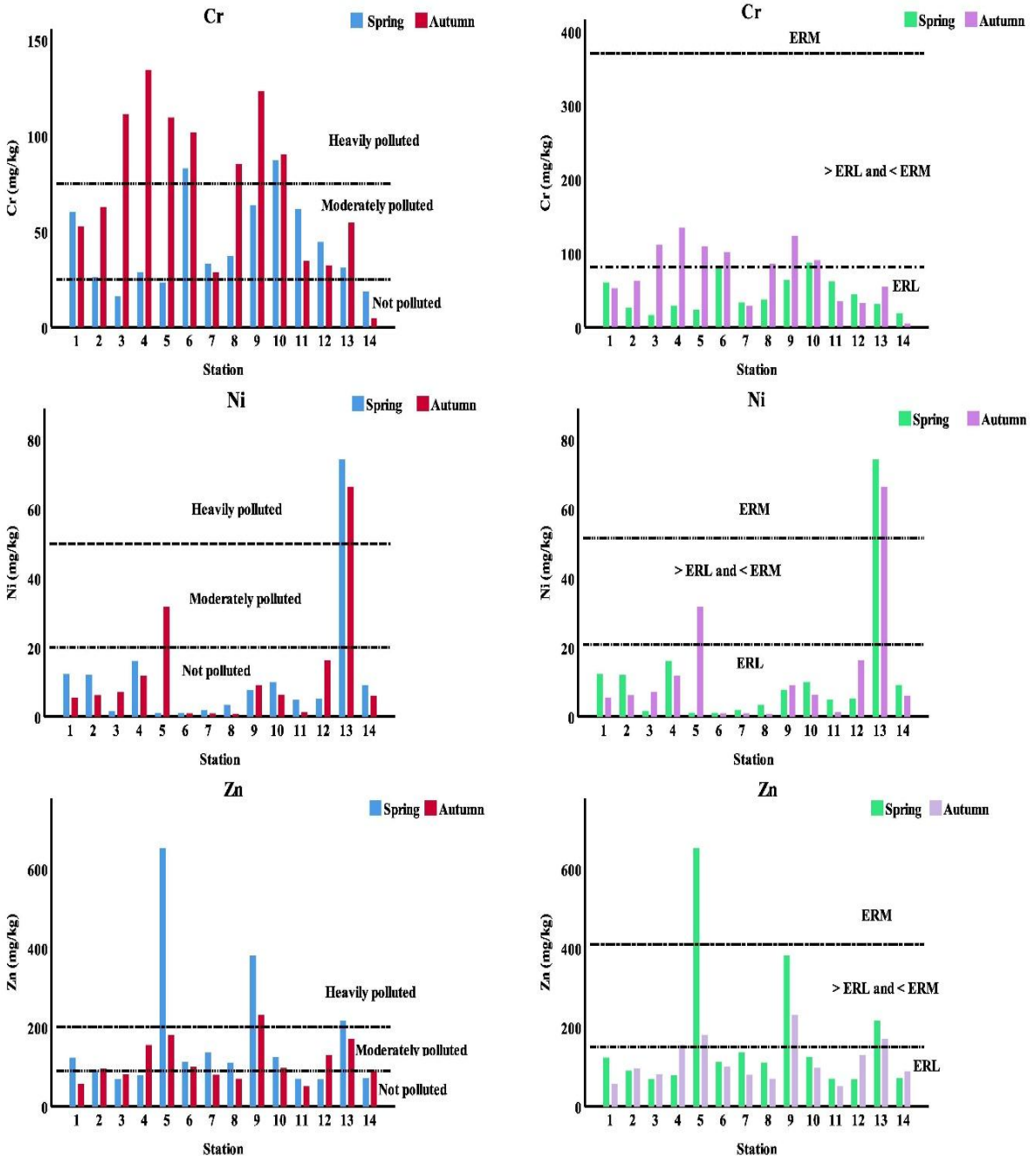

Fig. 6 Concentrations of (Cr, Ni, and Zn) in sediments along the Egyptian Red Sea coast are comparable to USEPA and US NOAA guidelines.

3.5. Assessment of sediment contamination

3.5.1. Contamination Factor *(CF)*

The C_f index is used to show the contamination degree with a single metal **(Hakanson, 1980)**. Individual C_f is a useful method for estimating pollution levels over time and determining the pollution status of individual substances (**Loska *et al.*, 1997)**. It is calculated using the following ratio:

$$\mathbf{C_f} = \frac{C_i}{C_b}$$

Where C_f is contamination factor, C_i is the concentration of metal of interest at a site and C_b is the concentration of the same metal at a background or reference site. the concentration of elements in the average shale background concentrations of global sediments **(Turekian and Wedepohl, 1961)** was chosen as the background levels of sedimentary metal in the present study. According to **Hakanson (1980)** values of the contamination factor (C_f) are classified into four groups as follows: $C_f < 1$ low contamination factor; $1 \leq C_f < 3$ moderate contamination factors; $3 \leq C_f < 6$ considerable contamination factors; $C_f \geq 6$ very high contamination factor.

The calculated values of C_f are shown in (Table 4 & Fig. 7) in the form of a Box Whiskers plot; the contamination factor values are low (Cf <1) for Ni in both seasons and Cr in the spring season at all sampling sites. While the contamination factor falls between low and moderate ($1 \leq C_f < 3$) for Zn in both seasons and Cr in the spring season.

The highest value of contamination factor was observed for Ni at station 13 in both seasons, and for Zn at stations 5 and 9 in the spring season. The calculated mean values of C_f of heavy metals in the study area was found to fall into the following sequence: Zn (1.73) > Cr (0.49) > Ni (0.17) in the spring season whilst in the autumn season the mean values of C_f are ordered as follows: Zn (1.19) > Cr (0.81) > Ni (0.18).

3.5.2. Enrichment factor (EF)

To evaluate the quantity of contaminants in the environment, the enrichment factors were determined by comparing the abundance of species in source material to that found in the Earth's crust **(Atgin *et al.*, 2000)**. Because the Fe distribution was not associated with other heavy elements, **(Deely and Fergusson, 1994)** suggested Fe as an acceptable normalising element factor. Because Fe has a very high natural content, it is unlikely to be significantly enriched in sediments from anthropogenic sources **(Niencheski *et al.*, 1994)**.

The EF is determined by the following equation by **Muller (1981)**:

$$EF = \frac{\left(C_{sample} / Fe_{sample}\right)}{\left(C_{reference} / Fe_{reference}\right)}$$

Where C_{sample} and $C_{reference}$ represents the concentration of the element in sediment sample and reference or background environment, respectively **(Turekian and Wedepohl, 1961)**. Fe_{sample} and $Fe_{reference}$ are the Fe concentration in the sampling site and Fe concentration in the reference environment. EF is classified into seven types as suggested by **Birch and Davies (2003)**. EF<1 indicates no enrichment, EF< 3 is minor enrichment, EF = 3-5 is moderate enrichment, EF = 5-10 is moderately severe enrichment, EF= 10-25 is severe enrichment, EF= 25-50 is very severe enrichment and EF>50 is extremely severe enrichment.

The computed metal EFs in the surface sediments of the Egyptian Red Sea coastal area represented in (Table 5) showed that the ranges (average) of EF for Ni, Cr, and Zn are 0.11–4.15, 0.95–12.18, and 6.03–44.06, respectively, with an order of Zn (14.23) > Cr(5.08) > Ni(1.28) in the spring season whilst, in the autumn season the ranges (average) of EF for Ni, Cr, and Zn are 0.12–4.85, 0.39–21.12, and 6.34–19.65, respectively, with an order of Zn (11.52) > Cr(8.90) > Ni(1.40).

Table (5) & Fig. (8) show that Ni reflects no (EF < 1), minor (EF < 3) and (3-5) moderate enrichment status represented in total sediment locations in both seasons by 50%, 36% and 14%, respectively. Zn shows moderately severe (5–10), severe (10–25) and very severe enrichment (25–50) in the spring season and moderately severe (5–10), severe (10–25) enrichment status in the autumn season represented in total sediment locations by (22%, 71 and 7%, respectively in the spring season) (50% and 50%, respectively in the autumn season). Cr shows no (EF < 1), minor (EF < 3), moderate (3-5), moderate-severe (5–10) and severe enrichment (10–25) in both seasons represented in total sediment locations by (7%, 21%, 29%, 36% and 7% respectively in the spring season) (7%, 14%, 7%, 22 and 50%, respectively in the autumn season).

Severe enrichment (EF= 21.86) and very severe enrichment (EF= 44.06) was obtained at a station (9; fishermen harbour) and station (5; Hurghada shipyard), respectively during the spring season, indicating strong anthropogenic input of Zn in these sites.

3.5.3. Pollution index (PI) and modified pollution index (MPI)

The average value of each element's contamination factor ($C_{f\ average}$) is used by PI. However, while calculating a weighted average, it also considers the maximum value of CF ($C_{f\ max}$). The quantification of sediment quality is identified by PI using a weighted average. **(Nemerow, 1991)** used the equation below to calculate it.

$$\mathbf{PI} = \sqrt{\frac{\left(C_{f\,average}\right)^2 + \left(C_{f\,max}\right)^2}{2}}$$

where $C_{f\ average}$ and $C_{f\ max}$ represent the average of contamination factors and maximum contamination factor, respectively.

Brady *et al.* (2015) recently proposed a modified pollution index (MPI), which is an improvement on the pollution index that calculates enrichment factors rather than contamination factors. This takes into account background concentrations as well as sediments' complex, non-conservative behavior. Another benefit is that the sediment qualification level has been changed to provide a more precise sediment contamination qualifying. Unlike the low trigger value of 3 used for PI, this is unlikely to overestimate sediment contamination. it was calculated by the equation:

$$MPI = \sqrt{\frac{(EF_{average})^2 + (EF_{max})^2}{2}}$$

where $EF_{average}$ and EF_{max} represent average of enrichment factors and maximum enrichment factor, respectively. The threshold values of sediment classification for PI and MPI are: PI <0.7 and MPI <1 represent unpolluted, 0.7 < PI < 1 and 1 < MPI < 2 indicate slightly polluted, 1 < PI < 2 and 2 < MPI < 3 represent moderately polluted, 3 < MPI < 5 represents moderately heavily polluted, 2 < PI < 3 and 5 < MPI < 10 indicate heavily polluted, and PI >3 and 10< MPI represent severely polluted sediment.

In this study, both pollution index (PI) and modified pollution index (MPI) (Tables 4&5 and Figs. 9&10) showed that red sea coast sediment is polluted. For PI, stations (5 and 9 in the spring season were severely polluted with the remaining sites being moderately polluted in (stations 1,7, and 10 in the spring season, stations 3,4, 5, 9, 12 and 14 in the autumn season and station 13 in both seasons) or slightly polluted in (station 4 in the spring season, station 10 in the autumn season and stations 2,6 and 8 in both seasons) or unpolluted in (stations 3, 11, 12 and 14 in the spring season and stations 1, 7 and 11 in autumn season). Similarly, MPI revealed that (stations 1, 10 and 11 in the spring season and stations 3, 4, 5, 6 and 9 in both seasons) were severely polluted. In addition, MPI discriminates between moderately-heavily polluted at (station 14 in the spring season) and, heavily polluted at (stations 1, 10 and 14 in the autumn season and stations 2,7,8, 12 and 13 in both seasons).

Table 4 contamination factors (Cf) and pollution Load Index (PLI) and Pollution index (PI) along the area of investigation in the spring &autumn season.

Station	Cf Ni		Cf Cr		Cf Zn		PI	
	Spring	Autumn	Spring	Autumn	Spring	Autumn	Spring	Autumn
1	0.18	0.08	0.67	0.58	1.30	0.59	1.05	0.51
2	0.18	0.09	0.29	0.70	0.94	1.00	0.74	0.82
3	0.02	0.11	0.18	1.23	0.72	0.84	0.55	1.01
4	0.24	0.17	0.32	1.49	0.81	1.63	0.74	1.39
5	0.02	0.47	0.26	1.21	6.86	1.89	5.14	1.58
6	0.02	0.01	0.92	1.13	1.17	1.05	0.97	0.95
7	0.03	0.01	0.37	0.32	1.43	0.83	1.10	0.65
8	0.05	0.01	0.41	0.95	1.16	0.73	0.91	0.78
9	0.11	0.13	0.71	1.37	4.00	2.42	3.05	1.95
10	0.15	0.09	0.97	1.00	1.31	1.01	1.09	0.87
11	0.07	0.02	0.69	0.38	0.74	0.53	0.63	0.44
12	0.08	0.24	0.49	0.36	0.71	1.36	0.59	1.06
13	1.09	0.98	0.35	0.60	2.28	1.80	1.83	1.50
14	0.13	0.09	0.21	0.05	0.75	0.93	0.59	0.71
Min	0.02	0.01	0.18	0.05	0.71	0.53	0.55	0.44
Max	1.09	0.98	0.97	1.49	6.86	2.42	5.14	1.95
Mean	0.17	0.18	0.49	0.81	1.73	1.19	1.35	1.02

Table 5 Enrichment factor (EF) and modified pollution index (MPI) in the surface sediments of the Egyptian Red Sea coastal area in the spring & autumn season.

Station	EF Ni		EF Cr		EF Zn		MPI	
	Spring	Autumn	Spring	Autumn	Spring	Autumn	Spring	Autumn
1	1.86	1.45	6.93	10.52	13.44	10.69	10.85	9.26
2	2.15	0.77	3.53	5.96	11.43	8.51	9.03	7.01
3	0.45	1.80	3.32	21.12	13.38	14.44	10.29	17.33
4	4.15	1.86	5.59	16.03	14.25	17.48	11.55	14.91
5	0.11	4.85	1.65	12.65	44.06	19.65	32.97	16.42
6	0.17	0.16	9.52	13.52	12.12	12.57	10.00	11.39
7	0.23	0.12	2.96	3.04	11.55	8.04	8.87	6.26
8	0.46	0.12	3.81	10.98	10.80	8.50	8.42	9.04
9	0.62	1.05	3.85	10.82	21.86	19.15	16.65	15.39
10	1.50	0.58	9.81	6.28	13.29	6.34	11.04	5.46
11	1.28	0.40	12.18	8.29	13.07	11.57	11.16	9.47
12	0.84	1.63	5.33	2.45	7.68	9.30	6.33	7.29
13	3.01	4.18	0.95	2.59	6.27	7.69	5.04	6.42
14	1.08	0.69	1.66	0.39	6.03	7.32	4.74	5.54
Min	0.11	0.12	0.95	0.39	6.03	6.34	4.74	5.46
Max	4.15	4.85	12.18	21.12	44.06	19.65	32.97	17.33
Mean	1.28	1.40	5.08	8.90	14.23	11.52	11.21	10.09

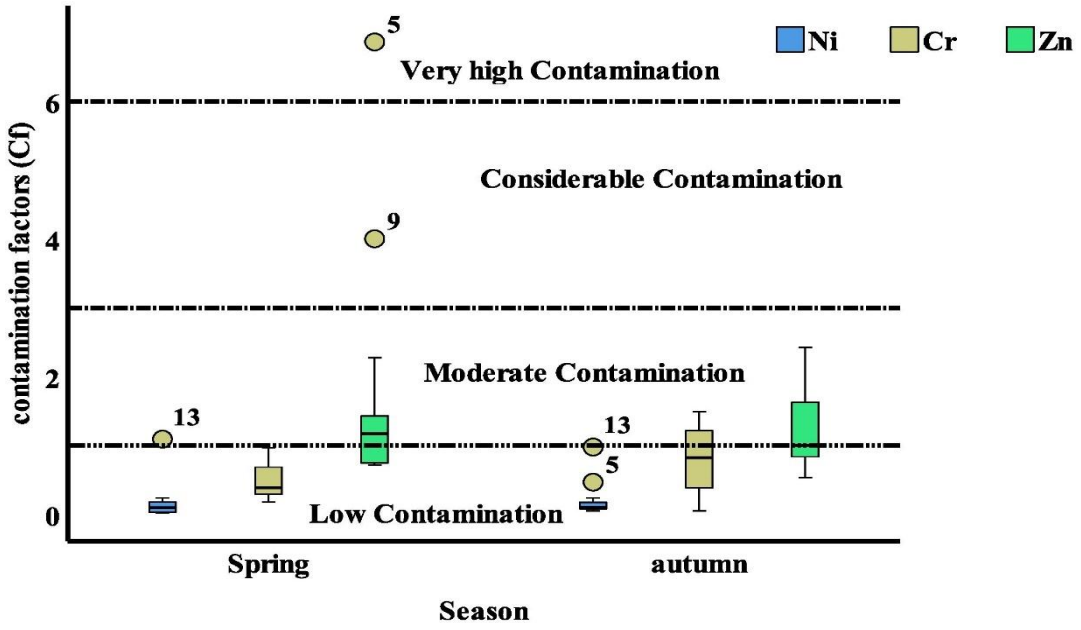

Fig. 7 Contamination Factor of Individual elements (Ni, Cr, and Zn) in sediment samples in the spring & autumn season.

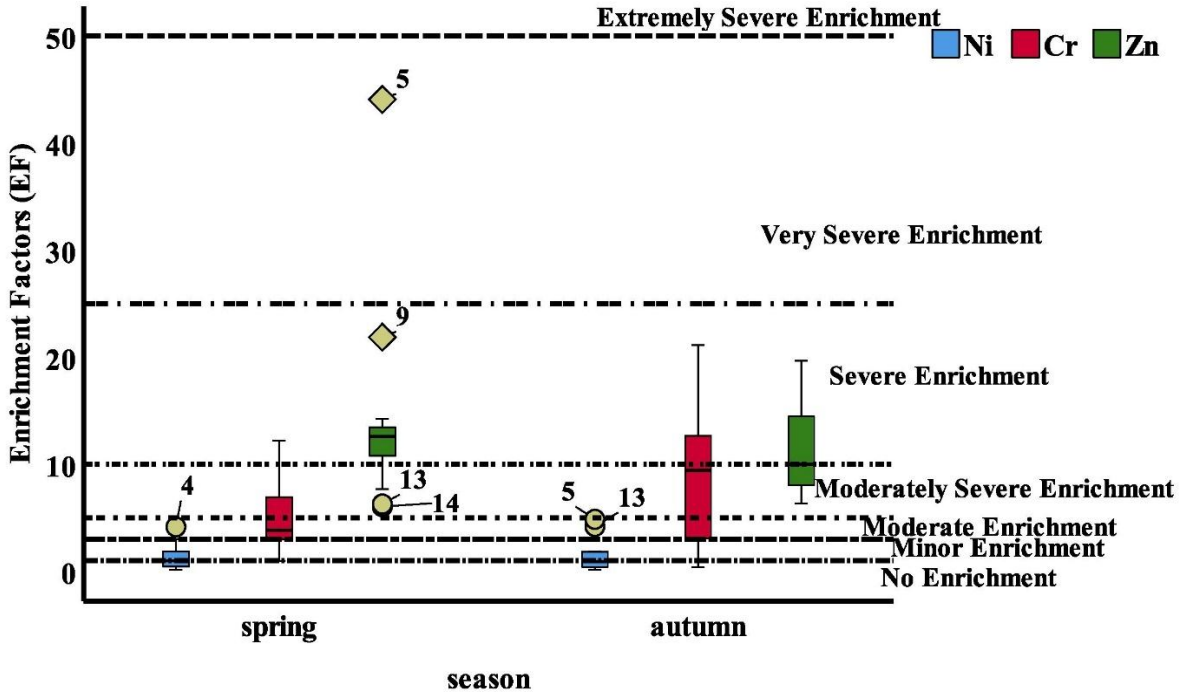

Fig. 8 The metal Enrichment factors (EF) of heavy metals (Ni, Cr, and Zn) in the surface sediments of the study area in the spring & autumn season

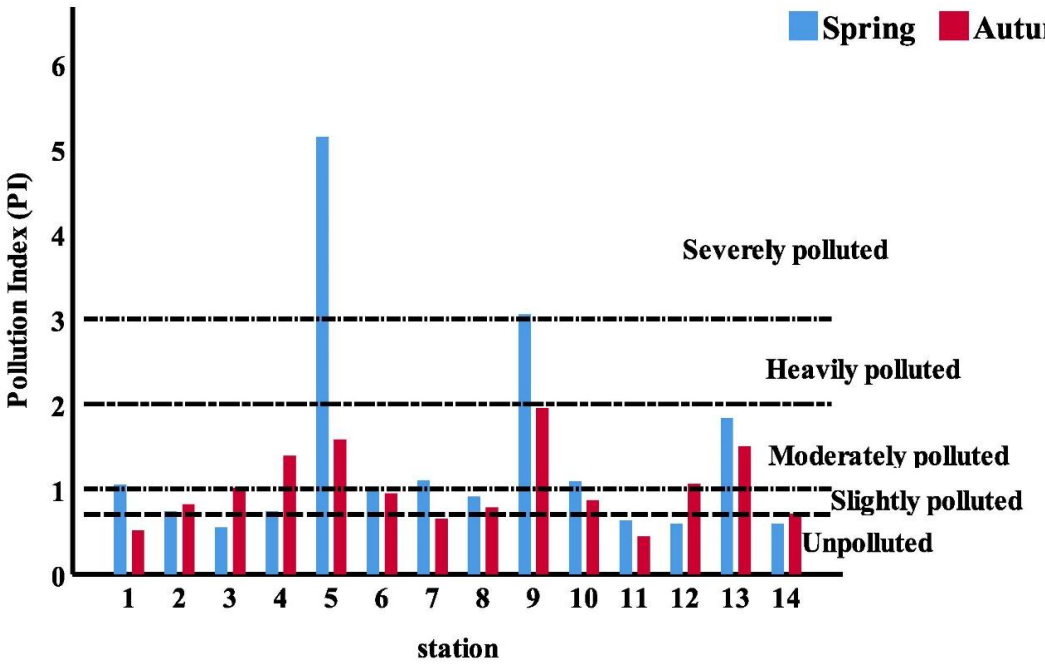

Fig. 9 pollution index (PI) of Ni, Cr and Zn for sediments of the study area in the spring& autumn season.

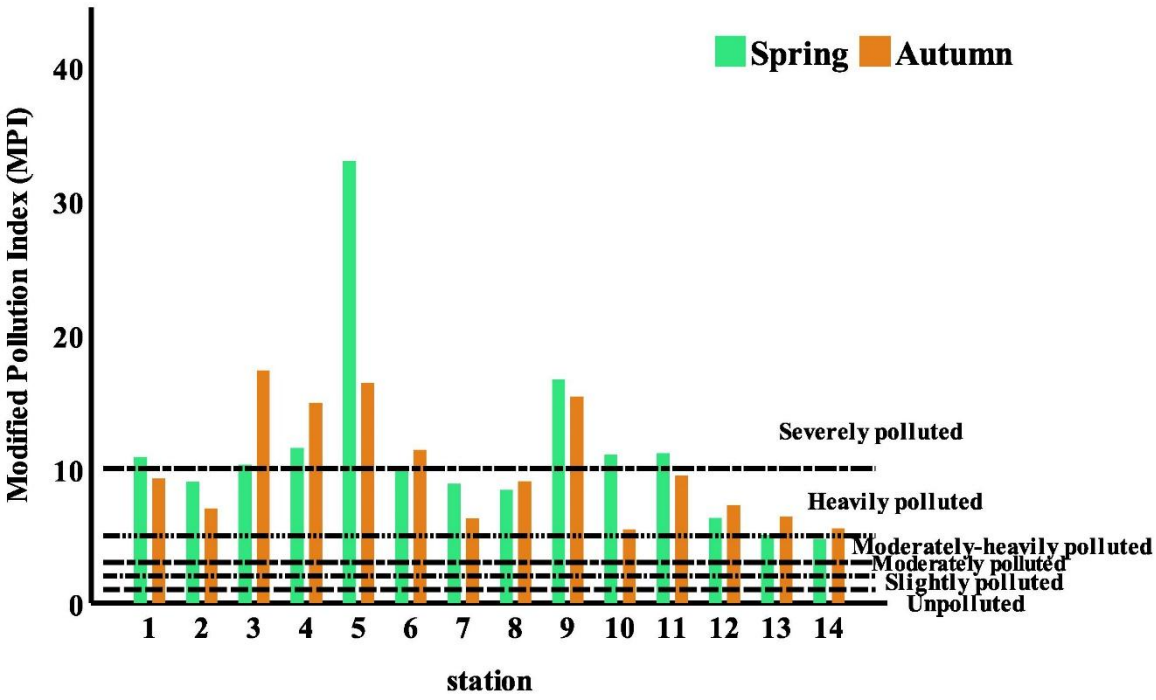

Fig. 10 Modified pollution index (MPI) of Ni, Cr and Zn for sediments of the study area in spring& autumn season

CONCLUSION

The ecological risks of Zn, Ni, and Cr in fourteen surface sediment samples collected from the Egyptian Red Sea coast during spring and autumn 2015 were evaluated using different analyses methods. However, the enrichment factor (EF), contamination factor (CF), pollution index (PI) and modified pollution index (MPI)were the methods used. The determined heavy metals had the order of Zn> Cr> Ni in both seasons. The statistical analyses showed some relations among Zn and Ni in the autumn season and Zn with TOM in both seasons reflecting their similar pollution effects and distribution of Zn were controlled by the organic matter content. USEPA, National Oceanographic and Atmospheric Administration (NOAA) guidelines and background were used to estimate the quality of the collected sediment samples. Interestingly, the average Ni and Cr concentrations were lower than the minimum and maximum permissible contents for sediment quality guidelines. whilst the average values of Zn is higher than the minimum permissible contents for (SQG) in both seasons. Application of NOAA SQGs revealed that Cr, Ni and Zn had adverse effects on the benthic organisms at certain sites.

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