

## **Seasonal Variation of Metallic Contamination of Water and Sediments in Navigation Canal and Industrial Zone South Port Said, Egypt**

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### **Authors' contributions**

*This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.*

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### **ABSTRACT**

In the present study, water and sediment samples were collected from Navigation Canal and from Industrial Zone South Port Said to assess heavy metals contamination. It was shown that, the highest mean concentration of heavy metals in water samples was observed in summer, and the lowest mean was observed in winter. It has been made evident that the industrialization in Industrial Zone South Port Said was responsible for the present deteriorating conditions. However, it was shown that, the highest mean concentration of heavy metals in sediment samples was observed in winter, and the lowest mean was observed in summer. Pollution status was evaluated using some indices: geo-accumulation index (Igeo), contamination factor (CF), pollution load index (PLI) and ecological risk index (RI). Based on Igeo, all metal values were unpolluted. On the basis of the

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values of CF, sediments are high in winter and low in summer. Metals concentrations were in the following order: Ni > Fe > Mn > Pb > Cu > Zn > Co > Cd. According to CF classification, Ni contamination was considerable. RI of winter season can be classified as moderate pollution. No pollution was classified for PLI in all seasons. The decrease in PLI and RI values were indicated dilution and dispersion of metal content with increasing distance from source areas. It is suggested that PLI can give an indication about the trend spatially and temporarily. In addition, it also provides significant data and advice to the policy and decision makers on the contamination degree of the area.

**Keywords:** Heavy metals; pollution; industrial activities; sediment quality.

## 1. INTRODUCTION

Heavy metals in aquatic environment have received extensive attention because they are toxic, non-biodegradable in the environment and easy to accumulate and magnify in organisms [1]. Concentrations of heavy metals in aquatic ecosystems have increased considerably due to the inputs of industrial waste, sewage runoff and agriculture discharges [1]. The most anthropogenic sources of metals are industrial, petroleum contamination and sewage disposal [2]. Increased industrial activities have led to pollution stress on surface water both from industrial, agricultural and domestic sources [3]. Heavy metals contamination in sediments is a critical factor for evaluating potential environment effects because of the associated bio-toxicity, high environmental stability and high occurrence of bioaccumulation in the food chain. Studies have shown that heavy metal toxicity and accumulations do not only depend on metal concentrations but also on other factors [4]. Some heavy metals, such as Pb and Cd, are toxic to biota even at very low concentrations, the toxic heavy metals, which affect the ecosystem, may lead to bioaccumulation and bio-magnification. Some others, such as zinc and copper, are biologically major constituents of aquatic ecosystems [5]. Pollution of the lake environment by heavy metals has received considerable attention by the scientific community because of their resistance to decomposition, toxicity and ecological effects to living organisms. Although heavy metals are naturally occurring through geochemical weathering processes of rocks, they may also be added by anthropogenic inputs [6]. Heavy metals may affect organisms directly by accumulating in the body or indirectly by transferring to the next trophic level of the food chain. Being non-biodegradable like many organic pollutants, they can be concentrated along the food chain,

producing their toxic effects at area often far away from the source of pollution [7]. Manzala Lake is connected with the Mediterranean Sea by outlet of a small Navigating Canal namely Al-Qabouti area. This outlet allows an exchange of water between the Lake and the Mediterranean Sea. This makes the Northern portion of Lake to be characterized by high salinity [8]. El- Moselhy and Gabal [9] found that the highest values of metals were observed at stations influenced by various pollution sources such as harbours sewage and industrial drains. The present study aims to evaluate heavy metals contaminations in water and sediments of Navigation Canal and industrial zone of South Port Said.

## 2. MATERIALS AND METHODS

### 2.1 Study Area

Selected sites (1, 2 and 3) inside the Industrial Zone of South Port Said and the sites (4, 5 and 6) of Navigation Canal (connection to the Mediterranean and Manzala Lake) at EL-Qabouti area; located between 31°12' to 31°14' N and 32°16' to 32°17' E. The **site 1** (Lift station 1), **site 2** (The well are 100 meters away from Lift station 1), **site 3** (station raise 2) to withdraw all the waste. the **site 4** (down of main pipe collected with water body), the **site 5** at 500m from the main pipe towards the east of the Suez Canal and so, the **site 6** at 500m after the main pipe towards the west of Manzala Lake. Water and sediment samples were illustrated in Table 1 and Fig. 1.

### 2.2 Sample Collection

Water and bed sediments samples were collected for a year during 2017. Water samples were collected in 125 ml sterile glass bottles from 20 cm below the water surface to avoid floating

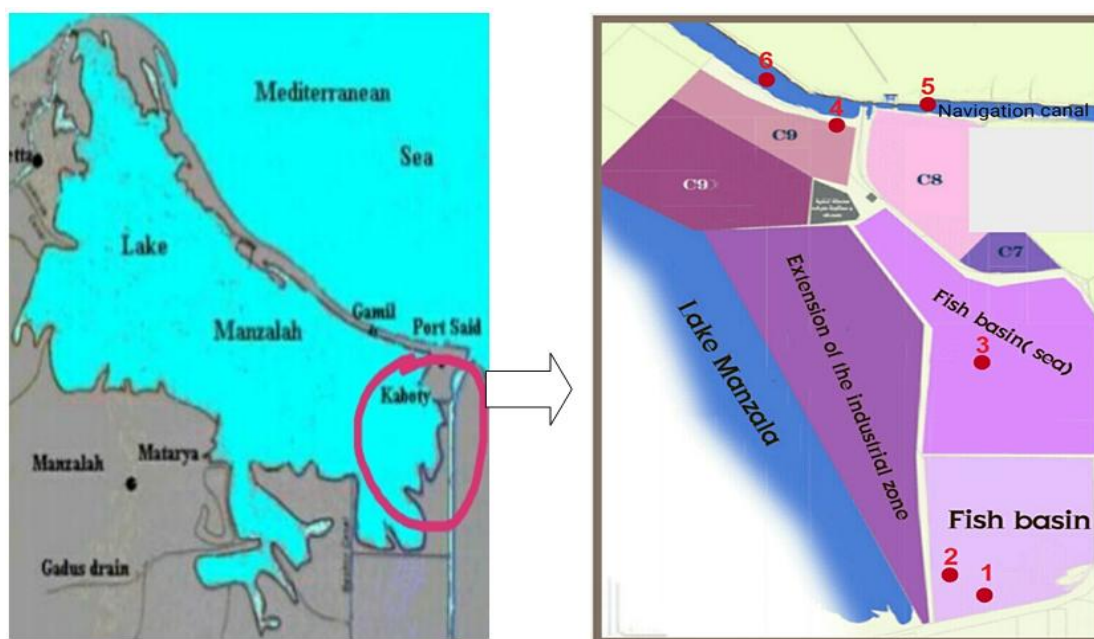


Fig. 1. Map shows the study area locations

material. Bed sediment samples were air dried and sieved through a 0.2 mm sieve. The fine earth was then used for the analysis. Particles larger than 0.2 mm mesh size were discarded.

Table 1. Water and sediment samples locations of the study area

Station	Co ordinates
1	31°12' 13.89" 32°17' 62.85"
2	31°14' 45.06" 32°16' 57.97"
3	31°13' 29.42" 32°17' 30.11"
4	31°17' 25" 32°9' 51.65"
5	31°13' 57.53" 32°17' 43.3"
6	31°14' 8.35" 32°16' 55.85 "

## 2.3 Sample Analysis

Eight heavy metals (Fe, Cu, Mn, Cd, Ni, Zn, Co and Pb) were analyzed in water and sediments. Water samples were being filtered using filtration system through 0.45  $\mu\text{m}$ -pore-diameter filter paper then analyzed for trace elements using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Exactly 0.25 gm of bed sediment sample is placed in Teflon vessel with

5 ml  $\text{HNO}_3$  (65%), 2 ml  $\text{HF}$  (40%) and 2 ml  $\text{H}_2\text{O}_2$  (30%) to determine heavy metals concentrations of bed sediments using method as described in [10] using the Inductively Coupled Plasma-Emission Spectrometry (ICP-OES) with Ultra Sonic Nebulizer (USN).

## 2.4 Quality Assessment of Sediment Samples

Sediments are usually considered as the vital sink for heavy metals, which can be sensitive pointers for monitoring contaminations in aquatic environment [11]. To assess the contamination degree of heavy metals in the sediment samples, some indices were remodelled in this study. Classification of these indices is shown in Table 2.

### 2.4.1 Geoaccumulation Index ( $I_{\text{geo}}$ )

An index of geo-accumulation ( $I_{\text{geo}}$ ) was originally defined in order to determine and define metal contamination in sediments, by comparing current concentrations with pre-industrial levels.

$$I_{\text{geo}} = \text{Log}_2 (C_n/1.5B_n)$$

Where,  $C_n$  is the measured concentration of geochemical background value in average shale heavy metals in sediments,  $B_n$  is the

**Table 2. Classification of ecological indices**

Type	Range	Level	Type	Range	Level
<b>Igeo</b>	<b>Igeo</b> ≤ 0	Unpolluted	<b>RI</b>	<b>RI</b> ≤ 150	Low
	0 < <b>Igeo</b> ≤ 1	Unpolluted to moderately polluted		150 < <b>RI</b> ≤ 300	Moderate
	4 < <b>Igeo</b> ≤ 5	Heavily to extremely polluted		300 < <b>RI</b> ≤ 600	High
	<b>Igeo</b> > 5	Extremely polluted		<b>RI</b> > 600	Serious
<b>CF</b>	<b>CF</b> < 1	Low contamination factor			
	1 ≤ <b>CF</b> < 3	Moderate contamination factors			
	3 ≤ <b>CF</b> < 6	Considerable contamination factors			
	<b>CF</b> ≥ 6	Very high contamination factor			
<b>PLI</b>	<b>PLI</b> > 1	Polluted			
	<b>PLI</b> < 1	No pollution			

of element ( $n$ ) and 1.5 is the background matrix correction due to erogenous effects ie Factor 1.5 is used because of possible variations in background values for a given metal in the environment as well as very small anthropogenic influences.

#### 2.4.2 Contamination factor (CF)

The level of contamination can be expressed by the contamination factor (**CF**); [12]. **CF** is the ratio obtained by dividing the concentration of each metal in the sediment by the baseline or background value. The background value corresponding to the baseline concentrations reported by Turekian and Wedepohl [13] and is based on element abundances in sedimentary rocks (shale).

#### 2.4.3 Pollution load index (PLI)

The **PLI** proposed by Tomilson et al. [12] provide some understanding to the public of the area about the quantity of a component in the environment. The **PLI** of a single site is the root of number of metals ( $n$ ) of multiplied together by contamination factor (**CF**) values.

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n}$$

Where,  $n$  is the number of metals (eight in the present study) and **CF** is the contamination factor.

#### 2.4.4 Potential ecological risk index (RI)

Sediment contamination degree caused by heavy metals, potential ecological risk index (**RI**), which was developed based on sedimentary theory, was introduced to assess the ecological risk degree of heavy metals in the present

sediments. Potential ecological risk index was originally proposed by Hökanson [14] and had been widely used in sediment heavy metal pollution assessment. The value of **RI** can be calculated by the following formulas:

$$C_f^i = \frac{C_R^i}{C_B^i},$$

$$E_r^i = T_r^i \times C_f^i,$$

$$RI = \sum_{i=1}^m E_r^i,$$

$T_r$  is the toxic-response factor for a given heavy metal,  $C_f$  is the contamination factor.

### 2.5 Statistical Analysis

One-way ANOVA and Duncan multiple range test were used to evaluate the significant difference in the concentration of different study sites. A probability at level of 0.05 or less was considered significant [15].

## 3. RESULTS AND DISCUSSION

### 3.1 Heavy Metals in Water Samples

Heavy metals contamination is becoming a serious threat and great problem to both the naturally stressed marine ecosystems and humans that rely on marine resources for food, industry and recreation. Heavy metals are introduced to coastal and marine environments through a variety of sources and activities including sewage and industrial effluents, brine discharges, coastal modifications and oil pollution. Table 3 shows concentration of heavy

metals in water samples. The present study was classified into two sectors (Industrial Zone and Navigation Canal). Industrial Zone includes (1, 2 and 3 sites). Mean concentrations of iron (mg/l) in sites (1, 2 and 3). In site (1) were 3.753, 5.088, 11.64 and 7.224; for (2) were 3.582, 4.776, 11.45 and 6.898 and for (3) 4.518, 6.790, 9.24 and 8.678 mg/l in winter, spring, summer, and autumn, respectively. On the other hand, Navigation Canal (sites 4, 5 and 6 sites) the mean concentrations of iron in site (4) were 4.410, 5.161, 10.84 and 7.36; for (5) were 1.479, 2.321, 4.108 and 2.892 and for (6) were 2.424, 3.819, 6.786 and 5.881 mg/l during winter, spring, summer and autumn respectively. The highest mean concentration was in summer, on the other hand the lowest mean was observed in winter. Mean concentrations of lead in sites (1, 2 and 3). In site (1) were 0.066, 0.122, 0.153 and 0.138 ; for (2) were 0.064, 0.119, 0.146 and 0.136 and for (3) 0.03 , 0.077, 0.163 and 0.124 mg/l in winter, spring, summer, and autumn, respectively. The highest mean concentration in summer and the lowest mean was observed in winter. On the other hand, Navigation Canal include (4, 5 and 6 sites). Mean concentrations of lead in site (4) were 0.052, 0.106, 0.133 and 0.128; for (5) were 0.008, 0.033, 0.084 and 0.065. For site (6) were 0.013, 0.071, 0.096 and 0.083 mg/l during winter, spring, summer and autumn respectively. It was showed that, the highest mean concentration in summer, on the other hand the lowest mean was observed in winter. Mean concentrations of cadmium in sites (1, 2 and 3). In site (1) were ND, 0.005, 0.016 and 0.009.; for (2) were 0.001, 0.008, 0.019 and 0.012. For site (3) were 0.04, 0.049, 0.077 and 0.056 mg/l in winter, spring, summer, and autumn, respectively. It was showed that, the highest mean concentration in summer, on the other hand the lowest mean was observed in winter. On the other hand, navigation canal includes (4, 5 and 6 sites). Mean concentrations of lead in site (4) were 0.028, 0.031, 0.043 and 0.037; for (5) were 0.008, 0.012, 0.021 and 0.015. For site (6) were 0.013, 0.019, 0.025 and 0.022 mg/l during winter, spring, summer and autumn respectively. It was showed that, the highest mean concentration in summer, on the other hand the lowest mean was observed in winter. Mean concentrations of Manganese in sites (1, 2 and 3). In site (1) were 0.417, 0.511, 0.895 and 0.602; for (2) were 0.398, 0.472, 0.881 and 0.587, while (3) 0.502, 0.618, 0.79 and 0.658 mg/l in winter, spring, summer, and autumn, respectively. It was showed that, the highest mean concentration in summer, on the

other hand the lowest mean was observed in winter. On the other hand, Navigation Canal includes (4, 5 and 6 sites). Mean concentrations of lead in site (4) were 0.49, 0.516, .911 and 0.715; for (5) were 0.161, 0.21, 0.316 and 0.241 and for (6) were 0.303, 0.347, 0.522, and 0.46 mg/l during winter, spring, summer and autumn respectively. It was showed that, the highest mean concentration in summer, on the other hand the lowest mean was observed in winter. Mean concentrations of copper in sites (1, 2 and 3). In site (1) were 0.033, 0.037, 0.068 and 0.045 for (2) were 0.04, 0.042 and 0.071 and 0.051 for (3) were 0.072, 0.118, 0.167 and 0.136 mg/l in winter, spring, summer, and autumn, respectively. It was showed that, the highest mean concentration in summer, on the other hand the lowest mean was observed in winter. On the other hand, Navigation Canal include (4, 5 and 6 sites). Mean concentrations of lead in site (4) were 0.038, 0.0063, 0.089 and 0.069; for (5) were 0.011, 0.017, 0.026 and 0.019 and for (6) 0.028, 0.036, 0.05 and 0.04 mg/l during winter, spring, summer and autumn respectively. It was showed that, the highest mean concentration in summer, on the other hand the lowest mean was observed in winter. Mean concentrations of Zn in sites (1, 2 and 3). In site (1) were 1.219, 1.114, 3.15 and 2.18; for (2) were 1.185, 0.988, 2.7 and 1.44 and for (3) 1.13, 3.312, 5.11 and 3.577 mg/l in winter, spring, summer, and autumn, respectively. On the other hand, Navigation Canal include (4, 5 and 6 sites). Mean concentrations of Zn in site (4) were 1.164, 2.46, 3.86 and 2.54; for (5) were 0.318, 0.519, 0.811 and 0.588 and for (6) were 0.622, 1.16, 1.56 and 0.718 mg/l during winter, spring, summer and autumn respectively. It was showed that, the highest mean concentration in summer, on the other hand the lowest mean was observed in winter. Mean concentrations of nickel in sites (1 and 2), the values of nickel were  $dl < 0$  in winter, spring, summer and autumn. But It is worth to mention that, nickel values at site (3) were 0.004, 0.007, 0.012 and 0.009 mg/l in winter, spring, summer, and autumn, respectively. While the nickel concentration was in the sites 4, 5 and (6) were collected from Navigation Canal were  $dl < 0$  during winter, spring, summer and autumn. It was showed that, the highest mean concentration at site (3) in summer, on the other hand the lowest mean was observed in winter. Mean concentrations of cobalt in site 1 were  $dl < 0$  in winter and spring, but the mean concentrations were recorded 0.008 and 0.003 mg/l in summer and autumn, respectively. The mean concentrations of cobalt

in site (2) were the highest mean value of cobalt were  $dl < 0$  in the winter and spring, but the mean concentrations were recorded 0.014 and 0.006 in the summer and autumn, respectively. It is worth to mention that, the mean concentrations of cobalt in site (3) were 0.02, 0.027, 0.038 and 0.032 mg/l in winter, spring, summer, and autumn, respectively. Also results revealed that, the mean concentrations of cobalt in site (4) were recorded during winter, spring, summer and autumn; being 0.008, 0.01, 0.017 and 0.013 mg/l respectively. On the other hand mean concentration of cobalt in site (5) were recorded 0.001, 0.001, 0.003 and 0.002 mg/l during winter, spring, summer and autumn respectively. While the results showed that, the mean concentrations of cobalt in site (6) were 0.002, 0.003, 0.005 and 0.003 mg/l during winter, spring, summer and autumn respectively. It was showed that, the highest mean concentration in the summer, on the other hand the lowest mean was observed in the winter. Finally, the result showed that lead values at sites 1, 2 and 3 are over the permissible limits of [16] (0.1 mg/l except the winter season). Also the results showed that lead values at sites 4, 5 and 6 are within the

permissible limits of [17] (0.1 mg/l). This means that the water in studied Navigation Canal is not polluted by Pb. Iron values at the industrial effluents in sites 1, 2 and (3) were out the permissible limits of [16] ( $< 1.0$  mg/l), this might be due to the sites which house many industries and include a large amount of iron concentrations. The values at sites 4, 5 and 6 were out the permissible limits [17] ( $< 1.0$  mg/l). The values at sites 4, 5 and 6 are within the permissible limits of [17] ( $< 1.0$  mg/l) of amendment [18]. Cd values at sites 4, 5 and 6 were exceeded the permissible limits of [17] the value  $< 0.003$  mg/l except at site (5). Copper values at sites 4, 5 and 6 were within the permissible limits of [17] (0.05 mg/l). It is worth to mention that nickel values at the industrial effluents at sites 1, 2 and (3) are within the permissible limits of [16] (0.1 mg/l). Generally, the values of zinc at sites 1, 2 and 3 were higher than the permissible limits of [16] (not detection limit) in the four seasons. Zinc values at site 4 were higher than the permissible limits of [17] (2.0 mg/l), while the values at site (5) within the permissible limits, but the values at site (6) were out the permissible limits except for winter.

**Table 3. Concentrations of heavy metals (mg/L) in water samples**

Season	Sample location	Cu	Zn	Ni	Mn	Co	Cd	Pb	Fe
<b>Winter</b>	site 1	0.033	1.219	ND	0.417	ND	ND	0.066	3.753
	site 2	0.04	1.185	ND	0.398	ND	0.001	0.064	3.582
	site 3	0.072	1.13	0.004	0.502	0.02	0.04	0.03	4.518
	site 4	0.038	1.164	ND	0.49	0.008	0.028	0.052	4.41
	site 5	0.011	0.318	ND	0.161	0.001	0.008	0.008	1.479
	site 6	0.028	0.622	ND	0.303	0.002	0.013	0.013	2.424
<b>Spring</b>	site 1	0.037	1.114	ND	0.511	ND	0.005	0.122	5.088
	site 2	0.042	0.988	ND	0.472	ND	0.008	0.119	4.776
	site 3	0.118	3.312	0.007	0.618	0.027	0.049	0.077	6.798
	site 4	0.063	2.46	ND	0.516	0.01	0.031	0.106	5.16
	site 5	0.017	0.519	ND	0.21	0.001	0.012	0.033	2.321
	site 6	0.036	1.16	ND	0.347	0.003	0.019	0.071	3.819
<b>Summer</b>	site 1	0.068	3.15	ND	0.895	0.008	0.016	0.153	11.64
	site 2	0.071	2.7	ND	0.881	0.014	0.019	0.146	11.45
	site 3	0.167	5.11	0.007	0.79	0.038	0.077	0.163	9.29
	site 4	0.089	3.86	ND	0.911	0.017	0.043	0.133	10.84
	site 5	0.026	0.811	ND	0.316	0.003	0.021	0.084	4.108
	site 6	0.051	1.56	ND	0.522	0.005	0.025	0.096	6.786
<b>Autumn</b>	site 1	0.045	2.18	ND	0.602	0.003	0.009	0.138	7.224
	site 2	0.051	1.44	ND	0.587	0.006	0.012	0.136	6.898
	site 3	0.136	3.577	0.009	0.658	0.032	0.056	0.124	8.678
	site 4	0.069	2.54	ND	0.715	0.013	0.037	0.128	7.36

site 5	0.019	0.588	ND	0.241	0.002	0.015	0.065	2.892
site 6	0.04	0.718	ND	0.46	0.003	0.022	0.083	5.88

**Table 4. Concentrations of heavy metals (µg/g) in sediment samples and the toxicity guidelines: The effect range low (ERL) and effect range medium (ERM)**

Season	Sample location	Fe	Cu	Zn	Ni	Mn	Co	Cd	Pb
<b>Winter</b>	site 4	149170	42.16	139.7	18.91	710.7	7.1	2.91	49.17
	site 5	59430	11.58	65.39	3.87	176.2	1.2	0.61	9.43
	site 6	74680	21.36	71.49	4.21	388.4	1.36	0.83	14.68
<b>Spring</b>	site 4	142650	34.55	126.9	17	590.2	6.9	2.65	42.65
	site 5	48120	10.33	60.91	3.26	144.8	1.13	0.52	8.12
	site 6	61630	19.75	69.32	3.59	320.9	1.45	0.71	12.63
<b>Summer</b>	site 4	123110	29.69	102.4	12.6	381.6	3.4	1.4	24.11
	site 5	14260	8.51	48.38	2.61	95.14	0.73	0.32	4.26
	site 6	25960	16.93	53.91	3.13	170.5	0.91	0.42	8.96
<b>Autumn</b>	site 4	131420	31.79	111.5	14.6	427.7	4.2	1.54	31.42
	site 5	26190	9.12	51.93	2.82	121.8	0.81	0.36	6.19
	site 6	54230	17.35	59.88	3.25	218.4	1.01	0.47	10.43
	<b>ERL</b>	-	34	150	20.9	-	-	1.2	46.7
	<b>ERM</b>	-	270	410	51	-	-	9.6	218

**Table 5. Contamination factor (CF) of heavy metals in sediment**

Season	Sample location	Fe	Cu	Zn	Ni	Mn	Co	Cd	Pb
<b>Winter</b>	site 4	2.01	0.94	0.84	9.70	2.46	0.37	0.28	1.47
	site 5	0.80	0.26	0.21	2.03	0.47	0.06	0.06	0.69
	site 6	1.01	0.47	0.46	2.77	0.73	0.07	0.06	0.75
	<b>Mean</b>	1.27	0.56	0.50	4.83	1.22	0.17	0.13	0.97
<b>Spring</b>	site 4	1.92	0.77	0.69	8.83	2.13	0.36	0.25	1.34
	site 5	0.65	0.23	0.17	1.73	0.41	0.06	0.05	0.64
	site 6	0.83	0.44	0.38	2.37	0.63	0.08	0.05	0.73
	<b>Mean</b>	1.21	0.52	0.46	4.61	1.15	0.17	0.13	0.94
<b>Summer</b>	site 4	1.66	0.66	0.45	4.67	1.21	0.18	0.19	1.08
	site 5	0.19	0.19	0.11	1.07	0.21	0.04	0.04	0.51
	site 6	0.35	0.38	0.20	1.40	0.45	0.05	0.05	0.57
	<b>Mean</b>	1.08	0.49	0.41	4.00	1.01	0.15	0.12	0.88
<b>Autumn</b>	site 4	1.77	0.71	0.50	5.13	1.57	0.22	0.21	1.17
	site 5	0.35	0.20	0.14	1.20	0.31	0.04	0.04	0.55
	site 6	2.01	0.94	0.84	9.70	2.46	0.37	0.28	1.47
	<b>Mean</b>	1.14	0.52	0.42	4.27	1.09	0.16	0.13	0.92

**Table 6. Geoaccumulation index (I<sub>geo</sub>) of heavy metals in sediments samples**

Season	Sample location	Fe	Cu	Zn	Ni	Mn	Co	Cd	Pb
<b>Winter</b>	site 4	0.13	-0.2	-0.25	0.81	0.21	-0.6	-0.73	-0.01
	site 5	-0.52	-0.77	-0.86	0.13	-0.5	-1.38	-1.42	-0.34
	site 6	-0.17	-0.5	-0.52	0.27	-0.31	-1.32	-1.38	-0.3
	<b>Max</b>	0.13	-0.2	-0.25	0.81	0.21	-0.6	-0.73	-0.01
	<b>Min</b>	-0.52	-0.77	-0.86	0.13	-0.5	-1.38	-1.42	-0.34
<b>Spring</b>	site 4	0.11	-0.29	-0.33	0.77	0.15	-0.62	-0.78	-0.05
	site 5	-0.36	-0.82	-0.94	0.06	-0.57	-1.4	-1.5	-0.37
	site 6	-0.26	-0.53	-0.6	0.2	-0.38	-1.29	-1.45	-0.31
	<b>Max</b>	0.11	-0.29	-0.33	0.77	0.15	-0.62	-0.78	-0.05
	<b>Min</b>	-0.36	-0.82	-0.94	0.06	-0.57	-1.4	-1.5	-0.37
	site 4	0.04	-0.36	-0.52	0.49	-0.09	-0.92	-0.91	-0.014
	site 5	-0.89	-0.9	-1.13	-0.15	-0.85	-1.59	-1.59	-0.47

Season	Sample location	Fe	Cu	Zn	Ni	Mn	Co	Cd	Pb
Summer	site 6	-0.63	-0.6	-0.87	-0.03	-0.52	-1.5	-1.5	-0.42
	Max	0.04	-0.36	-0.52	0.49	-0.09	-0.92	-0.91	-0.014
	Min	-0.89	-0.9	-1.13	-0.15	-0.85	-1.59	-1.59	-0.47
Autumn	site 4	0.07	-0.33	-0.47	0.53	0.02	-0.83	-0.84	-0.11
	site 5	-0.63	-0.87	-1.02	-0.1	-0.69	-1.55	-1.56	-0.44
	site 6	-0.31	-0.59	-0.77	0.02	-0.46	-0.145	-1.5	-0.38
	Max	0.07	-0.33	-0.47	0.53	0.02	-0.145	-0.84	-0.11
	Min	-0.63	-0.87	-1.02	-0.1	-0.69	-1.55	-1.56	-0.44

Table 7. Ecological risk index (RI) and pollution load index (PLI) of sediment samples

Season	S. No	RI	PLI
Winter	site 4	311.24	1.24
	site 5	65.24	0.32
	site 6	89.71	0.44
	Mean	155.40	0.67
Spring	site 4	282.57	1.11
	site 5	55.71	0.27
	site 6	77.00	0.40
	Mean	148.12	0.64
Summer	site 4	151.15	0.75
	site 5	34.39	0.17
	site 6	46.59	0.26
	Mean	128.83	0.57
Autumn	site 4	167.57	0.85
	site 5	38.98	0.21
	site 6	52.04	0.31
	Mean	120.30	0.55

Table 8. One-Way ANOVA between mean concentrations of heavy metals

Season	Winter	Spring	Summer	Autumn	P-Value
Cu	0.037 <sup>a</sup>	0.052 <sup>a</sup>	0.079 <sup>a</sup>	0.060 <sup>a</sup>	0.308 <sup>ns</sup>
Zn	0.940 <sup>a</sup>	1.592 <sup>a</sup>	2.865 <sup>a</sup>	1.841 <sup>a</sup>	0.051 <sup>ns</sup>
Ni	0.004	0.007	0.007	0.009	--
Mn	0.379 <sup>b</sup>	0.446 <sup>ab</sup>	0.719 <sup>a</sup>	0.544 <sup>ab</sup>	0.019 <sup>*</sup>
Co	0.008 <sup>a</sup>	0.010 <sup>a</sup>	0.014 <sup>a</sup>	0.010 <sup>a</sup>	0.83 <sup>ns</sup>
Cd	0.018 <sup>a</sup>	0.021 <sup>a</sup>	0.034 <sup>a</sup>	0.025 <sup>a</sup>	0.542 <sup>ns</sup>
Pb	0.039 <sup>b</sup>	0.088 <sup>ab</sup>	0.129 <sup>a</sup>	0.112 <sup>a</sup>	0.0004 <sup>***</sup>
Fe	3.361 <sup>b</sup>	4.660 <sup>b</sup>	9.019 <sup>ab</sup>	6.489 <sup>a</sup>	0.0007 <sup>***</sup>

Values are significant at \* $P \leq 0.05$ , \*\* $P \leq 0.01$ , \*\*\* $P \leq 0.001$ .

### 3.2 Heavy Metals of Sediments in Navigation Canal

Table 4 shows concentration of heavy metals in sediment samples. Concentration of iron in bed sediment in the Navigation Canal include (4, 5 and 6 sites) were 149170, 142650, 123110 and 131420, for site (5) were 59430, 48120, 14260 and 26190 site (6) were 74680, 61630, 25960 and 54230  $\mu\text{g/g}$  during winter, spring, summer and autumn respectively. It was

showed that, the highest mean concentration in winter, on the other hand the lowest mean was observed in summer. Concentration of lead in bed sediment in the Navigation Canal include (4, 5 and 6 sites) were 49.17, 42.65, 24.11 and 31.42 for site (5) were 9.43, 8.12, 4.26 and 6.19 site (6) were 14.68, 12.63, 8.96 and 10.43  $\mu\text{g/g}$  during winter, spring, summer and autumn respectively. It was showed that, the highest mean concentration in winter, on the other hand the lowest mean was observed in



summer. Concentration of cadmium in bed sediment in the Navigation Canal include (4, 5 and 6 sites) were 2.91, 2.65, 1.4 and 1.54, for site (5) were 0.61, 0.52, 0.32 and 0.36 for site (6) were 0.83, 0.71, 0.42 and 0.47 µg/g during winter, spring, summer and autumn respectively. It was showed that, the highest mean concentration in winter, on the other hand the lowest mean was observed in summer. Concentration of manganese in bed sediment in the Navigation Canal includes (4, 5 and 6 sites) were 710.7, 590.2, 381.6 and 427.7, for site (5) 176.2, 144.8, 95.14 and 121.8, site (6) were 388.4, 320.9, 170.55 and 218.4 µg/g during winter, spring, summer and autumn respectively. It was showed that, the highest mean concentration in winter, on the other hand the lowest mean was observed in summer. Concentration of copper in bed sediment in the Navigation Canal include (4, 5 and 6 sites) were 42.16, 34.55, 29.69 and 31.79, for site (5) were 11.58, 10.33, 8.51 and 9.12 site (6) were 21.36, 19.75, 16.93 and 17.35 µg/g during winter, spring, summer and autumn respectively. It was showed that, the highest mean concentration in winter, on the other hand the lowest mean was observed in summer. Concentration of zinc in bed sediment in the navigation canal include (4, 5 and 6 sites) were 139.7, 126.7, 102.4 and 111.5, for site (5) were 65.39, 60.91, 48.38 and 51.93, for site (6) were 71.49, 69.49, 53.91 and 59.88 µg/g during winter, spring, summer and autumn respectively. It was showed that, the highest mean concentration in winter, on the other hand the lowest mean was observed in summer. Abd and Hegazy [19] reported that Zn levels ranged from 54.52 to 352.20 with a mean value of 129.23 µg/g for Burullus and 2.43 to 157.70 with a mean value of 23.94 µg/g for Manzala. Concentration of nickel in bed sediment in the Navigation Canal include (4, 5 and 6 sites) were 18.91, 17, 12.6 and 14.6, for site 5 were 3.87, 3.26, 2.61 and 2.82, site 6 were 4.21, 3.59, 3.13 and 3.25 µg/g during winter, spring, summer and autumn respectively. It was showed that, the highest mean concentration in winter, on the other hand the lowest mean was observed in summer. Concentration of cobalt in bed sediment in the Navigation Canal include (4, 5 and 6 sites) were 7.1, 6.9, 3.4 and 4.2, for site 5 were 1.2, 1.13, 0.73 and 0.81, site (6) were 1.36, 1.45, 0.91 and 1.01 µg/g during

winter, spring, summer and autumn respectively. It was showed that, the highest mean concentration in winter, on the other hand the lowest mean was observed in summer. Heavy metals contamination in sediment could affect the water quality and bioaccumulation of metals in aquatic organisms [20].

### 3.3 Quality Assessment of Sediment

#### 3.3.1 Geoaccumulation index

Igeo of Fe was: -0.17 to 0.13, -0.36 to 0.11, -0.89 to -0.9 and -0.63 to -0.87 in winter, spring, summer and autumn respectively. Cu values were: -0.77 to -0.2, -0.82 to -0.29, -0.9 to -0.36 and -0.87 to -0.33 in winter, spring, summer and autumn respectively. Zn values were: -0.17 to 0.13, -0.36 to 0.11, -0.89 to -0.9 and -0.63 to -0.87 in winter, spring, summer and autumn respectively. Ni values were: 0.13 to 0.81, 0.06 to 0.77, -0.15 to 0.49 and -0.1 to 0.53 in winter, spring, summer and autumn respectively. Mn values were: -0.5 to 0.21, -0.57 to 0.15, -0.85 to -0.09 and -0.69 to 0.02 in winter, spring, summer and autumn respectively. Cobalt values were: -1.36 to -0.6, -1.4 to -0.62, -1.59 to -0.92 and -1.55 to -0.145 in winter, spring, summer and autumn respectively. Nikle values were: 0.13 to 0.81, 0.06 to 0.77, -0.15 to 0.49 and -0.1 to 0.53 in winter, spring, summer and autumn respectively. Cd values were: -1.42 to -0.73, -1.5 to -0.78, -1.59 to -0.91 and -1.56 to -0.84 in winter, spring, summer and autumn respectively. Pb values were: -0.34 to -0.01, -0.37 to -0.05, -0.047 to -0.014 and -0.44 to -0.11 in winter, spring, summer and autumn respectively. The results for all metals based on Igeo values were unpolluted according to Table 5. [21] found that Igeo values in sediments of Damietta Nile Branch of Fe ranged from -2.20 to -1.15, Cu ranged from -1.42 to -0.006, Mn ranged from -1.11 to 0.664, Zn ranged from -1.36 to -0.735 and lead ranged from -2.35 to -0.674.

#### 3.3.2 Contamination factor

Result of the present study indicates that the CF values of all metals are ranged from 0.12 to 4.83. The mean values of the Cf are found: Fe: 1.27, 1.21, 1.08 and 1.14 in winter, spring, summer and autumn respectively. Cu: 0.56, 0.52, 0.49 and 0.52 in winter, spring, summer and autumn respectively. Zn: 0.50, 0.46, 0.41 and 0.42 in winter, spring, summer and autumn respectively. Ni: 4.83, 4.61, 4.0 and 4.27 in winter, spring,

summer and autumn respectively. Mn: 1.22, 1.15, 1.01 and 1.09 in winter, spring, summer and autumn respectively. Co: 0.17, 0.17, 0.15 and 0.16 in winter, spring, summer and autumn respectively. Cd: 0.13, 0.13, 0.12 and 0.13 in winter, spring, summer and autumn respectively. Pb: 0.97, 0.94, 0.88 and 0.92 in winter, spring, summer and autumn respectively. On the basis of the values of Cf, sediments are high in winter and low in summer. It was indicated that metals in the following order: Ni > Fe > Mn > Pb > Cu > Zn > Co > Cd Table 6. According to Cf classification, it was showed that Ni was Considerable contamination. Abd and Hegazy [19] showed that the contamination factor of Fe, Cu, Mn, and Pb in all samples along the coastal zone from Damietta to Port Said showed low contaminated expect Zn showed a considerable contamination.

### 3.3.3 Pollution load index and ecological risk

On the present study, RI values were 155.40, 148.12, 128.83 and 120.30 in winter, spring, summer and autumn respectively. According to the classification, it was showed that RI of winter season classified as moderate pollution as in Table 2. PLI values in the present study were 0.67, 0.64, 0.57 and 0.55 in winter, spring, summer and autumn respectively. According to the classification, it was showed that PLI classified as no pollution in all season as in Table 7. The decrease in PLI and RI values indicating dilution and dispersion of metal content with increasing distance from source areas. PLI can give indication about the trend spatially and temporarily. In addition, it also provides significant data and advice to the policy and decision makers on the contamination degree of the area. Abd [22] mentioned that PLI along the three Northern Delta lakes in Egypt were classified as a moderate contamination as a result of inputs from anthropogenic sources. Our results of the ecological risk assessment were in compatible to some extent with that obtained by Goher et al. [23]. PLI can give indication about the trend spatially and temporarily. In addition, it also provides valuable information and advice to the policy and decision makers on the pollution level of the area.

### 3.4 Toxicity Guidelines

To evaluate heavy metals contamination in sediments and their effect on the biodiversity community in the investigated area, metal concentration was compared to the toxicity

guidelines: the effect range low (ERL) and effect range medium (ERM) [24]. Copper concentrations lower than ERL except station (4) in winter and spring season, but copper in all stations is lower than ERM which confirm that no effect on biodiversity in the study area. Zn and Ni concentrations in all stations were lower than ERM and ERM which indicate that there is no adverse effect. On the other hand, Cd concentrations were lower than ERL except station (4) is more than ERL in all seasons. Pb shows no adverse effect on biota according to guideline classification Table 4. Metals which typically occur at higher than normal concentrations in anthropogenic effluents. But at low concentrations some of these are essential for living organisms but at high concentrations they may be toxic, whereas, others are not essential for metabolic activity (e.g. Pb, Hg) and are toxic to cells even at quite low concentrations [25]. El-Zeiny and El-Kafrawy [26] recorded that the highest levels of toxic metals in bottom sediments is the main contributors to pollution of the coast of Damietta include industrial, shipping and local activities. The present study recommended that the rules should be established instructions to control human activities. Beheary and El-Matary [27] recorded that the degree of pollution by heavy metals at Manzala Lake were varied according to three indices.

### 3.5 Statistical Analysis

One-Way ANOVA between mean concentrations of different heavy metals shows that there were a high significant between Pb, Fe and their sites in all season which related to low difference among its concentrations as mentioned in Table 8.

## 4. CONCLUSION

It has been made evident that the industrialization in Industrial Zone South Port Said was responsible for the present environmental degradation. Pollution status was evaluated using some indices: geo-accumulation index (**I<sub>geo</sub>**), contamination factor (**C<sub>f</sub>**), pollution load index (**PLI**) and ecological risk index (**RI**). The results for all metals based on I<sub>geo</sub> values were unpolluted. On the basis of the values of Cf, sediments are high in winter and low in summer. It was showed that metals in the following order: Ni > Fe > Mn > Pb > Cu > Zn > Co > Cd. According to Cf classification, it was showed that Ni was considerable contamination. According to the

classification, it was showed that RI of winter season classified as moderate pollution. According to the classification, it was showed that PLI classified as no pollution in all season. The decrease in PLI and RI values indicating dilution and dispersion of metal content with increasing distance from source areas. PLI can give indication about the trend spatially and temporarily. In addition, it also provides significant data and advice to the policy and decision makers on the contamination degree of the area.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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