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Study on heavy metal pollution in Gaza fishing harbour along the Mediterranean Sea-Gaza beach, Palestine

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ABSTRACT

Gaza fishing harbour is one of the most polluted areas in the Mediterranean Sea along Gaza coast due to the adverse effect of effluents from land-based sources. Concentrations of Manganese (Mn), Zinc (Zn), Copper(Cu), Nickel (Ni), Cobalt (Co), Lead (Pb) and Cadmium (Cd) were determined in seawater and marine sediments from Gaza fishing harbour and the surrounding coastal area south east coast of the Mediterranean Sea from September 2013 to March 2014 for investigating the level of heavy metals pollution in the area. Heavy metal concentrations were measured using Flame Atomic Absorption Spectrophotometer (FAAS). Concentrations of the heavy metals in examined water and sediments were ranged as follows: {Mn 0.010 – 0.128; Cu 0.038-0.695; Zn 0.028 – 0.373; Ni 0.199-0.296; Co 0.071-0.166; Pb 0.159-0.588; Cd 0.074-0.949 :mg/l} and {Mn 13.92-96.84; Cu 1.2-81.20; Zn 3.33-101.89; Ni 0.6-24.51; Co 1.9-8.23; Pb 3.24-13.34; Cd 0.1-1.81 :mg/kg} respectively. Mean concentrations of heavy metals in marine sediments showed significant variations and they were significantly higher than their levels in the seawater. The results obtained in this study were compared with those reported in earlier studies and concluded that the area of the present study was in general considered a metal polluted area according to the EPA, WHO Australian and Israeli guidelines. Hence, a continued monitoring programme for heavy metals, inorganic and organic compounds in water and sediments in the Mediterranean Sea along Gaza coast is recommended.

Keywords: *Heavy metal pollution, Mediterranean Sea, Gaza fishing harbour, Seawater, Marine sediments.*

INTRODUCTION

Coastal areas provide several important benefits to human beings in terms of foodstuff resources and ecology amenities. The human beings activities may have significant adverse effects on the ecosystems health and the sustainability of resources (Franca et al. 2005). The Gaza fishing harbour and the surrounding coastal environment is facing large and serious threats from land-based pollution sources. The small Gaza Strip has rapidly growing population that already counts at about 1.8 million persons (PCBS, 2014). The limited land resources, the physical isolation of the area and the underdeveloped environmental management system has caused various serious problems. These problems lead to contamination of the fishing harbour, coastal zone and seawater as well as, marine sediments, deterioration of natural resources and natural habitats, and reduction of fish populations. The fishery and tourist sectors are directly under threat due to several adverse effects (MEnA, 2001).

The seawater and sediments quality in the fishing harbour along the coast of Gaza in the Mediterranean sea is highly polluted from untreated sewage of about 17 sewage outfalls discharging into the coastal waters more than 100,000m³/day (personal communication with Palestinian Water Authority and Gaza Municipality). The input of the sewage into the sea causes a number of deterioration effects on aquatic life; including phytoplankton, zooplankton, and crustaceans, macro-algae and fish species. The main causes of these disturbs are: biodegradable organics, refractory organics, dissolved in-organics, heavy metals, suspended solids, pathogens, nutrients, pesticides and the insecticides being used intensively in agriculture and some small-scale industries (MEnA, 2001).

According to Connell et al. (1999) and Franca et al. (2005) heavy metals may take place in the coastal and marine environment from natural changes and discharges or leachates from several anthropogenic activities. The contamination of normal waters by heavy metals adversely affects aquatic life and poses significant environmental jeopardies and concerns (Cajaraville et al. 2000 and Ravera, 2001). Monitoring programs and investigation on heavy metals in marine water environments have become commonly major due to alarms over accumulation and toxic effects in marine organisms and to humans over the food chain (Otchere, 2003). Mackevičiene et al. (2002) reported that contaminants can stay for several years in sediments of rivers and marine systems where they squeeze the possible to affect human health and the surrounding environment.

Sediments are an imperative basin of assortment of contaminants, predominantly heavy metals and may attend as a supplemented source for benthic organisms (Wang et al. 2007) particularly in estuarine ecosystems. Metals may be existing in the estuarine system as dissolved kinds, as free ions or materializing organic complexes with humic and fulvic acids. Additionally, many metals for example, Lead associate freely with particulates and become adsorbed or co-precipitated with carbonates, oxyhydroxides, sulphides and clay minerals. Accordingly, sediments accumulate contaminants and may deed as long-term stores for metals in the environment (Spencer and MacLeod, 2002). The incidence of higher concentrations of metals in sediments observed at the nethermost of the water column can be a significant indicator of man-induced pollution rather than natural enrichment of the sediment by environmental weathering (Davies et al. 1991; Chang et al. 1998). The analyses of marine water or sediment samples still are subject to a range of limitations, in that the methods do not allow for the estimation of the quantity of the metal which is biologically available (Etim et al. 1991). Heavy metals pollution in seawater and marine sediments in the Mediterranean Sea were studied (Nasr et al. 2015; Okbah et al. 2014; El-Serehy et al. 2012; El-Gohary et al. 2012; Yilmaz and Sadikoglu, 2011; Khaled and Ahdy, 2009; Abdallah, 2008; Herut and Halicz 2004; Massoud and Hassan, 2002).

The dissolved substances such as heavy metals in the seawater along Gaza coast and fishing harbour area may pose a threat not only to the marine ecosystem but also to the groundwater quality and may be dangerous to the humans by causing unpredictable human diseases. Consequently, the food chain of marine ecosystem of Gaza is may affected from several unknown factors. Few short term studies for monitoring and assessment of the seawater and on-shore soil quality along Gaza particularly the distribution of heavy metals have been conducted.

According to literature investigations, there is no study about the determination of the pollution levels of the heavy metals in seawater and sediments of Gaza fishing harbour area, hence, this study was undertaken. The present study aims to determine the variations and the distribution of seven selected heavy metals (Mn, Cu, Zn, Ni, Co, Pb and Cd) in surface seawater and marine sediments of Gaza fishing harbour and the surrounding area, as well the impact of pollutant sources on the water quality of the harbour.

MATERIAL AND METHODS

Study area

To assess the level of pollution in the seawater and marine sediments in the Mediterranean sea along Gaza coastal environment, hence, theGaza fishing harbour and the surrounding environment in north and south parts of the harbour area were selected as study area.

Gaza fishing harbour is located in the Mediterranean sea along Gaza coast. The harbour was constructed between 1994 and 1998 on a normal sandy beach supported by sand dunes. The length of the current main breakwater is 1,000 m and that of the protection breakwater is 300 m. The head of focal breakwater is at water depth of 9 m, and the entry of the harbour was 6 m deep when it was constructed. The entering of Gaza harbour is seaward from the shore to a distance of about 500 m (Abualtayef et al. 2012).

To investigate the general distribution of heavy metals pollutants in the seawater and marine sediments in the fishing harbour along Gaza city the data was collected from 5 locations inside the vicinity of the harbour and two locations in the north part of the harbour and one other location is located in the south part of the harbor. The total number of sampling sites is 8 locations (Fig.1).

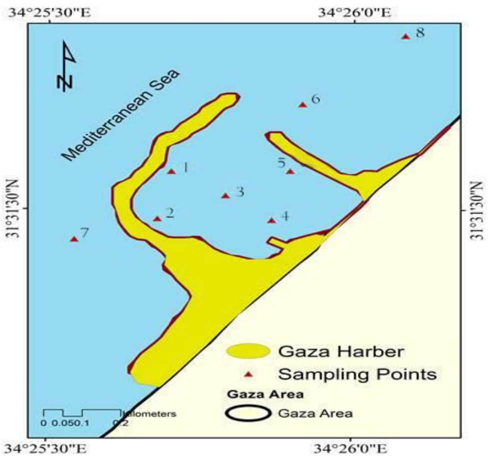

Fig1. *Map shows sampling stations in Gaza fishing harbour*

The sampling frequency during this study was three times started from September 2013 and ended on March 2014. The sampling covered three seasons summer, winter and spring seasons, first sampling was conducted on September, second sampling on November 2013 and the third sampling on March 2014.

Sampling and analytical methods

All samples were collected using 1.5 liter, polyethylene bottles, which was pre-washed with 10% nitric acid and deionized water. Before sampling, the bottles were rinsed at least for three times with water from the sampling location. The bottles were immersed to about 20-40 cm below the water surface to prevent contamination of heavy metals from air. All water samples were immediately brought to the laboratory where they were filtered through Whatmann No.41 (0.45 µm pore size) filter paper (Sadeghi et al. 2012).

The samples were acidified with 2 ml nitric acid for preventing precipitation of metals, reduce adsorption of the analytics onto the walls of containers and to avoid microbial activity, then water samples were stored at 4°C until the analyses process carried out.The standard addition technique was used in seawater samples due to the presence of high complex concentrations of cation and anion in seawater where their removal is very difficult. This technique assumes that added analytic were react exactly in the same manner during analysis as the analytic already in the sample. The calibration was carried out using standard solutions prepared from a multi-element standard solution. These standards were 10mg/l Mn, 20mg/l Cd, 6.5mg/l Co, 10mg/l Pb, 20mg/l Cu, 10mg/l Ni and 10mg/l Zn (APHA, 1998).

Different parameters like temperature, pH, DO, electrical conductivity and turbidity were recorded in the field using portable Hydrolab Surveyor (MS5 Surveyor Hach Environmental) and turbidity was measured with 2100P turbidmeter (HACH).

Bottom marine sediment samples were obtained from the same point where seawater samples were collected. At each point, three sediment samples were taken superficially by using pre cleaned 100 ml, wide mouthed, disposable plastic containers and packed separately in pre cleaned polyethylene bags. They were brought to the laboratory, dried in oven (at 105 ºC ±2 for 24hours) to constant weight and then sieved through a polyethylene sieve and mortar to remove large particles in order to obtain a homogenous fine powder. The samples were then pulverized in an agate mortar for 30 minutes. Dried samples were weighed around 4g accurately and transferred to Teflon containers. Then acid mixtures were added to samples. After the microwave digestion, all samples were diluted to 50 ml with 2% nitric acid. The digested solutions were stored in acid-treated falcon tubes at 4 0C prior to metal analysis by Flame Atomic Absorption Spectrophotometer UNICAM, 929 model (APHA, 1998).

Quality control

For checking efficiency of the digestion procedures and the subsequent recovery of the metal, homogeneous mixtures of five samples ofmarine sediments were picked up with multi element solution which consists of standard solutions for all metals measured during this study. The element solution was spiked in a mode to achieve ultimate concentrations of 1 and 4µg/g. In addition, a mixture without any metal was used for controlling purpose. All mixtures were prepared by the digestion method. The subsequent solutions were analyzed 3 times for metal concentrations agreeing with the same procedures as the samples to create assurance in the accuracy and consistency of the obtained data. The amount of spiked metal recovered after the digestion of the spiked samples was used to estimate percentage recovery as following:

% recovery= [(t-c)/t] 100

where t= concentration of a metal in treatment sample and c= concentration of a metal in control sample.

All samples of water and sediment analytical batches for the determination of Mn, Zn, Ni, Cu, Pb, Co and Cd concentrations were supplemented by blanks at a minimum rate of one blank per 5 samples. To validate the results obtained for the heavy metal elements each determination was conducted at three (3) times and compared with the results observed from the water and sediment samples for precision and accuracy. To minimize contamination, all glassware for the digestion process were first cleaned under running tap water and soaked in 10% (v/v) Nitric acid (HNO3) for 24 hours. They were then rinsed with distilled water followed by 0.5% (w/v) potassium permanganate (KMnO4).

Distilled water was used to finally rinse the glassware which was subsequently dried. The recovery percentage of various heavy metals found to follow the following order: Zn (99.80)>Pb (99)>Cu (98.33)>Mn (97.75)>Ni (96.83)>Cd (96)>Co (93.33). High recovery of samples ensure the accuracy of the analytical method used for digestion purpose during this work.

Data statistical analysis

The heavy metals data were entered as Microsoft Excel sheets uploaded to Statistical Package for Social Sciences (SPSS) windows version 19 and analyzed using min, max, mean and relative standard deviation statistics. In addition the Pearson correlation coefficient (a measure of linear association) and paired sample t test are used to detect significant variations of heavy metals elements among seawater and marine sediment samples.

RESULTS AND DISCUSSION

Hydrographic conditions

The obtained results of seawater physicochemical parameters along with statistical analysis are presented in Table 1.

Temperature is a significant biological factor, which plays an important role in the metabolic endeavors of the microorganisms (Sirajudeen and Mubashir, 2013). The surface water temperature varied from 17.9 $^{\circ}$C (winter) to 28 $^{\circ}$C (summer). The temperature shows regular seasonal variations, with the higher temperature during summer and lower temperature during winter season. This seasonal variation may be due to the increase in amount of sewage input and urban runoff. Generally surface water temperature is affected by the intensity of solar radiation, evaporation, inaccessibility, inflow of freshwater and cooling and mix-up with ebb and flow from adjacent neritic waters (Govindasamy et al. 2000).

The seawaters in Gaza fishing harbor is fairly turbid, while turbidity decreased away from the harbor area. There is considerable variation in turbidity among all locations while it is found to be higher in winter than summer. The turbidity values observed to be ranged between 1.52 and 12.9 NTU, with a mean value of 5.87 NTU. Almost 50% of the values found to be higher than the international standard (5NTU).

The measurements of electrical conductivity did not vary significantly among the eight locations data. It is observed that slightly higher values are obtained in September during end of summer season and these values decreased gradually in November during the rainy season.Electrical conductivity ranged between 55.8 and 60.6 mS/cm with a mean value of 57.62 mS/cm.

The investigation of pH is one of the most common tests in marine waters and a good indicator for water quality assessment. Fluctuations in the acidity or basicity of seawater can have intense effects on biological growth and activity of marine organism species and on the chemical reactions in the seawater column (Cormack, 1983). Most organisms have adapted to live in water of a specific pH in the range of 6.5-8.5. Most pH measurements were found to be in the acceptable range (7.5-8.5) as documented by Harvey (1955) for all locations during this study. The pH measured values found to be ranged between 7.57 and 8.15 with a mean value 7.89. The lowest value of pH (7.57) was observed in the month of November while the maximum pH (8.15) was observed in the month of September. The pH values do not show any definite trend for the two seasons during the study period.

The concentrations of dissolved oxygen (DO) ranged between 2.94 to 7.2 mg/l with a mean concentration of 5.22 mg/l. Close inshore and semi enclosed bodies of water, the introduction of sewage with its high content of organic carbon, nitrogen and phosphorus can have a serious effect on the oxygen level of seawater (Topping, 1976), which is quite evident from the data obtained for Gaza fishing harbor. Very low oxygen water and high organic wastes interact to form an anaerobic environment at certain locations in Gaza fishing harbor. During the sample collection it has also been observed that a thick layer of black mud persists at the bottom of harbor particularly at upper reaches of harbor. The smell of hydrogen sulphides is quite prominent during low tide. The concentration of dissolved oxygen gradually increases (4.20-7.11 mg/l) towards entrance of the open sea indicating decreased level of pollution.

Table1. *Statistical analysis summary for seawater physicochemical parameters*

Parameters	Min.	Max.	Mean ±SE	StDev
Temp (ºC)	17.9	28	22.99±0.85	4.17
pH	7.57	8.15	7.89±0.03	0.15
EC (μs/cm)	55.8	60.6	57.62±0.33	1.64
Turbidity (NTU)	1.52	13	5.90±0.67	3.31
DO (mg/l)	2.94	7.2	5.22±0.20	0.98

Distribution of heavy metals in seawater

Seawater samples were collected from the Gaza fishing harbor and the surrounding area and analyzed to determine the concentrationsof heavy metalelements including: Mn, Cu, Zn, Ni, Pb, Co and Cd. The results of heavy metals concentration determination in collected seawater samples are shown in Table 2. The mean concentrations of heavy metals Mn, Cu, Zn, Ni, Co, Pb and Cd were 0.067, 0.063, 0.028, 0.199, 0.071, 0.159 and 0.074 mg/L respectively.

Compared the concentrations of heavy metals in seawater of Gaza fishing harbor with some typical areas reported in the literature, the pollution of Gaza fishing harbor was more serious than several areas. This may be related to the semi-closed characteristics and the current of the Gaza fishing harbor area.

The Mn concentrations were similar to values recorded by Kim et al. (2010) from the Saemangeum coastal area in Korea with an average of (0.0626 mg/l), and closer to values reported by Khan and Saleem (1988) from Karachi harbor and Qari and Siddiqui (2008) from Karachi coastal areas. El-Serehy et al. (2012) reported high concentrations of Mn (170-198 mg/l) in the Mediterranean coastal waters eastern Nile Delta, as compared to the present study.

The copper concentrations were similar to values (0.05-0.43 mg/l) recorded by Qari and Siddiqui (2008) from Karachi coastal areas. Kim et al. (2010) reported low concentrations from the Saemangeum coastal area in Korea with an average of (0.57 µg/l) as compared to the present study. The concentrations of Cu are generally higher when compared with previous results obtained (an average of 4.72µg/l) from the seawater of Abu-Qir Bay in the Mediterranean Sea along Egypt coast (El-Goharyet al. 2011). El-Serehy et al. (2012) reported high concentrations of Cu with a mean value of (6.83 mg/l) in the Mediterranean coastal waters eastern Nile Delta, as compared to the present study. Higher concentrations of copper in the fishing harbor area of Gaza might be due to the agricultural, domestic and small-scale industries wastewaters discharged into the harbor vicinity. In addition to this high values of dissolved copper may be attributed to the occurrence of high amount of suspended matter during highest discharged period (heavy rains occurred in the region during the month of November, 2013).

Table2.*Statistical summary of heavy metal concentrations in seawater of Gaza fishing harbour and surrounding area*

Item	Mn mg/L	Cu mg/L	Zn mg/L	Ni mg/L	Co mg/L	Pb mg/L	Cd mg/L	Reference
Min	0.006	0.038	0.028	0.199	0.0712	0.159	0.0746	This study
Max	0.128	0.695	0.373	0.296	0.1408	0.5888	0.949	
Mean	0.067	0.094	0.066	0.25	0.11	0.29	0.23	
RSD%	45.65	138.93	77.77	9.57	19.80	29.47	114.03	
EPA Std.	-	0.045	1.18	0.12	-	0.05	0.01	USEPA 2000
WHO Std.	-	10	30	10	-	0.05	0.01	FAO/WHO 1984
Israeli Std.	-	5µg/l	40µg/l	10µg/l	-	5µg/l	0.5µg/l	Herut & Halicz 2004

The concentrations of Zn are very high when compared with the values recorded in Abu-Qir Bay that ranged between 0.0012 and 0.0927 mg/l in summer and winter seasons respectively with a mean value of 0.0046 and 0.0314 mg/l. Masood and Hassan (2002) recorded less concentration of Zn as compared to this study with an average of 0.0269 mg/l in the estuarine mouth of Rosetta estuary of the Nile and Mediterranean sea waters. The concentrations of Zinc are higher than the values (0.0207-0.05929 mg/l with a mean of 0.0335 mg/l) recorded by Abdullah (2008) at El-Max Bay in Egypt. The Zn concentrations also were higher when compared with values recorded by Kim et al. (2010) from the Saemangeum coastal area in Korea with an average of (0.29 µg/l). The Zn values are lower in concentrations as compared with the values (0.09-0.77 mg/l) recorded by Qari and Siddiqui (2008) from Karachi coastal waters. This high concentration of Zinc in the seawater surface may be due to the discharge of untreated domestic and urban wastewaters in the vicinity of Gaza fishing harbor.

The concentrations of Ni were closer to values (0.1-0.41 mg/l) documented by Qari and Siddiqui (2008) from Karachi coastal areas. Kim et al. (2010) reported low concentrations from the Saemangeum coastal area in Korea with an average of (0.53 & 0.83 µg/l) as compared with the present study.

The concentrations of Cobalt are very high when compared with the values recorded in the Saemangeum coastal area in Korea that ranged between 0.018-0.297 and 0.045-0.147 µg/l in May and July, 2006 respectively with a mean value of 0.130 and 0.091µg/l (Kim, et al. 2010). Herut and Halicz (2004) recorded less concentration of Cobalt as compared to this study with a range of 0.025-0.038 µg/l in the surface water from Gulf of Eilat and Mediterranean seawaters. The Cobalt concentrations are lower when compared with the concentrations (0.25-0.45 mg/l) documented by Qari and Siddiqui (2008) from Karachi coastal waters. This high concentration of Cobalt in the seawater surface may be due to the discharge of untreated domestic and urban wastewaters in the vicinity of Gaza fishing harbor.

The concentrations of Pb are very high when compared with the values recorded in Abu-Qir Bay that ranged between 0.013 and 0.028 mg/l in summer and winter seasons respectively with an average value of 0.022 and 0.015 mg/l. El-Bourarie et al. (2010) recorded less concentration of Pb as compared to this study with a range of 0.005-0.057 mg/l in the Nile River Delta Waters. The concentrations of Pb in this study are higher than the values ranged between 0.0026 and 0.0261 mg/l recorded by Abdullah (2008) at El-Max Bay in Egypt. The lead concentrations also were higher when compared with values recorded by Kim et al. (2010) from the Saemangeum coastal area in Korea ranged from 0.007-0.053 µg/l with an average of (0.015 µg/l). Herut and Halicz (2004) documented less concentrations of Pb as compared to our study with a range of 0.018-0.055 µg/l in the surface water from Gulf of Eilat and Mediterranean seawaters.

The Pb values in this study are lower in concentrations as compared with the mean value (9.39 mg/l) recorded by Yilmaz and Sadikoglu (2011) from the seawater of Kepez harbor of Canakkale in Turkey and values (ranged from 0.43-0.62 mg/l). The higher values of Pb concentration in the seawater surface might be due to the increase amount of agricultural, untreated domestic and urban wastewaters discharged in the vicinity of Gaza fishing harbor.

The concentrations of Cd during this study were very high when compared with the values documented in Abu-Qir Bay ranged between 1.18µg/l and 1.36µg/l during summer and with an average value of 0.57µg/l in winter and 1.26µg/l in summer season. The concentrations of Cd in the present study are higher than the values which ranged between 0.66 and 6.45µg/l recorded by Abdullah (2008) at El-Max Bay in Egypt. The cadmium concentrations level were also higher when compared with values recorded by Kim et al. (2010) from the Saemangeum coastal area in Korea ranged from 0.002-0.048 µg/l with an average of (0.057 µg/l). Herut and Halicz (2004) documented less concentrations of Cd as compared to this study with a range of 0.008-0.013 µg/l in the surface water from Gulf of Eilat and Mediterranean seawaters. The concentrations of cadmium in this study are lower in values as compared with the mean value (73.80 mg/l) documented by Yilmaz and Sadikoglu (2011) from the seawater of Kepez harbor of Canakkale in Turkey.

Distribution of heavy metals in marine sediments

The results of heavy metals concentration determination in collected marine sediment samples are shown in Table 3. The mean concentrations of heavy metals Mn, Cu, Zn, Ni, Co, Pb and Cd were found to be 42.42, 18.08, 26.55, 8.04, 4.20, 7.27 and 1.17 mg/kg respectively.

The concentrations of Mn are low when compared with the mean values recorded in El-Gamil coast in Egypt 198 and 170 mg/kg in summer and winter seasons respectively (El-Serehy et al. 2012). Kim et al. (2010) recorded higher concentrations of Mn as compared to this study with a range of 221-426 mg/kg with a mean value of 341 mg/kg in May 2006 and range of 211-429 mg/kg with a mean of 304mg/kg in August, 2006 in the Saemangeum coastal area of Korea. From the comparison results with the above mentioned studies it is clear that the level of contamination with manganese metal in the Gaza harbor area is low.El-Serehy et al. (2012) reported almost similar concentrations of Cu with a mean value of 15.3 and 13.3 mg/kg in winter and summer seasons respectively in the Mediterranean coastal waters eastern Nile Delta, as compared to the present study.

Table3. *Statistical summary of heavy metal concentrations in marine sediments of Gaza fishing harbour and surrounding area*

Item	Mn mg/kg	Cu mg/kg	Zn mg/kg	Ni mg/kg	Co mg/kg	Pb mg/kg	Cd mg/kg	Reference
Min	13.92	1.20	3.33	0.60	1.90	3.29	0.1	This study
Max	96.84	81.20	101.89	24.51	8.23	13.34	1.81	
Mean	42.42	18.08	26.55	8.04	4.20	7.27	1.17	
RSD%	57.72	130.57	113.93	78.21	53.69	32.97	33.55	
AustralianStd.	-	65	200	21	-	50	1.5	ANZECC 2000
EPA Std.	460	16	-	-	-	31	0.6	USEPA 2000

The concentrations of Ni were relatively similar when compared with the values (2.87-20.1 mg/kg with a mean value of 10.9 mg/kg) recorded by Kim et al. (2010) from the Saemangeum coastal area in Korea. Herut and Halicz (2004) were documented similar concentrations of Ni as compared to this study with a range of 2.2-21.14 mg/kg in the surface marine sediments from Gulf of Eilat and Mediterranean Sea.

The concentrations of cobalt were almost similar when compared with values ranged between 0.9 to 8.4 mg/kg recorded by Herut and Halicz (2004) for marine sediment samples collected from Gulf of Eilat and Mediterranean Sea. Kim et al. (2010) were also recorded relatively similar concentration values of cobalt when compared with this study with a mean value of 6.21 and 6.28 mg/kg during May and August of 2006 from the Saemangeum coastal area in Korea.

The Pb concentrations in marine sediments were similar to values recorded by Hutagalung and Manik (2002) from estuary of Digul Dan (Arafura Sea) in Indonesia with a range of 3.6-12.4 mg/kg and mean value of 7.8 mg/kg and closer to values documented by Razak (1986) from coast of Pantai Ujung Watu (Central Java) with a range between 1.1 and 10.9 mg/kg. Kim et al. (2010) reported higher values of Lead concentration with a range between 18.6-28.2 and 17.9-26.5 from the Saemangeum coastal area in Korea with an average of 22.4 and 22.3 mg/kg as compared to the present study and the Lead concentration were also low when compared with previous results (53.20-159.64 mg/kg during summer) obtained from the coastal zone of Abu-Qir Bay in the Mediterranean Sea (El-Gohary et al. 2011). Herut and Halicz (2004) were documented higher concentrations of Pb as compared to this study with a range of 1.0 to 164.3 mg/kg in the surface marine sediments from Gulf of Eilat and Mediterranean Sea.

The concentrations of Cd in this study are lower when compared with the values documented in Abu-Qir Bay ranged between 0.24mg/kg and 4.68mg/kg during summer and with an average value of 2.52mg/kg in winter and 2.80mg/kg in summer season (El-Gohary et al. 2011). El-Serehy et al. (2012) recorded higher concentration values of Cd as compared to our study with a range of 1.8-2.3 mg/kg and 1.4-2.0 mg/kg in the El-Gamil coastal waters during winter 2005 and summer 2006 in the Mediterranean Sea along Egypt.

The cadmium concentrations level were also higher when compared with values recorded by Kim et al. (2010) from the Saemangeum coastal area in Korea ranged from 0.05-0.14 µg/g with an average of (0.09 µg/g). Herut and Halicz (2004) documented less concentrations of Cd as compared to this study with a range of 0.03-1.60 mg/kg and average of 0.32 mg/kg in the surface marine sediments from Gulf of Eilat and Mediterranean Sea.

Data statistical analysis

Pearson’s correlation is used to detect linear correlations between various parameters and locations. Table 4 shows the Pearson's correlation between heavy metals (Mn, Cu, Zn, Ni, Co, Pb and Cd) and physicochemical parameters (temperature, turbidity, electrical conductivity, pH and dissolved oxygen) in seawater.

Table4. *Pearson's correlation coefficient among seven heavy metals and physicochemical parameters in Gaza fishing harbour and surrounding area*

	Mn	**Cu**	**Zn**	**Ni**	**Co**	**Pb**	**Cd**	**Temp**	**NTU**	**EC**	**pH**	**DO**
Mn	1											
Cu	0.07	1										
Zn	-0.21	-0.07	1									
Ni	0.50	0.06	-0.21	1								
Co	0.20	-0.02	-0.21	-0.25	1							
Pb	0.20	-0.13	-0.07	0.02	0.51	1						
Cd	0.27	-0.11	-0.13	-0.23	0.04	-0.09	1					
Temp	-0.53	0.02	0.21	-0.53	-0.39	0.16	0.03	1				
NTU	-0.46	-0.09	0.20	-0.28	0.16	0.10	-0.11	0.15	1			
EC	0.64	-0.12	-0.09	0.50	0.38	0.19	-0.14	-0.92	-0.23	1		
pH	-0.05	0.01	0.04	0.09	-0.23	0.04	-0.33	0.19	-0.19	0.06	1	
DO	0.63	-0.05	-0.15	0.52	0.13	-0.12	0.18	-0.71	-0.25	0.69	-0.16	1

The correlation coefficient matrix between heavy metal concentrations and the physicochemical characteristics of the seawater samples of Gaza fishing harbour and surrounding area showed some significant correlations, both positive and negative. Strong correlation found between Mn and dissolved oxygen; EC and temperature; Dissolved oxygen and temperature; dissolved oxygen and EC. Moderate negative correlation found between Mn and turbidity; Mn and temperature; Ni and temperature. Moderate positive correlation found between Mn and DO; Mn and EC; Mn and Ni; Ni and EC; Ni and DO; Co and Pb. These results can demonstrate that the seven elements measured in the present study have almost similar sources and having related sources can be associated to the geographical structure of the selected study area. Table 5 presents the Pearson's correlation coefficients among heavy metals (Mn, Cu, Zn, Ni, Co, Pb and Cd) elements in the marine sediments of Gaza fishing harbour area.

Table5. *Correlation coefficient matrix among seven heavy metals in Gaza fishing harbour marine sediments*

Heavy metals	**Mn**	**Cu**	**Zn**	**Ni**	**Co**	**Pb**	**Cd**
Mn	1						
Cu	0.65	1					
Zn	0.53	0.80	1				
Ni	0.70	0.83	0.59	1			
Co	0.89	0.81	0.51	0.82	1		
Pb	0.55	0.42	0.23	0.61	0.64	1	
Cd	0.47	0.32	0.35	0.57	0.35	0.43	1

It can be seen from Table 5 that all heavy metals are positively correlated. Significant correlation was found between Mn and Co (0.89); Cu and Zn (0.80); Cu and Ni (0.83); Cu and Co (0.81); Ni and Co (0.82); Mn and Ni (0.70). Moreover, moderate correlation was found between Mn and Cu (0.65); Mn and Zn (0.53); Mn and Pb (0.55); Zn and Ni (0.59); Zn and Co (0.51); Ni and Pb (0.61). The strong positive correlation between Cu, Co, Mn and Ni indicates that they mostly came from the same source, while the three heavy metals Zn, Pb and Cd, which show decreasing levels are moderately correlated indicating that these heavy metals probably have similar provenance.

The significant direct correlation between some of the metals in marine sediment samples calculated in the present study may be due to the existence of some of these metals in the same oxidation state reacting in similar manner to the aquatic environment or that the metals with high correlation coefficient occur together in a mineral and are co-leached into the aquatic environment consequently (Aiyesanmi, 2006).

Since it has been documented that correlations between metal pairs get weakened or alienated with anthropogenic effect thus, high correlation between these metals strongly recommends common lithological or crustal origin rather than anthropogenic contamination sources (Aiyesanmi, 2006).

The obtained results from statistical analysis may confirm that the seven heavy metal elements investigated in this study have similar sources and having similar sources can be related to same topographical area (El-Serehy et al. 2012).

Statistically, significance analysis (P values from the ANOVA-test) was performed between the all 8 sites for heavy metals in seawater and marine sediments. Though, there were differences in heavy metals concentrations between the different eight sites, these differences in most of heavy metal concentrations were not statistically significant among most of the locations ($P>0.05$). In addition significance analysis t-test was performed between seawater and marine sediment samples and results showed highly significance values of pv among all heavy metal elements except Zn element. Hence there is no heavy metal adding source in any of the eight sites chosen for this study.

CONCLUSION

Gaza fishing harbour is one of the most polluted areas due to the adverse effect of effluents from land-based sources. Domestic untreated wastewater and fishing activities may are the major sources of observed higher levels of heavy metals contamination.

The mean concentration values of metals in marine sediments were higher than those in water samples due to their metal mobilization from sediments to overlying water by action of pH and microbial activity.

The concentrations mean of the investigated metals in seawater were ranged in the order of Pb> Ni> Cd> Co> Zn> Mn> Cu and in marine sediments were Mn> Zn> Cu> Ni> Pb> Co> Cd.

The majority obtained concentration values of Cu, Mn, Ni, Zn, Pb and Cd investigated in the seawater and marine sediments samples were found to be higher than the limit values as compared with EPA, WHO, Australian and Israeli guidelines and standards for heavy metals level.

Investigations of the correlation between heavy metals recorded in this study showed both strong (significant) and weak relationships between several pairs of trace elements in the seawater and marine sediments of the samples collected from Gaza fishing harbor area. Statistically, significance analysis t test was performed between all study area sites for heavy metals in seawater and marine sediments. It was found that there are differences in heavy metals concentrations between the different eight sites, these differences in most of heavy metal concentrations were not statistically significant among most of the locations.

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