Risk Assessment of Heavy Metals in New Damietta Harbor along the Egyptian Mediterranean Coast

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Abstract

*Mediterranean coastal area. At the same time, little data are available for heavy metal pollution in this region. Studies on the environmental state of the Egyptian Mediterranean Coast have concentrated in the past mostly on simple environmental effects. Therefore, there is a demand for a current description of the heavy metal pollution likely caused through the regional development. The study area is at New Damietta Harbor (DH) that is considered as a semi-closed water body influenced by loading/unloading activities, municipal and agricultural waters resulting from Damietta Governorate. The study is mainly concerned with the contamination of surface waters, soil, and sediments by hazardous heavy metals, which are a widespread environmental problem in the marine and coastal environment at the Egyptian Mediterranean Coast. The purpose of this study was set to: 1. Evaluate the levels and the spatial distribution of heavy metals from water, soil, and sediments of the New Damietta harbor and offshore harbor water, which affect the Egyptian Mediterranean Coast, and 2. Compare the heavy metals in the harbor sediment and at the Egyptian Mediterranean Coast with international standards in order to determine the best available methodology for assessing the sediment toxicity. The analytical data revealed a marked increase in the levels of Cd , Hg, Pb, Ni, Cr, and Zn. On the other hand, the EF of Cu showed low value; less than unity indicate that the metal is incorporated in the sediment dominantly as lithogenous material. The high values of EFs showed the accumulation of trace metals in the sediments of study area. The magnitude of pollution by the metals can be arranged in the following sequence: **Cd > Hg > Pb > Cr > Ni > Zn > Cu .** The study concluded that the concentrations of heavy metals (Cd, Cr, Cu, Hg, Ni, Pb, and Zn) in water at all locations inside the harbor were within the limits (with few exceptions due to dredging activities). Heavy metals in the points recorded offshore for water and sediment were within the limits as well in all locations to the benefit of the Mediterranean Coastal environment. Finally, it is recommended to add a chapter, contains the limits for water quality criteria in harbors water in Egyptian Environmental Law of 1994.*

Keywords: Egyptian Mediterranean Coast, Water Quality, Risk Assessment of Heavy Metals, Marine Zones, New Damietta Harbor

1. Introduction

The Egyptian Mediterranean coast extends between longitude $25^0 \, 30^/$ E and $34^0 \, 15^/$ E, and northward to latitude 33^0 N. It has a surface area of about 154,840 km^2 and its water volume is 224,801 km^3 (Said and Rajkovic, 1996) The coastal zone of Egypt on the Mediterranean extends from Rafah in the eastern region to El-Salloum to in the western region for over 1200 km. It hosts five large lakes; namely Bardawil, Manzala, Burullus, Edku and Maryut, which represent about 25% in area of the total wetland of the Mediterranean. It also hosts a number of important residential and economic centers of the country including the cities of Alexandria, Matruh, Damietta, Rosetta, Port Said, and Al Arish. Activities on the coastal zone include fishing, industrial activities, tourism, trading and agricultural activities in the delta region (SMART, 2005).

The maritime transport in the eastern Mediterranean, including oil tankers, commercial ships and passenger ships, affects the coast to a large extent. The entire beaches are permanently polluted by oil lumps, litter and plastic debris even in the very far remote areas of the coast where there are no known activities (Table 1). The marine environment (as a part the coastal zone) is of great economic and environmental significance. This zone in Egypt is currently under sever and ever increasing pressure.

Table 1: Description of the Egyptian Mediterranean Coast and sources of marine pollution

Region	Sources of pollution	Main sites of pollution
Western Region	• Industrial and domestic wastewater from residential and tourist resort areas. • Much of the wastewater is discharged into the coastal lakes, which are connected to the sea. • Shipping activities	El-Nobarreya drain El-Mex Out fall Abu Qir Drain (El-Amiaa) Lake Edku outlet Western harbour El-Dikhaila harbour Eastern Harbour
Middle Region	• Nile water and agricultural drains contaminated with hazardous industrial waste, domestic sewage, organic matter, fertilizers and pesticides. • Lake Manzalah receives the sewage from Cairo via El-Baqar canal • Shipping activities	Rosetta branch of River Nile Damietta branch of River Nile Outlet from Lake El-Manzala (El-Gamil outfall) Burullus outlet New Damietta Port
Eastern Region	• Oil production and oil terminals • Shipping activities	Port said

Table 2: Total trace metal concentrations (μg/g dry weight) in surficial sediments along the Egyptian Mediterranean Coastal area

Region	Station	Fe	Mn	Zn	Cu	Ni	Cr	Co	Pb	Cd
Western Region	**Min.**	243	17.2	2.05	0.46	1.65	4.08	0.43	4.41	0.06
	Max.	11,478	527	62.2	26.3	19.4	85.5	6.63	53.7	0.47
	Average	4,646	209	23.4	7.93	8.81	24.8	2.46	18.9	0.29
	SD									
Middle Region	**Min.**	9,654	257	10.5	3.44	36.3	79.0	7.94	4.61	0.04
	Max.	38,045	823	29.8	17.3	60.3	298	26.4	8.83	0.23
	Average	25,516	597	21.9	9.86	49.5	147	17.0	6.70	0.12
	SD	10,090	204	6.81	4.47	8.64	84.7	6.91	1.37	0.07
Eastern Region	**Min.**	1,422	54.8	2.61	1.57	27.8	72.4	1.93	3.34	0.04
	Max.	33,971	1086	30.1	11.4	47.4	284	17.1	6.67	0.18
	Average	17,697	570	16.3	6.48	37.6	178	9.50	5.01	0.11
	SD	23,016	729	19.4	6.94	13.9	150	10.7	2.35	0.10
All Regions	**Min.**	243	17.2	2.05	0.46	1.65	4.08	0.43	3.34	0.04
	Max.	38,045	1,086	62.2	26.3	60.3	298	26.4	53.7	0.47
	Average	13,256	381	22.2	8.46	25.9	82.7	8.24	13.2	0.22
	SD	12,911	305	15.8	6.22	21.0	90.2	8.40	11.9	0.15

A number of factors contribute to this situation: a) rapid urbanization of the coast; b) pollution from residential, commercial and industrial activities, c) tourism development, d) resources users, and e) continuous development in hazards prone areas, among others. Pollution is originated from the discharge of huge amounts of wastewater (domestic, industrial and agricultural discharges) into the coastal water (Table 2) (UNEP, 2002).

The New Damietta Harbor was constructed in 1982 and is located about 10 km west of the Damietta Nile Branch. The harbor basin was constructed inland and its entrance protected by two breakwaters. The western breakwater extends about 1500 m parallel to the navigation channel, attaining the 7-m depth contour. The eastern one is about 500 m long, perpendicular to the shoreline, and tends to about 3 m water depth contour. The navigation channel extends offshore to the middle shelf of about 15 m. Since January 1984, the channel of the harbor has experienced sedimentation and subsequently threatening the navigation activities (Shereet, 2009).

New Damietta Harbor is considered as semi-closed water body influenced by loading/unloading activities, municipal and agricultural waters resulting from Damietta Governorate (Shereet, 2009). Damietta is an industrial center known for its furniture, leathers, textile and sweets industries in addition to dairy products and rice mills, and for its agricultural heritage. It is also a town of fishing industry with one of the largest fleets on the Mediterranean which accounts for half of the fishing boats of Egypt. Finally, it is well known for the port that the pollution in near-shore waters of the Mediterranean Sea has reached a critical level (Shereet, 2009).

Much of Damietta's coastal zone remains largely undeveloped because of threats to shoreline erosion and poor connections with the rest of Egypt. However, this situation is steadily changing since the construction of the new international coastal road from El Saloum to Rafah which has done much to improve the areas connectivity. Significant developments in the past two decades include the construction of Damietta Port, the establishment of New Damietta, offshore exploratory oil and gas activities, tourism and fishing activities.

The task of planning, managing and protecting the coastal zone is distributed among various ministries and bodies and governed by a number of national regulations. As a consequence, there is often insufficient cooperation and dialogue, which results in regulatory inconsistencies regarding planning, management and development of coastal zones. Furthermore, lack of environmental controls and standards, and environmental awareness amongst building licensing authorities, as well as absence of a National Land Use Plan have led to unplanned urban growth which has in turn placed a burden on coastal zone environments, contributing to traffic congestion and increased population densities.

Erosion is now a significant environmental problem affecting Damietta's coastal zone. Indeed the shoreline east of Damietta Promontory has retreated more than 500m in a little over 10 years (1983 to1995).In response coastal defenses have been built west of the promontory. Two other successful shoreline protection measures also worth mentioning include pilot groin defenses in Ras El Bar and a sea wall defense system in Ezbet El Borg. Both these initiatives were built by the governorate's Shoreline Protection Authority.

Increasing levels of development and persistent sources of pollution (from various drains and factories into the Nile, commercial activities around Damietta Port, sewage and agricultural drainage sources and oil and gas related industries) have all had an effect on the coastal zone ecosystems and levels of biodiversity. Along the coast, levels of pollution have led to an increase in the number of grey mullet fish and Cardium snails and a decrease in the number of Anguilla eels, crabs and sparidack fish etc. A similar trend is also being experienced in Lake Manzala where levels of polluted drain water etc being dumped into the lake have threatened the number of some species and increased the numbers of others.

A solution to improving the quality of water in the coastal zone and lake Manzala may not be far away however, as a 100 hectares of engineered wetland facility designed to treat 25,000 m3 of polluted drain water per day gets underway in Port Said. Another issue of some concern facing the livelihoods of fishing communities on Lake Manzala is that land reclamation and siltation processes have shrunk the size of the lake by an average of 5.2 km^2 pa. Efforts to halt the reclamation process need to be taken soon to protect the future livelihoods of the lakes fishing communities.

Both Damietta's industrial zones face a number of pollution control issues. This is mainly due to incomplete infrastructure which has made it difficult for industries to comply with environmental standards. In New Damietta's industrial zone, for instance wastewater is not treated before it reaches the city's compact wastewater treatment unit. However, this situation will soon be resolved once the new wastewater treatment plant is completed by the end of 2005. Damietta's Industrial Free Zone on the other hand has recently put in place a sewage system that transports sewage to Ras El Barr. As far as solid waste disposal is concerned neither zone has an organized formal solid waste management system, instead the responsibility of waste disposal falls on individual industrial facilities that transfer it to the City Dump. Other issues that need to be addressed include the high cost of industrial land in both zones (New Damietta LE180/ m^2, Free the high cost of land and electricity has certainly contributed to low occupancy rates in both the Free Zone [>5%] and New Damietta [28%]. Indeed, in some cases high prices have led facilities to change their activity to storage, work by batch order or close down altogether. To encourage further industrial development in both these zones land prices and power costs will need to be reduced. The Governorate has asked the two industrial zones to lower their land prices but to date no action has been taken. While growth in the dedicated industrial zones faces the above constraints, small and medium industries in Damietta continue to grow. An attempt to assimilate the increase in the MSMEs outside residential areas is currently being considered through the conversion of 80 Feddans of land into a zone for new MSME facilities on the Ras El Bar-Damietta road.

The main objectives of the present study were to characterize the soil, water, and sediment pollution with heavy metals and compare it with the permissible international limits in particular for offshore locations in order to figure out its impacts on the Mediterranean Sea pollution.

1.1 The Effect of Different Heavy Metal Pollution on Fish in the Egyptian Mediterranean Coast

The Fishery area of Damietta is one of the most productive coastal zones with high biological diversity for fishes. Cartilaginous fishes (Sharks, and rays), Crustaceans and shrimps, Bivalve and Gastropod Mollusca are present in abundant numbers. There is a large number of bony fish species (e.g. Sardines, Red Mullet, Sea Bream, King Fish, Cuttle Fish, Cutlass Fish, Rabbit Fish, Red Barracuda, Lizard Fish, Sea Bass, Blue Fish, and others.).

The total fish production was 45156 tons, of which Al Borg Village fish production accounted for 12388 tons (about 27.4%) of the total production and the majority was from Mullets fishes and shrimps (2714 and 2139 tons respectively) representing about 39.18% of its total catch. The heavy metals, As, Cd, Pb and Hg are most toxic to all human beings, animals, fishes and environment. The excess levels of heavy metals cause severe toxicity. Though some heavy metals are essential for animals, plants and several other organisms, all heavy metals exhibit their toxic effects via metabolic interference and mutagenesis. The Pb and Hg cause severe toxicity in all. Fishes are not the exception and they may also be highly polluted with heavy metals, leading to serious problems and ill-effects. The heavy metals can have toxic effects on different organs. They can enter into water via drainage, atmosphere, soil erosion and all human activities by different ways.

Table 3: International guideline for heavy metals in water, sediment and fish

Heavy Metals	Water	Sediment	Shrimp Tissues
	Maximum Limit WHO/USEPA (mg/l)	Maximum Limit WHO/USEPA (mg/kg)	Maximum Limit WHO/USEPA (mg/kg)
Cr	0.1	25	1
Mn	0.5	30	1
Ni	0.02	20	0.5-1
Cu	0.05	25	30
Zn	3	123	100
Cd	0.01	6	1
Pb	0.05	10	2
As	0.03	3	-

Table 4: Comparison between heavy metals concentrations obtained in Mediterranean Sea Egypt with those obtained by other authors in Mediterranean Sea

Location	Cd	Cr	Cu	Co	Mn	Ni	Pb	Zn	Reference
Mediterranean Sea Egypt	0.04–0.47	4.08–297.95	0.46–26.26	0.43-26.26	17-1086	1.65–60.25	3.34–53.67	2.05–62.21	[48]
Malaga bay Mediterranean Sea Spain	0.021–0.283	4.31–26	6.57–21.2	-	-	9.48–40.2	7.92–37.1	-	[6]
Mediterranean Sea Morocco	0.14–0.27	88.40–160.97	4.09–29.12	18.06-31.7	256.56-651.66	3.19–79.89	33.11–47.97	64.82–110.77	[26]
Mediterranean Sea Turkey	-	-	-	238-1192	283-1192	28–240	91.3–751	86–970	[29]
Ivra Complex Italy	-	2568–2984	-	100-117	968-1053	2040–2438	0.25	-	[37]
Mediterranean Sea Libya	5–10.5	14.8–24.9	9.1–22.7	8.2-18.1	14.3-49.4	11.6–29.9	8.9–56.9	11.6–30.5	[38]
Eastern Mediterranean Sea Egypt	1.8–2.3	-	4–9.4	-	200.8-254.3	-	18.4–24.8	33.1–42.2	[40]

With increasing heavy metals in the environment, these elements enter the biogeochemical cycle leading to toxicity in animals, including fishes. Table 3 shows the International guideline for heavy metals in water, sediment and fish.

Table 4 shows a Comparison between heavy metals concentrations obtained in Mediterranean Sea Egypt with those obtained by other authors in Mediterranean Sea. It is clear that Libyan Mediterranean coast. Whereas, Co, Mn and Ni showed concentrations lower than those reported in Ivra complex, Italy. On the other hand, the values of Cd, Cr, Cu, Co, Ni, and Pb obtained at the Moroccan Mediterranean coast were very close to those obtained in Mediterranean Sea Egypt. However, the Cr concentrations were higher in the Egyptian Mediterranean coast than those measured in Malaga Bay, and the Libyan Mediterranean coast.

2. Materials and Methods

2.1 Sampling locations and Preparation

According to field sampling plan the following samples were collected:

- Four stations for water samples were selected representing the harbor properly, and three stations were added to cover the open water just outside the harbors. These stations were selected for evaluating the interface between the different water masses inside and outside the harbor. An additional station (station five) was selected at the basin situated in the internal channel, which joins the Damietta Branch of the River Nile to the Harbor.
- Six sediment cores were taken within the port and approach channel at different depths of 0-3 m.
- Ten sediment grabs were taken within the port and the approach channel.
- Heavy metals (Cd, Cr, Cu, Hg, Ni, Pb, and Zn) at all locations will measured in (µg/L), and (Hg is in ng/L).Figure 1 shows the spatial distribution of surface water temperature (°C) at different stations.

Figure 1: Locations of sampling stations

Offshore Water Sampling and Field Measurements

16 offshore stations were studied, the following activities were made: Recording the start and end of sampling time, station number and sea conditions, Recording the transparency of water (measured by lowering a Secchi disc from the lighted side of the vessel), collecting five-liter water sample by lowering a Neskin bottle (5 L capacity) at -5 m, In situ measuring temperature and pH using the multisensory Horiba, Measuring the dissolved oxygen (DO) using Winkler technique, and Fillin a 20 L jar with water from -5 m using the Neskin bottle sampler for toxicity test .

Field QC Samples and Collection Frequency

Data precision and accuracy evaluations were based on blanks from equipment rinsate, field and laboratory duplicates, and matrix spiking exercises. The QC samples were collected at following frequencies:

• One field duplicate for every 20 samples,
• One matrix spike sample and matrix spike duplicate per 20 samples, and
• One sediment grab equipment rinsate blank for every 20 samples.

The equipment rinsate blanks were collected from the gravity core and grab equipment by rinsing the equipment with deionized (DI) water after decontamination. The remaining QC samples were collected during taking. Homogenization process was performed in the laboratory. An equipment rinsate blank of sediment core was obtained by rinsing the sample handling equipment with DI water after decontamination. This blank was collected during core processing.

Field Logs

Field notes for documenting sampling activities were recorded in a separate printed format field logbook plot as follows: Name of the sampling vessel, list of scientific personnel aboard and the name of Survey Task Leader, prevailing weather conditions, sea conditions, station ID, date and time of sample collection, actual coordinates and water for each sampling location, QC information , sample ID (for grab samples), segmentation methods used for each core and sample IDs assigned, any field compositing that was performed, sample preservation methods, chain of custody information for samples collected on each day, and the signature of person maintaining the field logbook

Field Measurement Procedures

The vessel positioning and determination of the actual position of record for each sampling location was accomplished utilizing a differential-GPS unit with the capability of obtaining real-time sub-meter accuracy. Upon recovering the gravity core and securing the gear on

deck for inspection and servicing, the core nose was removed and the core liner immediately sealed by placing a plastic cap over the open end. The core liner was carefully removed from the barrel and measured to determine recovery length and percent recovery. The percent recovery for each core exceeded 80%; lesser values were considered insufficient for actual sample collection. No insufficient recovery was encountered during the present survey as we had to use a specialized diver to make sure that the core penetrated to the full length in the sediments. Additional attempts were made at the discretion of the Survey Task Leader in order to reach the amount of sediments needed for the examination as was designated by the sampling plan. The two attempts were generally considered to constitute for the completion of the sampling effort at each core designated station.

Sample Containers, Preservation, and Storage

Sediment cores were cut into individual segment lengths using a clean decontaminated Swiss made stainless blade. At each end of the segment a plastic cap was installed and fastened securely. Each sample was properly labeled and marked with the word UP to signify the top of core thus preserving the vertical orientation of each segment. Each segment was promptly placed into an ice box cooler and maintained on ice until properly transferred to the lab for processing.

Transportation
All samples were rapped with nylon sheets and cased in cartoon boxes sealed with colored tapes and were transported to the Labs in Alexandria in a coolant deepfreezes car with steel lockers.

2.2 Analytical Procedures and Instruments

Samples were filtered using filtration system through 0.45 µm pore diameter filter disc and then analyzed for heavy elements using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, Perkin Elmer Optima 3000) with ultrasonic nebulizer (USN). This Nebulizer decreases the instrumental detection limits by 10%.

2.2.1. Method

Analysis of heavy metals – The analytical procedures following these criteria:

(a) The limits of detection and quantification are determined for each targeted heavy metal;
(b) The recovery for each targeted heavy metal is between 75 and 125%;
(c) The repeatability of the method is less than 15% RSD; and
(d) A linear response is obtained from the analytical detector within the calibration range.

Reagents – All reagents used were of analytical grade or equivalent and free from any contaminant, which may interfere with the analysis.

Apparatus – Before using the laboratory wares, which have been in contact with the samples, the standard and test solutions, they were cleaned with diluted acids and then rinsed with distilled and de-ionized water.

Preparation of test sample – Representative CMM samples were cut into pieces before grinding, if necessary. Samples were powdered before analysis. Whenever possible, the quantity of sample to be powdered was at least five times as much as those needed for the analysis.

Procedure – The following procedures are applied for the quantitative determination of As, Cd, and Pb contents in samples. The procedures for the analysis of some samples is modified and adopted on demand.

Microwave assisted acid digestion – 0.5 g of the sample was weighed in a PTFE microwave digestion vessel and 7.5 mL of nitric acid add. The vessel was allowed to stand a while until the reaction ceases, then all vessels were sealed properly and placed in vessel modules in the turntable of the microwave unit. Digestion program was started, selecting low-pressure or high-pressure microwave assisted acid digestion depending on the type of microwave digestion vessel available in the individual laboratory. Upon the completion of the program, the mixture was cooled and the vessel was vented manually. The digested sample solution was transferred to a 50 mL volumetric flask and made up to the mark with DI water, then the solution was transferred to a centrifuge tube and centrifuged for 5 min. 10 mL of this solution was pipetted into another 50 mL volumetric flask and made up to the mark with DI water. With this, the test solutions for subsequent instrumental analysis were prepared.

2.2.2 Mercury Analytical Method

Mercury is measured by Flow Injection Analysis-Mercury System Atomic Absorption Spectrometry. The FIMS spectrometer consisted of a flow injection system to prepare the samples for the spectrometer and an AAS specifically designed to measure the absorption of mercury. Samples were collected in polyethylene bottles and stored at 4 °C for a maximum of 28 days. Samples were preserved at time of collection with 2.5 mL of HNO_3 and 5 mL of H_2SO_4.

A Laboratory Control Sample (LCS) was prepared and analyzed for each analyte using the same sample preparations, analytical methods, and QA/QC procedures employed for the test samples. One LCS was prepared and analyzed for each sample batch at a frequency of one LCS for each 20 samples or less. The LCS were within ± 20% of the true value for an aqueous LCS or within the control limits established by the supplier for a solid LCS. If not, the sample batch was reanalyzed. To determine mercury, weigh 3.00 ± 0.01 g into the digestion flask, moisten the samples with a few drops of water, add 21

mL HCl and 7 mL HN03. Pipette 10 mL HN03 into the absorbing vessel. Before analysis, hydroxylamine hydrochloride was added to reduce excess permanganate, and the sample was diluted to 50 ml with deionized water. Total mercury was determined by CVAAS using a Perkin Elmer flow-injection mercury system, FIMS 400 (detection limit of 0.01 ng/g). Standard reference material was used to evaluate the analytical accuracy within 5%. The concentrations measured were 1.32F0.14 Ag/g Hg and 0.60F0.07 Ag/ g Hg, dry weight, with recovery rates of 94% and 102%, respectively. Moisture was determined by weight loss in a separate sub-sample by drying at 110 °C for 2 h.

2.2.3 Reagents and standards

All reagents and standards where be prepared using standard operating procedures appropriate for the media. Reagents and standards for trace metal analyses were stored in trace metal cabinet or other trace metal free environments. All reagents and standards were sealed and transferred to the room containing solely the ICP-OES before analysis and were removed from the room upon completion of analysis.

2.2.4 Calibration and standardization Procedure

Preparation of Calibration Standards: For calibration of the instruments, a series of five standard solutions were prepared by serial dilution of the stock standard solution (1000 ppm) of the metals to be analyzed. The prepared metal concentrations include: 0.2, 0.5, 1, 1.5 and 2 ppm of Zn, Cu, Ni, Cr, Pb and Cd.

Preparation of Spiking Standards: For the spiking processes of the soil samples, a mixture of standard solution containing 1 mg/L of each Zn, Cu, Ni, Cr, Pb and Cd was prepared by serial dilution from 1000 mg/L stock standard solution in to 100 ml volumetric flask and diluting to the mark with double distilled water.

Method Validation: The proposed method was validated by evaluating different parameters as linearity, matrix effect, limit of detection (LOD), limit of quantitation (LOQ), accuracy (in terms of recovery) and precision (in terms of repeatability). Table 3 represent the Wavelength of detection, calibration curve equation, correlation coefficient (R) of the calibration curves, limit of detection (LOD) and limit of quantification (LOQ) obtained for each element. Table 4 shows the Metrological characteristics of the ICP-OES determination of metals in surface waters.

Table 5: Wavelength of detection, calibration curve equation, correlation coefficient (R) of the calibration curves, limit of detection (LOD) and limit of quantification (LOQ) obtained for each element

Element	Wave length (nm)	Calibration equation	R	LOD (µg/g)	LOQ (µg/g)
Zn	206.2	Y = 4226.9x + 26.3	0.9999	0.3	1.2
Cu	324.7	Y= 22876.2x + 180.1	0.9999	0.3	1.2
Ni	221.6	Y=2068.4x + 18.7	0.9999	0.6	1.9
Cr	206.5	Y=4570.1x + 60.3	0.9999	0.5	1.6
Pb	283.3	Y= 1050.3x + 23.4	0.9999	0.3	1.2
Cd	214.4	Y= 1617.2x + 17.8	0.9997	0.1	0.3

Table 6: Metrological characteristics of the ICP-OES determination of metals in surface waters

Element	λ [a]	Precision [b]	Trueness [c]	Trueness by Prof. Teste[d]	Linear range [e]	LOD [f]	LOQ [g]
	nm	%	%	%	mg/L	mg/L	mg/L
Cadmium	214.438	4	101	93	0.001 - 0.10	0.00073	0.0024
Chromium	267.716	4	101	94	0.002 - 0.10	0.00092	0.0031
Copper	324.754	5	102	100	0.002 - 0.20	0.00051	0.0017
Lead	220.353	4	100	100	0.005 - 0.10	0.0039	0.013
Nickel	231.604	9	100	92	0.005 - 0.10	0.0012	0.0040
Zinc	213.856	3	102	103	0.007 - 0.50	0.0012	0.0040

Laboratory Control Sample: The laboratory control sample (LCS) was analyzed in an identical manner as a sample and the results were used to assess accuracy and precision of the analytical method. In this work, three replicates of 0.5 g Li CO were spiked with 1.0 mg/L of₂ ₃ each of Zn, Cu, Ni, Cr, Pb and Cd. The spiked samples were digested like the soil samples including exposure to all glassware, digestion media, apparatus, solvents and reagents that are used with the soil samples. The percent

LCS recoveries for each metal of interest were calculated using the following equation:

$$\% R = \frac{LCS - MB}{S} \times 100$$

where: % R = percent recovery, LCS = Laboratory Control Sample Results,
S = amount of spike added and MB = results of the method blank

Instrument Calibration: The instrument was calibrated using calibration blank and five series of working standard solutions of each metal to be analyzed by using 0.2, 0.5, 1, 1.5 and 2 ppm of Zn, Cu, Ni, Cr, Pb and Cd. The response curves for standard solutions were recorded and all the necessary graph and calculation were done and the results are presented.

3. Results and Discussion

3.1 Copper

During the present study, copper concentrations in water ranged from 36.1 µg/l at station 1 to a value of 70.3 µg/L at station 5, while the average value was recorded as 46.8 µg/L. The distribution of Cu in port bottom sediments of Damietta Harbor ranged from 47.1 µg/g at station R6 to 7.25 µg/g at station R1, with an average of 20.1 µg/g. A decreasing trend of Cu concentrations was observed as moving away from the port area towards coastal waters. These trends of metal distributions are mostly related to the recent dumping of the dredged material on the port site.
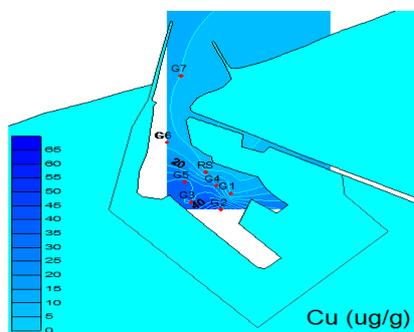
Figure 3: Distribution of Cu (µg/g) in marine bottom sediments of Damietta port

The concentrations of Cu were generally lower than those of the other investigated metals Cr, Zn, Ni and Pb, but higher than Cd. The Cu concentration ranged from 41.2 µg/g dry wt in core # 2 (1.5 - 2.0 m); to 4.35 µg/g dry wt core # 6 (2.00 - 3.00 m). Cu values were recorded in cores 3 and 2, while the lower values were recorded in core # 4 (Figure 4). This shows that the Cu concentration is much higher in Damietta port than across the access channel. However, these values are still in the range of the target values for the DUTCH standard.
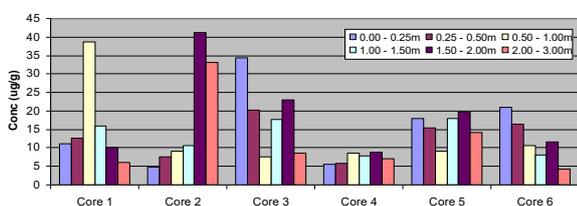

Figure 4: Distribution of Cu (µg/g) in different core segments at Damietta port

3.2 Lead

Very high concentrations of total lead were detected during the present work, which indicate the presence of a source for continuous lead input to the harbor. More investigations are needed for identifying the sources of this pollution. Lowest lead concentration was recorded at station 6 (129 µg/L), while the highest concentration was found at the station 5 (215 µg/L) at the internal channel. The average concentration attained a value of 176 µg/L. According to IARC (1980), lead levels in coastal waters ranged from 0.08 to 0.4 µg/L, with a background concentration in the Mediterranean, the Pacific and the Atlantic of 0.03-0.04 µg/l (below 1000 m).

The distribution of Pb in the coastal waters of Damietta Port showed a maximum at the station E1 (4.12 µg/L) and a minimum at the station R1 (1.33 µg/L), with an average value of 2.44 µg/L. The concentrations of Pb in the marine bottom sediments of Damietta port show a maximum at the station P2 (115 µg/g) and a minimum at the station R4 (5.35 µg/g), with an average of 47.1 µg/g. The distribution of Pb in marine bottom sediments of Damietta port is shown in Figure 5. The Pb concentration of marine sediment ranged from 107 µg/g at the station G8 to 26.5 µg/g at the station G1, with an average of 51.9 µg/g.
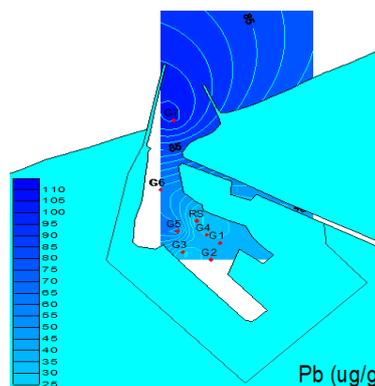

Figure 5: Distribution of Pb (µg/g) in marine bottom sediments of Damietta port

The distribution of Pb concentrations in different segments of the core samples is given Figure 6. The maximum detected concentration of Pb (128 µg/g dry wt.) was recorded in core # 1 (1.5 - 2.0 m), while the minimum content (3.08 µg/g dry wt.) was recorded in core # 6 (2.00 - 3.00 m).
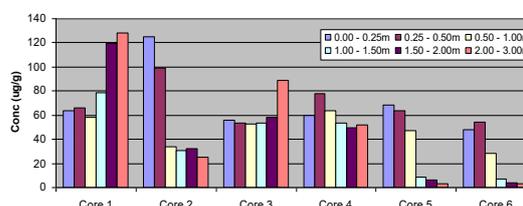

Figure 6: Distribution of Pb (µg/g) in different core segments at Damietta port

3.3 Cadmium

The obtained results of total cadmium during the present study showed that minimum concentration was recorded at station 5 (21.6 µg/L) belonging to the internal channel, while maximum concentration was detected in station 8 (30.2 µg/L), with an average value of 25.3 µg/L. Background levels of Cd in surface coastal waters was found to attain 0.05 µg/L, while they ranged in open ocean waters from 0.01 to 0.1 µg/L (Eisler, 1985). The distribution of Cd (µg/L) in the coastal waters of Damietta Port ranged from 0.41 µg/L at station E4 to 0.07 µg/l at station R2, with an average of 0.22 µg/L.

On the other hand, the distribution of Cd concentrations in marine bottom sediments of Damietta port ranged from 2.75 µg/g at station R4 to 0.44 µg/g at station R3, with an average of 1.22 µg/g. A decreasing trend of Cd concentration was observed as moving away from the port area towards the coastal waters (Figure 7). The Cd concentration in coastal waters of Damietta Port ranged from 2.39 µg/g at station G10 to 1.18 µg/g at station G3, with an average of 1.75 µg/g.
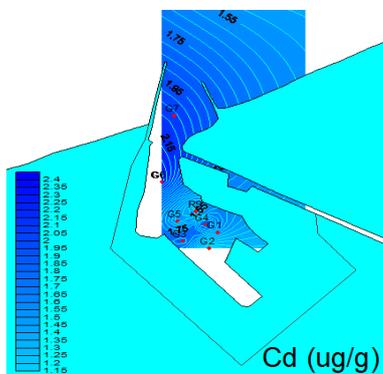

Figure 7: Distribution of Cd (µg/g) in marine bottom sediments of Damietta port

The distribution of the different Cd concentrations in the core sediment samples is given in Figure 8. The maximum detected Cd concentration of 5.60 µg/g dry wt. was recorded in core 4 at a depth 0.00 - 0.25 m, while the minimum one (0.02 µg/g dry wt.) was detected in core 2 (2.00 – 3.00 m).
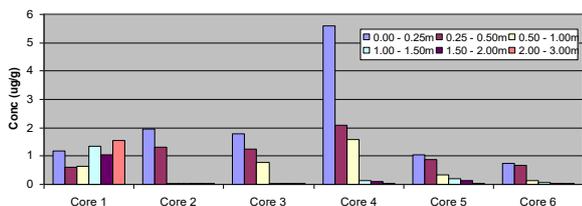

Figure 8: Distribution of Cd (µg/g) in different core segments at Damietta port

According to Figure 8, Core # 4 showed the highest Cd concentrations inside Damietta port, while the values

were much lower across the access channel. It is important to mention that even the higher values of Cd can still be considered as similar to the VORM target level for Cd (0.8 µg/kg).

3.4 Chromium (Cr)

The distribution of Cr in the coastal waters of Damietta Port ranged from 0.62 µg/L at the station E1 to 0.09 µg/L at the station R4, with an average value of 0.30 µg/L. On the other hand, the distribution of the Cr concentrations in the marine bottom sediments of Damietta port ranged from 603 µg/g at the station P4 to 171 µg/g at the station E2, with an average of 341 µg/g. The distribution of Cr concentrations in marine bottom sediments of Damietta port is shown in Figure 9. A decreasing trend of Cr concentration was observed as moving from the port area towards the coastal waters. In general, the levels of Cr are higher than the VORM values.
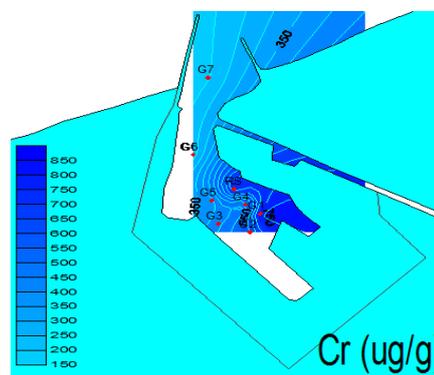

Figure 9: Distribution of Cr (µg/g) in marine bottom sediments of Damietta port

Cr Concentrations in the study area are generally higher than those of the other metals (Cd, Cu, Zn, Ni, and Pb). The distribution of the different Cr concentrations in the core sediment samples is given in Figure 10. The maximum detected Cr concentration of 928 µg/g dry wt. was recorded in core 2 (0.5-1.0m), while the minimum value of 161 µg/g dry wt. was recorded in core # 4 (0.0-0.25 m). The maximum Cr values were recorded in cores 1 and 2 while the lower values were recorded in core # 6. This shows that the Cr concentrations are much higher in Damietta port than across the access channel.
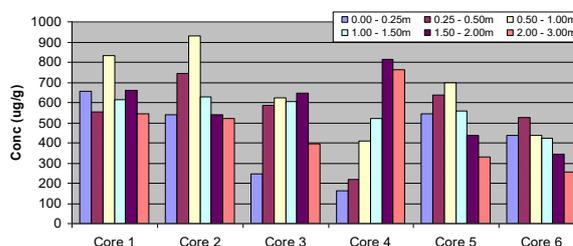

Figure 10: Distribution of Cr (µg/g) in different core segments of Damietta port

3.5 Mercury (Hg)

Mercury is probably one of the most investigated natural elements and potential contaminants in the world and, in particular, in the Mediterranean. The distribution of Hg in the coastal waters of Damietta Port ranged from 28.5 ng/L at station E3 to 9.52 ng/L at station R3, with an average value of 17.5 ng/L. These trends of metal distributions are mostly related to the recent dumping of the dredged material in the site. The concentrations of Hg were generally much lower than those of the other metals (Cr, Zn, Cu, Cd, As, and Ni). The distribution of the Hg concentrations in the marine bottom sediments of Damietta port ranged from 0.14 ng/g at station E2 to 0.05 ng/g at station R2, with an average of 0.10 ng/g.
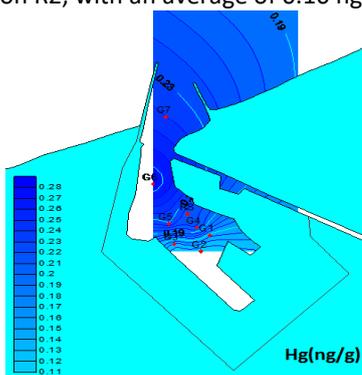

Figure 11: Distribution of Hg (ng/g) in marine bottom sediments of Damietta port

The distribution of Hg concentrations in the marine bottom sediments of Damietta port is shown in Figure 11. The distribution of the concentrations of Hg for the different segments of the core samples is given Figure 12. The maximum detected Hg concentration of 0.21 ng/g dry wt. was recorded in core 2 (0-0.25m) and core 5 (0.25 - 0.50 m), while the minimum content of 0.03 µg/g dry wt. was detected in core # 1 (2.00 - 3.00 m).
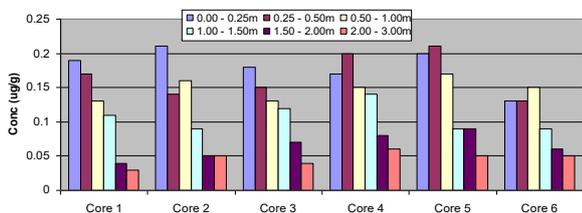

Figure 12: Distribution of Hg (ng/g) in different core segments at Damietta port

3.6 Nickel (Ni)

The distribution of Ni in coastal waters of Damietta Port ranged from 1.47 µg/L at the station E4 to 0.11 µg/L at the station R2, with an average value of 0.62 µg/L. These trends of metal distributions are mostly related to the recent dumping of the dredged material. The distribution of Ni concentrations in the marine bottom sediments of Damietta ranged from 347 µg/g at the station E3 to 106

µg/g at the station R2, with an average of 233 µg/g. A decreasing trend in Ni concentrations was observed moving away from the Damietta port towards the coastal waters along the access channel Figure 13.
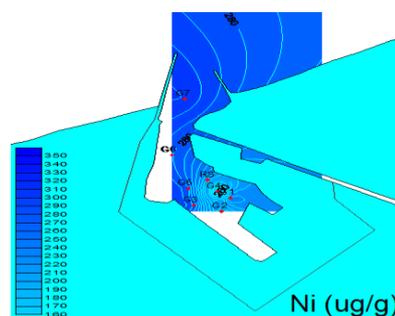

Figure 13: Distribution of Ni (µg/g) in marine bottom sediments of Damietta port

The distribution of Ni concentrations for the different segments of the core samples is given Figure 14. The maximum detected Ni concentration of 420 µg/g dry wt. was recorded in core 3 (0-0.25m), while the minimum content of 27 µg/g dry wt. was detected in core # 6 (2.00 - 3.00 m).
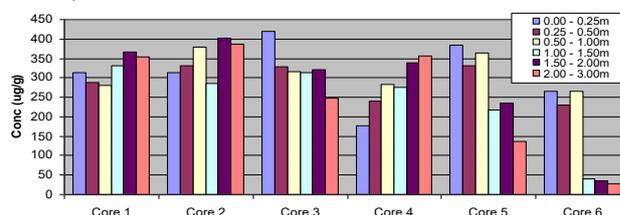

Figure 14: Distribution of Ni (µg/g) in different core segments at Damietta port

3.7 Zinc (Zn)

The distribution of Zn in the coastal waters of Damietta Port ranged from 28.0 µg/L at the station E1 to 10.5 µg/L at station R2, with an average value of 18.5 µg/L. These trends of metal distributions are mostly related to the recent dumping of the dredged material. The distribution of Zn concentrations in the marine bottom sediments of Damietta port ranged from 139 µg/g at station E4 to 27.1 µg/g at station R8, with an average of 79.1 µg/g.
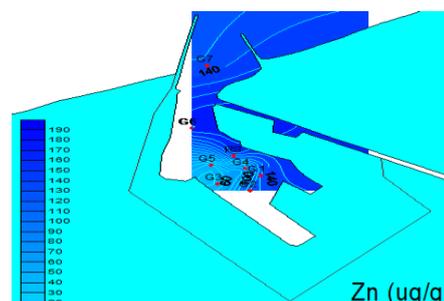

Figure 15: Distribution of Zn (µg/g) in the marine bottom sediments of Damietta port

The distribution of Zn concentrations in the marine bottom sediments of Damietta port is shown in Figure 15. The distribution of the total concentration of zinc in different core segments is given in Figure 16. The maximum detected Zn concentration of 144 µg/g dry wt. was observed in core #1 (0.5 - 1.0 m), while the minimum content of 52.8 µg/g dry wt. was detected in core # 1 (1.00 - 2.00 m). Zn concentrations in the sediments of the study area are less than the target values for the DUTCH standard for soil.

3.8 Summary of the Heavy metal pollution at New Damietta Harbor

The spatial variations of the total concentrations of the investigated heavy metals (Cd, Cr, Cu, Pb, Hg, Ni, and Zn) in the coastal area of Damietta port for both water (µg/L) and bottom sediments of Damietta port (µg/g) are given in Tables (7.1 to 7.3) respectively.
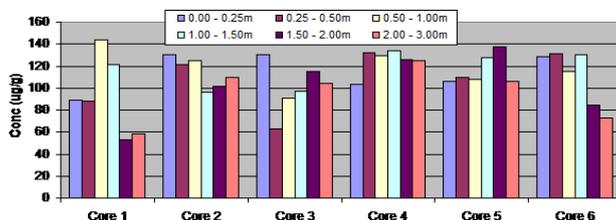

Figure 16: Distribution of Zn (µg/g) in different core segments at Damietta port

Table (7-1): Heavy metals concentrations (µg/L) in the coastal waters of Damietta port (Hg is in ng/L)

Station	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Pb (µg/L)	Hg (ng/L)	Ni (µg/L)	Zn (µg/L)
Average	0.24	0.22	0.30	1.18	2.44	17.49	0.62	18.50
Max	0.41	0.41	0.62	2.41	4.12	28.54	1.47	28.04
Min	0.10	0.07	0.09	0.48	1.33	9.52	0.11	10.47

Table (7-2): Heavy metals concentrations (µg/g) in the marine bottom sediments off Damietta port (Hg is in ng/g)

Station	Al %	As (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Pb (µg/g)	Hg (ng/g)	Ni (µg/g)	Zn (µg/g)
Average	4.90	7.40	1.22	341	20.1	47.1	0.10	233	79.1
Max	5.11	9.23	2.75	603	47.01	115	0.14	347	139
Min	4.57	4.88	0.44	171	7.25	5.35	0.05	106	27.1
DUTCH VALUES • Target • Intervention		29 55	0.8 12	100 380	36 190	85 530	0.3 10	35 210	140 720

Table (7-3): Heavy metals concentrations (µg/g) in the marine bottom sediments of Damietta port and the access channel ((Hg is in ng/g)

Metal	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Pb (µg/g)	Hg (ng/g)	Ni (µg/g)	Zn (µg/g)
Average	1.75	460	23.7	51.9	0.19	256	102
Max	2.39	821	65.3	107.	0.28	346	181
Min	1.18	191.	8.50	26.5	0.11	137	29.5
DUTCH VALUES • Target • Intervention	0.8 12	100 380	36 190	85 530	0.3 10	35 210	140 720

The average maximum concentration of heavy metals in the coastal waters of Damietta Port was recorded for Zn and Hg (18.5 µg/L and 17.5 ng/L respectively). The average minimum values were recorded for As, Cd and Cr (0.24, 0.22 and 0.30 µg/L respectively) (Table 7-1). In general, the existing and the proposed sites showed the highest concentrations of heavy metals as compared to those of the reference stations.

The average maximum concentration of heavy metals in the marine bottom sediments of Damietta Port was recorded for Cr and Ni (341 and 233 µg/g respectively) (Table 7-2). The average minimum values were recorded for Cd and Hg (1.22 µg/g and 0.10 ng/g respectively) (Table 7-2). In general, the existing and the proposed sites showed the highest concentrations of heavy metals as compared to those of the reference stations. However,

the recorded metals' concentrations are lower than the DUTCH Standard for soil.

The average maximum concentration of heavy metals in the marine bottom sediments at Damietta Port and along the access channel was recorded for Cr and Ni (460 and 256 µg/g respectively) (Table 7-3).

The average minimum values were recorded for Cd and Hg (1.75 µg/g and 0.19 ng/g respectively). In general, the existing and the proposed sites showed the highest concentrations of heavy metals as compared to those of the reference stations. The distribution of each element at different sites of Damietta port and its access channel, and in the coastal waters of Damietta port is given below. Except for Cr, the recorded metals' concentrations are lower than the DUTCH Standard for soil (so called VROM). The concentrations of the metals are less than the target values of VROM standard.

3.9 Comparison of the Heavy metal pollution at Mediterranean Region with the Study Area

Table 8 shows that Western harbor, Egypt is considered as polluted with Pb when compared the upper crusts (20 µg/g) [47], average shale (20 µg/g) [49], and the mean sediments (19 µg/g) [41]. The level of Pb in sediments of the Middle and the Eastern region were in agreement with levels, which indicate its normal concentrations and reflect the background concentrations in sediments. Sadiq *et al*. (2003) reported that low concentrations of Pb still might pose a threat to life in marine environment compared with other heavy metals. Table 8 further shows that the values obtained in this study are in agreement with the results of Alomary and Belhadj for the coast of Algeria (2007) and lower than the results obtained by Gargouri *et al*. (2010) for the coast of Sfax, Tunisia, (Caredda *et al*. (1999) for Sardinia, Italy, Fernex *et al*. (2001) for Mediterranean Sea, France, Feldstein *et al*. (2003) and higher than the results reported by Sabhi *et al*. (2000) for the Moroccan Mediterranean coast.

Table 8: Concentration of heavy metals (µg/g) in sediments of the New Damietta Harbor compared with other locations along the Mediterranean coast

Location	Cd	Cu	Cr	Ni	Zn	Pb
New Damietta Harbor	0.44-2.7	7.25-47.1	8.5-65.2	106-347	27.1-139	5.35-115
Western harbor, Egypt [19]	0.61-2.44	39.2	33-649	13-53	58.5-382	38-1,070
Western harbor, Egypt [36]	0.07-0.64	0.3-19	NA	NA	0.23-4.74	NA
Pasajes harbor, Spain [33]	1.2-6.64	25-3,726	NA	17-99	477-1,390	45-346
Coast of Sfax, Tunisia [23]	5.5.07	13-29	41-82	Jul.55	39-117	18-88
Taranto Gulf, Italy [13]	NA	42.4-52.3	75.2-103	47.9-60.7	86.8-129	44.7-74.8
Nables Harbor, Italy [3]	0.2-2.5	40-415	10.3-162	NA	41-1,196	37-314
El-Mex Bay, Egypt [1]	4.3-11.9	11.5-52.2	27.6-115	NA	89.3-592	NA
Algeciras Bay, Spain [17]	0.1-22	05.25	30-251	19-144	33-117	12.39
Mediterranean Sea, Algeria [5]	0.1-2.3	1.1-10.4	2.6-18.9	0.8-54.9	5.3-45.7	1.3-11.5
Mediterranean Sea, France [21]	0.15-3.4	14-82.6	NA	NA	29.4-509	20.1-394
Sardina, Italy [14]	0.21-13.4	2.77-51.3	NA	0.9-51.3	198-3,239	74-772
Abu Qir Bay, Egypt [31]	0.08-3.54	0.95-127	4.66-186	2.05-40.5	5.77-717	2.71-129
Themaikos Gulf, Greece [57]	0.3-8.4	32-130	21-470	63-130	84-537	38-190
Moroccan Med. Coast[43]	0.03-0.25	1.2-6.7	NA	NA	9.2-37.7	0.18-0.25

NA: Not available

Assessment of the Metals in the Investigated Area

To assess the anthropogenic influence in the study area, enrichment factors were calculated for the investigated total metals according to Szefer *et al*., (1998). The enrichment factor (EF) was calculated according to the following equation:

EF = (Ms /ALS) / (M$_b$ / Al$_b$)

Where Ms: Concentration of metal in sediment sample
ALS: % of Al in sediment sample
M$_b$: background concentration of metal

Al$_b$: background % of Al

EFs of unity indicate that the metal is incorporated in the sediment dominantly as lithogenous material, whereas EFs much greater than unity indicate that the element is incorporated in the sediment dominantly as anthropogenic material (Glasby and Szefer, 1998).

The background levels of total metals concentration recorded by Wedepohl (1969 – 1974) in the earth's crust are presented in Table (9). The enrichment factor was calculated depending on the average concentration of the two regions; the offshore region and the other region from G1 to G10 sediment samples.

Table 9 : Enrichment Factor (EF) calculated for surficial sediments of the study area

Trace Metals	Concentration of the earth's crust (Wedepohl: 1969 – 1974)	EF (Coastal area)	EF inside Damietta Port (G1 – G10)
Zn µg/g	100.00	1.2	1.6
Cu µg/g	100.00	0.3	0.4
Cr µg/g	200.00	2.5	3.5
Cd µg/g	0.20	8.9	12.2
Pb µg/g	19.00	3.6	4.1
Ni µg/g	150.00	2.4	2.6
Hg µg/g	0.08	2.0	4.1

The analytical data revealed a marked increase in the levels of Cd, As, Hg, Pb, Ni, Cr, and Zn. On the other hand, the EF of Cu showed low value; less than unity indicate that the metal is incorporated in the sediment dominantly as lithogenous material. The high values of EFs showed the accumulation of trace metals in the sediments of study area. The magnitude of pollution by the metals can be arranged in the following sequence:

Cd > As > Hg > Pb > Cr > Ni > Zn > Cu

Conclusions

The average maximum concentrations of heavy metals in the marine bottom sediments of Damietta Port were recorded for Cr and Ni as 341 and 233 µg/g, respectively. The average minimum values were recorded for Cd and Hg as 1.22 µg/g and 0.1 ng/g, respectively.

The distribution of each element at different sites of the Damietta port and its access channel, and in the coastal waters of Damietta port is high with regard to the concentrations of the heavy metals away from the harbor towards the Mediterranean Sea site. The distribution of different trace elements in the study area was highly related to the dredging process and its dumping on the site of Damietta port. If it is considered that the concentrations of the trace metals, reported for water–quality criteria (WQC), are 20 mg/L for Zn, 10 mg/L for Cu, 2 mg/L for Ni, and 10 mg/L for Pb, the concentrations found in this investigation are lower than the values given in the water–quality criteria.

The study area lies within the Middle region and its resulted that from this study and previous studies that the distribution of Fe, Mn, and Ni, among the three regions of the study area was similar and arranged as the following: Middle region> Eastern region> Western region.

The analytical data revealed a marked increase in the levels of Cd, Hg, Pb, Ni, Cr, and Zn. On the other hand, the EF of Cu showed low value; less than unity indicate that the metal is incorporated in the sediment dominantly as lithogenous material. The high values of EFs showed the accumulation of trace metals in the sediments of study area. The magnitude of pollution by the metals can be arranged in the following sequence:

Cd > Hg > Pb > Cr > Ni > Zn > Cu

While, the distribution of Zn, Pb, Cd are also similar and arranged as the following: Western region> Middle region> Eastern region. Copper was distributed among the three regions of the study area as the following: Middle region > Western region > Eastern region. The distribution of chromium was different from the other elements and its distribution among the different regions of the study area was as the following: Eastern region> Middle region> Western region.

Recommendations

From the outcomes of this study, the authors draw a number of recommendations as given below

- Egyptian Environment Law number 4 of the year 1994, enacted by the Minister of Environmental Affairs after consulting the Board of Directors of the Environmental Affairs Agency, should include the limits for water quality inside the harbor as it only specifies the criteria and specifications for certain substances when discharged into the marine environment.
- Egyptian Environment Law number 4 of the year 1994 only gives limits in cases, when discharged into the marine environment, which is not permitted, except at a minimum distance of 500 meters from the shoreline, and may not affect fishing zones, bathing zones or nature reserves in order to preserve the economic or aesthetic value of the area it should mention marine quality.
- This Egyptian Environment Law number 4 only contains just one chapter for pollution from ships. In this chapter, it recommends to identify the limits for oil pollution and the environmental monitoring plan in harbor waters.
- This Environment Law should also specify the water quality standards for coastal waters and marine outfalls, as in the coastal segment, marine water is subject to several types of uses. Depending of the types of uses and activities, water quality criteria should have specified in order to determine its suitability for a particular purpose. ***Class designated for best use recommendation to be as follows:***
- *Salt pans, Shell fishing, Maricultural and Ecologically Sensitive Zone,*

- *Bathing, Contact Water Sports and Commercial fishing,*
- *Industrial cooling, Recreation (non-contact) and Aesthetics,*
- *Harbors, and*
- *Navigation and Controlled Waste Disposal.*
- National institutions carrying out marine pollution monitoring and research should be supported, further developed and, when necessary, newly established in order to formulate and to conduct pollution control and to develop abatement measures.
- The state authorities should commit themselves with international agreements and national environmental laws and regulations.
- A Management Information System should be established that stores all previous information and data that will help in future developments, management and restoration of the Egyptian Mediterranean coastal zone.
- Suitable monitoring systems should be installed for the determination of trace metals in fish, water and sediments in the study area for the purpose of public and environmental health.
- More investigations about the currents and water budget in the area are needed to recognize and evaluate the research findings.
- More investigations should have done on fish especially on the around coast area as the heavy metals, As, Cd, Pb and Hg are most toxic to all human beings, animals, fishes and environment, the excess levels of heavy metals cause severe toxicity.

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