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Assessment of organic and inorganic pollutants in the offshore sediments, Dubai, UAE.

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United Arab Emirates University
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ASSESSMENT OF ORGANIC AND INORGANIC POLLUTANTS IN

THE OFFSHORE SEDIMENTS, DUBAI, U.A.E.

By

Haifa Darwish Ahmad Al Darwish

A thesis
Submitted to

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2004

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**United Arab Emirates University
2003/2004**

DEDICATION

To the person who is so missed to me . . . .

Who means everything to me . . . .

To the source of my power and pride . . . .

Who gave without limitations . . . .

Cared without Hesitation . . . .

To my first teacher . . . . To my great father.

Haifa Al Darwish

ACKNOWLEDGEMENTS

ABSTRACT

The investigated area covers the maximum fragments of Dubai offshore in the Arabian Gulf. The sediment samples were collected from fifteen stations starting by Al-Mamzar mouth and ending by Ras Ghantoot in order to assess the organic and inorganic pollutants affecting the coastal region in Dubai.

The textural class was determined through grain-size analysis and the mineral composition was identified by X-ray diffraction. The organic pollutants were characterized through the determination of total organic carbon (TOC), total Kjeldahl nitrogen (TKN), total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and individual polychlorinated biphenyls. On the other hand the inorganic pollutants were carried out by determination of some major oxides and trace elements concentrations, including heavy metals.

The present study indicates that most of the investigated area is covered by unpolluted sediments except for the northeastern part of the investigated area, which reflects a heavy polluted case. High levels of TOC, TKN, TPH, PAHs and PCBs, in addition to Cu, Pb and Zn were reported at station 6 (Al-Hamriya St 3). Al-Hamriya St 3 represents the most contaminated station. But the highest values of TKN, Fe, Mg, Cr, Ni and V were reported at stations located in the southwestern part (Dewa and Dubal).

High positive correlation between TPH and TOC suggests that TOC could be used as indicator of oil pollution in heavily oiled sediments. The frequency distribution of pollutants in the study area and the high relative S.D suggest an anthropogenic source. The association of copper, lead and zinc with TPH and TOC in absence of V and Ni

suggests that these pollutants are not related to crude oil and can be attributed to the presence of other contaminants. The negative correlation between Na and each of TPH, TOC, TKN, Cu, Pb and Zn may be give evidence of freshwater input.

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CHAPTER I

INTRODUCTION

1.1 General

INTRODUCTION

1.1 General

As the use of coastal areas has increased for residence, recreation and commerce purposes, pollution of coastal waters has increased as well. Coastal waters are in greater risk of being polluted than the open ocean for two reasons:

(i) More pollution is dumped into coastal waters than into the open ocean;

(ii) Coastal waters are not well circulated as the open ocean.

Thus, many of the concerns of pollution are focused on coastal waters (Thurman and Trujillo, 1999). As far as the marine environment is concerned, there is a great difficulty in assessing the degree to which pollution is occurring. Therefore, scientists cannot tell how these pollutants have altered the marine environment.

In essence, there is no adequate baseline studies from which scientists can compare polluted versus unpolluted regions. And since the marine environment is affected by decade- to century- long cycles, it is difficult to determine whether a change is due to a natural biologic cycle or whether it is caused by any number of introduced pollutants, many of which combine to produce a new compound (Thurman and Trujillo, 1999). The majority of new chemical compounds created each year are organic (carbon-containing) complexes. Many thousands of these compounds, both naturally occurring or synthetic, are widely used as herbicides and pesticides, as well as in a variety of industrial processes. Some are carcinogenic, some are directly toxic to humans or other organisms and others make water unpalatable. Some also accumulate in organisms as the heavy metals do.

Oil spills, are one source of organic compound pollution. At least as much additional oil pollution occurs each year from the careless disposal of used crankcase oil, dumping of bilge from ships and the runoff of oil from city streets during rainstorms (GESAMP, 1993 and Montgomery, 1995). Oil is a complex mixture of hydrocarbons and other substances, including the elements oxygen, nitrogen and sulfur with various trace metals. The other kind of organic compound pollution is polychlorinated biphenyles (PCBs). The laboratory tests revealed that PCBs have been implicated in reproductive and immunological abnormalities observed in terrestrial bird and in marine mammal populations. Also caused stomach, and liver ailments and other problems (Boon *et al.*, 1992 and Montgomery, 1995). Many of the inorganic industrial pollutants are potentially toxic metals. Manufacturing, mining and mineral-processing activities can all increase the fluxes of these naturally occurring substances into the environment and locally increase concentrations from harmless to toxic levels (Montgomery, 1995).

The organic compounds have fertilizing effect on the marine environment. The breakdown of excess organic matter not only consumes oxygen, but also releases a variety of compounds into the water, among them nitrates, phosphates and sulfates. Their abundance in water strongly encourages the growth of plants, including algae. This development is known as eutrophication of the water; the water itself is then described as eutrophic. Decomposition of algal plants can lead to severe depletion of oxygen in the water column, which cause mortality among fish (Montgomery, 1995). Reproductive, developmental and behavioural processes are very sensitive to exposure to hydrocarbons. The acute toxicity occurs due to components of the water-soluble fractions and dependent upon conditions and duration of exposure based on GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Pollution, 1993) reports.

Heavy metals such as Cd, Pb, Ni, V, Cu, Cr and Zn have toxic effect on the ecosystem.

Heavy metals are persistent toxicants and accumulate in living tissues for many years; the high concentrations of trace metals can cause acute damage to aquatic life. Mining and processing heavy metals in particular can increase the rate at which the heavy metals weather out of the rock into the environment. Some industries have also discharged concentrated doses of heavy metals into water bodies. Petroleum production, fertilizers and chemical industry are another sources of heavy metals to the marine environment (Montgomery, 1995). Studies of trace elements have also included the possibility that the transfer of these elements through food chains may adversely affect human health. The effects of lead on marine biota have been reviewed by GESAMP (1985). Most of the acute toxicity experiments with marine organisms indicated that effects were seen only after exposure to high concentrations.

In light of a high production of petroleum from the Arabian Gulf countries together with the transportation of increasingly large quantities, an increase in petroleum hydrocarbon levels in the marine environment of United Arab Emirates along the Arabian Gulf is expected (Shriadah, 1998a). In addition due to the industrial activities which, concentrated around Dubai Creek, Al-Hamriya and Dry Docks, it is expected that these areas may show high levels of organic and in organic pollutants. Besides affecting human health through the food web these pollutants pose a great threat to marine ecosystem in different ways and reduce the recreational utility of coastal waters.

1.2 Literature Review

Several researchers provided significant information on the concentration of petroleum hydrocarbon and heavy metals in the sediments in many parts of the world. Such studies reflected the levels of oil and trace metal pollution in the Gulf post- 1991war. Fowler *et al.* (1993) concluded that the post-war levels of PAHs in sediments were no higher than

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concentrations, which have been reported for coastal areas in northern Europe and the United States. Also his observations have demonstrated that concentrations of trace metals are somewhat elevated in heavily oiled sites of nearshore Gulf sediments.

Literathy (1993) provided a reasonable interpretation for the low level of petroleum-related compounds post- 1991 war. This was referred to the high rate of oil degradation and transformation due to the high temperature and strong solar radiation intensity, which result in fast photo-oxidation of poly aromatic compounds.

Basaham and Al-Lihaibi (1993) reported that trace metals concentrations in the sediments of Western Gulf showed a spread of values that was related to the variable sediment composition. The total and non-detrital element concentrations in the different types of sediments were within the range published in the literature for unpolluted areas.

Massoud et al. (1996) suggested that polluted areas reflected the direct effect of the 1991 Kuwait oil slick. The high levels of TPH found at muddy sediments. On other hand TOC measurements were not found to be useful indicators of petroleum hydrocarbon pollution in these marine sediments throughout the Arabian Gulf.

There is few data available on the levels of hydrocarbons in the sediments, especially from the Arabian Gulf coasts of UAE. Information on the hydrocarbons and heavy metals, biological productivity, and biodiversity of Dubai coastal region has been published by the EPSS (Environment Protection and Safety Section) of Dubai Municipality as annual reports (Dubai Municipality, 1996).

Valuable information on trace metals contents in bottom sediments of the Arabian Gulf were provided by Al-Abdali et al. (1996). With exception of Fe, all chronic and present-day trace metal concentrations were found to be within the permissible natural background

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levels in offshore areas. This indicates that the oil slick had minimal effect on the state of pollution by trace metals in the Arabian Gulf.

Shriadah (1998a) reported, based on data provided from several areas around the world, that most of the sediments collected from the Arabian Gulf coasts of UAE contained quantifiable amount of petroleum hydrocarbons. Also he found in his study on the levels and distribution of petroleum hydrocarbons in the coastal waters and sediments of the UAE in the Arabian and the Gulf of Oman that the sediments contained appreciable quantities of petroleum hydrocarbons. Total organic carbon could be considered as an indicator of hydrocarbon contamination only when the total petroleum hydrocarbons are present in high levels.

Al-Qubaisi (2001) reported that the concentration of organic carbon in the coastal areas of UAE were comparable with the data which, described by previous researchers on the same environment. The low values of various metals indicate that sediments of the offshore of UAE have minimum metal pollution accumulations except of Ni (Al-Qubaisi, 2001).

Data on heavy metal pollution in bottom sediments in Dubai coastal region has been provided by El-Sammak (2001). He concluded that the results were comparable to the previous published data, especially those on the same area. The discrimination of the area into two regions is mostly based on the organic matter, carbonates, and the variation in the metal contents. The lowest values for pollution load index (PLI) were found in lagoon area, while the highest values were found in the creek channel.

Recent report on the level of heavy metals in Dubai Creek has been published by Deshgooni (2002). It was concluded that there are two distinct geochemical zones characterize Dubai Creek. One identified as a polluted upstream region, and the other one is comparatively less

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polluted downstream region. The level of heavy metals is 8 times higher in the downstream and 23 times higher in upstream than the reference station of Dubai Coastal Environment. After the Gulf War 1991, many investigators concerned about the marine pollution and the effects of Kuwait oil slick on the marine environment and aquatic life.

1.2.1 Oil Pollution

Several studies have thrown light on the level of hydrocarbons and heavy metals in sediments. Many investigators have examined the impact of the 1991 Gulf War on marine environment. Hydrocarbon distribution in surface sediments from Kuwait, Bahrain and Oman Coastal zones (before the Gulf War) were documented by Mille *et al.* (1992). Gundlach *et al.* (1993) reported the distribution of oil along the Saudi Arabian Coastline as a result of the Gulf war oil spills. Literathy (1993) assessed the environmental consequences of the 1991 Gulf war. Gupta *et al.* (1993) reported the state of oil pollution in the northern Arabian Sea after 1991 Gulf oil spill. There is also a study proposed by Sauer *et al.* (1993) on hydrocarbon source identification and weathering characterization of intertidal and subtidal sediments along the Saudi Arabian coasts after the Gulf war oil spill. Michel *et al.* (1993) investigated contamination of the nearshore subtidal sediments of Saudi Arabia as a result of the Gulf war oil spill. Ehrhardt and Burns (1993) studied hydrocarbon pollution and the related photo-oxidation products in Saudi Arabian Gulf coastal waters. Massoud *et al.* (1996) studied the Total Petroleum Hydrocarbon (TPH) and the Total Organic Carbon (TOC) contents in the bottom sediments of the Arabian Gulf as indicators of oil pollution and implications for the effect and fate of the Kuwait oil slick. Shriadah (1998a) measured the concentrations of petroleum hydrocarbons along the Arabian Gulf coast of the United Arab Emirates. Study on the levels and distribution of petroleum hydrocarbons in the coastal waters and sediments of the United Arab Emirates in the Arabian Gulf and Gulf of Oman were carried out by Shriadah (2000). Paimpillil and

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Dennis (2002) conducted a study on the contamination of the coastal aquifer of Yanbu (Red Sea) region with oil seeping from the nearby landfills.

1.2.2   Trace Elements

On the other side, trace metals in sediments in the Arabian Gulf have been subjected to several investigations. Earlier study has been carried out by Abaychi and Douabul (1986) on the trace element geochemical associations in the Arabian Gulf. Fowler *et al.* (1993) assessed the temporal and spatial trends of petroleum hydrocarbons and trace metals in nearshore Gulf sediments and biota before and after the 1991 war. Al-Arfaj and Alam (1993) discussed the chemical characterization of sediments from the Gulf area after 1991 oil spill. Price (1993) performed a study on human impacts and management initiatives in the Gulf. Al-Abdali *et al.* (1996) used trace metal contents of bottom sediments of the Arabian Gulf as indicators of pollution and implications for the effect and fate of the Kuwait oil slick. Heavy metal characterization in the mangrove sediments of the United Arab Emirates shoreline was carried out by Shiradah (1998b). El-Sammak (2000) investigated the geochemical associations in the marine sediments of Ras Al-Kheimah, UAE. Recent study carried out by Al-Muzaini and Beg (2002) on contamination of toxic trace metals in the coastal sediments of the Shuaiba Industrial Area in Kuwait.

There are few published materials on the assessment of heavy metals offshore area of Dubai. Al-Qubaisi (2001) assessed the metals pollution in sediments of the coastal areas, UAE, including Abu Dhabi, Dubai and Sharjah. El-Sammak (2001) determined the extent of heavy metals pollution in bottom sediments of the Dubai creek. Deshgooni (2002) studied the modeling and assessment of the in environmental capacity in Dubai Creek, United Arab Emirates. There are no significant published data on the assessment of organic pollutants on offshore of Dubai.

1.2.3   The Effect on Marine Life

There are also many studies have documented the effects of organic and inorganic pollutants on aquatic life. Ismail (1992) carried out a study on macrobenthic invertebrates near sewer outlets in Dubai Creek. Adverse influence of the Kuwait oil well fires on fisheries in western Gulf has been investigated by McCain *et al.* (1993). Gerges (1993) studied the impacts of the 1991 Gulf War on the environment of the region (general observations). The effects of Gulf war oil spill on the zooplankton distribution and coral reefs in the NW Gulf have been documented by Al-Yamani *et al.* (1993) and Downing and Roberts (1993). Polycyclic aromatic hydrocarbons in edible tissue of fish from the Gulf after the 1991 oil spill have been investigated by Al-Yakoob *et al.* (1993). Evans *et al.* (1993) reported a short-term damage to coastal bird populations in Saudi Arabia and Kuwait following the 1991 Gulf War marine pollution. Also Symens and Evans (1993) recorded the adverse impact of the Gulf War oil spills on the tern populations in the northern Arabian Gulf during the breeding season. The assessment of the toxicity of Kuwait crude oil on the photosynthesis and respiration of seagrasses of the Northern Gulf has been investigated by Durako *et al.* (1993). Atlas (1995) reviewed the petroleum biodegradation and oil spill bioremediation in the marine environment. Wright (1995) investigated the trace metals and their major ion interactions in some aquatic animals.

1.3 Area of Study

Dubai is the second largest emirate in the seven-member federation. Dubai is the center of trade and tourism in the United Arab Emirates. Today Dubai is a very prosperous city with a bustling commercial life. It is a place for oil drilling, trade activities, shopping arcades, industrial areas and busy ports, and it is the leading entry to the region (Figure 1.1).

In its natural state, the approximately 70 km long Dubai coastline consisted primarily of long sandy beaches backed by dunes. This would have allowed wide-open views along the beach and out to sea. The infrastructural developments related to trade, fishing and tourism have led to significant changes in Dubai coastal region over recent years. Such developments included the construction of the major ports Jebel Ali and Al-Hamriya Port as well as Dry Docks; the construction of several recreational and fishing harbours; improvements to Dubai Creek; and the construction of the Al-Mamzar beaches and development of Al-Mamzar lagoon (Mocke *et al*, 2002).

Khor Dubai extends about 14 km deep in the dry land to divide the town into two zones: Deira and Bur Dubai. The daily life of Dubai has been closely associated with the Khor. In modern history, the Khor has been associated with political history of Dubai, being a support and a natural extension for the vital navigation front of the emirate as against the Iranian shores. Also it has provided a major port for the strategic location of the town along the old route between Europe and India (Figure 1.2). Thus becoming a nucleus that turned Dubai into a chandlery station first, then a commercial center that has no peer in the Gulf today.

According to the statistical survey for the Emirate of Dubai 2000, which conducted by Dubai Municipality, Dubai has a total population of 862,387 people, 97.3 percent of them live in urban areas while the rest, 2.7 percent, live in rural areas. Due to the rapid growth of the industrial activities in the study area and the urbanization, it is expected that such activities can introduce large quantities of both organic and inorganic compounds such as PAHs, PCBs, TPH, TOC, TKN and heavy metals. Figure 1.3 and Table 1.1 summarizes the total usage of Dubai coastal resource along 66 km as it was documented by Mocke *et al*. (2002).

Figure 1.1: *Map showing Dubai location in the Arabian Gulf*

Figure 1.2 : *Map showing Dubai location in the world*

Figure 1.3: *Map showing the usage of Dubai Coastal Region*

Table 1.1 : *Dubai coastal resource usage*

Coastal use		Length (km)	Total length (km)
Industrial	Ports	9.7	
	Fishing harbour	2.3	
	Other (Dewa, Dubal…)	8	
		Total industrial	20
Private	Hotels/ clubs	7.6	
	Residences	8.9	
		Total private	16.5
Public	Beach Parks	2.2	
	Free access	11.8	
		Total public	14
		Sanctuary (Jebel Ali)	15.5
		Grand Total	66

The study area is affected by many recognized sources of inputs such as treated water from Al-Awir STP, surface runoff during rainfall, grazing and painting wooden ship and other navigation activities at Al-Hamriya Port and Dry Docks (Table 1.2)

Table 1.2 : *The types of input into the study area*

Location	Description of the region
Al-Mamzar (mouth- mid – end)	Residence region there are no industrial activities. The input are from: 1) Surface runoff during rainfall. 2) Groundwater from Al Mamzar area.
Al-Hamriya (St 1- St 2-St 3)	Presence of Al Hamriya Port for commercial shipping. The input are from: 1) Grazing and painting wooden ship. 2) Deck drainage and bilge water. 3) Navigation route. 4) Fishing village. 5) Groundwater from Al Hamriya fish and vegetable market. 6) Surface water during rainfall.
Dry Docks	The input is from: 1) Repairing oil tankers and other ships.
Jumeirah Beach Hotel	There is no industrial activity. The input are from: 1) Groundwater from Jumeirah region 2) Surface water during rainfall.
D.E.W.A.	The input is from: 1) Desalination water (increase temperature).
D.U.B.A.L.	The input are from: 1) Groundwater from Aluminum industry. 2) Desalination water
Jebel Ali Hotel Ras Hisyan Ras Ghantoot	These three stations are called Jebel Ali Sanctuary. And are used as background or reference.
Dubai approach	The station is far from any coastal inputs.
Neptune wreck.	Position of old sinking ship.

(Source: Dubai Municipality. 2002)

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1.4 Geomorphology of the Arabian Gulf

The Arabian Gulf is described as a semi enclosed area with a low rate of water exchange. Most of its regions have a high salinity and temperature. With its shallow nature, all its parts lie within the photic zone and arid setting. The Gulf is principally a sedimentary basin whose substrate is mainly biogenic, with outcrops of older limestone (Sheppard, 1993). The Gulf has a rough complicated bottom, which varies considerably from area to area. Thus, there are scattered small islands and coral reefs, rocks and shallows, which are the main characteristics dominating the Gulf's seabed. The Gulf is divided into four main areas depending on variations in depth of water (Figure 1.4) these are:

(1) *The coastal area*, this extends from the seashore to a depth of 15–20 meters, its width varying from place to place. It is at its narrowest on the Iranian coast but it increases near the Bahrain, where it is generally covered with coral reefs and rocks.

(2) *The shallows*, this extends from 15–20 to 40–50 meters in depth. At its widest it extends over 160,935 square meters in the south and southwest of the Gulf. The seabed tends to be rough.

(3) *The transitional zone*, in this zone the seabed is irregular and covered by a mixture of coral reefs, mud and sand. The southern extension of this zone is somewhat smoother.

(4) *The deep area*, at the bottom of the U-shaped basin of the maximum depth of 91 meters is reached. The depth decreases towards the head of the Gulf, and this area can be divided into two zones. In the north, where the depth ranges between 50 and 65 meters the seabed is flat and covered by river deposits, although there are certain areas of coral reefs. The southern zone ranges from 70–110 meters, but it has an irregular seabed. The depth in some parts reaches 200 meters but it is insignificant areas. Overall the Gulf is a shallow marginal area and has an irregular seabed.

A high salinity, which in general is similar to, but lower than, other inland seas, characterizes the Gulf water's. Nevertheless, the Gulf is still considered to be an area of high salinity. This is due to the relatively small fresh water inflow and the high temperatures, which increase evaporation in excess of fresh water inflow. The salinity of the deeper water does differ slightly from that at the surface. Shallower areas tend to have higher salinity than the deeper ones. Most salt concentration in the Gulf comes from the Arabian Sea and the Gulf of Oman, through the Straits of Hormuz. The Gulf has a narrow link with the Indian Ocean through the Straits of Hormuz. These straits are the crucial area for currents, because they carry the ocean's influence into the Gulf waters. The high temperature and the high rate of evaporation increase the salinity and density of the surface water (al-Abdul-Razzak, 1984).

The coastal sector of UAE is a low-lying area with extensive tidal flats, lagoons and sand dunes (Al-Qubaisi, 2001). The energy of the coastal area and the marine system of UAE comes from water movement along the coasts or in the near shore zone. Along the Arabian Gulf and Oman Gulf coasts, there are three coastal processes: (1) alongshore current moving eastwards in the Arabian Gulf; (2) wave action and (3) tidal action. The energy of each process depends on several variables, wave velocity, configuration of the coastline, relief, lithology, and structure of the coastal area and the nature of marine sediments (Embbabi and Sharkawi, 1989).

In general water quality (physico-chemical) at the coastal belt monitoring stations of Dubai is normal. Variation in pH ranges from 8.1 to 8.4, due to buffering action of bicarbonate-carbonate system, which indicates to an alkaline medium. Salinity variation is wide and lies in a range of 41.2 to 43.1‰. The high salinity is noticed in the bottom water at Dewa. Dissolved oxygen is good at all stations of the coastal belt. Turbidity variation at all

sampling stations is in the range of 1.0–1.5 NTU. Levels of Total nitrogen, Nitrate-nitrogen and Phosphate-phosphorous are low. Variations in the levels of phytoplankton pigment are low (Dubai Municipality, 1996)
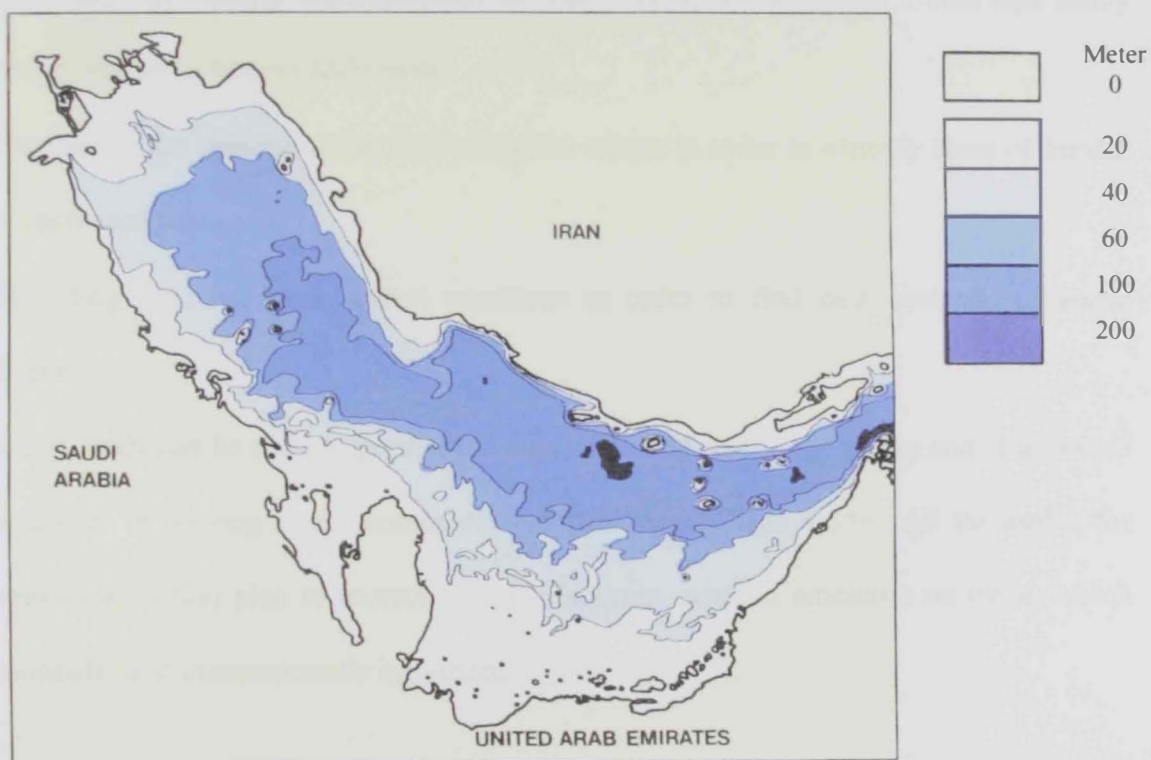
Figure 1.4 : *Map of the Arabian Gulf showing variations in water depth*

1.5 Aim of Study

The present work aims at initiating and conducting a baseline field assessment of the pollutants effecting the marine environment. The particular target is to assess organic and inorganic pollutants in bottom sediments in the offshore of Dubai. The specific aims of this study are:

- Providing appropriate measurements of TOC, TPH, TKN, PAHs, PCBs and heavy metals values in bottom sediments.

- Comparing the present values with standard values in order to identify areas of impact or increased risk.

- Providing input to management questions in order to find new methods of waste disposal.

Also, this study can be used to predict the environmental risk in the future and is expected to be useful in solving some coastal-related problems. This study will be useful for preparation an action plan to protect marine resources, with an emphasis on those, which are nationally and internationally important.

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CHAPTER II

MATERIALS AND METHODS

MATERIALS AND METHODS

2.1 Sediment Sampling

2.1.1 Sample Collection

The collection of sediment samples covered the offshore line of Dubai. The samples were collected from fifteen stations along Dubai coastal area. A Van Veen grab sampler made from stainless steel was used to obtain bottom sediments. The sediment samples were collected over three months period of time, starting in January to March 2002. Each sample was stored in clean aluminum foil and kept frozen in an airtight plastic bag before grain-size analysis. The sediments samples dried in oven under mild temperature before sieving analysis and was kept freeze-dried unlit required for future use.

2.1.2 Sampling Stations

The locations of the different stations are given in Table 2.1. All the samples were collected from offshore region only two samples obtained from inshore region, which are Dubai approach and Neptune Wreck. Ten stations were located at the northern parts of the study area and only five stations were located at the southern parts (Figure 2.1).

Table 2.1 : *Sampling locations*

Stations	Location	Stations	Location
1	Al-Mamzar mouth	2	Al-Mamzar mid
3	Al-Mamzar end	4	Al-Hamriya station 1
5	Al-Hamriya station 2	6	Al-Hamriya station 3
7	Dry Docks	8	Jumeirah Beach Hotel
9	D.E.W.A.	10	D.U.B.A.L.
11	Jebel Ali Hotel	12	Ras Hisyan
13	Ras Ghantoot	14	Dubai approach
15	Neptune Wreck		

Figure 2.1 : *Map showing sampling site along Dubai coastline*

The map contains the following labels:

- N (compass, pointing north)
- Arabian Gulf
- ○ Sampling Station
- Palm Island
- Jebel Ali
- Scale in meter 1:5500 m

Legend:
1. Mamzar mouth
2. Mamzar mid
3. Mamzar end
4. Hamriya St 1
5. Hamriya St 2
6. Hamriya St 3
7. Dry Dock
8. Jumeirah beach
9. Dewa
10. Dubai
11. Jebel Ali Hotel
12. Ras Hisyan
13. Ras Ghantoot
14. Dubai approach
15. Neptune Wreck

2.2 Analytical Methods

2.2.1 Grain Size analysis

The collected samples were dried in oven under moderately temperature about 70 ° C in order to remove any water molecules before sieving process. According to ROPME (Regional Organization for the Protection of Marine Environment, 1999) sieve analysis of sand was done by using a sample splitter, about 100 grams of sample was obtained and weighed the split sample to the nearest 0.01 gram. A clean set of sieves with height of 1 φ intervals were selected. The sample was replaced into the top sieve after arranged the sieves based on mesh number. The sieves were placed in mechanical shaker; fasten very tightly, and sieved for 15 minutes. Each sieve was emptied onto a large sheet of paper; the sieve brush was used to remove all particles from the bottom of the sieves. The dry weight percentage of the size fractions retained on each sieve was calculated. For the muddy samples, which contains more than 20% mud, pipette analysis is the most common method used for determining the grain-size distribution of sediments > 4 φ. Sediment samples should be air-dried. 50 grams of the sample were obtained and placed in a 500 ml beaker and dispersed in distilled water. This suspension was stirred vigorously by using glass rod starting from the bottom and working up to the top until all the materials were distributed uniformly. After dispersion wet sieving was used to separate the sand from mud using 230 mesh. The fraction retained on the sieve was dried and subjected to sieve analysis. The dispersed fraction passing the 230 mesh during wet sieving, was poured in an Andreason Sedimentation Cylinder. Distilled water was added to bring the volume to exactly to 500 ml and stirred 2–3 minutes. After 20 seconds of stirring, the pipette was inserted to depth of 20 cm and 10 ml exactly were withdrawn.

2.2 Analytical Methods

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This first withdrawal is very important step, as it represents the total fraction finer than 4 φ. The pipette was removed, the suspension was expelled into a weighing beaker of 30 ml. 10 ml of distilled water were sucked up to rinse out the pipette and the rinsing water was expelled into the same beaker. Withdrawals were continued at specified time intervals and new beaker was used for each withdrawal. The beakers were placed in an oven with cover glass on top and evaporated to near dryness (24 hr at 100–130 ° C). The beakers were removed from the oven, let cool to room temperature and weighed to 0.001 g on a precision balance. All beakers were weighed at nearly same time. This method was detailed by MOOPAM (Manual of Oceanographic Observation and Pollutant Analysis Methods, 1999). The most commonly used method for the calculation of statistical size parameters is the graphical method curves and histograms. The grain-size statistical parameters: Graphic mean " M_z ", Inclusive Graphic Standard Deviation " σ_1", Inclusive Graphic Skewness "Sk_1 " and Graphic Kurtosis " K_G" were calculated according to the equations described by MOOPAM (1999).

2.2.2 Determination of Total Organic Carbon (TOC)

The readily oxidizable organic carbon content is determined by the Walkey-Black Method (1947), adopted and modified by Jackson (1958). This method differentiates humus matter from extraneous sources of organic carbon such as graphite and coal. The Walkey-Black method utilizes exothermic heating in the sample. This method based on oxidation the sample with potassium dichromate and concentrated H_2SO_4, followed by the titration of excess dichromate with 0.5N ferrous ammonium sulfate solution to a sharp, 1 drop, end point. Oxidation of Cl- can be prevented by the use of Ag_2SO_4 in the digestion mixture. The organic carbon was determined by using the following analytical procedure:

From dried and sieved sediment sample, a 0.5 gram was placed in a 500 ml Erlenmeyer flask. Then 10 ml of 1N $K_2Cr_2O_7$ solution were added by burette to the sediment and swirling the flask mixed the two. Followed by the addition of 20 ml of concentrated H_2SO_4 by burette and were mixed by gentle rotation of the flask for about one minute. This was done carefully, to insure complete mixing of the reagents with the sediment; while avoiding throwing the sediment onto the sides of the flask out of contact with the reagents. The mixture was allowed to stand for 30 minutes. A standardization blank without sediment was run with each new batch of samples. After 30 minutes, the solution was diluted to 200 ml with distilled water and 10 ml of 85% H_3PO_4 and 0.2 g of NaF. Then 15 drops of the diphenylamine indicator were added to the sample flask. The solution was back titrated with the 0.5 N ferrous ammonium sulfate solution to a one-drop end point (brilliant green). The color of solution progressed from an opaque green-brown, to green upon the addition of approximately 10 ml of the ferrous solution. The color continued to shift upon titration to a bluish-black-gray; at this point the addition of 10–20 drops of ferrous solution shifted the color to a brilliant green giving one-drop end point. The results of analysis were calculated using the following equation:

% Organic carbon =10 (1-T/ S) [1.0 N (0.003) (100/W)]

Where

T= Sample titration, ml ferrous solution

S= Standardization blank titration, ml ferrous solution

The T/S factor canceled out the effect of the ferrous solution normality

0.003=12/4,000= meq weight of carbon

1.0 N = normality of ($K_2Cr_2O_7$)

10   = volume of ($K_2Cr_2O_7$) in ml

W = weight of sediment sample in grams.

2.2.3. Determination of Total Kjeldahl Nitrogen (TKN)

The total nitrogen includes organic and inorganic nitrogen, were determined according to Kjeldahl method (EPA, 1993) using block digestion and steam distillation. This method requires the digestion of the sample using strong acid at high temperatures. Careful handling of the solutions, for added protection, acid digestions should be performed in a fume hood with adequate ventilation. Eye protection should be worn at all times and care should be taken when handling hot digestion tubes. The procedure of Kjeldahl analysis is given as a following:

One gram of the sample was prepared and weighed to an accuracy of 0.1 mg into a digestion tube. Sample preparation for Kjeldahl analysis should be carefully followed to avoid errors in the final result. By using Kjeltec 1035, 2300 or 2400 these weights can be automatically entered into the memory of the system for automatic result calculation. Two Kjeltabs Cu 3.5 (alternatively 7 g K_2SO_4 and 0.8 g Cu SO_4 x $5H_2O$) were added. Then 12 ml of concentrated H_2SO_4 were added carefully (samples containing high-fat 15 ml H_2SO_4 were used) and the wet sample with the acid was shook gently. The exhaust is automatically attached when using a Lift System. A Controller and Flow Regulator would set the water aspirator to full effect. The digestion was continued until all samples were clear with a tube-green solution. Then 75 ml of deionized water were added to the tubes. The digestion tube was placed in the distillation unit and the system was closed safety. After that 50 ml of 40% NaOH were dispensed into the tube. The steam valve was opened on the Kjeltec 1002 and distilled for approximately 4 minutes. The distillate was titrated with standardized HCl acid (0.1 N or 0.2 N). The results were calculated according to the

following equations:

%N $= [(T-B) \times N \times 14.007 \times 100] /$ weight of sample in mg

% Protein $= \% N \times F$

mg N/ liter $= [(T-B) \times N \times 14.007 \times 1000] /$ volume of sample in ml

g N/ liter $= [(T-B) \times N \times 14.007] /$ volume of sample in ml

mg N/ 100 ml $= [(T-B) \times N \times 14.007 \times 100] /$ volume of sample in ml .

Where:

T = Titration volume for sample (ml)

B = Titration volume for blank (ml)

N= Normality of acid to 4 places of decimal

F= Conversion factor for Nitrogen to Protein Depending on sample.

2.2.4 Determination of Total Petroleum Hydrocarbons (TPH)

The quantification of TPH (Total Petroleum Hydrocarbons) as it is described by ROPME (1999) was carried out using Nicolet Infrared Spectrophotometer. This method can be used when relatively polar, heavy petroleum fractions are present, or when the levels of non-volatile greases over the solubility limit of the solvent. This method is not recommended for determination of low-boiling fractions that volatilize at temperatures below $70\,^{\circ}$ C. This method is not intended for use on highly contaminated waters, elutriates, or sediments (ROPME, 1999). The samples, which are analyzed by this method, should be " clean" sediments. The details of procedure are demonstrated below:

From the homogenized, field-moist sediment 20 ± 0.5 g were weighed and placed in a 150 ml beaker. The sample was acidified to pH 2 with approximately 0.3 ml concentrated HCl. Then 25 g of Mg $SO_4 \cdot H_2O$ were added to the acidified sample and stirred to create a

smooth paste. The paste was spread on the sides of the beaker to dry, usually 15–30 minutes or until the material has solidified. The solids were transferred to a mortar and ground to a fine powder, then transferred to a paper extraction thimble. The beaker and the mortar were wiped with pieces of filter paper moistened with the solvent (hexane) and the paper was added to the thimble. The thimble was filled with glass wool (or glass beads), placed in a soxhlet apparatus and extracted using fluorocarbon-113 for 4 hours. By using grease-free cotton, the extract was filtered into a volumetric flask and diluted to volume with fluorocarbon-113. If the final filtrate is turbid, is refiltered into a clean flask. About 5–10 ml solution from the volumetric flask were discarded, 3 g silica gel were added for drying the sample and stirred by stirring bar. The solution was stirred for a minimum of 5 minutes on a magnetic stirrer. After the silica gel has been settled in the sample extract, a clean cell was filled with solution. Cell size of 10 ml was used for the samples, which contain more than 8 mg/kg and cell size of 50 ml used for the samples, which contain less than 8 mg/kg of TPH. The absorbance of the extract was measured at an excitation wavelength of 310 µm and emission wavelength of 360 µm. If the absorbance exceeds 0.8, an appropriate dilution should be prepared and the sample should be reanalyzed.

2.2.5 Determination of Polycyclic Aromatic Hydrocarbons (PAHs)

The instrumental quantitation and identification of PAHs (Polycyclic Aromatic Hydrocarbons) were carried out using HPLC with fluorescence detector (High Performance Liquid Chromatography, Figure 2.2). This method is applicable to determine the PAHs in soils, sediments, water and wastes. It is recommended to determine the first highly 16 pollutant PAHs, which are mentioned below:

Naphthalene – Acenaphthylene – Acenaphthene – Fluorene – Phenanthrene – Anthracene – Fluoranthene – Pyrene – Benzo(a)anthracene – Chrysene – Benzo(b)fluoranthene – Benzo(k)fluoranthene – Benzo(a)pyrene – Dibenzo(a,h)anthracene – Benzo(g,h,i)perylene – Indeno(1,2,3-cd)pyrene.

The sample was prepared as described below:

From the solid sample 5 g ± 0.5 g were weighed accurately, blended with equal quantity of anhydrous sodium sulfate and placed in an extraction thimble. Approximately 70 ml of the extraction solvent (Hexane:Acetone, 50:50) were added. The sample was extracted in a soxhlet extraction apparatus for 2 hours (boiling for 1 hr and rinsing for 1 hr). The extract was transferred to a 10 ml volumetric flask. Then 2 ml of the extract were placed into a concentrator and evaporated carefully under nitrogen to reduce the solvent to about 0.5 ml and the residue was dissolved in acetonitrile. The Sample extract was cleaned-up (necessary in case of sediment and biota) before proceeding with analysis, using Solid Phase Extraction (SPE) using PAH SPE columns. Then a 20 µl aliquot of extract was injected into HPLC. The above listed compounds were detected by ultraviolet (UV) and fluorescence detectors simultaneously (ROPME, 1999).

Figure 2.2 : *Schematic of High Performance Liquid Chromatography apparatus (Source: Skoog, Principles of instrumental analysis, 1998)*

2.2.6 Determination of Polychlorinated Biphenyls (PCBs)

The determination of PCBs (Polychlorinated Biphenyls) was carried out using GC-ECD (Gas Chromatography with Electron Capture Detector, Figure 2.3) with capillary column-Sil/ length 30 m and diameter 0.32 mm. The condition of the GC is given below:

Carrier gas: Helium

Flow rate: 1.5 ml/min

Make-up gas: Ar/CH_4 at flow rate recommended by the manufacturer (between 30 to 60 ml/min)

Injector Temperature: 225 ° C

Detector temperature: 300 ° C

Initial temperature: 100 ° C, hold 2 minutes

This method is applicable for determination of PCBs in soils, sediments and water. It is recommended for determination of 20 PCBs congeners with priority pollutants which are listed below:

PCB 8 – PCB 18 – PCB 28 – PCB 44 – PCB 52 – PCB 60 – PCB 77 – PCB 101 – PCB 105 – PCB 118 – PCB126 – PCB 128 – PCB 138 – PCB 153 – PCB 170 – PCB 180 – PCB 187 – PCB 195 – PCB 206 – PCB 209.

Polychlorinated biphenyls were determined by using the following analytical procedure:

From the solid sample 5 g ± 0.5 g were blended with 5 g ± 0.5 g of anhydrous sodium sulfate and extracted using solid-liquid extraction system (automated soxhlet). Approximately 70 ml of the extraction solvent (1:1 Hexane:Acetone) were added to the sample, and extracted for 2 hours (boiling for 1 hr and rinsing for 1 hr). After extraction

the sample, the extract was cleaned-up and evaporated carefully. The residual 2–5 ml of the solvent after evaporation was collected. The system was opened and the cups were removed. The extract was quantitatively transferred to a 10 ml measuring cylinder. The cups were rinsed using hexane and the rinsates was added to the measuring cylinder at a fixed volume of 10 ml. A portion to a 2 ml were transferred to the Gas Chromatography autosampler vial, 1 µl was injected in GC-ECD and subjected to compounds detection and identification (ROPME, 1999).
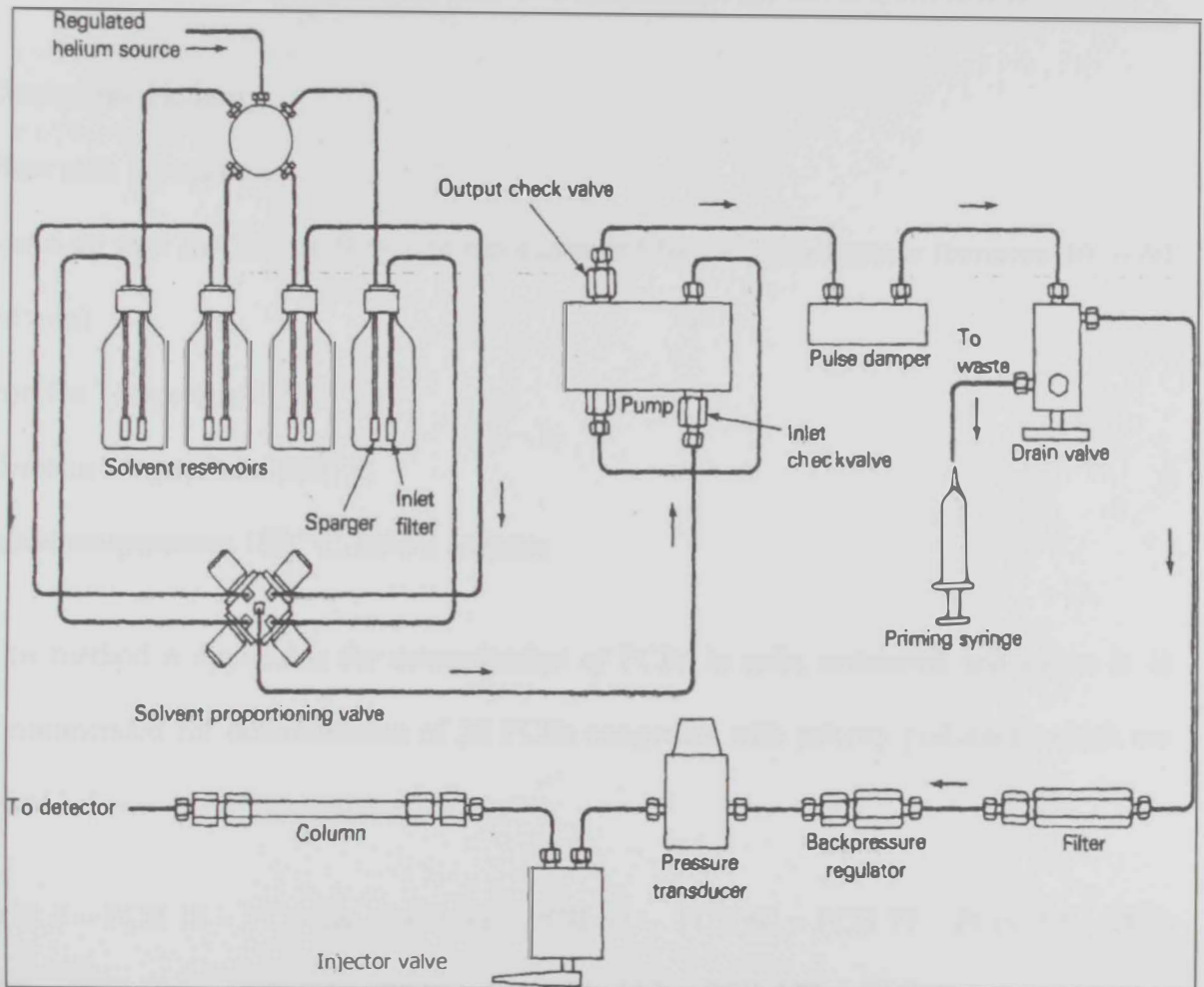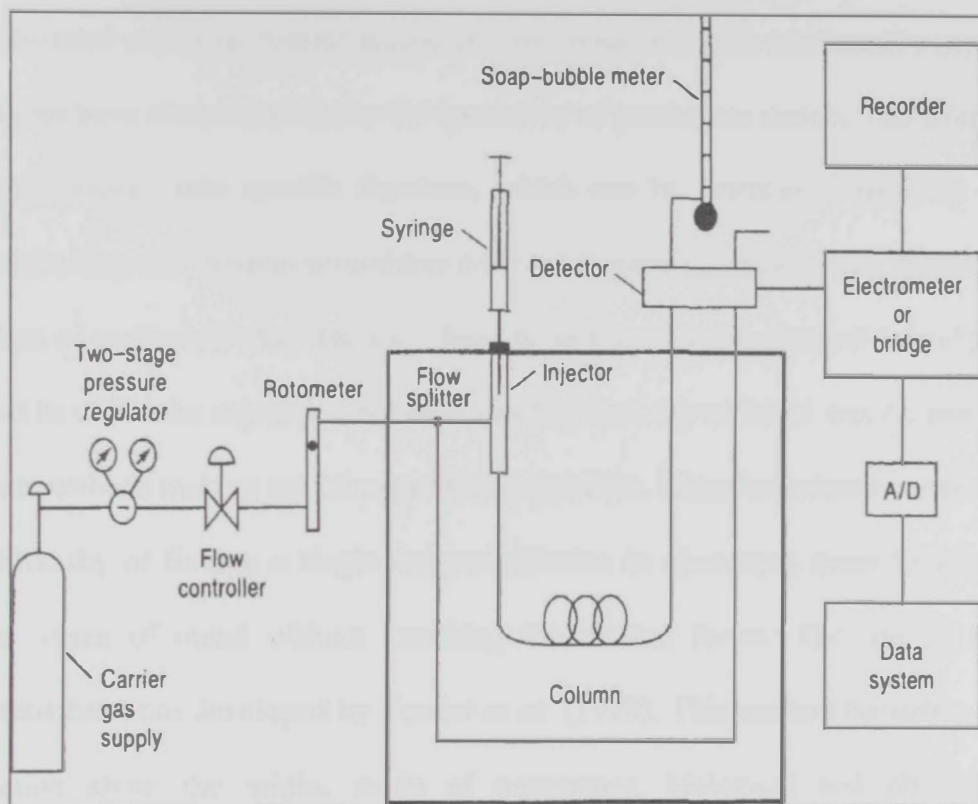
Figure 2.3 : *Schematic of Gas Chromatography apparatus (Source: Skoog, Principles of instrumental analysis. 1998)*

2.2.7 Determination of Major Oxides and Trace Elements Concentrations

Most studies dealing with particulate metals in natural water systems (metals associated with suspended matter or bottom sediments) are concerned with total metal concentration. Few studies have aimed to evaluate the speciation of particulate metals. The solid material can be partitioned into specific fractions, which can be extracted selectively by using appropriate reagents. Several procedures have been recently proposed for determining the speciation of particulate trace metals. These procedures can be grouped into (1) methods designed to effect the separation between residual and non residual metals, and (2) more elaborate methods making use of sequential extractions. These techniques, however, suffer from difficulty of finding a single reagent effective in dissolving quantitatively the non residual forms of metal without attacking the detrital forms. The use of sequential extractions has been developed by Tessier *et al.* (1979). This method furnishes a detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization, and transport of trace metals.

The sediment samples, bulk and fine fraction (230 mesh), which contain more than 10% silt-clay fraction (< 63 µm) have been subjected to dry sieving and analyzed to determine their major oxides and trace elements concentrations.

The major oxides and trace elements concentrations were determined by ICP (Inductively Coupled Plasma) involving nearly a direct aspiration of the aqueous solution at certain wavelength. For the trace metals a standard addition technique was employed because matrix effects, presumably due to material leached from the sediments, were observed. These effects would have contributed in many cases to an error of as much as 15%. For the metals present in high concentrations, the supernatant solution was diluted (20 x) with

deionized water and the concentrations were obtained directly from appropriate calibration curves prepared with the components of the extraction solution diluted by the same factor (Tessier *et al.*, 1979). For total or residual major oxides and trace elements analysis, the powder sample was digested with a 5:1 mixture of hydrofluoric and perchloric acids. For a one gram (dry weight) sample, the sediment was first digested in platinum crucible with a solution of concentrated $HClO_4$ (2 ml) and HF (10 ml) to near dryness; subsequently a second addition of $HClO_4$ (1 ml) and HF (10 ml) was made and again the mixture was evaporated to near dryness. Finally, $HClO_4$ (1 ml) alone was added and the sample was evaporated until the appearance of white fumes. The residue was dissolved in 12 N HCl and diluted to 25 ml. The resulting solution was then analyzed by ICP for major oxides and trace elements using the standard addition technique. The results were calculated using the following equations:

For the major oxides the percentage of weight was calculated as given below:

The oxide (wt%) = calculated conc. x volume x factor oxide / wt. of sediment x10000

For the trace elements the concentration (ppm) was calculated as given below:

The trace element (ppm) = calculated conc. x the volume/ wt. of sediment

2.2.8 Mineralogy

The collected samples were subjected to X-ray diffraction analysis to identify their mineral composition. A fully computerized Philips Diffractometer model PW/1840, with a Ni-filter, Cu-Kα radiation at 40 KV, 30 mA and scanning speed of 0.02°/S was applied on the ground bulk samples. The diffraction peaks between $2\theta = 2°$ and $2\theta = 60°$ were recorded.

The mineral composition of the samples was identified by comparing the obtained data with standard data.

2.2.9 Statistical Analyses

Microsoft Office EXCEL software was used for plotting the chart of sediment quality parameters.

Microsoft Office EXCEL 2000 [TM] software was also used for plotting histogram and pie charts of total organic carbon, total petroleum hydrocarbon, total nitrogen, polychlorinated biphenyls, individual polychlorinated biphenyls and polycyclic aromatic hydrocarbon compounds.

SURFER 7.01 [TM] program was used for mapping the total organic carbon, total petroleum hydrocarbon, total nitrogen, polycyclic aromatic hydrocarbon compounds, polychlorinated biphenyls and individual polychlorinated biphenyls.

STATISTICA [TM] Program was used to carry out univariate, biavariate and multivariate statistical analyses for the obtained geochemical data such as histogram, factor analysis, regression analysis, and correlation matrix.

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CHAPTER III

RESULTS OF ANALYSES

THE ANALYSES RESULTS

3.1 Grain Size Distribution

Sediment is little more than eroded particles and fragments of dust and other debris. Not only do particles of sediment come from worn pieces of other rocks, they also are derived from living organisms, from minerals dissolved in water, and even from outer space. Based on the sediments composition can be classified into:

1) Lithogenous, which compose of rock fragments, quartz, clay and volcanic ash;

2) Biogenous, which compose of calcareous ooze and siliceous ooze;

3) Hydrogenous, which compose of manganese nodules, phosphorite, calcium carbonate, metal sulfides and evaporites such as gypsum and halite;

4) Cosmogeneous, which compose of iron-nickel spherules and iron-nickel meteorites.

Sediment is constantly settling through the water onto sea floor, acting like a library of earth history (Thurman & Trujillo, 1999). Sediments can act as an indicator of overall environmental contamination in marine ecosystems because many toxic contaminants, which do not dissolve readily in water, become attached to sediments and organic material and settle to the bottom. One of the most important properties of sediment is its texture. The sediment size indicates the energy condition under which a deposit is laid down (Thurman & Trujillo, 1999).

The grain-size analysis of the present work revealed the texture of sediments in the study area. The samples obtained from Dubai offshore were divided into five groups based on

their textural characteristics. Table 3.1 demonstrates these groups, locality and percentage of each group from the studied stations.

Table 3.1 : The textural character in the study area

Textural character	Locality	Percentage of studied stations
1.Gavel sand	Cover each of: 1. Al-Mamzar mouth (St 1) 2. Dry Docks (St 7) 3. Ras Hisyan (St 12) 4. Dubai approach (St 14) 5. Neptune Wreck (St 15)	33.3%
2. Sand	Cover each of: 1. Al-Mamzar mid (St 2) 2. Al-Hamriya St 2 (St 5) 3. Dewa (St 9) 4. Jebel Ali Hotel (St 11) 5. Ras Ghantoot (St 13)	33.3%
3. Gravel muddy sand	Cover each of: 1. Al-Mamzar end (St 3) 2. Jumeirah Beach (St 8)	13.3%
4. Muddy sand	Cover each of: 1. Al-Hamriya St 1 (St 4) 2. Al-Hamriya St 3 (St 6)	13.3%
5. Mud	Cover: 1. Dubal (St 10)	6.67%

Most of the samples are classified as gravel sand and sand, which cover about 67% of the study area. This is in general agreement with the published works (Massoud *et al.*, 1996; Al-Abdali *et al.*, 1996 and Al-Ghadban *et al.*, 1996) on the sediments of the Arabian Gulf where coarse sandy sediments are mainly found in the southern regions of the Gulf and the fine clay silt sediments are mainly concentrated in the northern regions.

The data obtained from sieving analysis were used to chart cumulative curves on probability paper. The percentiles, which obtained from the curves, are used to calculate grain-size statistical parameters (Table 3.2) by using the equations adopted by Folk & Ward (1957). The histograms were constructed (Figure 3.1) to show the variation in grain-size distribution at different stations in the study area.

Values of graphic mean M_z (a description of size class) occupy the range from 0.03 φ to 3.95 φ with an average of 1.85 φ and standard deviation (S.D) of 1.15. Station 1 showed the minimum value, whereas the maximum value was found at station 10. Depending on M_z values, the samples were classified into: *1) Coarse sand,* samples collected from Al-Mamzar mouth (Figure 3.1A), Jebel Ali Hotel (Figure 3.1K), Ras Hisyan (Figure 3.1L) and Neptune Wreck (Figure 3.1O); *2) medium sand,* samples collected from Dewa (Figure 3.1I), Ras Ghantoot (Figure 3.1M) and Dubai approach (Figure 3.1N); *3) fine sand,* samples collected from Al-Mamzar mid (Figure 3.1B), Al-Hamriya stations (Figure 3.1D-F), Dry Docks (Figure 3.1G) and Jumeirah Beach (Figure 3.1H); *4) very fine sand,* samples collected from Al-Mamzar end (Figure 3.1C) and Dubal (Figure 3.1J).

Values of inclusive graphic standard deviation σ_I (a measure of sorting) occupy the range from 0.52 φ to 1.97 φ with an average of 1.15 φ and S.D of 0.43. The minimum value was calculated for station 8, whereas the maximum value was at station 14. σ_I values showed that the samples which being: *1) Poorly-sorted,* were collected from Al-Mamzar mouth

and end, Al-Hamriya St 1 and 3, Dry Docks, Jebel Ali Hotel, Ras Hisyan, Dubai approach and Neptune Wreck; 2) *moderately-sorted* samples were collected from Al-Mamzar mid, Al-Hamriya St 2, Dewa and Dubal; and finally 3) *moderately well-sorted* samples were collected from Jumeirah Beach and Ras Ghantoot. Generally most of the samples are classified by being poorly-sorted.

Values of inclusive graphic skewness SK_I (a measure of symmetrical degree of the distribution curve) vary from - 0.81 to 0.26 with an average of - 0.2 and S.D of 0.25. Referred to Folk & Ward (1957) formula, the present samples showed the following distribution curves: 1) *Fine-skewed curve*, for the sample of Al-Hamriya St 1; 2) *near symmetrical curve*, for the samples of Al-Mamzar mid, Jumeirah Beach, Dewa and Neptune Wreck; 3) *coarse-skewed curve*, for the samples of Al-Hamriya St 2 and 3, Ras Hisyan, Ras Ghantoot and Dubai approach; finally, 4) *very coarse-skewed curve*, for the samples of Al-Mamzar mouth and end, Dry Docks, Dubal and Jebel Ali Hotel. Hence, the majority of the samples are described as coarse to very coarse skewed.

Values of graphic kurtosis K_G (a measure of sharpness of the curve peak) range between 0.71 to 5.53 with an average of 1.53 and S.D of 1.15. Station 14 showed the minimum value, the maximum value was calculated for station 10. The samples obtained from Dubai offshore have the following curves of distribution: 1) The samples collected from Al-Hamriya St 3 and Dubai approach, characterized by having *platykurtic* distribution curves; 2) The samples collected from Jumeirah Beach, Dewa and Ras Ghantoot have *mesokurtic* distribution curves; 3) The samples collected from Al-Mamzar mouth, mid and end, Al-Hamriya St 1 and 2, and Ras Hisyan have *leptokurtic* distribution curves; 4) The samples collected from Dry Docks, Jebel Ali Hotel and Neptune Wreck have *very leptokurtic* distribution curves; 5) The sample collected from Dubal has *extremely leptokurtic* distribution curves.

Table 3.2 : *Grain size cumulative weight, percentile and statistical parameters of Dubai sediments.*

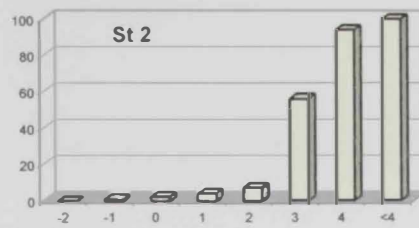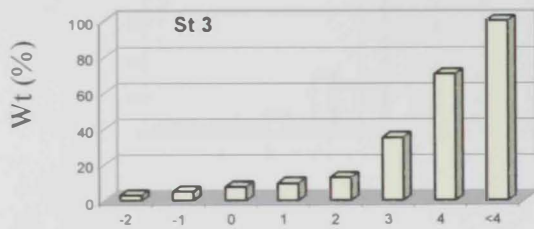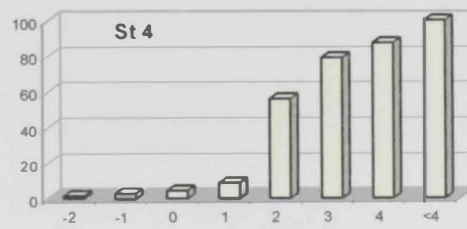| Stations	Locality	Cumulative wt%								Percentile							Statistical Parameter			
		-2φ	-1φ	0φ	1φ	2φ	3φ	4φ	$<4\varphi$	5	16	25	50	75	84	95	M_z	σ	SK_1	K_G
1	Al-Mamzar mouth	9.1	15.8	36.1	80.4	97.7	99.7	99.9	100	- 2.5*	- 1.3	- 0.6	0.3	0.8	1.1	1.7	0.03*	1.24*	- 0.33	1.23
2	Al-Mamzar mid	0	1.1	2.3	4.1	7.4	55.7	93.7	99.7	1.3	2.4	2.6	3	3.5	3.7	4.1	3.03	0.75	- 0.07	1.28
3	Al-Mamzar end	3	5	7.6	9.6	12.8	35	70.2	100	- 1.2	2.1	2.5	3.3	4	4.1	4.3	3.17	1.33	- 0.42	1.50
4	Al-Hamriya St 1	1.3	2.7	4.4	8.6	55.8	78.8	87.2	100	0.1	1.2	1.4	1.9	2.9	3.5	4.2	2.20	1.20	0.26	1.12
5	Al-Hamriya St 2	0.4	2	3	5.9	18.8	77.3	96.9	99.7	0.7	1.9	2.1	2.6	3.1	3.3	3.7	2.60	0.80	- 0.13	1.23
6	Al-Hamriya St 3	0	3.88	8.63	19.38	38.13	59.38	68.75	99.87	- 0.8	0.5	1.1	2.6	4.1	4.2	4.5	2.43	1.73	- 0.21	0.72
7	Dry Docks	5.2	9.3	14.1	21.4	32.7	63.3	93.3	99.8	- 2.3	0.3	1.7	2.5	3.2	3.6	4.2	2.13	1.81	- 0.41	1.78
8	Jumeirah Beach	0	0.4	0.8	1.4	10.3	70.3	99.4	99.9	1.8	2.2	2.4	2.7	3.1	3.2	3.6	2.70	0.52	0.00	1.05
9	Dewa	0	1.9	6.4	33.3	83.3	96.8	99.5	99.8	0	0.5	0.8	1.4	1.9	2.2	2.9	1.37	0.86	- 0.01	1.08
10	Dubal	0	0.2	0.6	1.6	7.2	8.4	9.2	100	1.8	3.1	4.2	4.3	4.4	4.45	4.5	3.95	0.75	- 0.81	5.53
11	Jebel Ali Hotel	1.9	3.3	8.3	29.9	80.1	99.4	99.9	100	- 1	- 0.5	0.9	1.3	1.8	2	2.4	0.93	1.14	- 0.40	1.55
12	Ras Hisyan	5.5	12.1	30.5	71.5	92.8	98.4	99.3	99.7	- 2.2	- 0.7	- 0.3	0.6	1.2	1.6	2.4	0.50	1.27	- 0.17	1.26
13	Ras Ghantoot	0	1.7	7.5	29.6	77.6	99.7	100	100	0	0.5	0.9	1.3	1.7	1.9	2.3	1.23	0.70	- 0.14	1.18
14	Dubai approach	5.3	18.5	35.1	47.3	57.5	76.6	97.2	99.8	- 2.1	- 1.1	- 0.5	1.3	2.9	3.2	3.8	1.13	1.97	- 0.13	0.71
15	Neptune Wreck	2.6	10.2	33.1	71	93.2	98.5	99.7	99.9	- 1.6	- 0.7	0.3	0.4	1.2	1.5	2.3	0.40	1.14	- 0.01	1.78

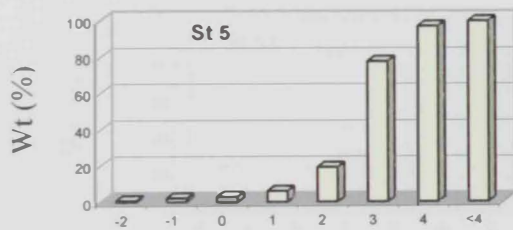* Values in φ
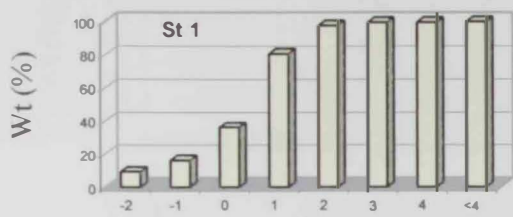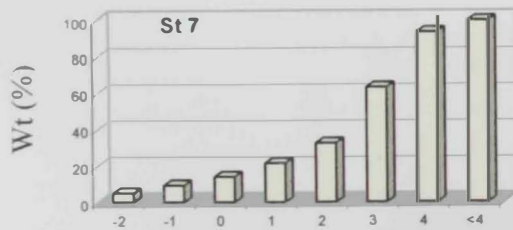
40

A.
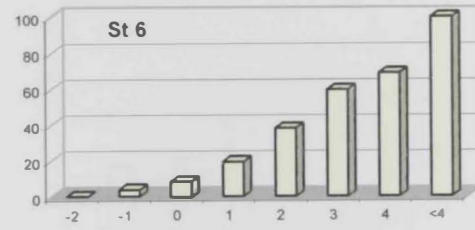
Grain size (φ)

B.

Grain size (φ)

C.

Grain size (φ)

D.

Grain size (φ)

E.

Grain size (φ)

F.

Grain size (φ)

G.

Grain size (φ)

H.
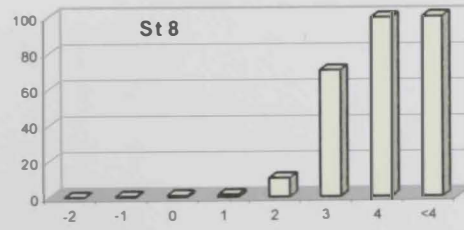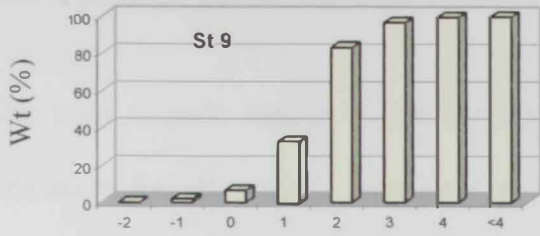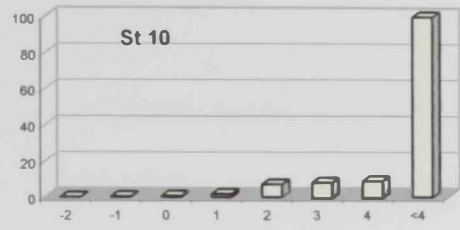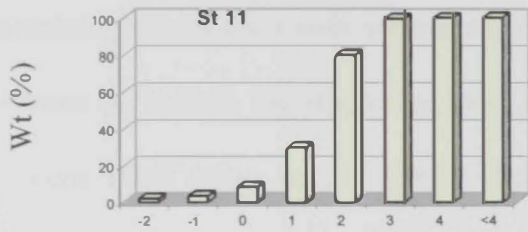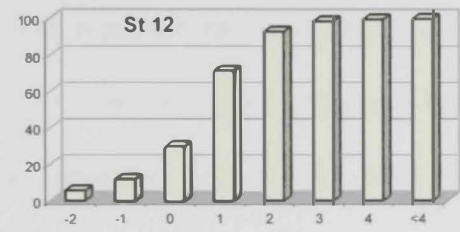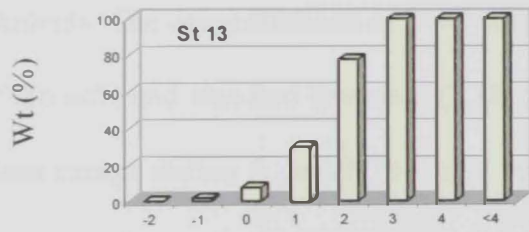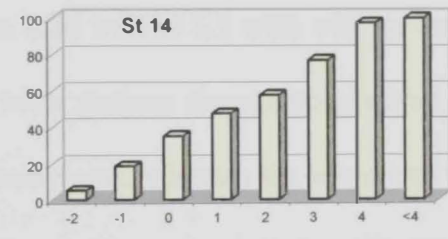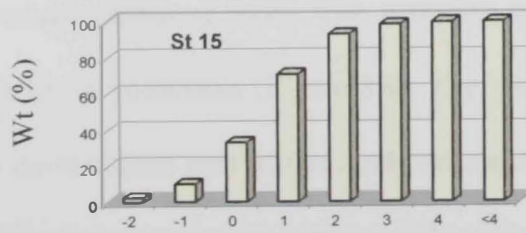
Grain size (φ)

Figure 3.1 : *Histograms representing grain size distribution in Dubai sediments*

3.2. Total Organic Carbon (TOC)

The total organic carbon value indicates the sum of organic carbon and represents a measure for all organic substances in sediments. These substances can be of natural origin like humic acids, mineral oils, solvents, pesticides, polyaromatic hydrocarbons or chlorinated organic compounds. Domestic and industrial wastewaters also contribute to organic contaminants in various amounts. Industrial waste effluents may contain carbon-containing compounds with various toxicity levels. The input of organic matter to coastal systems is, indeed, the triggering mechanism leading to the ecological consequences of concern (Dell'Anno *et al.*, 2002). Both of these situations can create unfavorable conditions for aquatic life, such as oxygen reduction and hypoxia up to mortality of marine organisms and biodiversity loss (Cloern, 2001).

Table 3.3 illustrates the data obtained from determination of organic carbon in Dubai sediments. The concentrations of TOC vary between 0.16 wt% to 5.9 wt% with an average of 0.86 wt% and standard deviation (S.D) of 1.44. Most stations showed comparable TOC values except station 6, which provided the maximum value, whereas the minimum value was reported at station 1. The variation in TOC concentration was plotted in (Figure 3.2), while the percentage of TOC at different stations of the study area is demonstrated in Figure 3.3. It is worthy to note that station 6 (Al-Hamriya St 3) approximately contributed by half of total percentage (46%) of TOC. The mapping survey was used to show the distribution of TOC in Dubai sediments (Figure 3.4). The concentration of TOC markedly increases towards the northeastern part of the study area around Al-Hamriya St 3 (St 6). Such increase may be due to navigation activities and the daily usage of Al-Hamriya Port.

Table 3.3 : *Concentrations of total organic carbon in Dubai sediments*

Stations	Locality	TOC wt%
1	Al-Mamzar mouth	0.16
2	Al-Mamzar mid	0.44
3	Al-Mamzar end	0.52
4	Al-Hamriya St 1	1.21
5	Al-Hamriya St 2	1.41
6	Al-Hamriya St 3	5.9
7	Dry Docks	0.55
8	Jumeirah Beach	0.25
9	Dewa	0.23
10	Dubal	0.63
11	Jebel Ali Hotel	0.37
12	Ras Hisyan	0.27
13	Ras Ghantoot	0.23
14	Dubai approach	0.44
15	Neptune Wreck	0.34
Average ± S.D		0.86 ± 1.44

Wt % x 10^4 = mg/kg = µg/g = ppm = ppb x 10^{-3} = µg/kg x 10^{-3}
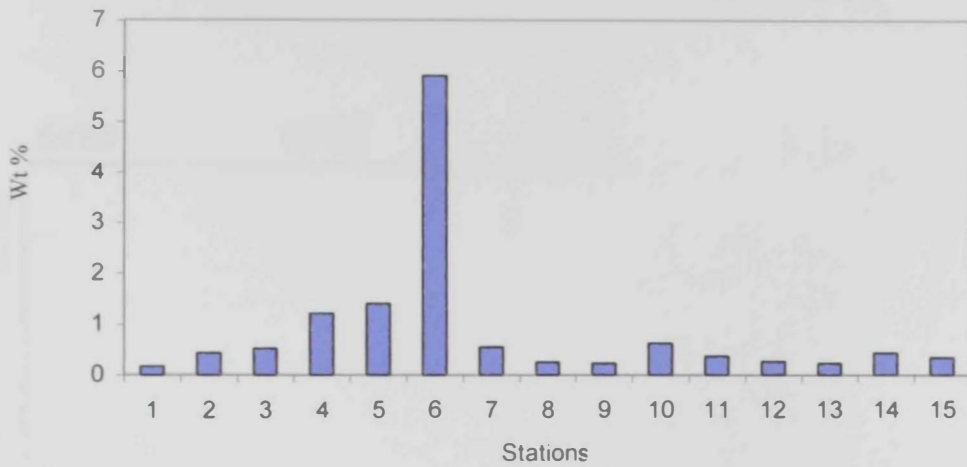
Figure 3.2 : *Concentrations of total organic carbon (wt %) in Dubai sediments*
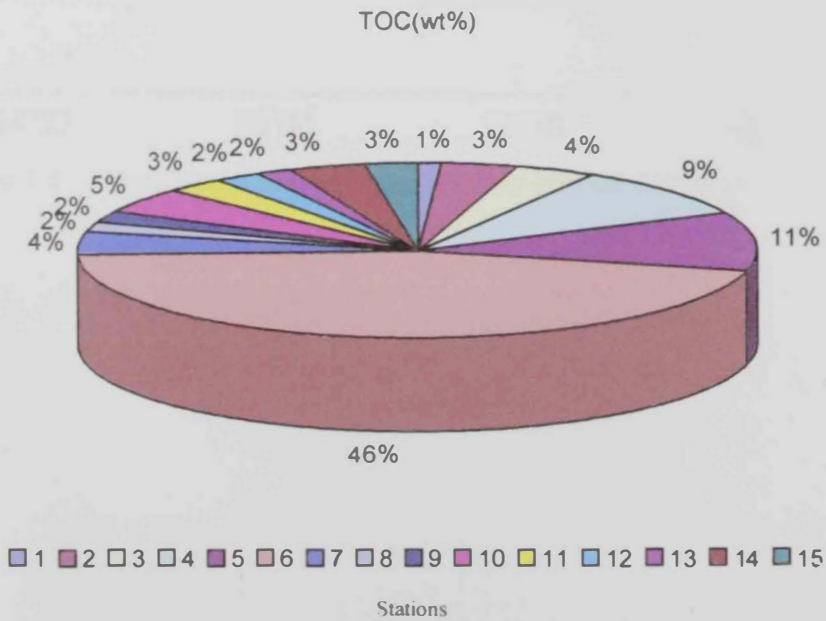
Figure 3.3 : *The percentage of total organic carbon in each station*
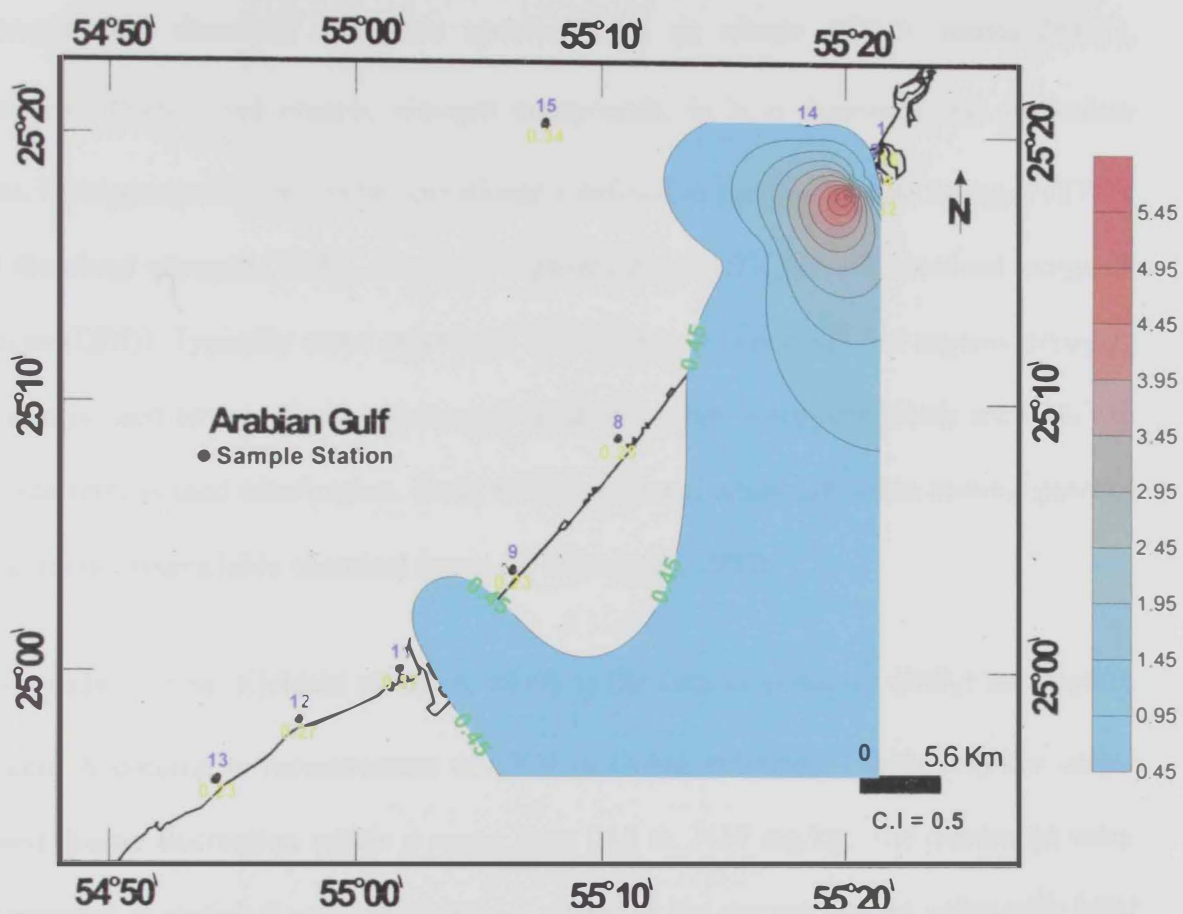
Figure 3.4 : *Distribution map of total organic carbon (wt%) in Dubai sediments*

3.3 Total Kjeldahl Nitrogen (TKN)

The elemental gas dinitrogen (N_2) is the most abundant but least reactive form of nitrogen in the global environment. However, many biochemical transformations can convert dinitrogen into dissolved inorganic species; such as nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+) and organic nitrogen compounds, in both dissolved and particulate forms. Nitrogen speciation can be operationally defined as total particulate nitrogen (TPN), total dissolved nitrogen (TDN), dissolved organic nitrogen (DON) and dissolved inorganic nitrogen (DIN)). Typically some organisms fix nitrogen to either NH_4^+ or organic nitrogen, the term is used ammonification (nitrogen fixation); other organisms nitrify the NH_4^+ to NO_3, the term is used nitrification. Both, nitrification and ammonification convert gaseous nitrogen into bioavailable chemical forms (Wilson *et al.*, 1993).

TKN stands for total Kjeldahl nitrogen, which is the sum of ammonia (NH_3) and organic nitrogen. According to measurement of TKN in Dubai sediments (Table 3.4) the values showed drastic fluctuation within a range from 218 to 2457 mg/kg. The maximum value was reported at station 9, whereas station 6 provided the second highest value with 2222 mg/kg. The minimum value was recorded at station 1 with an overall average of 696 mg /kg and S.D of 697. The variation in TKN concentrations was illustrated in Figure 3.5, while Figure 3.6 demonstrates the percentage of TKN in each station. Each of Dewa (St 9) and Al-Hamriya St 3 (St 6) represent more than I/5 (23% & 21% respectively) of total TNK values. The areal distribution map of TKN (Figure 3.7) indicates remarkable increases towards the northeastern represented by Al-Hamriya St 3 (St 6) and southwestern represented by Dewa (St 9) parts of the study area.

Table 3.4 : *Concentrations of total Kjeldahl nitrogen in Dubai sediments*

Station no.	Locality	TKN mg/kg
1	Al-Mamzar mouth	218
2	Al-Mamzar mid	420
3	Al-Mamzar end	410
4	Al-Hamriya St 1	931
5	Al-Hamriya St 2	814
6	Al-Hamriya St 3	2222
7	Dry Docks	523
8	Jumeirah Beach	234
9	Dewa	2457
10	Dubal	265
11	Jebel Ali Hotel	385
12	Ras Hisyan	324
13	Ras Ghantoot	330
14	Dubai approach	507
15	Neptune Wreck	402
Average ± S.D		696 ± 697

mg/kg = μg/g = ppm
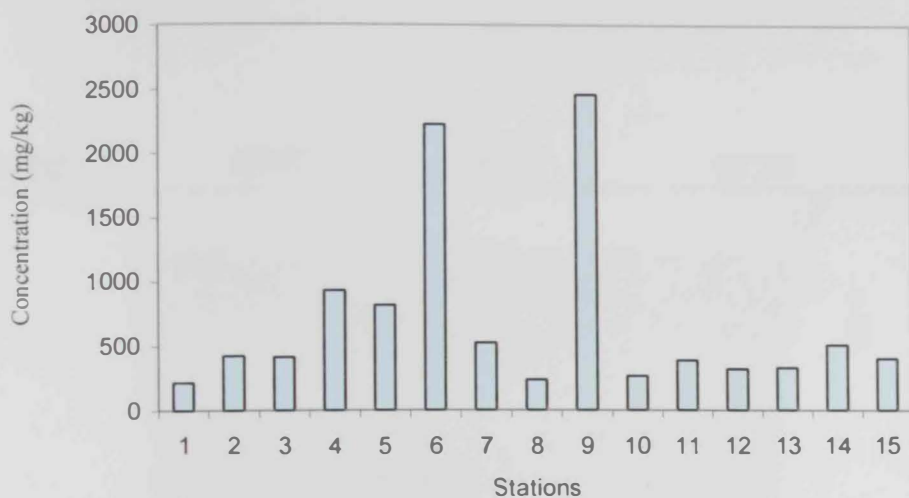
Figure 3.5 : *Concentrations of total Kjeldahl nitrogen (mg/kg) in Dubai sediments*
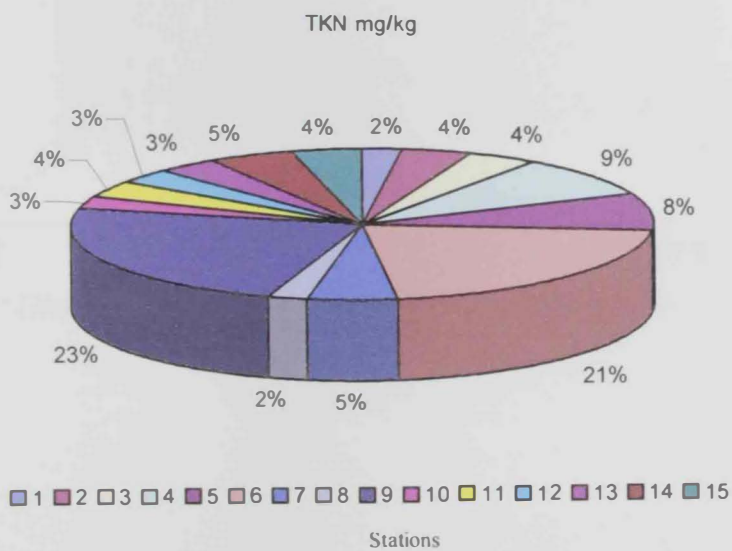
Figure 3.6 : *The percentage of total Kjeldahl nitrogen in each station*

49
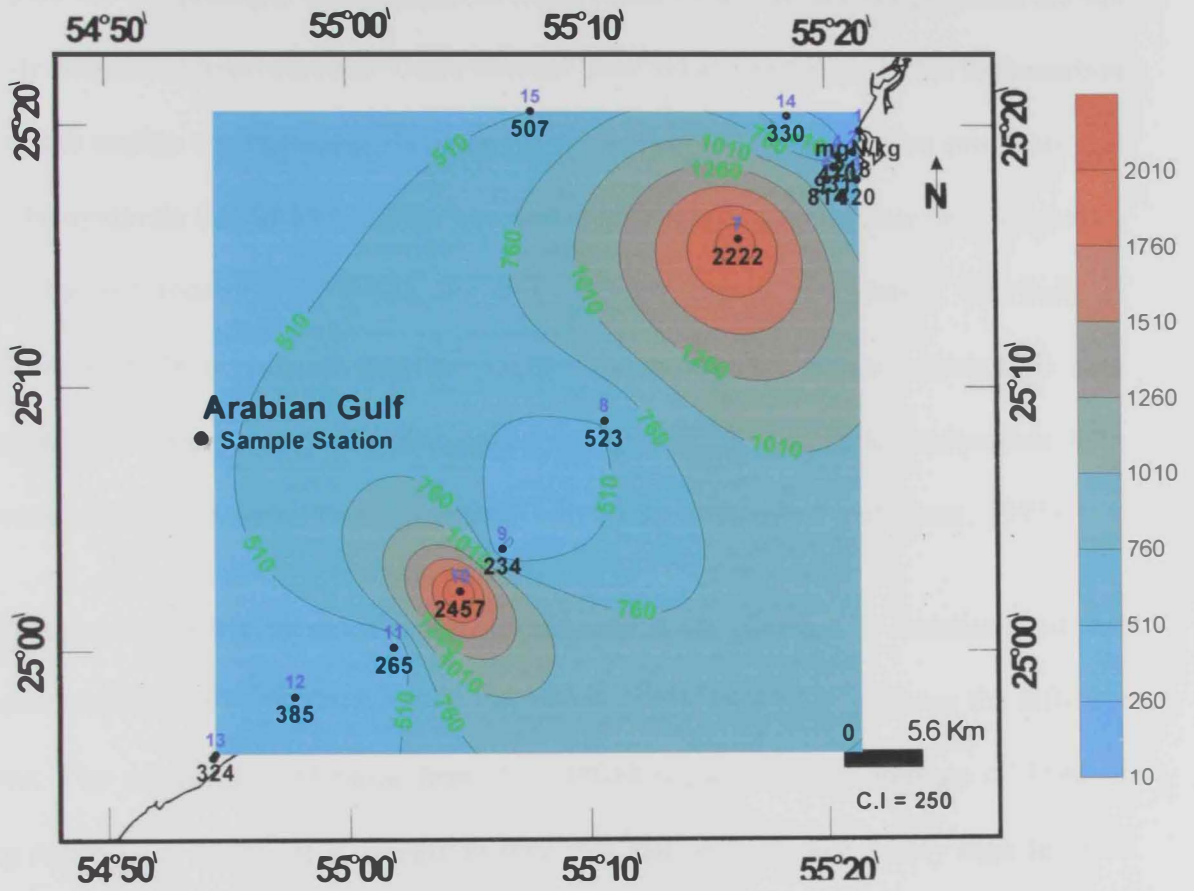
Figure 3.7 : *Distribution map of total Kjeldahl nitrogen (mg/kg) in Dubai sediments*

3.4 Total Petroleum Hydrocarbons (TPH)

Hydrocarbons, chemical compounds composed exclusively of the elements carbon and hydrogen, are the principal components of fossil fuels. Crude oil and oil products are not the only sources of hydrocarbons. Other sources exist which contribute to the hydrocarbon load of the marine environment. These derive from incomplete combustion processes and recent biosynthesis (GESAMP, 1993). The fate of petroleum hydrocarbons once they enter the marine environments is similar to that of many organic pollutants. The bulk of petroleum initially introduced into the water column rapidly becomes associated with hydrophobic organic matter and suspended particulates, the volatile compounds then evaporate and the non-volatiles are deposited into sediment (Capone and Bauer, 1992).

The spectrophotometric measurement of Dubai sediments (Table 3.5) demonstrated that the concentrations of total petroleum hydrocarbons (TPH) vary widely among the different stations. The values of TPH range from 2 to 48018 mg/kg, with an average of 3590.43 mg/kg and S.D of 12353. It is worthy to note that station 6 showed a very high level of TPH (48018 mg/kg) compared with other stations (Figure 3.8), whereas a very low level was recorded at station 4 and other stations showed slightly and moderately levels of TPH (Figure 3.9). The percentage of TPH in Dubai sediments is demonstrated in Figure 3.10 , 9/10 (90%) of TPH values in the study area was provided by Al-Hamriya St 3 (St 6) and 1/10 (10%) was in Al-Hamriya St 2 (St 5). The distribution map showed that TPH in Dubai sediments is concentrated in the northeastern part of the study area, which may reflect a heavily polluted area around Al-Hamriya St 2 and 3 (St 5 & 6). Al-Hamriya St 3 (St 6) represents the center anomalous area whereas the other parts of the study area vary between moderately polluted, slightly polluted and unpolluted by TPH (Figure 3.11).

Table 3.5 : *Concentrations of total petroleum hydrocarbons in Dubai sediments*

Station no.	Locality	TPH in soil mg/kg
1	Al-Mamzar mouth	50
2	Al-Mamzar mid	39
3	Al-Mamzar end	39
4	Al-Hamriya St 1	2
5	Al-Hamriya St 2	4888
6	Al-Hamriya St 3	48018
7	Dry Docks	134
8	Jumeirah Beach	146
9	Dewa	223
10	Dubal	47
11	Jebel Ali Hotel	6.44
12	Ras Hisyan	113
13	Ras Ghantoot	108
14	Dubai approach	20
15	Neptune Wreck	23
Average ± S.D		3590.43 ± 12353

mg/kg = µg/g = ppm
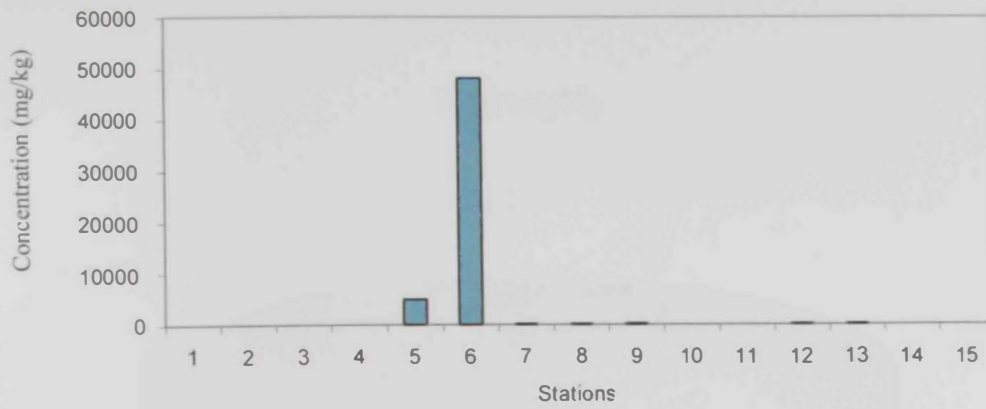
Figure 3.8 : *Concentrations of total petroleum hydrocarbons (mg/kg) in Dubai sediments*
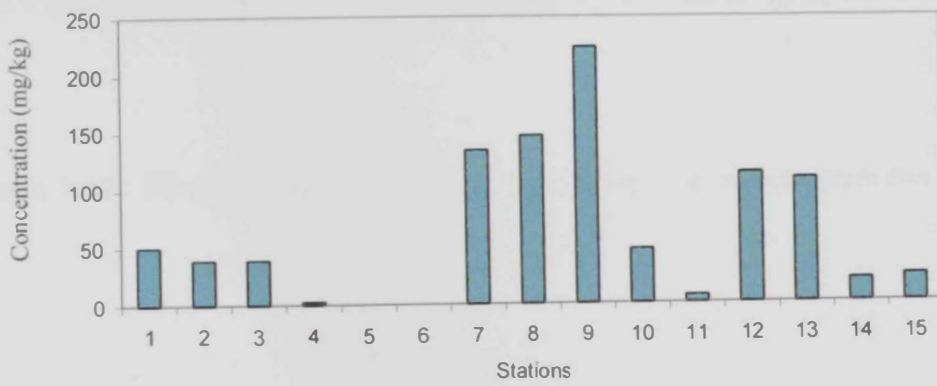
Figure 3.9 : *Concentrations of total petroleum hydrocarbons (mg/kg) at different stations except station 5 and 6*

TPH mg/Kg

Trace values

10%

90%

□ 1 ■ 2 □ 3 □ 4 ■ 5 □ 6 ■ 7 □ 8 ■ 9 ■ 10 □ 11 □ 12 ■ 13 ■ 14 ■ 15
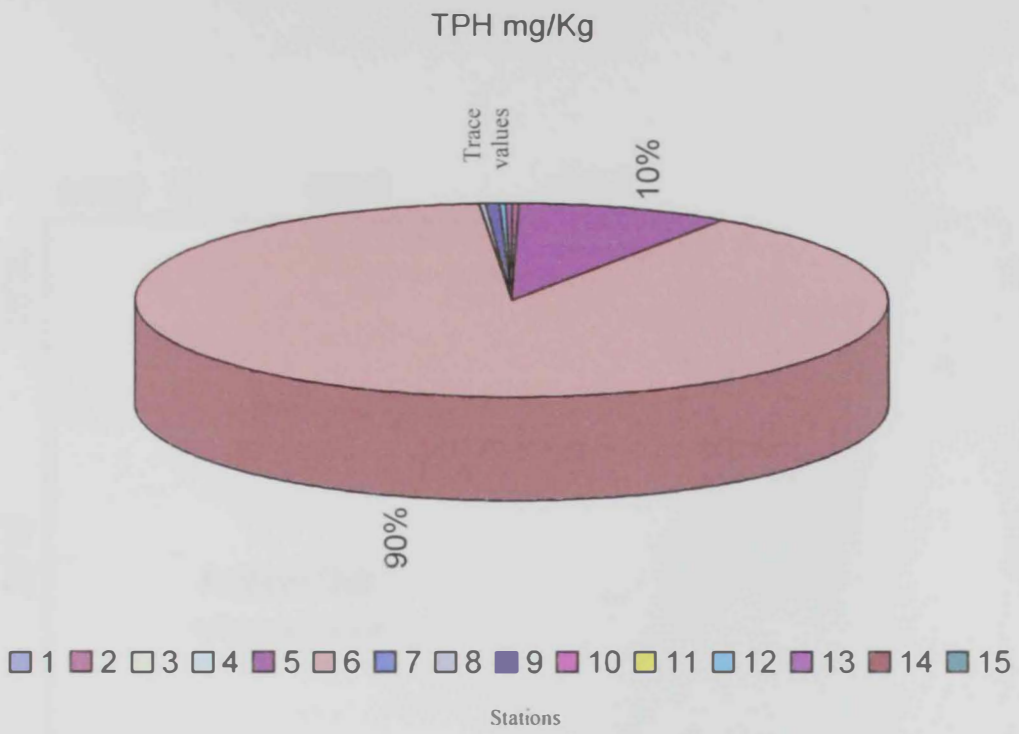
Stations

Figure 3.10 : *The percentage of total petroleum hydrocarbons in each station*
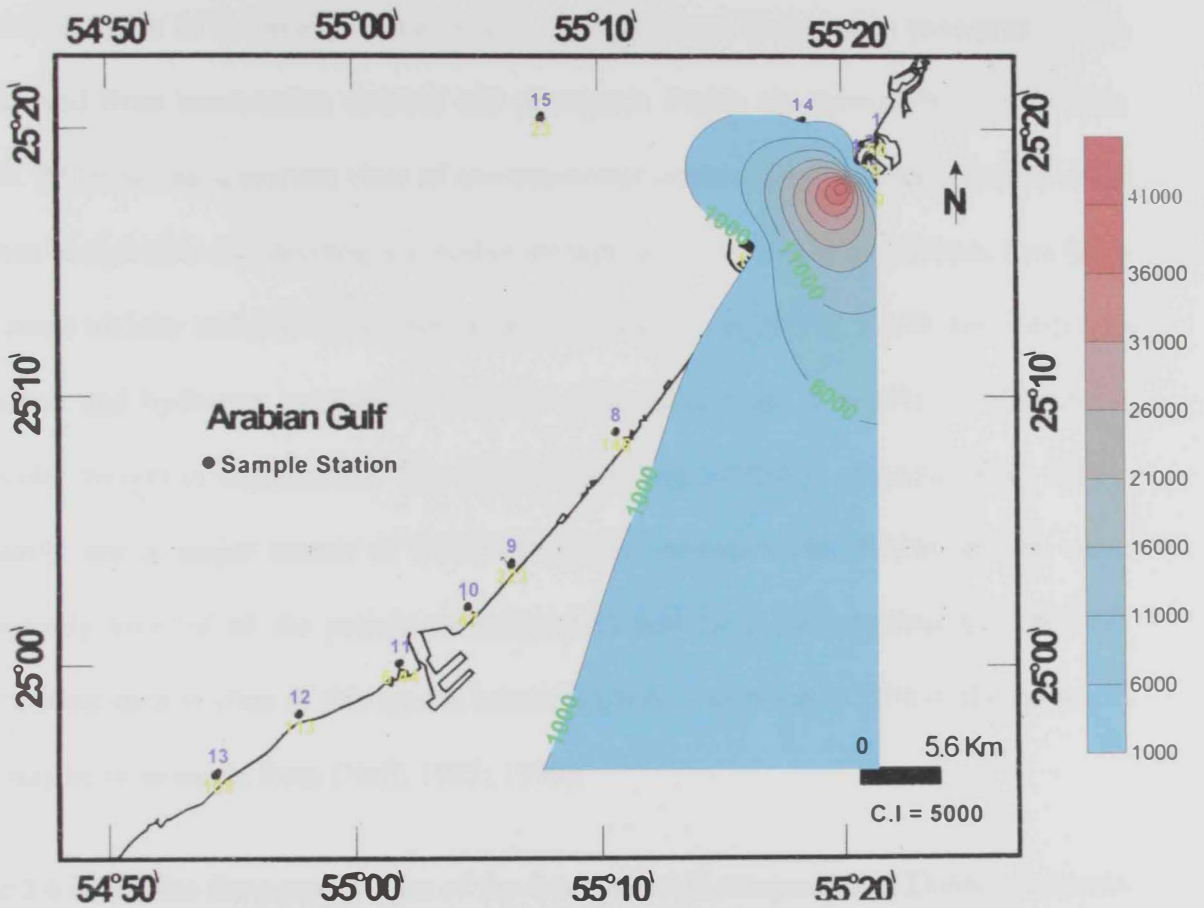
Figure 3.11 : *Distribution map of total petroleum hydrocarbons (mg/kg) in Dubai sediments*

3.5 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons are a class of organic pollutants that are released into the environment in large quantities, mainly due to human activities. There are two primary sources of PAHs to the marine environment, pyrogenic and petrogenic: pyrogenic PAHs are derived from combustion sources and petrogenic PAHs are derived from petroleum inputs. PAHs are an important class of environmental contaminants to study because some of these compounds are carcinogenic and/or mutagenic to mammals. In addition, they have both acute toxicity and sub-lethal effects on some aquatic organisms. PAHs are composed of carbon and hydrogen, arranged in two or more fused rings. The PAH of the lowest molecular weight is naphthalene. The largest fused-ring system is graphite (Witt, 1995). Oil spills are a major source of PAH in aquatic environments. PAHs are the most biologically toxic of all the petroleum compounds and the most notorious and common carcinogenic hydrocarbon of this type is benzo(a)pyrene. As much as 75% of the carbon in coal may be in aromatic form (Neff, 1985; 1990).

Table 3.6 illustrates the concentration of the detected PAH compounds in Dubai sediments. The total PAHs (TPAHs) vary from 0.09 to 161.72 ppm with an average of 11.83 ppm and S.D value of 41.6. The maximum concentration was found at station 6, whereas the minimum value was reported at station 14. Benzo(g,h,i)perylene, benzo(k)fluoranthene and chrysene reflected significant levels (Figure 3.12) especially in station 6. Also pyrene, dibenzo(a,h)anthracene, naphthalene, fluoranthene and benzo(a)pyrene showed their highest levels at the same station. The other compounds vary in concentration between low and very low. Figure 3.13 represents the percentage of TPAHs in each station of the study area. It is clear here that Al-Hamriya St 3 (St 6) constitutes more than 9/10 (92%) of TPAHs values in Dubai sediments. The description of each compound is given below:

3.5.1 Naphthalene

It is a polycyclic aromatic hydrocarbon (PAH) with two aromatic rings (Figure 3.14A). Naphthalene is noncarcinogenic PAH but also toxic to some organisms. The exposure to naphthalene can cause colon, and liver damage; leukemia and DNA damage (Rowat SC., 1998). Naphthalene was detected at five stations (1, 3, 5, 6 & 14) with concentrations vary between low and very low within a range from 0.1 to 6.6 ppm. The maximum value was reported at station 6 and the minimum value at station 14 (Figure 3.15A). The mapping of naphthalene is showing a trend of increasing towards the northeastern part (Figure 3.16).

3.5.2 Fluorene

It is a polycyclic aromatic hydrocarbon (PAH) with one five-membered and two six-membered rings (Figure 3.14B). Fluorene was reported only in two stations (6 & 5) of the study area, at very low levels 0.78 & 0.24 ppm respectively (Figure 3.15B).

3.5.3 Phenanthrene

It is a polycyclic aromatic hydrocarbon (PAH) with three aromatic rings (Figure 3.14C). Phenanthrene is noncarcinogenic PAH, but also toxic to some organisms. Phenanthrene occurs in fossil fuels and is present in products of incomplete combustion. Phenanthrene is one of a number of PAHs on EPA's priority pollutant list (ATSDR, 1990). Phenanthrene was recorded at five stations (1, 3, 5, 9 & 15) with very low concentrations. The highest value was 0.32 ppm and reported at station 5 (Figure 3.15C). The mapping survey also shows an increase towards the northeastern part of the study area (Figure 3.17).

3.5.4 Fluoranthe

It is a polycyclic aromatic hydrocarbon (PAH) with one five-membered and three six-membered rings (Figure 3.14D). Fluoranthene is noncarcinogenic PAH, but also toxic to some organisms. Fluoranthene was detected in six stations (3, 5, 6, 9, 10 & 15) of the study area at very low concentrations; the highest recorded value was 3.9 ppm at station 6, whereas the minimum concentration (0.04 ppm) was provided by stations 3 and 10 (Figure 3.15D). The distribution map demonstrates that its values increase towards the northern parts particularly around Al-Hamriya stations (Figure 3.18).

3.5.5 Pyrene

It is a polycyclic aromatic hydrocarbon (PAH) with four aromatic rings (Figure 3.14E). Pyrene is noncarcinogenic PAH but also toxic to some organisms. Pyrene levels in Dubai sediments range from 0.03 to 13.7 ppm. Pyrene was found at five stations (3, 5, 6, 9 & 10) with a relative wide range from 0.03 ppm at station 3 to 13.7 ppm at station 6 (Figure 3.15E). Its distribution map exhibits an increasing trend towards the northeastern part of the study area around Al-Hamriya stations (Figure 3.19).

3.5.6 Benzo(a)anthracene

It is a polycyclic aromatic hydrocarbon (PAH) with four aromatic rings (Figure 3.14F). Benzo(a)anthracene was detected only at two stations (9 & 10) of the study area with very low concentrations of 0.2 ppm and 0.04 ppm respectively . The distribution was only limited to the western parts of the study area (Figure 3.15F).

3.5.7 Chrysene

It is a polycyclic aromatic hydrocarbon (PAH) with four aromatic rings (Figure 3.14G). Chrysene is a ubiquitous environmental contaminant formed primarily by the incomplete combustion of organic compounds. Although it is present in coal and oil, the presence of chrysene in the environment is mainly due to anthropogenic activities (ATSDR, 1990). Chrysene is carcinogenic, causing tumors in fish and other animals, and are acutely toxic to some organisms. The measurement of chrysene in Dubai sediments showed that its values vary between very low and high. Chrysene was reported at seven stations (1, 3, 5, 6, 9, 10 & 15) with values range between 0.02 ppm at stations 1 and 3 to 35 ppm at station 6 (Figure 3.15G). The distribution map of chrysene displays a northeastern increasing trend around Al- Hamriya stations (Figure 3.20).

3.5.8 Benzo(b)fluoranthene

It is a polycyclic aromatic hydrocarbon (PAH) with one five-membered and four six-membered rings (Figure 3.14H). Benzo(b)fluoranthene was detected only at four stations (5, 7, 9 & 10) of the study area. The values vary from 0.03 ppm at station 10 to 3.1 ppm at station 5 (Figure 3.15H). Also, its distribution map shows an increasing trend towards the northeastern parts of the study area around Al-Hamriya stations (Figure 3.21).

3.5.9 Benzo(k)fluoranthene

It is a polycyclic aromatic hydrocarbon (PAH) with one five-membered and four six-membered rings (Figure 3.14I). There is no commercial production or known use of this compound. Benzo(k)fluoranthene is found in fossil fuels and occurs usually in products of incomplete combustion and in soils, groundwater, and surface waters at hazardous waste sites (ATSDR, 1990). In initiation-promotion assays, benzo(k)fluoranthene was active as

an initiator of skin carcinogenesis. In a short-term assay, hepatic and lung tumors occurred in newborn mice. Benzo(k)fluoranthene was detected at six stations (5, 6, 7, 8, 9 & 15) . Its values occupy the range from 0.02 ppm at station 15 to 43 ppm at station 6, which showed significant level, whereas this compound was found by trace quantities in other stations (Figure 3.15I). The distribution map of benzo(k)fluoranthene shows an increasing towards the northeastern parts around Al-Hamriya stations (Figure 3.22).

3.5.10 Benzo(a)pyrene

It is a polycyclic aromatic hydrocarbon (PAH) with five aromatic rings (Figure 3.14J). Benzo(a)pyrene is carcinogenic, causing tumors in fish and other animals, and are acutely toxic to some organisms. This compound was found only at three stations (6, 9 & 10) of the study area, with values varying from 0.05 ppm at station 10 to 2.34 ppm at station 6 (Figure 3.15J).

3.5.11 Dibenzo(a,h)anthracene

It is a polycyclic aromatic hydrocarbon (PAH) with five aromatic rings (Figure 3.14K). Dibenzo(a,h) anthracene was recorded at three stations (5, 6 & 9). Its values range from 0.03 ppm at station 9 to 10.5 ppm at station 6 (Figure 3.15K).

3.5.12 Benzo(g,h,i)perylene

It is a polycyclic aromatic hydrocarbon (PAH) with six aromatic rings (Figure 3.14L). There is no known commercial production or use of benzo(g,h,i)perylene. It occurs naturally in crude oils and is present in products of incomplete combustion and in coal tar. Benzo(g,h,i)perylene is one of a number of PAHs on EPA's priority pollutant list (ATSDR, 1990). There is lack of data on the acute, sub-chronic, chronic, developmental, or

reproductive toxicity of benzo(g,h,i)perylene by other routes of exposure in humans or animals. The measurement of benzo(g,h,i)perylene in Dubai sediments demonstrated that, the concentrations vary between very low and high. Benzo(g,h,i)perylene was detected at five stations (5, 6, 7, 10 & 15). The compound values vary widely from 0.03 ppm at station 15 to 46 ppm at station 6 (Figure 3.15L). The distribution map of benzo(g,h,i)perylene exhibits an increasing trend towards the northeastern parts of the study area around Al-Hamriya stations (Figure 3.23).

3.5.13 Indeno(1,2,3-cd)pyrene

It is a polycyclic aromatic hydrocarbon (PAH) with one five-membered and four six-membered rings (Figure 3.14M). This compound was detected only at five stations (1, 5, 7, 9 & 10) of the study area; with trace concentrations varying from 0.02 ppm at station 10 to 0.3 ppm at station 5 (Figure 3.15M).

Table 3.6 : *Concentrations of polycyclic aromatic hydrocarbons (ppm) in Dubai sediments*

	Locality / Compounds	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(a)pyrene	Dibenzo(a,h)anthracene	Benzo(g,h,i)perylene	Indeno(1,2,3-cd)pyrene	Total PAHs
1	Al-Mamzar mouth	0.19	nd	nd	nd	0.02	nd	nd	nd	nd	0.02	nd	nd	nd	nd	nd	0.03	0.26
2	Al-Mamzar mid	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
3	Al-Mamzar end	0.1	nd	nd	nd	0.03	nd	0.04	0.03	nd	0.02	nd	nd	nd	nd	nd	nd	0.22
4	Al-Hamriya St 1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
5	Al-Hamriya St 2	2.3	nd	nd	0.24	0.32	nd	0.44	0.92	nd	1.3	3.1	0.56	nd	0.18	2.9	0.3	12.56
6	Al-Hamriya St 3	6.6	nd	nd	0.78	nd	nd	3.9	13.7	nd	34.8	nd	43	2.34	10.5	46.1	nd	161.72
7	Dry Docks	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.08	0.05	nd	nd	0.14	0.03	0.3
8	Jumeirah Beach	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.05	nd	nd	nd	nd	0.05
9	Dewa	nd	nd	nd	nd	0.13	nd	0.25	0.23	0.2	0.13	0.12	0.08	0.23	0.03	nd	0.1	1.5
10	Dubal	nd	nd	nd	nd	nd	nd	0.04	0.04	0.04	0.03	0.03	nd	0.05	nd	0.08	0.02	0.33
11	Jebel Ali Hotel	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
12	R as Hisyan	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
13	Ras Ghantoot	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
14	Dubai approach	0.09	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.09
15	Neptune Wreck	nd	nd	nd	nd	0.06	nd	0.14	nd	nd	0.15	nd	0.02	nd	nd	0.03	nd	0.4

nd (Not detected)   ppm = $\mu g/g$ = mg/kg = ppb x 10^{-3} = $\mu g/kg$ x 10^{-3}

Average ± S.D	11.83 ± 41.6

62
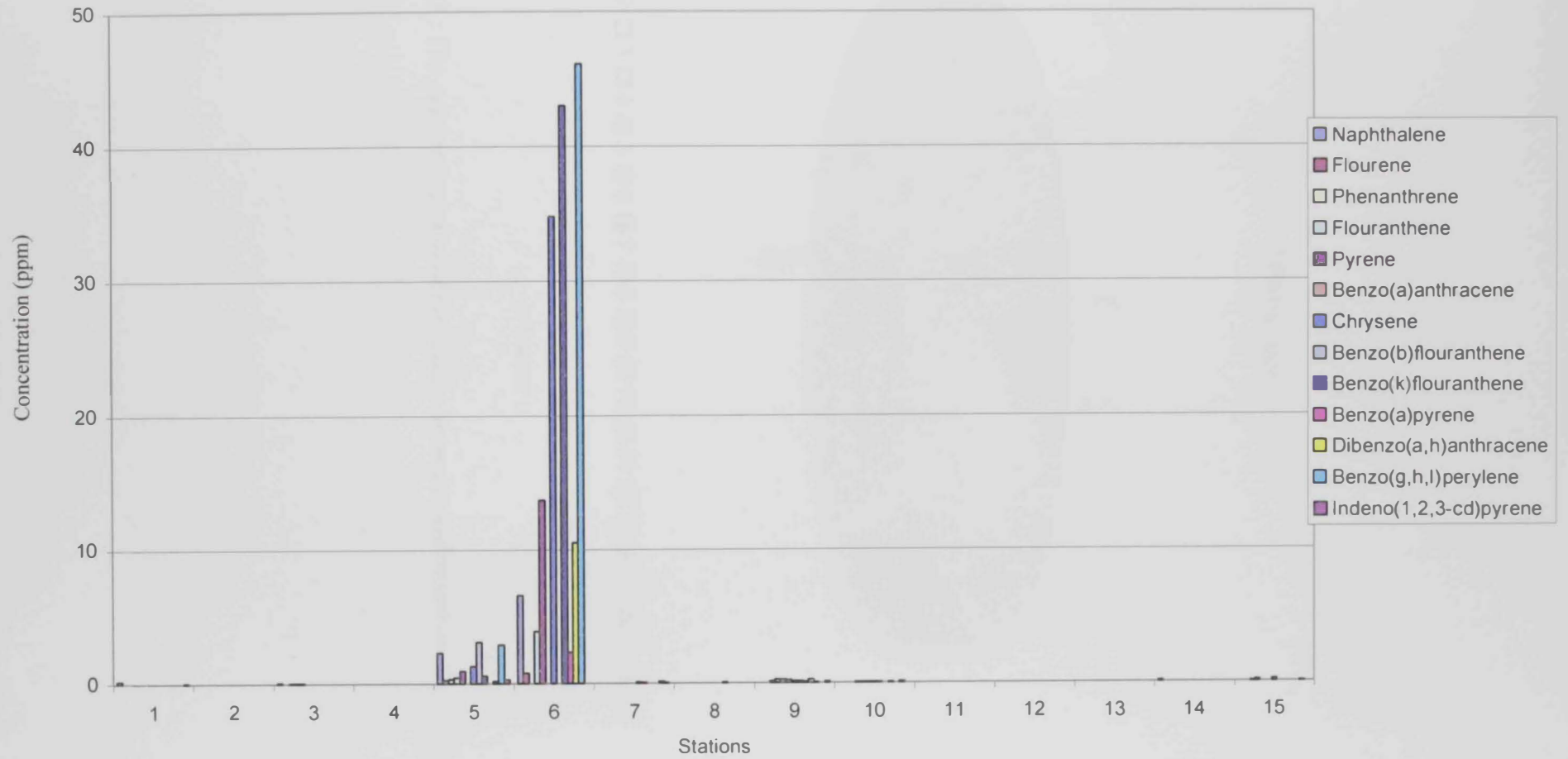
Figure 3.12 : *Concentrations of polycyclic aromatic hydrocarbon compounds (ppm) in Dubai sediments*

TPAHs (ppm)
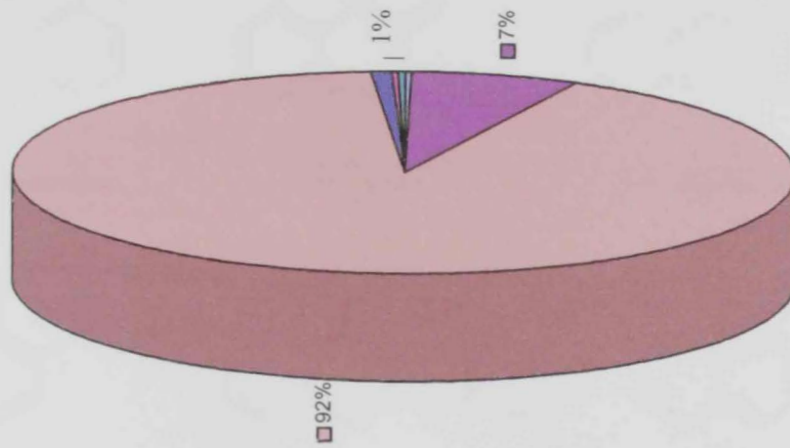
□1 ■2 □3 □4 ■5 □6 ■7 □8 ■9 ■10 ■11 □12 ■13 ■14 ■15

Stations

Figure 3.13 : *The percentage of total polycyclic aromatic hydrocarbons in each station*
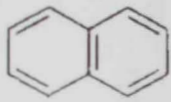
A. Naphthalene
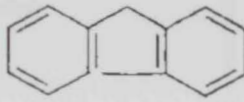
B. Fluorene
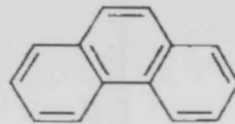
C. Phenanthrene
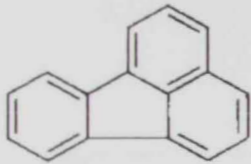
D. Fluoranthene
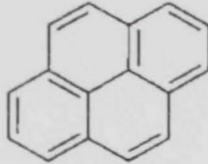
E. Pyrene
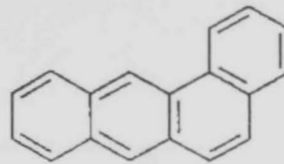
F. Benzo(a)anthracene
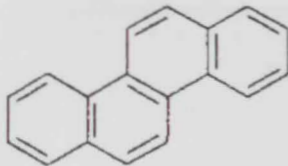
G. Chrysene
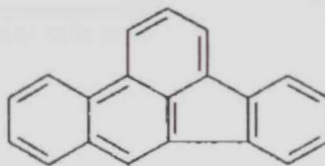
H. Benzo(b)fluoranthene
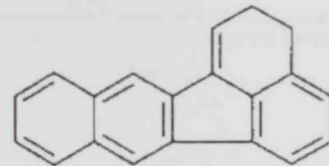
I. Benzo(k)fluoranthene
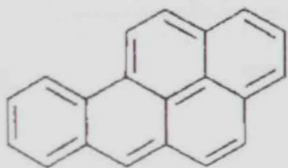
J. Benzo(a)pyrene
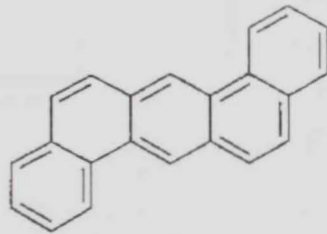
K. Dibenzo(a,h)anthracene
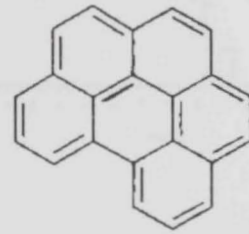
L. Benzo(g,h,i)perylene
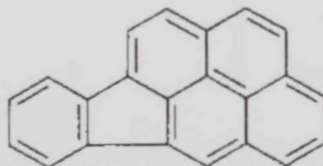
M. Indeno(1,2,3-c,d)pyrene

Figure 3.14 : *The structural formula of PAH compounds (Source: Witt, 1995)*
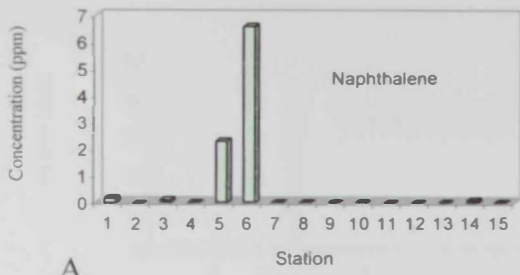
A.
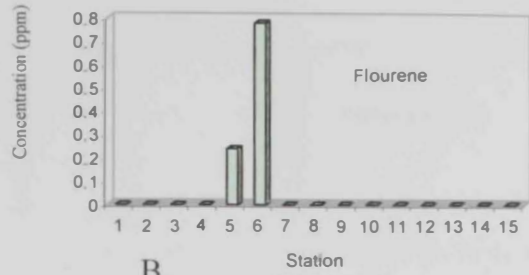
B.
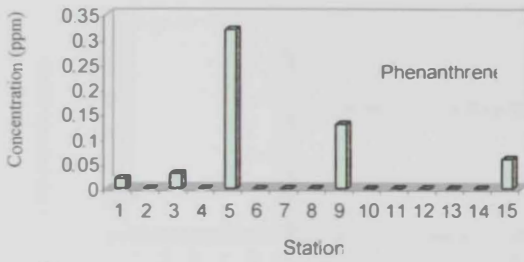
C.
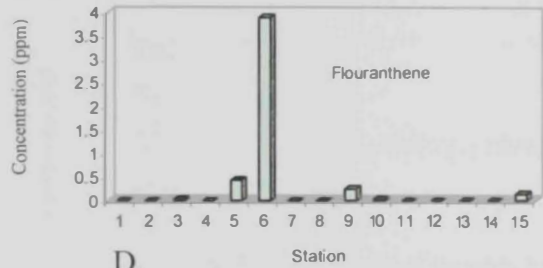
D.
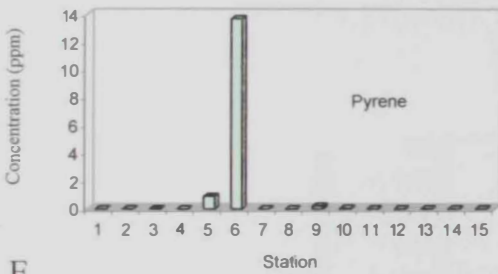
E.
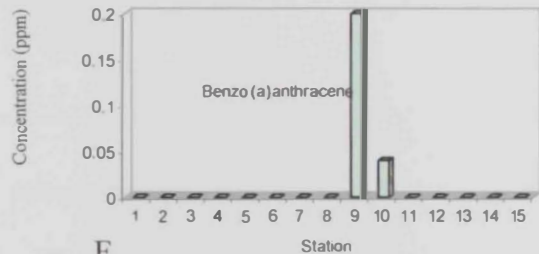
F.
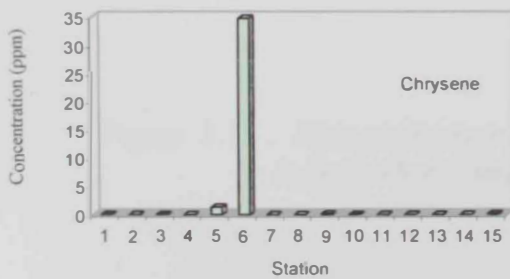
G.
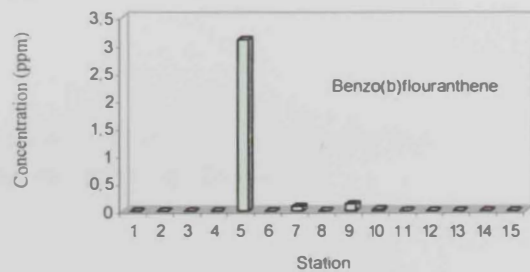
H.
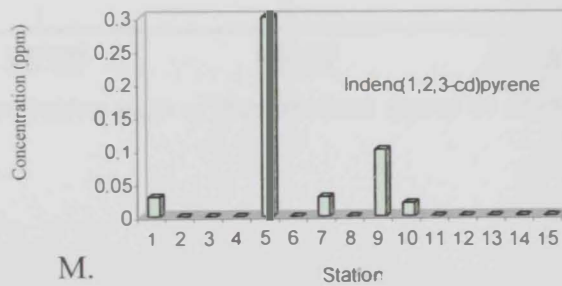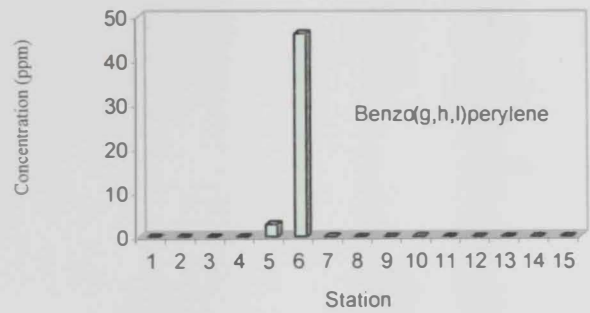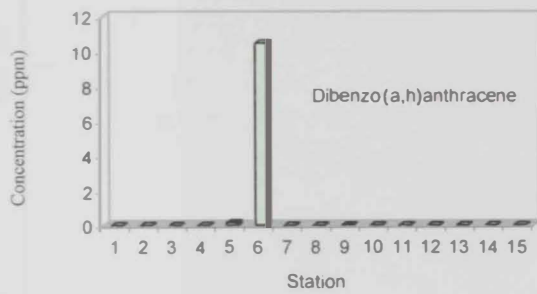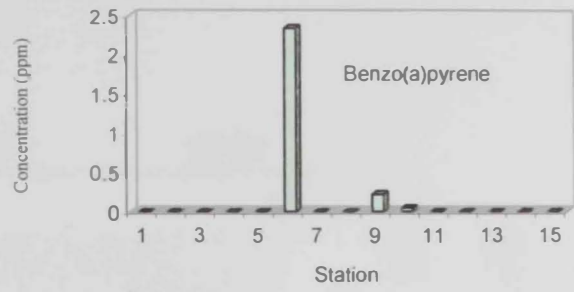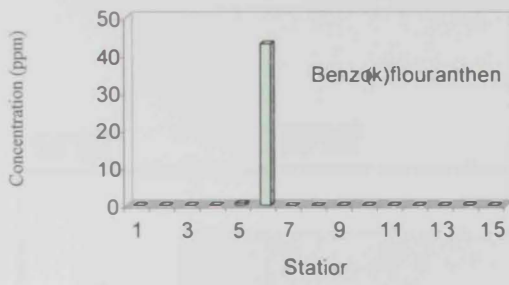
Figure 3.15 : *Histograms representing concentrations of polycyclic aromatic hydrocarbon compounds (ppm) in Dubai sediments*
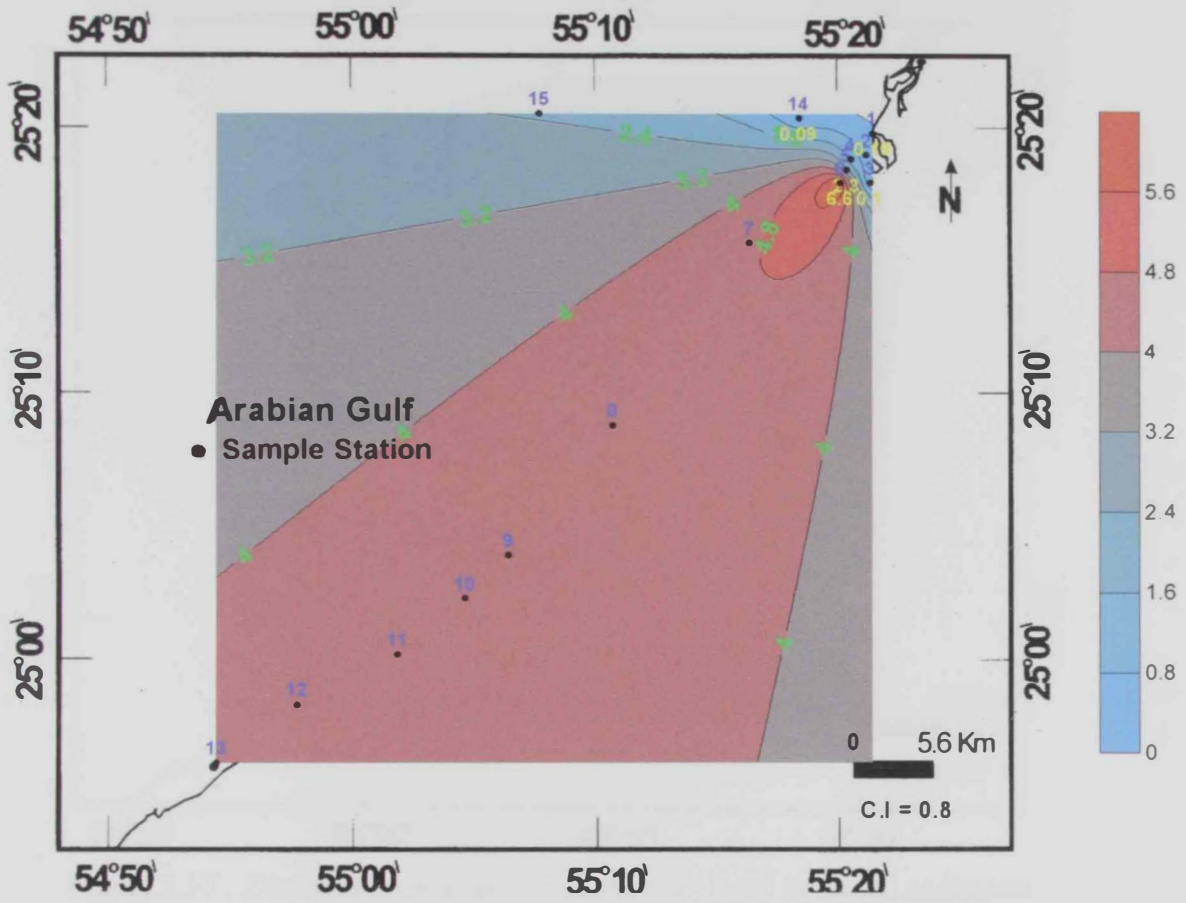
Figure 3.16 : *Distribution map of naphthalene (ppm) in Dubai sediments*
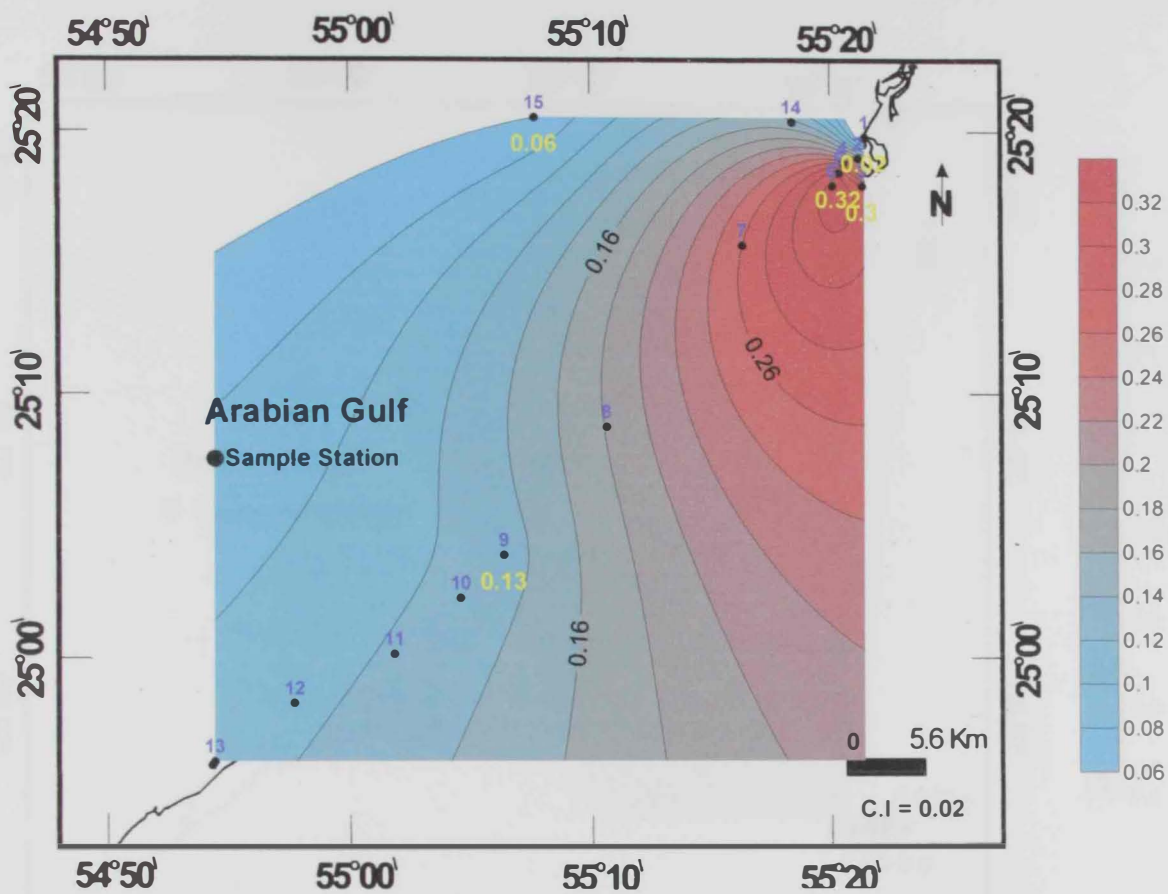
Figure 3.17 : *Distribution map of phenanthrene (ppm) in Dubai sediments*
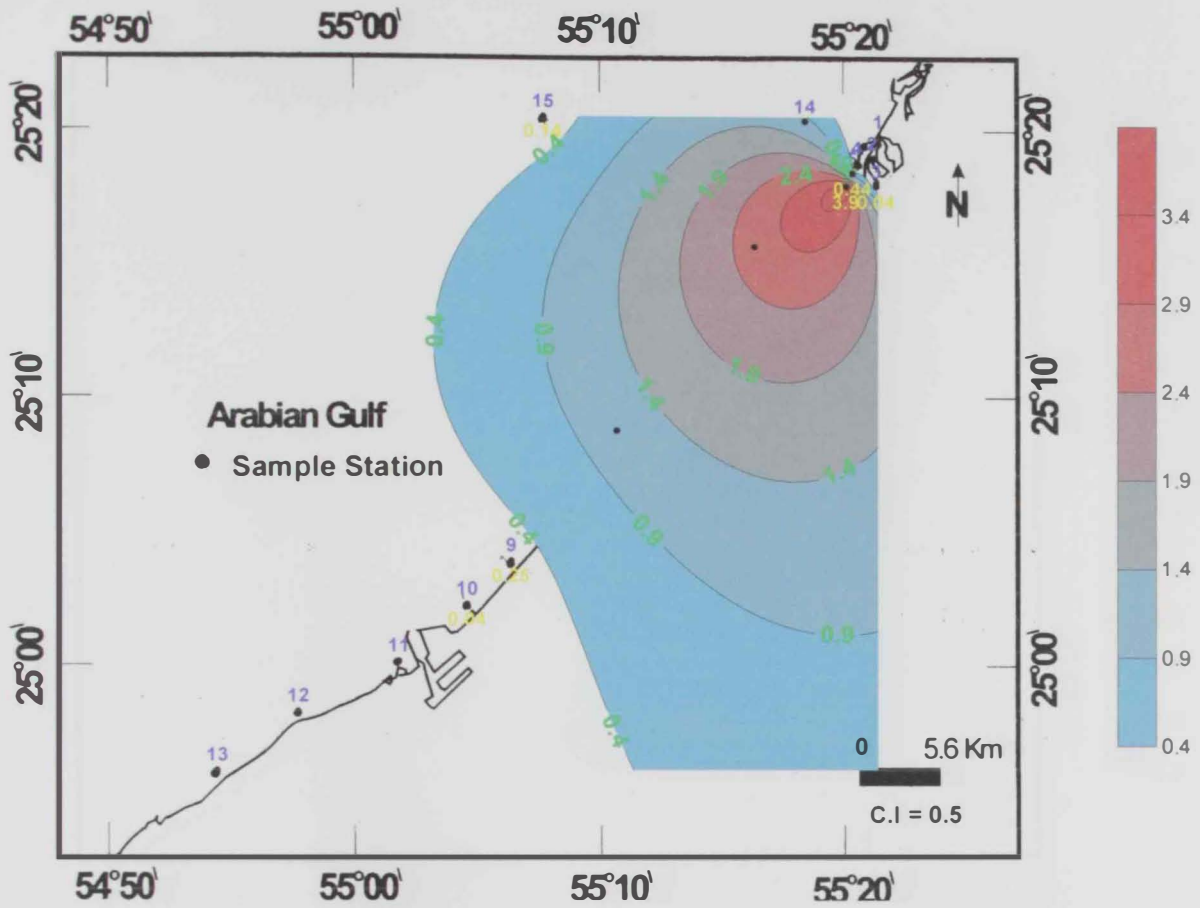
Figure 3.18 : *Distribution map of flouranthene (ppm) in Dubai sediments*
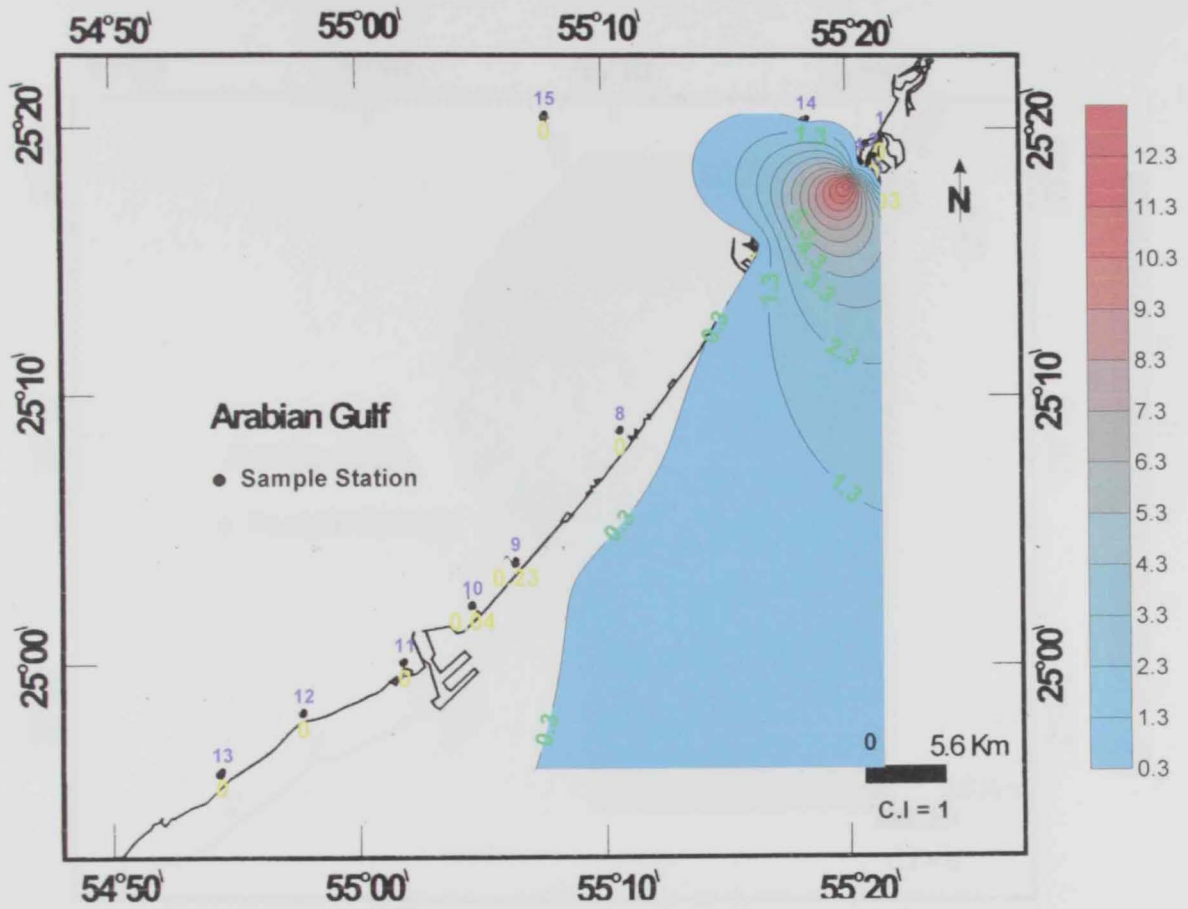
Figure 3.19 : *Distribution map of pyrene (ppm) in Dubai sediments*
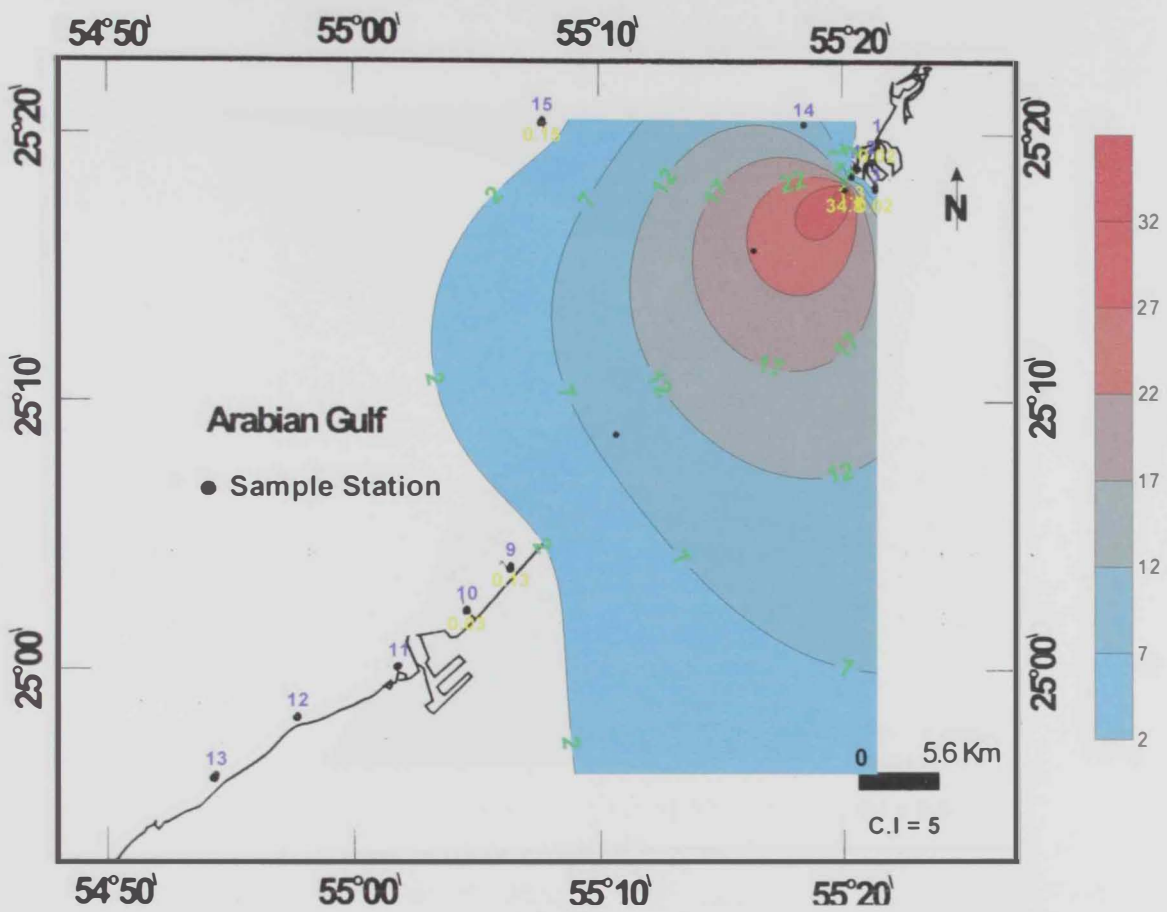
Figure 3.20 : *Distribution map of chrysene (ppm) in Dubai sediments*
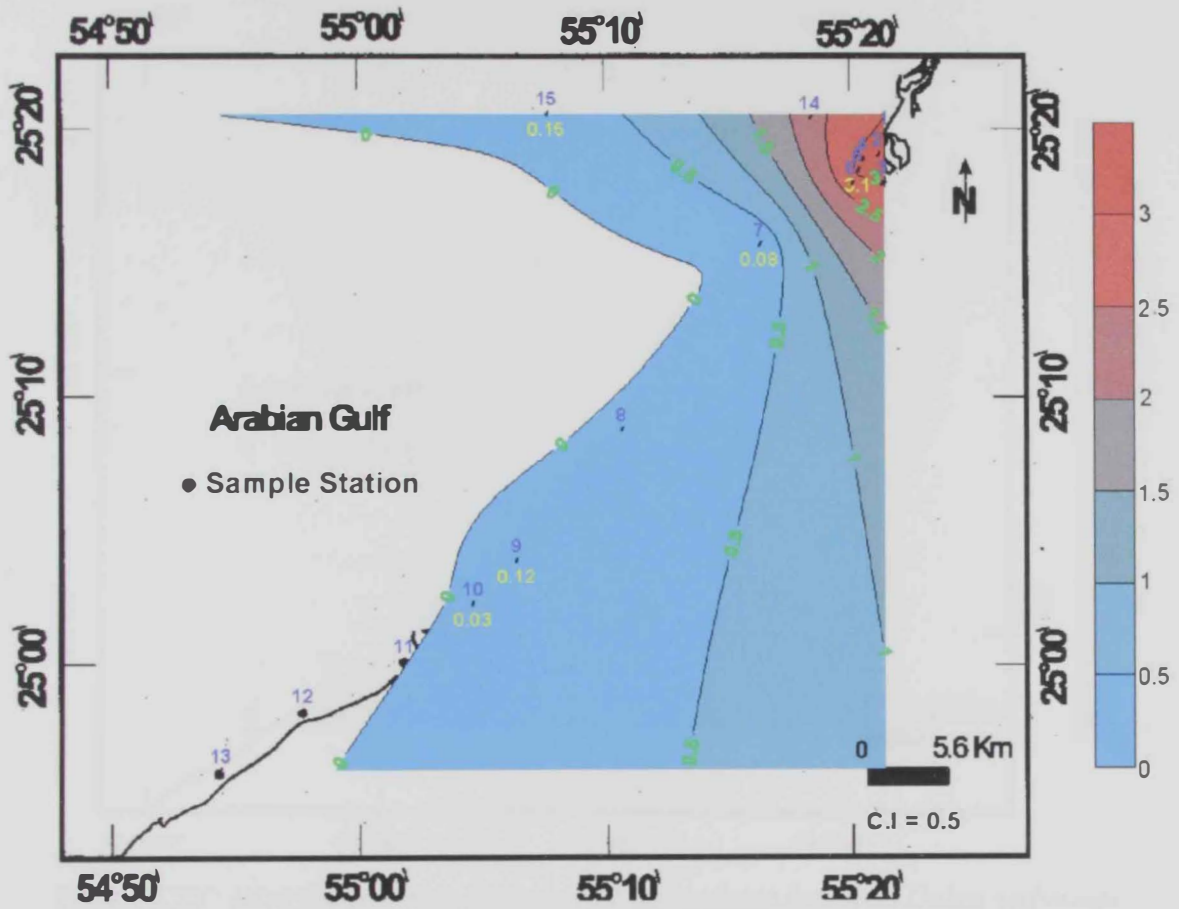
Figure 3.21 : *Distribution map of benzo(b)fluoranthene (ppm) in Dubai sediments*
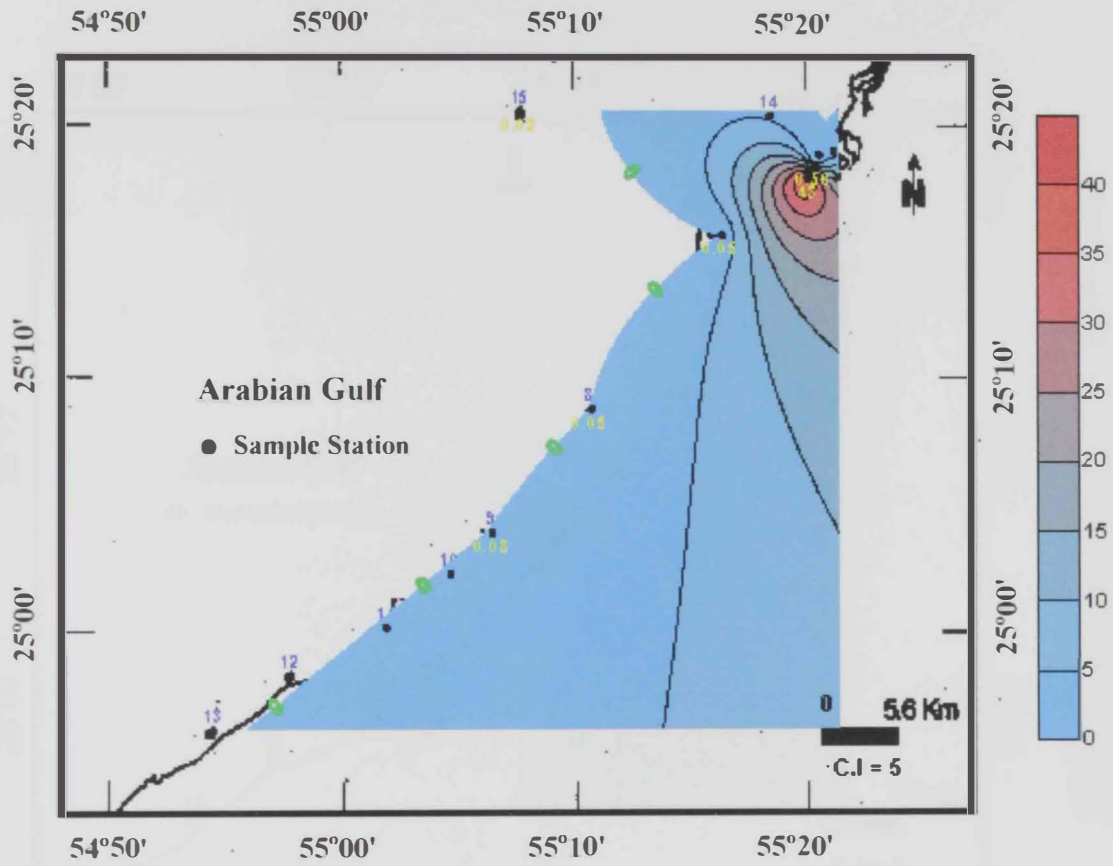
Figure 3.22 : *Distribution map of benzo(k)fluoranthene (ppm) in Dubai sediments*
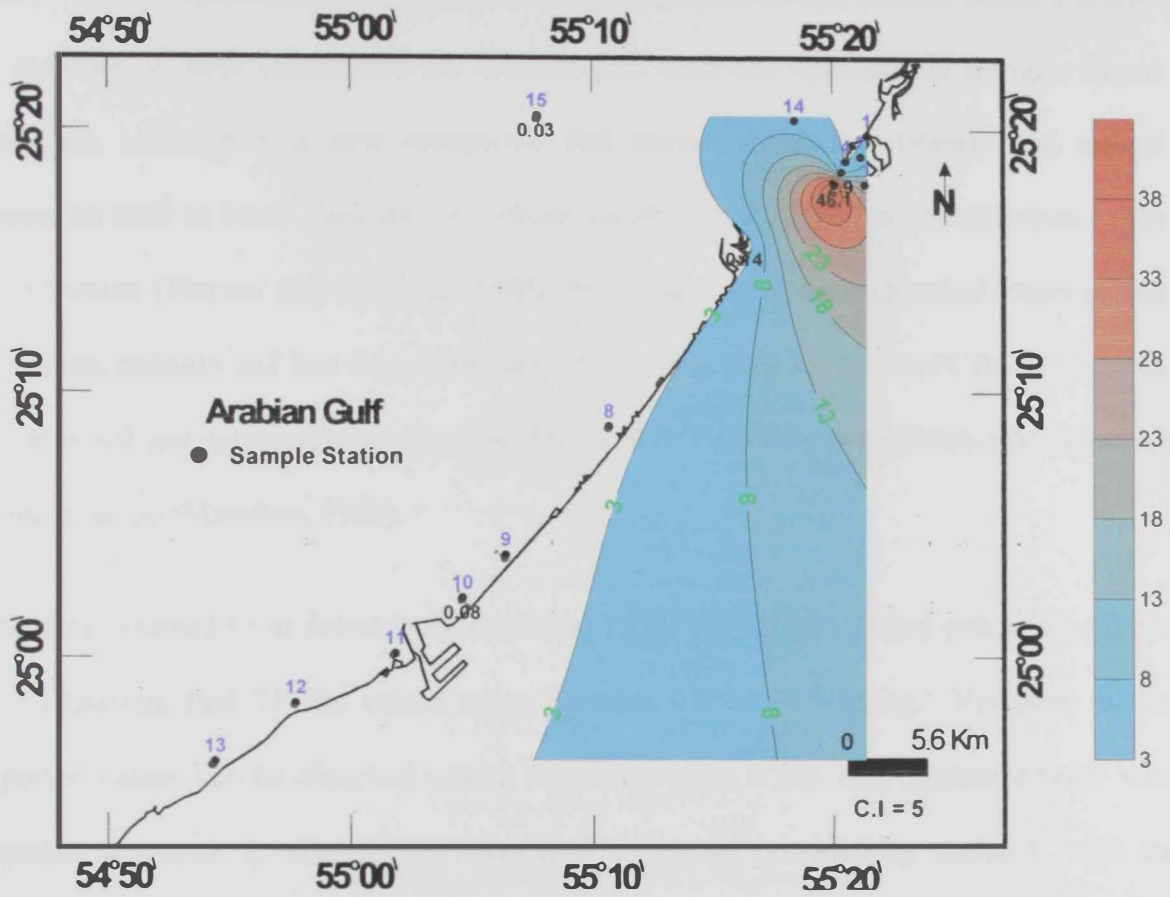
Figure 3.23 : *Distribution map of benzo(g,h,i)perylene (ppm) in Dubai sediments*

3.6 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are mixtures of synthetic organic chemicals with the same basic chemical structure and similar physical properties ranging from oily liquids to waxy solids. Polychlorinated biphenyls are organic chemicals that contain bound chlorine. A majority of these compounds are artificial and enter the environment through human activities, although it is now recognized that marine algae, invertebrates and natural processes such as forest fires also contribute variable quantities of organochlorines to the environment (Haynes and Johnson, 2000). PCBs have very high chemical, thermal and biological stability and low vapor pressure. These properties led to use PCBs in hundreds of industrial and commercial application. The presence of PCBs is a reflection of industrial contamination (Manahan, 1993).

The data obtained from determination of total PCBs (TPCBs) in Dubai sediments (Table 3.7) illustrates that TPCBs values range between 0.8 to 93.3 µg/kg. Variation in the reported values can be observed among stations (Figure 3.24). The minimum value was reported at station 2, whereas the maximum value was provided by station 6, with an average of 17.17 µg/kg and S.D of 25.7. The percentage of TPCBs in Al-Hamriya St 3 (St 6) constitutes more than 1/3 (36%) from an overall PCBs values in Dubai sediments (Figure 3.25), while Figure 3.26 demonstrates the distribution of TPCBs in the study area. The mapping showed that TPCBs concentration increases towards the northeastern part and nearly disappears from the southwestern parts of the study area. The highest values concentrated around Al-Hamriya St 3 (St 6).

Table 3.7 : *Concentrations of polychlorinated biphenyls in Dubai sediments*

Station no.	Locality	PCBs (µg/kg)
1	Al-Mamzar mouth	7.21
2	Al-Mamzar mid	0.8
3	Al-Mamzar end	9.05
4	Al-Hamriya St 1	34.9
5	Al-Hamriya St 2	34.6
6	Al-Hamriya St 3	93.3
7	Dry Docks	46
8	Jumeirah Beach	2.34
9	Dewa	nd
10	Dubal	8.38
11	Jebel Ali Hotel	nd
12	Ras Hisyan	nd
13	Ras Ghantoot	nd
14	Dubai approach	9.8
15	Neptune Wreck	11.1
Average ± S.D		17.17 ± 25.7

nd (Not detected)

$\mu g/kg = ppb = ppm \times 10^{3} = \mu g/g \times 10^{3}$
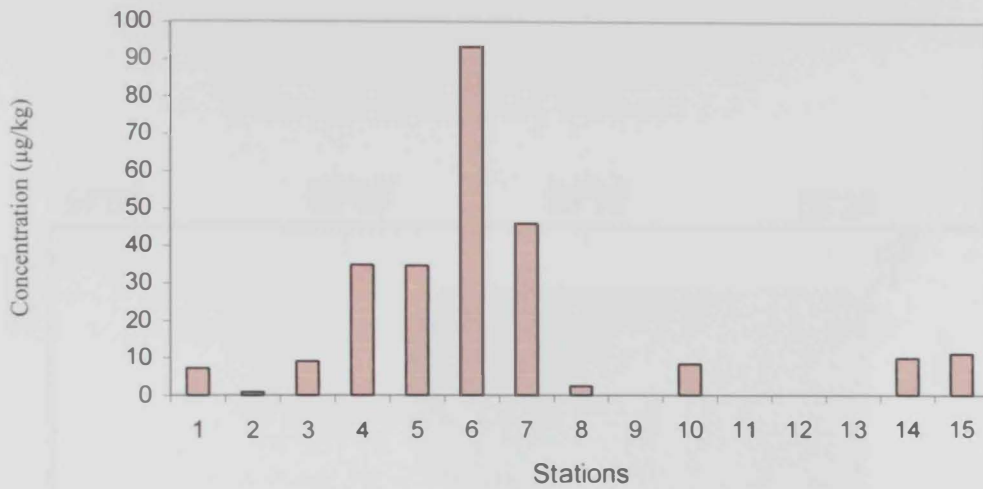
Figure 3.24 : *Concentrations of polychlorinated biphenyls* (μg/ kg)*in Dubai sediments*

PCBs (μg/ kg)
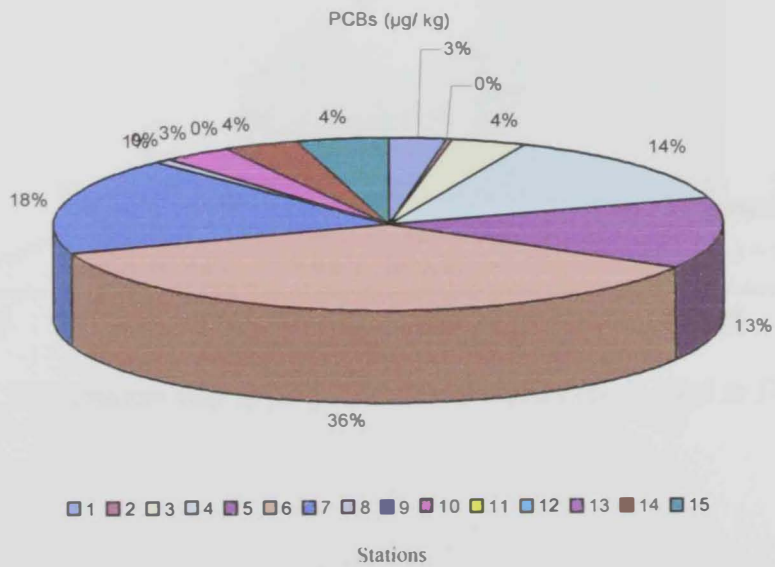
Stations

Figure 3.25 : *The percentage of polychlorinated biphenyls in each station*
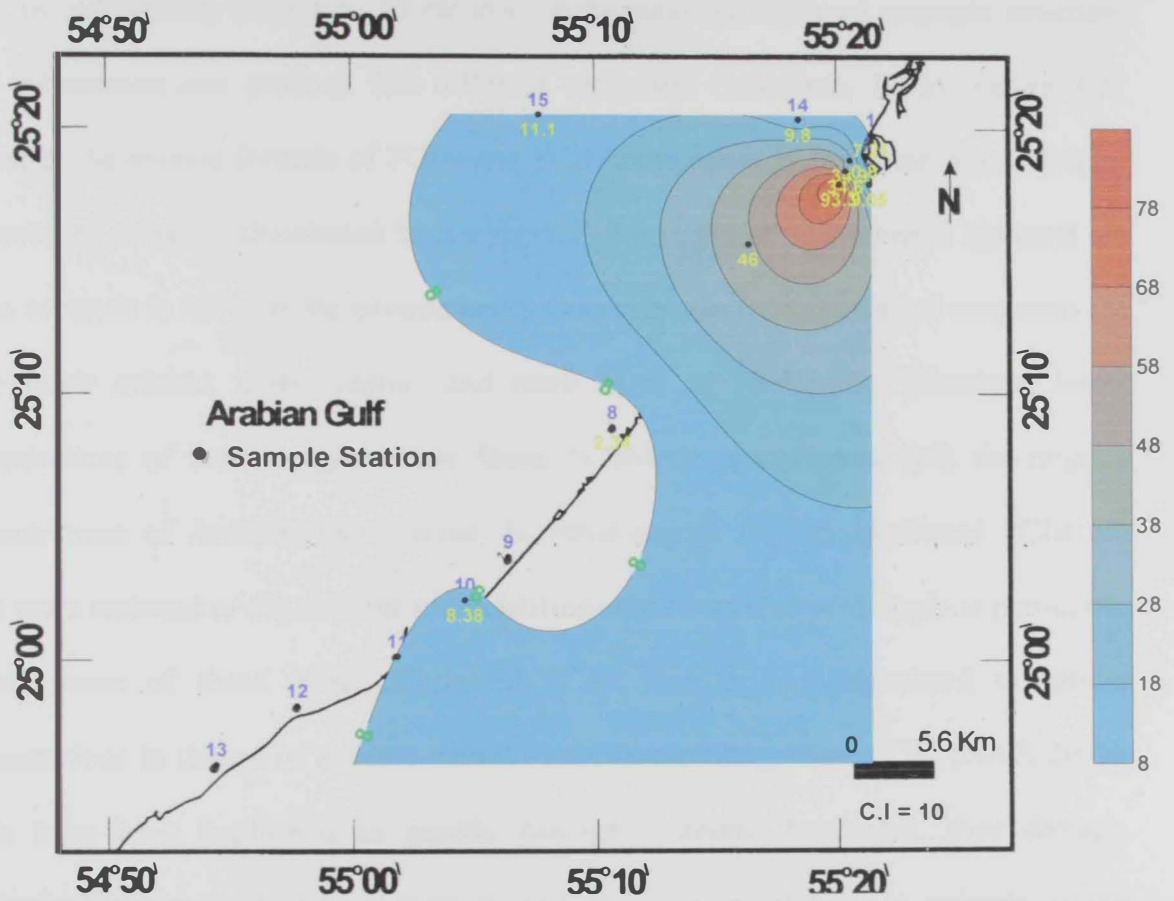
Figure 3.26 : *Distribution map of polychlorinated biphenyls (µg/kg) in Dubai sediments*

3.6.1 Individual Polychlorinated Biphenyls

Polychlorinated biphenyls have been found throughout the world in water, sediments, bird and fish tissue, these compounds constitute an important class of special wastes. They are made by substituting from 1 to 10 chlorine atoms onto the biphenyl aromatic structure. This substitution can produce 209 different congeners (Manahan, 1993). Figure 3.27 illustrates the general formula of PCBs and PCB homologues in the environment (hepta-[7], octa-[8] nona-[9] chlorinated biphenyls and the single decachlorinated biphenyl are not as common in use of in the environment). Generally, the less-chlorinated congeners are more water soluble, more volatile, and more likely to biodegrade. Therefore, lower concentrations of these congeners are found in sediments compared with the original concentrations of Aroclors that entered the environment. Higher-chlorinated PCBs are often more resistant to degradation and volatilization and sorb more strongly to particulate matter. Some of these more chlorinated PCBs tend to bioaccumulated to greater concentrations in tissues of animals than do lower-molecular-weight PCBs (NAP, 2001). PCBs have been implicated in genetic damage, immune depression, liver damage, respiratory problems, short-term memory and excess pigmentation. In animals: tumor growth, behavioural changes, reproductive abnormalitities, fetal death and increased infection (Livingston, 1976; Rowat S.C, 1998).

Table 3.8 illustrates the chemical names of individual PCBs based on the number and position of chlorine atom onto the biphenyl aromatic structure. General observation on the detected individual PCBs in Dubai sediments (Table 3.9) showed that PCB 180 provided the highest values (Figure 3.28). PCBs congeners, except for PCB 180, PCB 52 and PCB 8, showed limited distribution in Dubai sediments and the detected compounds also were found in limited stations.

General formula of PCBs
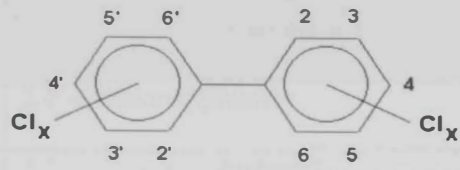
monochlorobiphenyls   trichlorobiphenyls   tetrachlorobiphenyls
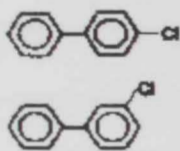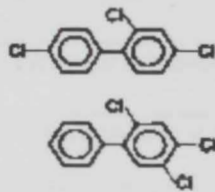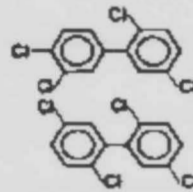
2.4.5 trichlorobiphenyls

dichlorobiphenyls
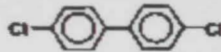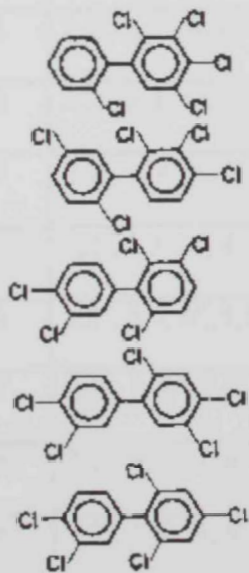
pentachlorobiphenyls   hexachlorobiphenyls
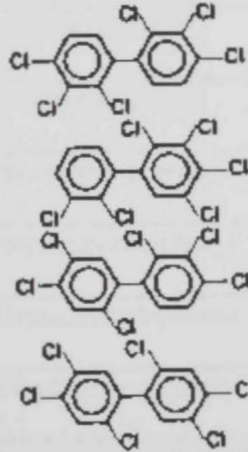
Figure 3.27 : *Structural formula of PCBs and PCB homologues (Source: NAP, 2001)*

Table 3.8 : *Chemical names of individual polychlorinated biphenyls*

Commercial name	Chemical name
PCB 8	2,4'-Dichlorobiphenyl
PCB 18	2,2', 5-Trichlorobiphenyl
PCB 28	2,4,4'-Trichlorobiphenyl
PCB 44	2,2', 3,5'-Tetrachlorobiphenyl
PCB 52	2,2', 5,5'-Tetrachlorobiphenyl
PCB 66	2,3', 4,4'-Tetrachlorobiphenyl
PCB 77	3,3', 4,4'-Tetrachlorobiphenyl
PCB 101	2,2', 4,5,5'-Pentachlorobiphenyl
PCB 105	2,3,3', 4,4'-Pentachlorobiphenyl
PCB 118	2,3', 4,4', 5-Pentachlorobiphenyl
PCB 126	3,3', 4,4', 5-Pentachlorobiphenyl
PCB 128	2,2', 3,3', 4,4'-Hexachlorobiphenyl
PCB 138	2,2', 3,4, 4', 5'-Hexachlorobiphenyl
PCB 153	2,2', 4, 4',5, 5'-Hexachlorobiphenyl
PCB 170	2,2', 3,3', 4, 4',5-Heptachlorobiphenyl
PCB 180	2,2', 3,4, 4', 5,5'-Heptachlorobiphenyl
PCB 187	2,2', 3, 4', 5,5', 6-Heptachlorobiphenyl
PCB 195	2,2', 3,3', 4, 4', 5,6-Octachlorobiphenyl
PCB 206	2,2', 3,3', 4, 4', 5,5', 6-Nonachlorobiphenyl
PCB 209	2,2', 3,3', 4, 4', 5,5', 6,6'-Decachlorobiphenyl

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3.6.1.1 PCB 8 (2,4'-Dichlorobiphenyl)

The concentrations of PCB 8 vary in a restricted range (7.08 to 10.79 µg/kg). This compound was detected only in four stations (3, 4, 7 & 14) of the study area; the highest value was reported at station 4 and the lowest value was found at station 14 (Figure 3.29A). The distribution map of PCB 8 shows an increasing trend towards the northern parts of the study area around Al-Hamriya St 1 (Figure 3.30).

3.6.1.2 PCB 44 (2,2', 3,5'-Tetrachlorobiphenyl)

This compound was detected in station 8 at very low level of 2.34 µg/kg (Figure 3.29B).

3.6.1.3 PCB 52 (2,2', 5,5'-Tetrachlorobiphenyl)

This compound was recorded only in four stations (1, 4, 7 & 15); the values vary widely between 2.51 to 27.1 µg/kg. The highest value was recoded at station 7, whereas the lowest value was reported at station 1 (Figure 3.29C). The distribution map of PCB 52 shows an increasing trend towards the eastern parts of the study area (Figure 3.31) around Dry Docks (St 7).

3.6.1.4 PCB 66 (2,3', 4,4'-Tetrachlorobiphenyl)

This compound was detected only in station 5 with very low concentration of 1.62 µg/kg (Figure 3.29D).

3.6.1.5 PCB 10 (2,2', 4,5,5'-Pentachlorobiphenyl)

This compound was found only in station 15 with very low concentration of 1.91 µg/kg (Figure 3.29E).

3.6.1.6 PCB 105 (2,3,3', 4,4'-Pentachlorobiphenyl)

This compound was reported only in three stations (6, 7 & 10) at very low levels with range from 1 to 1.52 µg/ kg (Figure 3.29F).

3.6.1.7 PCB 118 (2,3', 4,4', 5-Pentachlorobiphenyl)

This compound was detected only in two stations (5 & 6) with very low concentration of 2.04 and 2.19 µg/kg respectively (Figure 3.29G).

3.6.1.8 PCB 128 (2,2', 3,3', 4,4'-Hexachlorobiphenyl)

This compound was detected only in station 15 with very low concentration of 1.71 µg/kg (Figure 3.29H).

3.6.1.9 PCB 138 (2,2', 3,4, 4', 5'-Hexachlorobiphenyl)

This compound was found only in two stations (6 & 7) at very low levels with range from 1.22 to 1.75 µg/kg (Figure 3.29I).

3.6.1.10 PCB 153 (2,2', 4, 4',5, 5'-Hexachlorobiphenyl)

This compound was detected in four stations (4, 5, 6 & 15) of the study area; and with very low concentration range from 1.08 to 2.31 µg/kg (Figure 3.29J). The highest value was reported at station 5, whereas the lowest value was reported at station 15. The distribution map of PCB 153 shows an increasing trend towards northern parts around Al-Hamriya stations (Figure 3.32).

3.6.1.11 PCB 180 (2,2', 3,4, 4', 5,5'-Heptachlorobiphenyl)

This compound exhibited the highest value and widest distribution. The values vary between very low, low and high within a range from 0.8 to 86.52 µg/kg. The highest value was recorded at station 6, whereas the lowest value was reported at station 2 (Figure 3.29k). The distribution map of PCB 180 exhibits an increasing trend towards the northeastern parts of the study area. The highest three values were concentrated in Al-Hamriya stations (Figure 3.33).

3.6.1.12 PCB 187 (2,2', 3, 4', 5,5', 6-Heptachlorobiphenyl)

This compound was detected only in station 7 with very low concentration of 0.94 µg/kg (Figure 3.29L).

Table 3.9 : *Concentrations of individual polychlorinated biphenyls (µg/ kg) in Dubai sediments*

	Locality / Compounds	PCB 8	PCB 18	PCB 28	PCB 44	PCB 52	PCB 66	PCB 77	PCB 101	PCB 105	PCB 118	PCB 126	PCB 128	PCB 138	PCB 153	PCB 170	PCB 180	PCB 187	PCB 195	PCB 206	PCB 209
1	Al-Mamzar mouth	nd	nd	nd	nd	2.51	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	4.7	nd	nd	nd	nd
2	Al-Mamzar mid	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.8	nd	nd	nd	nd
3	Al-Mamzar end	9.05	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
4	Al-Hamriya St 1	10.79	nd	nd	nd	3.24	nd	nd	nd	nd	nd	nd	nd	nd	1.36	nd	19.5	nd	nd	nd	nd
5	Al-Hamriya St 2	nd	nd	nd	nd	nd	1.62	nd	nd	nd	2.04	nd	nd	nd	2.31	nd	28.63	nd	nd	nd	nd
6	Al-Hamriya St 3	nd	nd	nd	nd	nd	nd	nd	nd	1.52	2.19	nd	nd	1.75	1.28	nd	86.52	nd	nd	nd	nd
7	Dry Docks	9.7	nd	nd	nd	27.1	nd	nd	nd	1	nd	nd	nd	1.22	nd	nd	6	0.94	nd	nd	nd
8	Jumeirah Beach	nd	nd	nd	2.34	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
9	Dewa	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
10	Dubal	nd	nd	nd	nd	nd	nd	nd	nd	1.35	nd	nd	nd	nd	nd	nd	7.02	nd	nd	nd	nd
11	Jebel Ali Hotel	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
12	Ras Hisyan	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
13	Ras Ghantoot	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
14	Dubai approach	7.08	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	2.72	nd	nd	nd	nd
15	Neptune Wreck	nd	nd	nd	nd	2.66	nd	nd	1.91	nd	nd	nd	1.71	nd	1.08	nd	3.71	nd	nd	nd	nd

nd (Not detected)   µg/kg = ppb = ppm x 10^3 = µg/g x 10^3
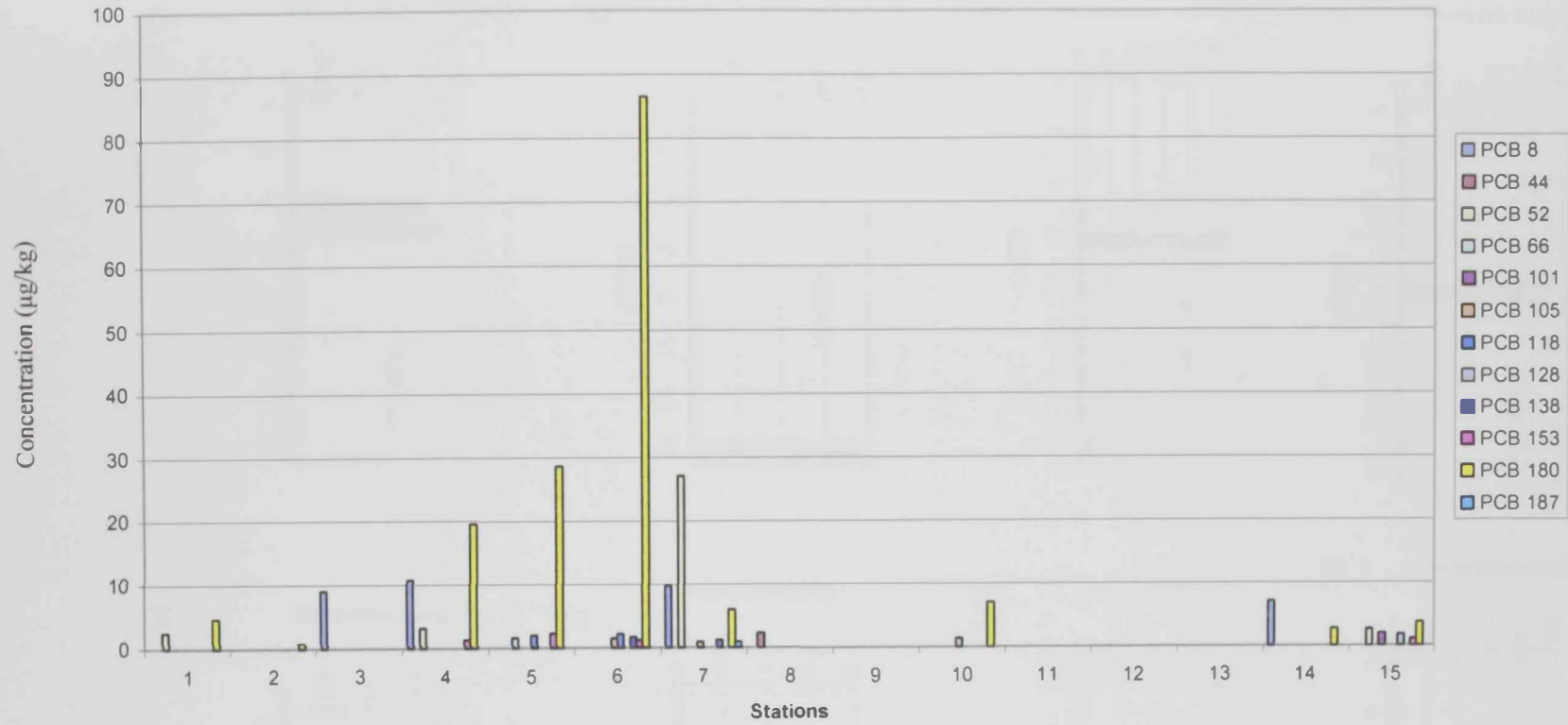
Figure 3.28 : *Concentrations of individual PCBs (μg/kg) in Dubai sediments at different stations*

A.

B.

C.

D.

E.

F.

G.

H.

88
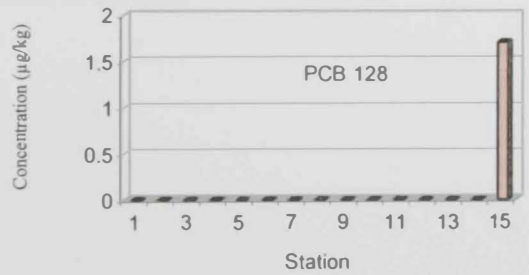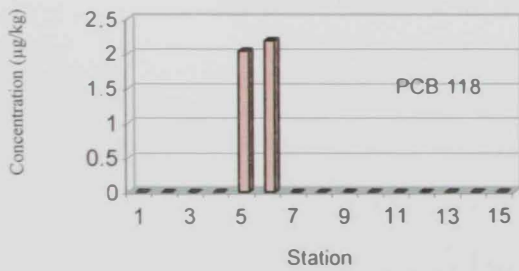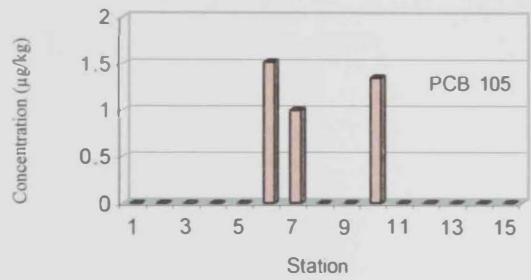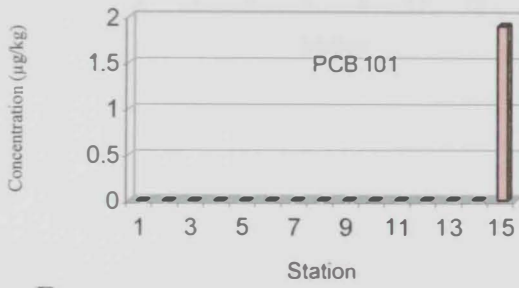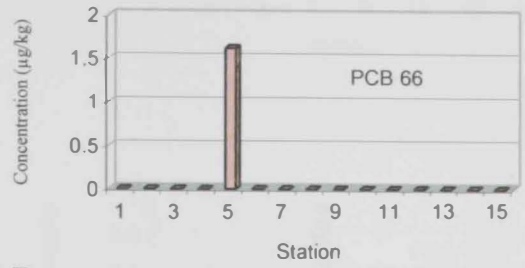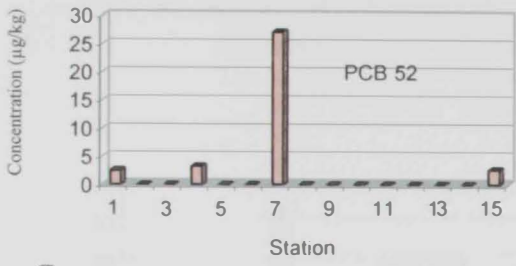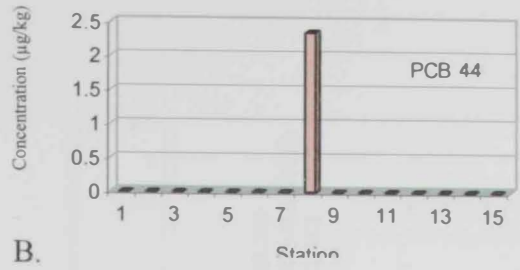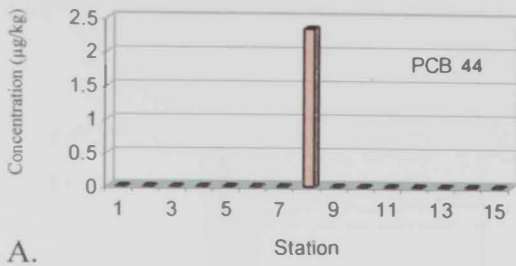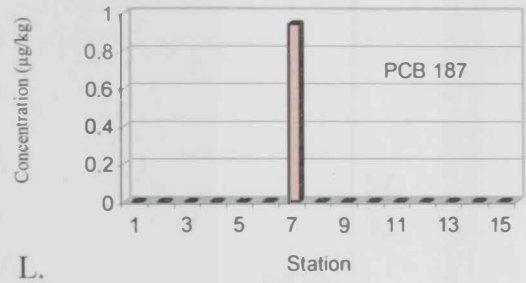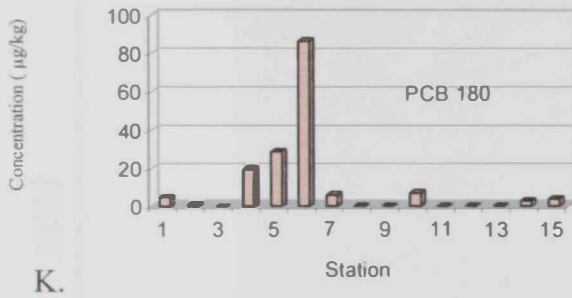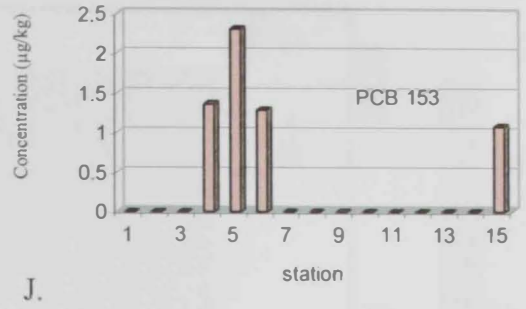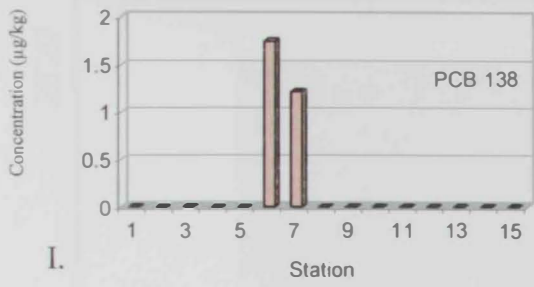
Figure 3.29 : *Histograms representing concentrations of individual polychlorinated biphenyl compounds (µg/kg) in Dubai sediments*
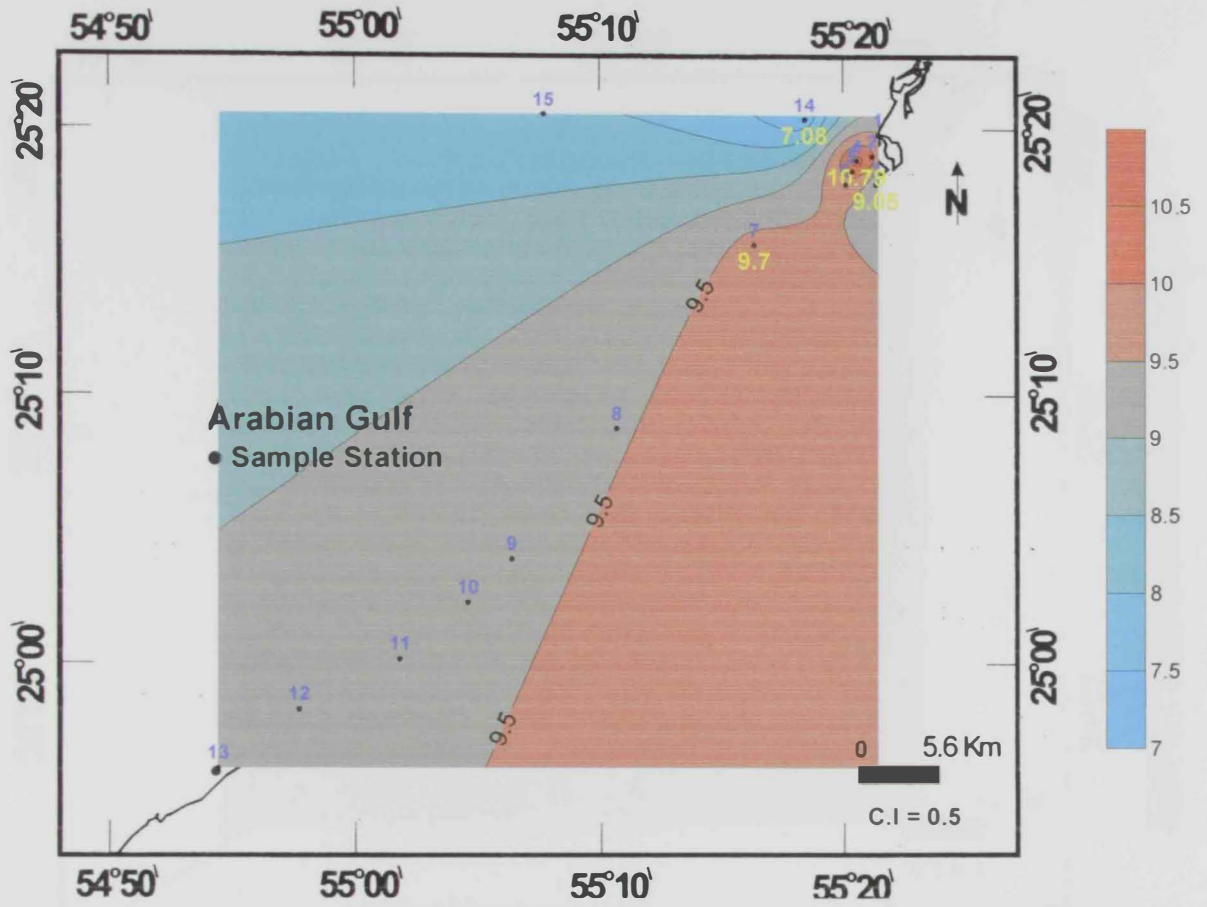
Figure 3.30 : *Distribution map of PCB 8 (µg/kg) in Dubai sediments*
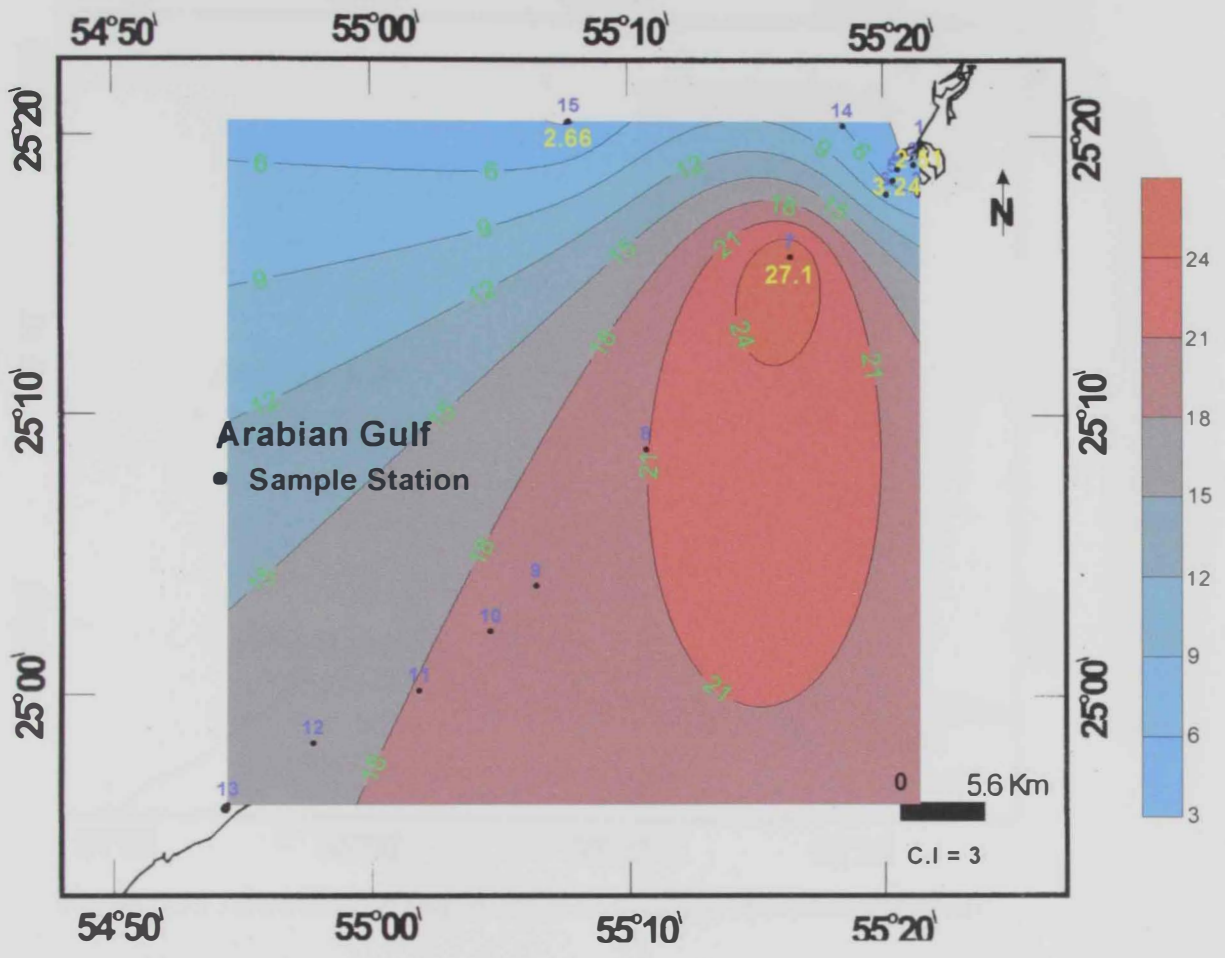
Figure 3.31 : *Distribution map of PCB 52 (µg/kg) in Dubai sediments*
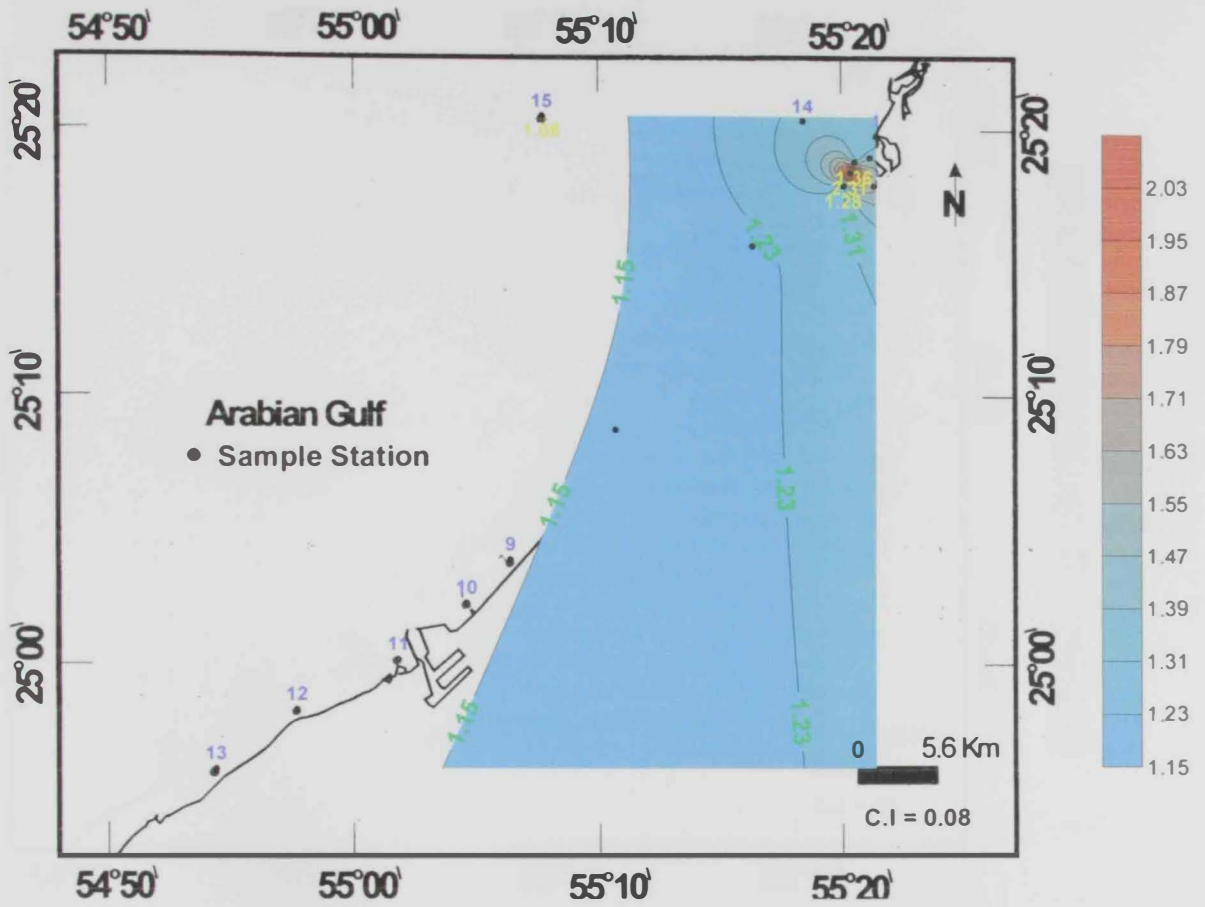
Figure 3.32 : *Distribution map of PCB 153 (µg/kg) in Dubai sediments*
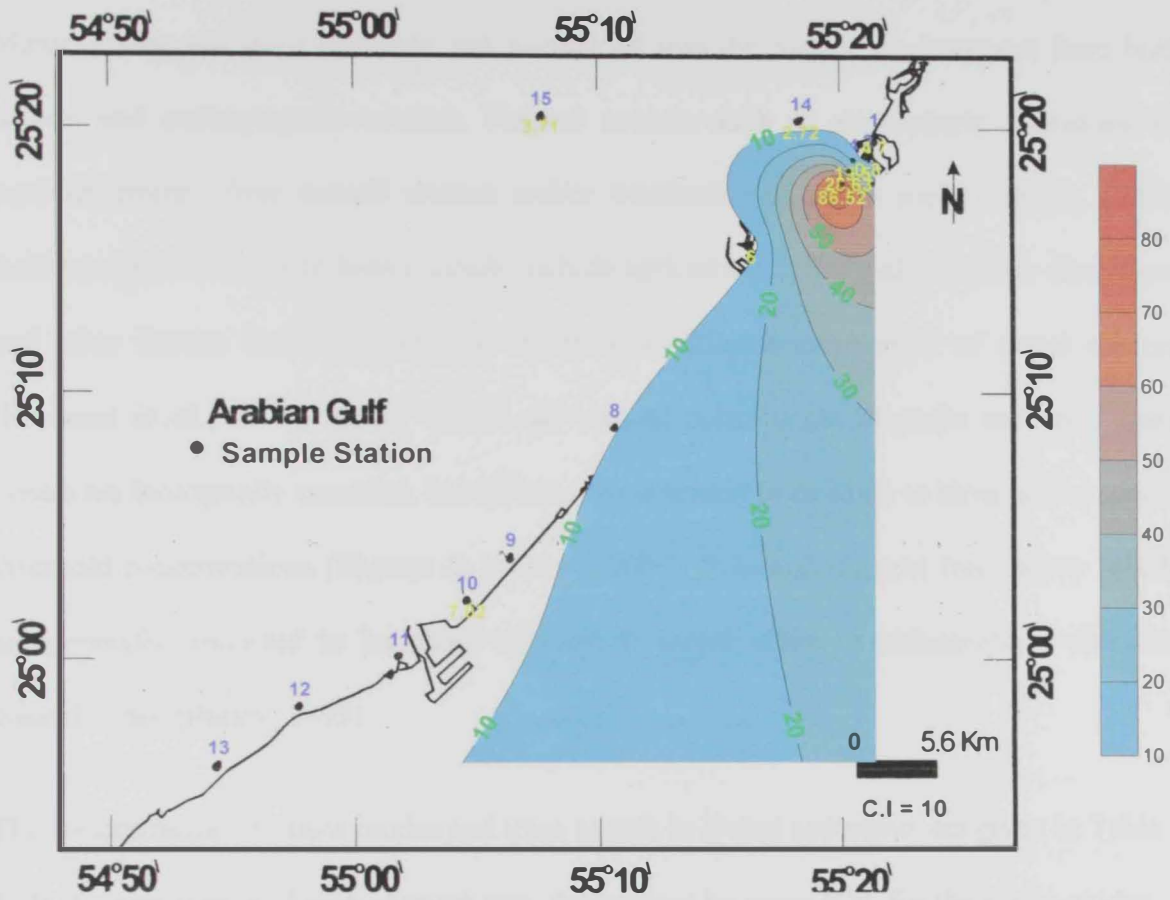
Figure 3.33 : *Distribution map of PCB 180 (μg/kg) in Dubai sediments*

3.7 Element Distribution

Major, minor and trace elements, are introduced into the marine environment from both natural and anthropogenic sources. Natural sources such as atmospheric deposition of particles emitted from natural sources and/or weathering of parent rocks (Nriagu, 1989). Anthropogenic sources of heavy metals include agriculture, industrial, domestic discharges and other human activities can also result in significant enrichment of metal content (Bloemen *et al.*, 1995). Heavy metals are natural constituents of rocks and soil, many metals are biologically essential, but all have the potential to be toxic to biota above certain threshold concentrations (Haynes & Johnson, 2000). Potential impacts from heavy metals are generally restricted to locations adjacent to major cities or industrialized areas on coastal fringe (Batley, 1995).

The concentration of major oxides and trace metals in Dubai sediments are given in Table 3.10. An absorbance of each element was determined by using ICP, for the major oxides the obtained value was multiplied by factor oxide, which vary from oxide to another.

3.7.1 Major Oxides

3.7.1.1 Silica (SiO$_2$)

The values of SiO$_2$ in the collected samples show a restricted variation and lie within the range from 49.52 to 66.99 wt%, with an average of 56.68 wt% and standard deviation (S.D) of 5.47. The maximum value was reported at station 8 and the minimum value was found at station 11. The fine fractions (230 mesh) of the samples of stations 5 and 8 reflected lower concentrations, whereas the samples of stations 2 and 14 have relatively

higher silica values than the bulk samples. Station 9 has significantly higher silica value than its corresponding bulk samples (Figure 3.34A).

3.7.1.2 *Alumina* (Al_2O_3)

The highest value of Al_2O_3 was reported at station 3 and the lowest value at station 15. The values range between 0.04 to 2.44 wt%, with an average of 0.86 wt% and S.D of 0.78. The Alumina concentration in the fine fractions of stations 2 and 8 decreased but significantly increased in stations 5, 9 and 14 (Figure 3.34B)

3.7.1.3 *Iron oxide* (Fe_2O_3)

Iron oxide shows the maximum value at station 10, whereas the minimum values were reported at stations 11 and 13. The values range between 0.04 to 1.76 wt%, with an average of 0.52 wt% and S.D of 0.53. The fine fraction contents of Fe_2O_3 show higher concentration in stations 2 and 5 and significantly higher levels in stations 9 and 14 compared with those of the bulk samples, whereas the concentration of Fe_2O_3 in the fine fraction of station 8 has lower value than the bulk sample (Figure 3.34C).

3.7.1.4 *Magnesium oxide* (MgO)

The values of MgO fluctuate among stations. Station 10 has remarkable higher level (3.09 wt%) relative to other stations. The minimum value was recorded at stations 1 and 9. The values range from 0.49 to 3.09 wt% with an average of 0.97 wt% and S.D of 0.65. The Magnesium oxide concentrations in the fine fractions are significantly lower than those of the bulk samples except for stations 8 and 9 (Figure 3.34D).

3.7.1.5 Calcium oxide (CaO)

Calcium oxide is the second oxide in abundance after SiO_2. Calcium oxide values show nearly similar concentrations in most stations. The values lie within the range from 25.13 to 48.55 wt%, with an average of 39.33 wt% and S.D of 7.05. The maximum value was recorded at station 11 and the minimum value was found at station 10. The fine fractions reflected lower levels of CaO, except for station 8, where CaO value is higher in its fine fraction (Figure 3.34E).

3.7.1.6 Sodium oxide (Na₂O)

The values of Na_2O fluctuate with a limited range from 0.68 to 1.98 wt% with an average of 1.31 wt% and S.D of 0.42. The maximum value was found at station 7, whereas the minimum value was recorded at station 6. The concentrations of Na_2O in fine fractions are higher in stations 8, 9 and 14 but lower in stations 2 and 5 compared with their bulk samples (Figure 3.34F).

3.7.1.7 Potassium oxide (K₂O)

Potassium oxide values show a wide variation among stations. The maximum value was reported at station 3, whereas the minimum value was recorded at station 15. The values range between 0.1 to 0.77 wt%, with an average of 0.35 wt% and S.D of 0.24. Potassium oxide concentration in the fine fractions was significantly higher than the bulk samples except for station 8 showed lower value (Figure 3.34G).

Table 3.10 : *Concentration of major oxides (wt%) and trace elements (ppm) in Dubai sediments*

Stations Elements \ Locality	Bulk Sample															Fine Fraction (230 mesh)					Ms	Range of bulk samples (n =15)	Average ± S.D of bulk samples (n =15)
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	F2	F5	F8	F9	F14			
	Mamzar mouth	Mamzar mid	Mamzar end	Hamriya St 1	Hamriya St 2	Hamriya St 3	Dry Dock	Jumeirah Beach	Dewa	Dubai	Jebel Ali Hotel	Ras Hisyan	Ras Ghantoot	Dubai approach	Neptune Wreck	Mamzar mid	Hamriya St 2	Jumeirah Beach	Dewa	Dubai approach	Canadian marine sediments		
Major Oxides (wt%)																							
SiO_2	53.58	57.51	58.83	58.11	61.57	55.11	58.38	66.99	50.31	66.96	49.52	49.58	54.39	56.29	53.07	66.67	61.33	61.31	70.46	60.49	87.1	49.52–66.99	56.68 ± 5.47
Al_2O_3	0.15	1.90	2.44	1.15	0.79	0.94	1.70	1.06	0.12	1.61	0.10	0.07	0.05	0.75	0.04	1.59	2.98	1.03	1.31	13.5	5.42	0.04–2.44	0.86 ± 0.78
Fe_2O_3	0.07	0.62	0.85	0.52	0.86	1.03	1.20	0.40	0.05	1.76	0.04	0.05	0.04	0.18	0.07	0.63	0.90	0.34	0.45	0.94	3.55	0.04–1.76	0.52 ± 0.53
MgO	0.49	0.79	1.19	0.82	0.88	0.87	1.37	0.56	0.49	3.09	0.52	0.94	0.53	1.07	0.87	0.49	0.75	0.58	0.59	0.93	0.90	0.49–3.09	0.97 ± 0.65
CaO	44.72	36.70	34.13	38.11	33.67	41.07	34.70	29.38	47.76	25.13	48.55	47.70	43.70	39.97	44.59	28.54	31.98	34.93	25.39	33.98	0.83	25.13–48.55	39.33 ± 7.05
Na_2O	0.84	1.80	1.80	0.84	1.86	0.68	1.98	1.22	1.14	0.87	1.16	1.55	1.18	1.48	1.25	13.8	1.53	1.43	1.27	1.74	1.02	0.68–1.98	1.31 ± 0.42
K_2O	0.14	0.67	0.77	0.45	0.38	0.30	0.67	0.39	0.13	0.61	0.11	0.11	0.11	0.27	0.10	0.68	0.53	0.38	0.53	0.56	1.17	0.1–0.77	0.35 ± 0.24
Trace Elements (ppm)																							
Ba	23	64	71	52	63	63	83	35	12	95	11	12	11	29	12	63	84	57	43	36	565	11–95	42 ± 29
Cd	0.1	0.2	0.2	0.2	0.3	0.4	0.3	0.1	0.1	0.3	0.1	0.1	0.1	0.1	0.1	0.2	0.3	0.2	0.2	0.1	0.6	0.1–0.4	0.2 ± 0.1
Cr	6	24	31	20	22	23	45	48	7	173	5	6	5	16	5	30	33	48	46	22	62	5–173	29 ± 42
Cu	1	5	7	36	72	157	88	0	2	10	1	1	1	2	2	4	67	2	4	3	31	1–157	26 ± 46
Mn	20	108	120	58	55	55	130	100	13	145	9	8	9	45	8	143	93	153	115	75	125	8–145	75.6 ± 51.6
Ni	2	13	18	12	16	17	32	6	2	159	2	2	2	7	2	14	19	7	9	9	29	2–159	19 ± 39
Pb	1	3	4	10	18	35	20	1	1	4	1	2	1	1	1	2	20	2	2	2	10	1–35	7 ± 10
Sr	4582	2350	1990	3545	3335	4105	1561	2975	5035	1212	5201	4165	4800	2760	3985	1350	3000	2515	2310	3290	53	1212–5201	3440 ± 1269
V	2	11	15	8	10	14	20	8	2	27	2	2	2	5	2	13	13	12	10	7	142	2–27	9 ± 8
Zn	6	18	22	67	145	415	132	9	6	38	6	6	6	8	20	15	123	11	12	10	86	6–415	60 ±108

Wt % x 10^4 = ppm = µg/g

97

A.

B.

C.

D.

98
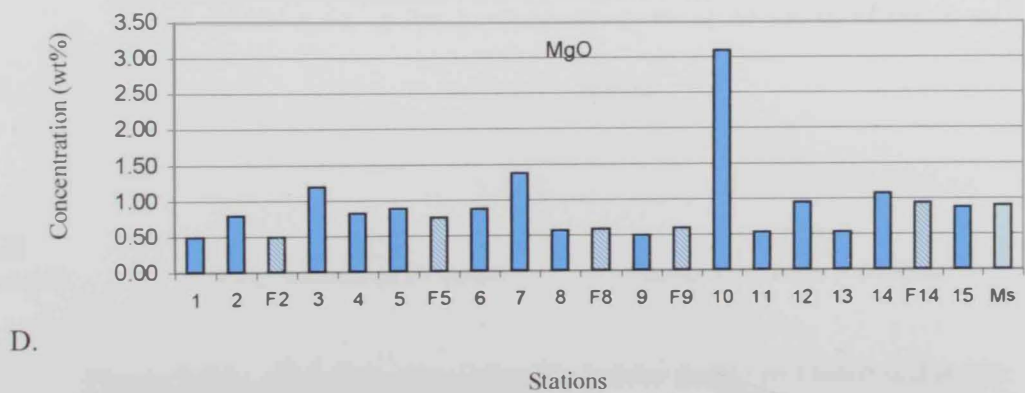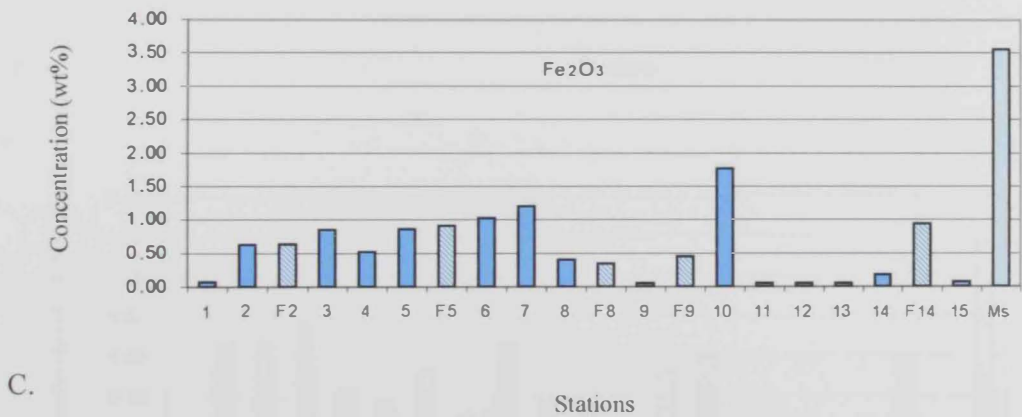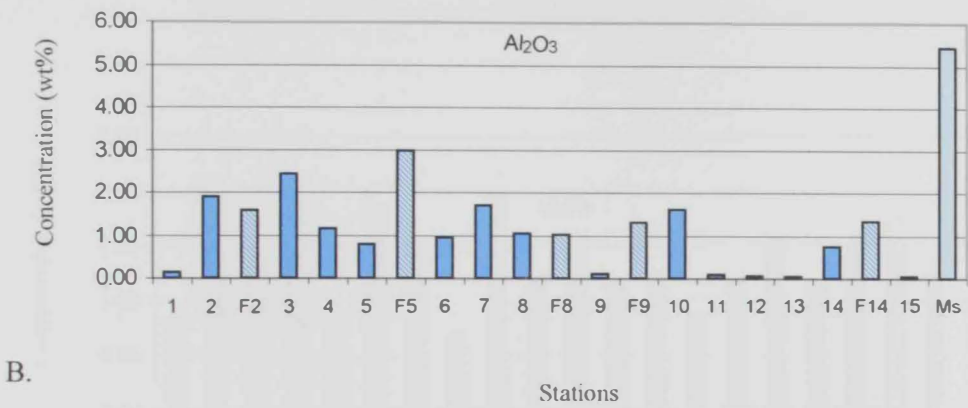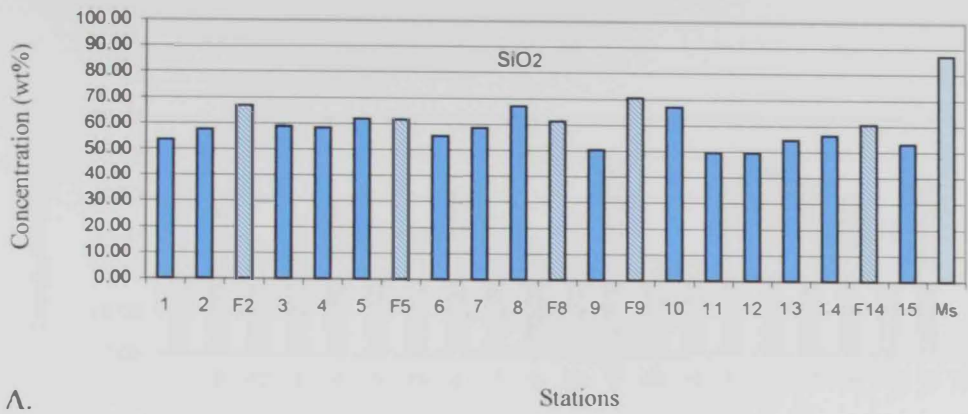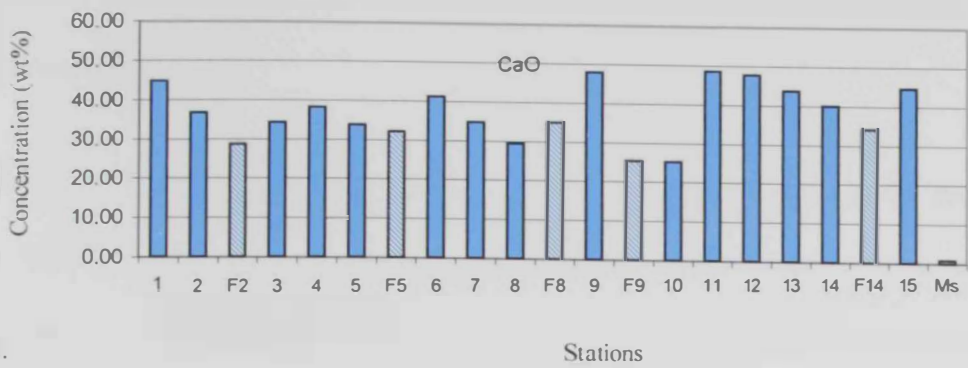
E.
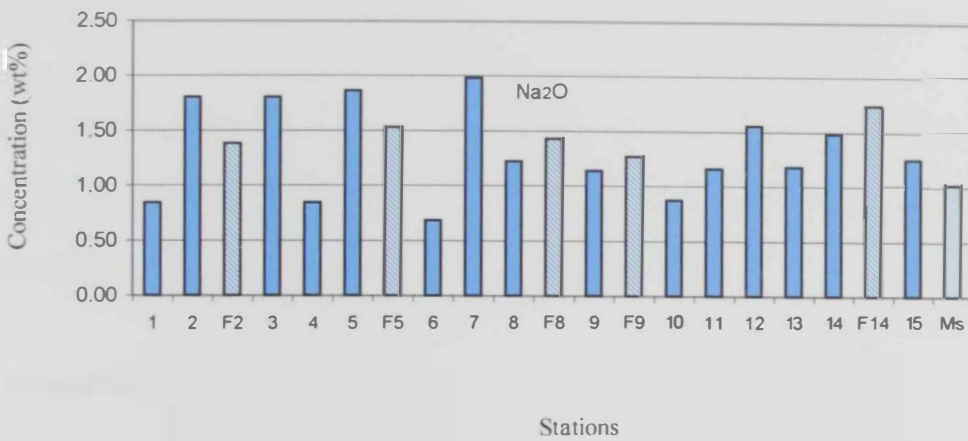
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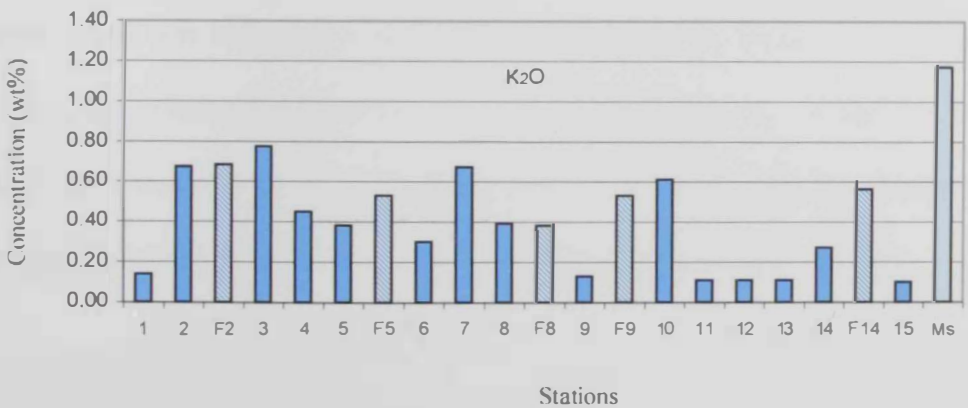
G.

Bulk sample   Fine fraction (230 mesh)   Canadian marine sediments

Figure 3.34 : *Concentration of major oxides (wt%) in Dubai sediments*

3.7.2 Trace Elements

3.7.2.1 Barium (Ba)

Barium shows wide variation among stations, within a range from 11 to 95 ppm. The maximum value was recorded at station 10 and the minimum values were reported at stations 11 and 13. An overall average is 42 ppm and S.D is 29. Barium concentrations in the fine fractions show significantly higher levels than the bulk samples (Figure 3.35A).

3.7.2.2 Cadmium (Cd)

The values of cadmium showed very low abundances and very limited variations; ranged from 0.1 to 0.4 ppm. Therefore Cd values in Dubai sediments could be ignored. The fine fractions showed agreement with the bulk samples (Figure 3.35B).

3.7.2.3 Chromium (Cr)

The values of chromium vary widely among stations, within a range from 5 to 173 ppm. The maximum value was recorded at station 10 with remarkable higher level compared to other stations. The minimum values were reported at stations 11, 13 and 15, with an average of 29 ppm and S.D of 42. Chromium concentrations in the fine fractions were higher and significantly higher at station 9 than the bulk samples (Figure 3.35C).

3.7.2.4 Copper (Cu)

Copper values show an increase from station 1 to 6. The maximum value was recorded at station 6, whereas stations 1, 11, 12 and 13 have the minimum values. The values show wide variations from 1 to 157 ppm with an average of 26 ppm and S.D of 46. The fine fractions of samples 8, 9 and 14 show slightly higher concentrations, whereas the fine of

stations 2 and 5 show lower concentration than the bulk (Figure 3.35D).

3.7.2.5 *Manganese* (Mn)

Manganese values fluctuate among stations, with relatively high levels in some stations
and low in others. The Mn values range from 8 to 145 ppm with an average of 75.57 ppm
and S.D of 51.6. The maximum value was reported at station 10 and the minimum value
was found at station 12. The concentrations of Mn in the fine fractions in general were
higher than the bulk sample, and significantly higher for station 9 (Figure 3.35E).

3.7.2.6 *Nickel* (Ni)

Nickel values show significant abundance at station 10, which represents the maximum
value (159 ppm), whereas the minimum values were reported at six of the studied stations
(1, 9, 11, 12, 13 & 15). The values range from 2 to 159 ppm, with an overall average of 19
ppm and S.D of 39. The concentrations in fine fractions were relatively higher than the
bulk samples (Figure 3.35F).

3.7.2.7 *Lead* (Pb)

Lead values from station 1 to 6 show an increase in concentration. The values were within
the range from 1 to 35 ppm. The maximum value was found at station 6, whereas the
minimum values were reported at seven of the studied stations (1, 8, 9, 11, 13, 14 & 15
respectively). The values range from 1 to 35 ppm, with   an average of 7 ppm and S.D
value of 10. Lead concentrations in the fine fractions show slightly higher values than
those of the bulk samples (Figure 3.35G).

3.7.2.8 Strontium (Sr)

The values of Sr are very high compared with other trace elements concentrations. The values have the range from 1212 to 5201 ppm. The maximum value was recorded at station 11 and the minimum value was reported at station 10, with an overall average of 3400 ppm and S.D value of 1269. Strontium concentrations in the fine fractions show significant lower values compared to the bulk samples (Figure 3.35H).

3.7.2.9 Vanadium (V)

Vanadium values range from 2 to 27 ppm; the maximum value was recorded at station 10, whereas the minimum values were found at six of the studied stations (1, 9, 11, 12, 13 & 15), with an overall average of 9 ppm and S.D of 8. The concentrations of V in the fine fractions are slightly higher and relatively higher in station 9 compared to the bulk samples (Figure 3.35I).

3.7.2.10 Zinc (Zn)

Zinc values vary widely among stations within a range of 6 to 415 ppm. The maximum value was recorded at station 6, whereas five stations (1, 9, 11, 12 & 13) have the minimum value, with an average of 60 ppm and S.D of 108. Zinc concentrations in the fine fractions are slightly higher compared to those of the bulk samples except for stations 5 and 2 in which the fine fraction has relatively lower level (Figure 3.35J).

A.

B.

C.

D.

E.

F.

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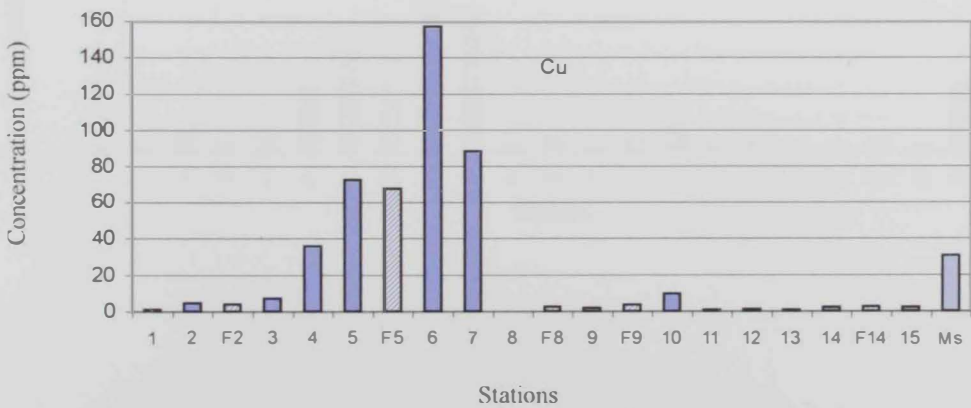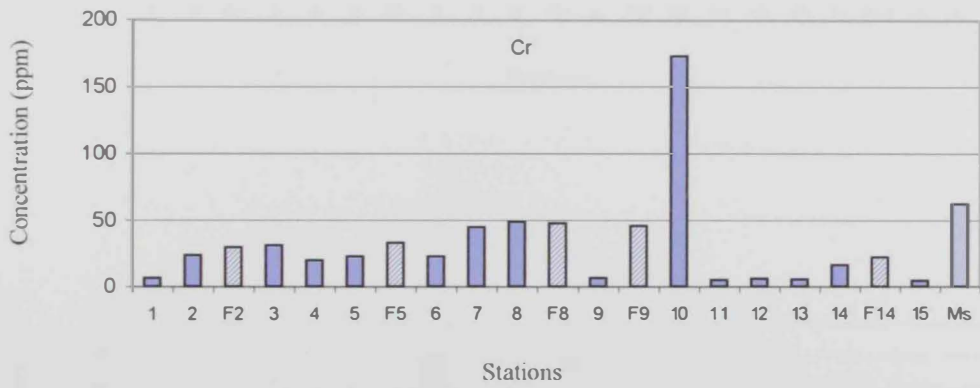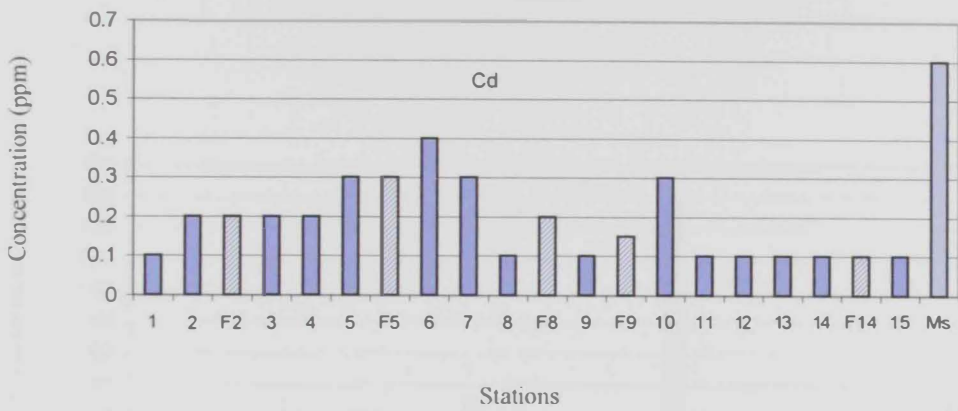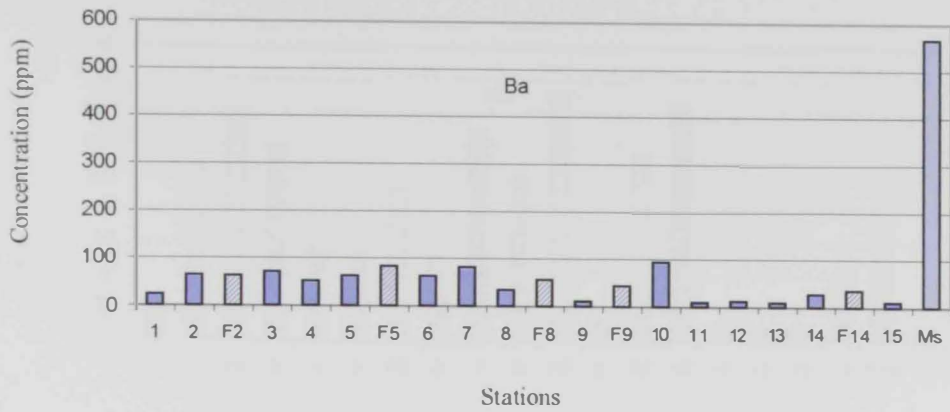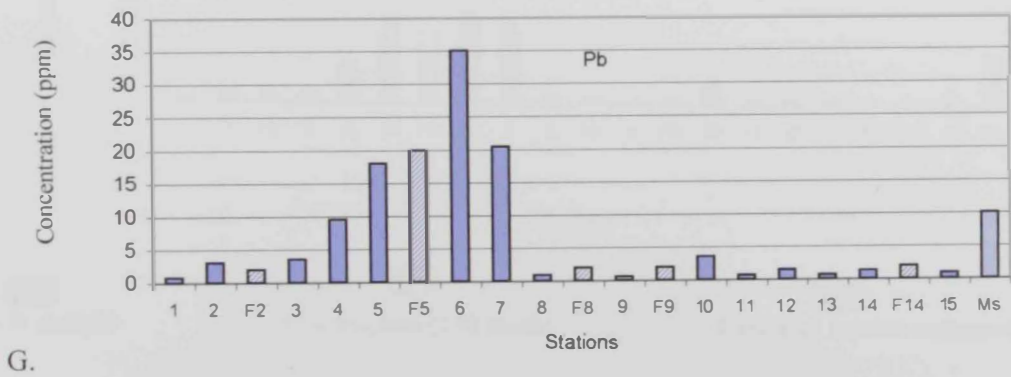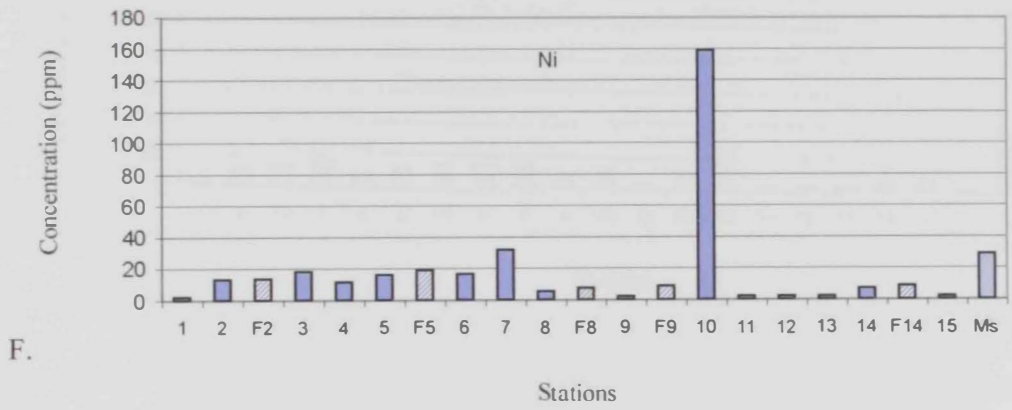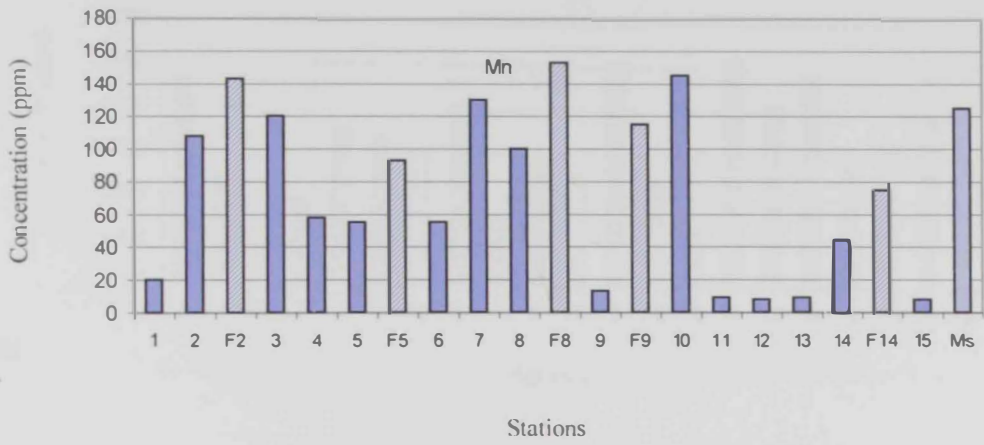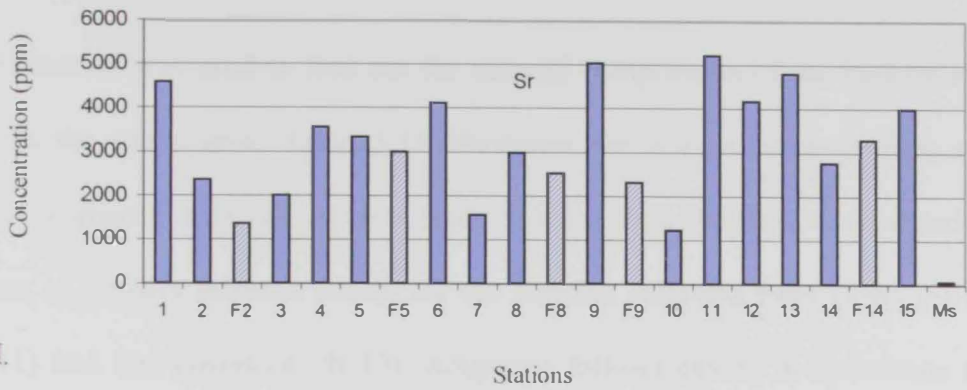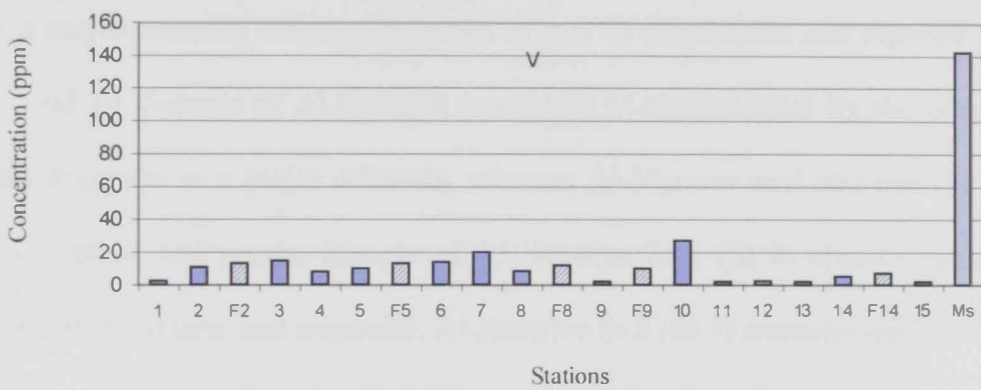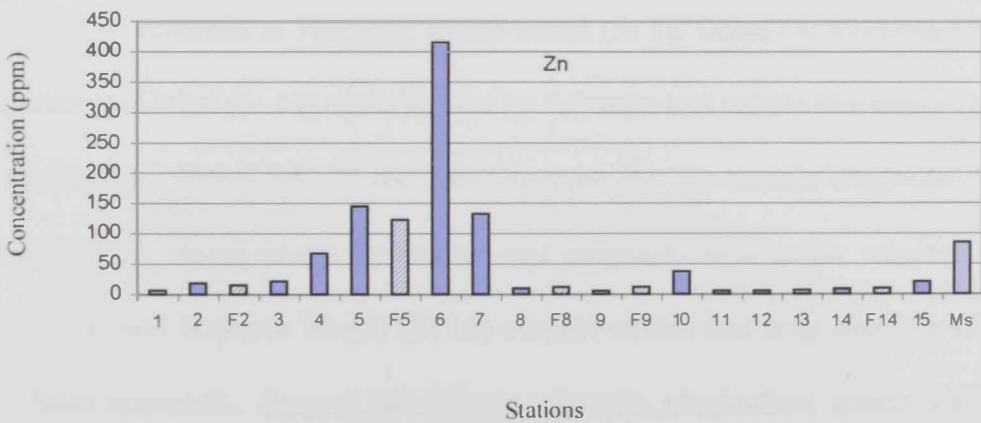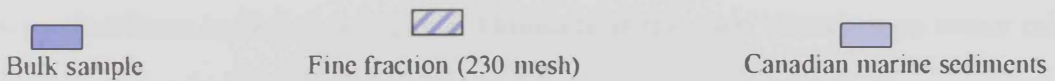
Figure 3.35 : *Concentration of trace elements (ppm) in Dubai sediments*

105

3.8 Mineral Composition

X-ray diffraction was used to find out the mineral composition of the various sediments samples in the study area. Table 3.11 illustrates the mineral compositions of Dubai sediments. In general carbonate mineral (calcite) is the most abundant mineral and found at all stations as a major mineral, except for the samples collected from Dewa (St 9), Jebel Ali (St 11) and Ras Ghantoot (St 13). Aragonite follows calcite in abundance as major mineral. Quartz is less common and distributed only at six of the studied stations (2, 3, 4, 6 & 14) as a major mineral, whereas dolomite is rare in distribution and reported only at stations 5 and 10. Sample of Al-Mamzar mouth (St 1) characterizes by the presence of calcite and aragonite as a major minerals, whereas Al-Mamzar mid and end (St 2 & 3) compose of calcite and quartz. Sample of Al-Hamriya St 1 (St 4) characterizes by the presence of calcite, quartz and aragonite; Al-Hamriya St 2 (St 5) contains calcite, dolomite and aragonite, whereas Al-Hamriya St 3 (St 6) characterizes by calcite and quartz as major minerals. Dry Docks sample (St 7) composes of calcite whereas aragonite and calcite are forming the major minerals at Jumeirah Beach Hotel (St 8). Dewa (St 9) characterizes by aragonite, whereas Dubal (St 10) characterizes by dolomite and calcite as a major minerals. Samples of Jebel Ali Hotel (St 11) and Ras Ghantoot (St 13) contain aragonite, whereas Ras Hisyan (St 12) characterizes by calcite and aragonite as a major minerals. Dubai approach (St 14) and Neptune Wreck (St 15) contain calcite and aragonite in addition of quartz at Dubai approach. Among subordinate minerals, plagioclase, quartz, calcite and dolomite distribute in Dubai sediments. Dolomite is the most abundant as minor mineral, whereas quartz, chromite, pyroxene, aragonite, plagioclase and amphibole are less abundant. Figure 3.36 demonstrates the X-ray of existing mineral based on the intensities of their strongest diffraction peaks.

Table 3.11 : *Distribution of major, subordinate and minor minerals in Dubai sediments*

Stations	Locality	Major mineral(s)	Subordinate mineral(s)	Minor mineral(s)
1	Al-Mamzar mouth	Calcite, Aragonite	Quartz, Plagioclase	Dolomite, Pyroxene
2	Al-Mamzar mid	Calcite, Quartz	Plagioclase	Dolomite, Chromite
3	Al-Mamzar end	Calcite, Quartz	. . . .	Dolomite, Aragonite, Plagioclase
4	Al-Hamriya St 1	Calcite, Quartz, Aragonite	Plagioclase, Dolomite	. . . .
5	Al-Hamriya St 2	Calcite, Dolomite, Aragonite	. . . .	Quartz, Chromite
6	Al-Hamriya St 3	Calcite, Quartz	Plagioclase, Dolomite	. . . .
7	Dry Docks	Calcite	Quartz	Dolomite, Aragonite
8	Jumeirah Beach	Aragonite, Calcite	Plagioclase	Dolomite, Pyroxene
9	Dewa	Aragonite	Calcite	. . . .
10	Dubal	Dolomite, Calcite	. . . .	Quartz
11	Jebel Ali Hotel	Aragonite	Quartz, Calcite	Amphibole
12	Ras Hisyan	Calcite, Aragonite	Quartz, Plagioclase	Dolomite
13	Ras Ghantoot	Aragonite	Calcite	Quartz
14	Dubai approach	Calcite, Quartz, Aragonite	. . . .	Dolomite, Chromite
15	Neptune Wreck	Aragonite, Calcite	. . . .	. . . .
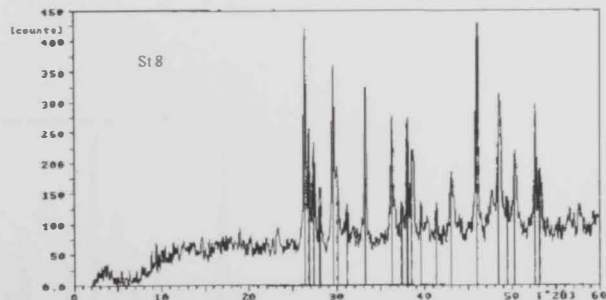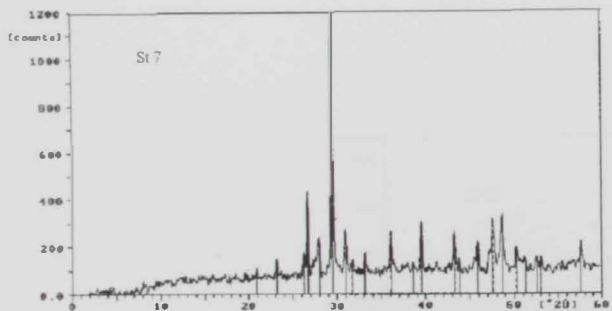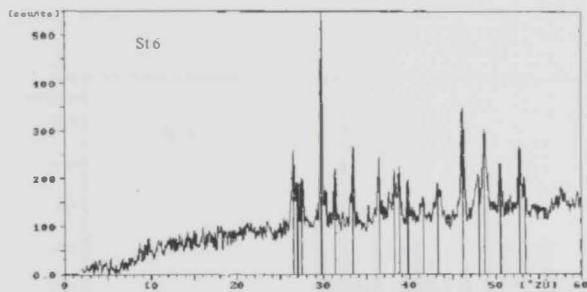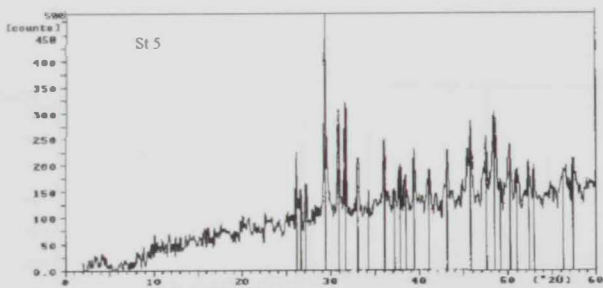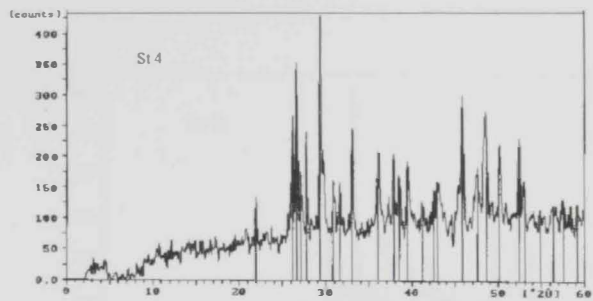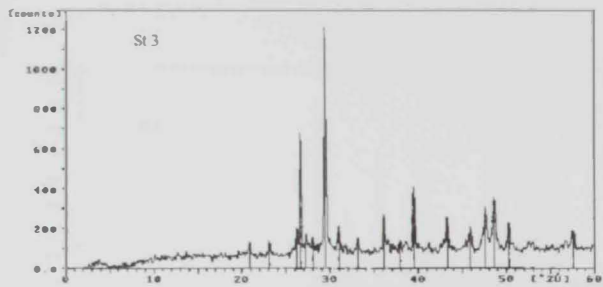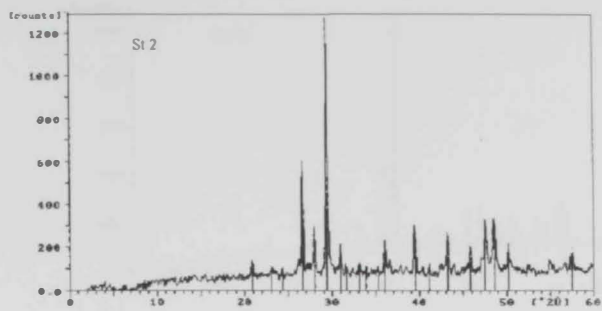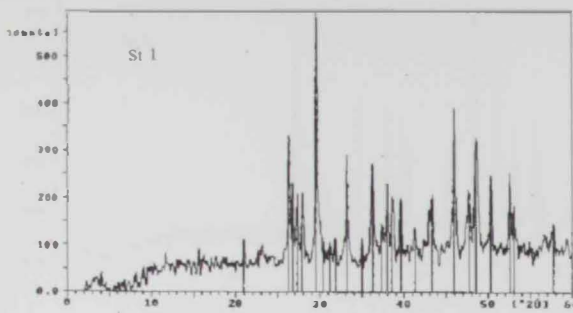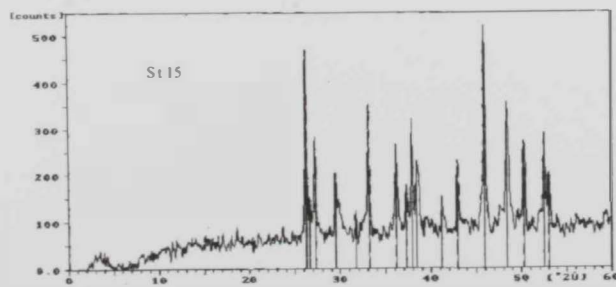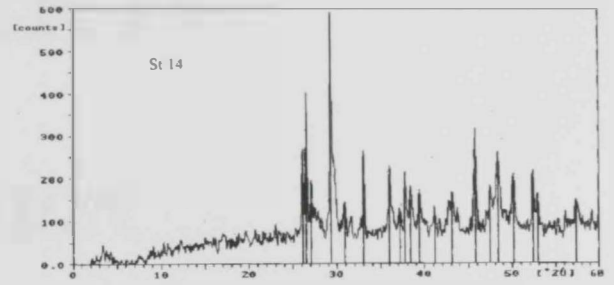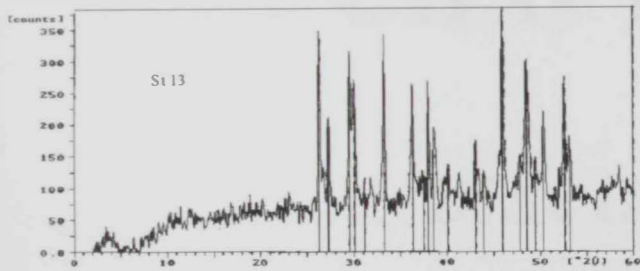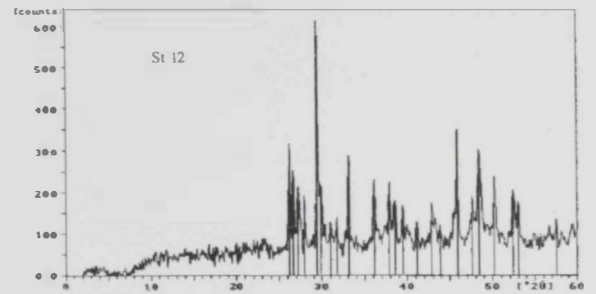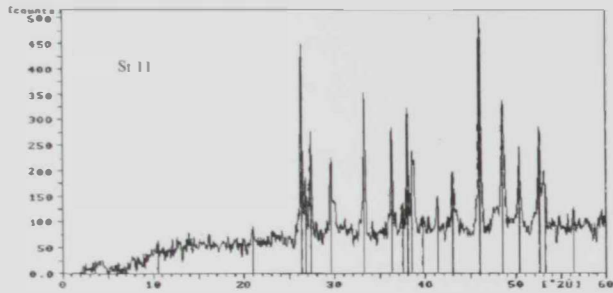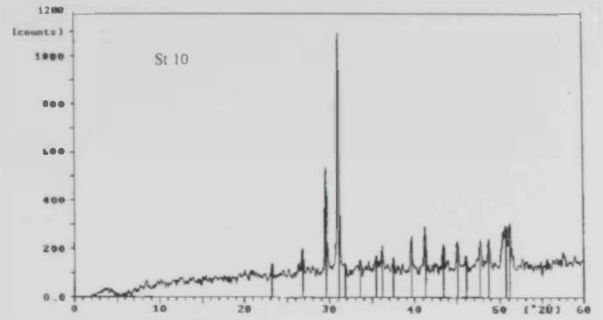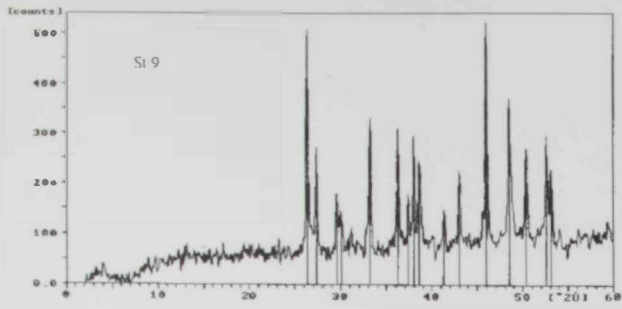
Figure 3.36 : *X-rays diffraction charts of different stations*

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CHAPTER IV

DISCUSSION

DISCUSSION

4.1 Introduction

The fate of organic and inorganic pollutants in the marine environment has been studied extensively in both qualitative and quantitative detail over the past 15 years. The ecological impacts are also better understood; many biological effects have been measured and some toxicological patterns have become apparent. Marine birds and mammals are visible victims of oil spills. The concern for chronic sublethal effects caused by these pollutants in low-energy, shallow coastal waters and shorelines is increasing (GESAMP, 1993).

In the comparison of anthropogenic and natural environmental factors, we can already recognize that the very rapid environmental development especially of coastal regions led to high quantity of anthropogenic input, which reflects a negative impact on coastal ecosystem and limit the survival capacity of organisms (Fellenberg, 2000).

Due to the increase in industrial development, the degree of pollution by fossil fuel-derived hydrocarbons showed an increasing tendency. The general distribution pattern of organic pollutants in the sediment reflects the pollutant discharge from industrial and urban sources (Hong *et al.*, 1995).

Contaminants in aquatic ecosystem, such as organochlorine, polychlorinated biphenyls and heavy metals, cause various harmful effects on human and wildlife. Monitoring aquatic

pollution is a crucial step in controlling water quality and in the management of aquatic and semi-aquatic wildlife (Yamaguchi *et al.*, 2002).

Some contaminants such as PAH compounds are adsorbed on suspended particles, and then settle and accumulate in bottom sediments. The contaminants in sediments are much less subject to degradation than if they were in the water column. The concentrations of contaminants in sediments are frequently used as indices of the rate of contaminant inputs into aquatic environments (Neff, 1985).

The studies and assessment of marine pollution are underpinned by a set of definitions, most of which have a basis in relation to chemical inputs. But some proposed biological organisms as agents of pollution in the marine environments. Such as introduction of non-indigenous species through wastewater discharges into marine environment (Elliott, 2003). Also the high nutrient supply supports a high level of primary productivity by phytoplankton, process described as eutrophication (Killops and Killops, 1993)

Historically, marine sediment is considered to be the ultimate sink for many classes of anthropogenic contaminants. However, recent studies (Loganathan & Kannan, 1991) have demonstrated that during the last decade environmental regulation has resulted in a reduction in the loading of waste from terrestrial sources, but the marine sediment reservoir could act as a non-point source, and has the potential to release the ' in-place contaminants' causing adverse effects to organisms and to human health through trophic transfer (Hong *et al*, 1995).

Sediment pollution was found to be complex as it is geographically not only limited to the introducing part, but also affects large scale of the marine environment. Sediment quality was strongly influenced by upstream input and partly by the asymmetric tide cycle,

resulting in accumulation of the finer sediments with the highest pollution load in the upstream part (Vandecasteele *et al.*, 2002).

Many attempts were made by several researchers to quantify the extent of petroleum hydrocarbon and heavy metal pollution in sediments. Kvenvolden *et al.* (1993); Al-Thukair and Al-Hinai (1993); De Domenico *et al.* (1994) and Simpson *et al.* (1995) determined the oil pollution and its impact on marine environment. Steimle *et al.* (1990); Niencheski *et al.* (1994); Depledge *et al.* (1995) and Ismail *et al.* (1995) assessed heavy metal pollution and its impact on the marine life in several areas around the world.

4.2 Natural Background Levels

The background levels (natural levels) are the concentrations of elements or compounds before any anthropogenic influences or the concentrations which have no or minimal effects on marine environment and aquatic life. In other word it is what be present without external perturbation. Also background concentration levels are defined as these concentrations commonly found in soils that considered clean and are a function of soil organic matter and clay content (Tack *et al.*, 1997). The assessment of pollutant values for different sources provide guideline and indicate threshold levels above which action must be taken to remediate the soil (Vandecasteele *et al.*, 2002).

4.2.1 Total Petroleum Hydrocarbons (TPH)

The Arabian Gulf has a long history of oil pollution, due to many reasons. About 2 Mbbls of oil discharge annually into the northern part of the Gulf (Literathy, 1993). Natural oil seeps are important sources of pollution in the region and constitute about 10% of the overall oil discharges (Al-Harmi, 1988). Pipeline accidents and shipping activities provide

another sources of oil pollution. Moreover, the petroleum industry provides other sources of pollutants in the region (Massoud *et al.*, 1996). A mixed petroleum product containing a broad spectrum of hydrocarbon classes is released to the marine environment where it may affect a variety of biological processes and be a potent cell mutagen and carcinogen (Capone & Bauer, 1992). Massoud *et al.* (1996) established the following values of TPH dry, silt/clay sediment fraction, as guidelines for pollution levels in bottom sediments of the Arabian Gulf:

10–15 µg/g   Unpolluted areas (natural back ground levels)

15–50 µg/g   Slightly polluted areas (upper permissible limits)

50–200 µg/g   Moderately polluted areas

> 200 µg/g   Heavily polluted areas.

In comparing these values with the values obtained from Dubai sediments, only Al-Hamriya St 1 (St 4) and Jebel Ali Hotel (St 11) have been attained the background levels. Al-Mamzar area (St 1, 2 & 3), Dubal (St 10), Dubai approach (St 14) and Neptune Wreck (St 15) are slightly polluted areas. Dry Docks (St 7), Jumeirah Beach (St 8), Dewa (St 9), Ras Hisyan (St 12) and Ras Ghantoot (St 13) are described as moderately polluted areas. Al-Hamriya St 2 (St5) showed high level (4888 µg/g), which described as heavily polluted area; but Al-Hamriya St 3 (St 6) provided unexpectedly high level of TPH (48018 µg/g), which can be described as over heavily polluted area. Bearing in mind the textural class in this station is muddy sand (25% mud and 71% sand), which has less ability in adsorption of TPH than the silt/clay.

Table 4.1 summarizes the data conducted by Shriadah (1998a) about the petroleum hydrocarbons pollutants along the Arabian Gulf coast of the UAE.

Table 4.1 : *The levels of TPH along the UAE coast (Shriadah, 1998a)*

Emirate	TPH μg/g
Ras Al-Khaimah	4.55–7.4
Umm Al-Quwain	4.51–7.03
Sharjah	5.99–7.25
Abu Dhabi	6.38–9.85

According to the pervious data proposed by Shriadah (1998a) the study area showed incomparable values. All the stations showed higher values with, levels vary between so high and slightly high except for Al-Hamriya St 1 (St 4) and Jebel Ali Hotel (St 11) were within the proposed range. The maximum value is 24009 times higher than the minimum value, which exhibits a very large scale of fluctuation.

Worldwide substantial data have been published regarding the concentrations of TPH in the marine sediments among these, petroleum hydrocarbons in surficial sediments from the coast of Oman range from 0.8 to 19 μg/g. Total hydrocarbon concentrations in uncontaminated sediments from coastal waters in Australia were in the range 0.2–5.0 μg/g (Shriadah, 1998a). Total petroleum hydrocarbons in surficial sediments from Port-of-Spain Harbour, ranged from 2.8–240.5 μg/g. Unusually high levels (28.2–17147.5 μg/g) of petroleum hydrocarbons were found in the Gulf of Paria, Trinidad (Shriadah, 1998a). The value of TPH in Al-Hamriya St 3 is 2.8 times higher than the value, which was reported in Gulf of Paria (17147 μg/g). Furthermore, Massoud *et al*. (1996) found TPH in heavily polluted area, which affected by Kuwait oil slick ranged from 266–1448 μg/g. The recorded value from Al-Hamriya St 3 is 33 times higher compared with last value (1448 μg/g). The concentrations of TPH in sediments at the most severely impacted areas along

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Saudi Arabian coast one year after the Gulf War oil spill were 10000 µg/g (Hayes *et al.*, 1993. This value is 4.8 times lower than TPH value at Al-Hamriya St 3, which confirms the pervious conclusion about abnormality of this value.

Based on the present data five moderately (108–223 µg/g) and heavily (4888–48018 µg/g) polluted regions are recognized in the study area. Three are located in the northeastern parts; one heavily polluted is located in the far northeastern part at Al-Hamriya St 2 and 3 (St 5 & 6). Another two are moderately polluted; one is located in the middle northeastern part at Dry Docks (St 7) and the other is located in the near northeastern part at Jumeirah Beach (St 8). In the southwestern parts there are two moderately polluted regions; one is located in the near southwestern part at Dewa (St 9) and the other is located at the far southwestern part at Ras Hisyan (St 12) and Ras Ghantoot (St 13).

The very high level of TPH at heavily polluted region in Al-Hamriya St 2 and unexpectedly high value in Al-Hamriya St 3 (represents 9/10 [90%] of total values of TPH in the study area) are majority attributed to the presence of Al-Hamriya Port. Navigation route, grazing, and ship painting, incomplete combustion of oil products, recent biosynthesis processes (GESAMP, 1993) and anthropogenic discharges could be the direct sources of pollution. Because of V and Ni are the largest trace metal constituents of crude oil, and hence their presence in high concentration in marine sediments may indicate direct input from oil pollutants (Al-Abdali *et al*, 1996). Therefore the relatively low values of V and Ni in Al-Hamriya St 2 (10 ppm and 17 ppm) and Al-Hamriya St 3 (14 ppm and 16 ppm) disprove the presence of natural seepage or any damages in oil pipelines (crude oil) and raise the suggestion of anthropogenic source.

The high levels of TPH in bottom sediments might also be a result of precipitation of thick residual oil components after the evaporation of the lower boiling-point components

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(Shriadah, 2000). Another interpretation for this huge value at Al-Hamriya St 3 is that level may have occurred as a temporal event during or shortly. The moderately polluted region at Dry Docks (St 7) is mostly attributed to the presence of dry docks, which might received petroleum input from tankers damage, water deballasting, tankers maintenance. Also nearby offshore discharge could provide another source. The moderately polluted regions at Jumeirah Beach (St 8), Dewa (St 9) and Ras Hisyan (St 12), and Ras Ghantoot (St 13), which are far from navigation route and oil activates, the private usage of the coast where many large hotels are constructed could act as a direct source of oil input.

4.2.2 Total Organic Carbon (TOC)

The organic matter content of sediments, quantified by the concentration of total organic carbon (TOC), is thought to play an important role in the accumulation and release of different micropollutants (Massoud *et al.*, 1996). Literathy *et al.* (1992) found that the natural background levels of TOC in the bottom sediments of the Kuwait marine environment are in the range of 0.5–0.8 wt%.

The data for Dubai sediments showed that all the stations were at background levels except for Al-Hamriya stations. TOC at Al-Hamriya St 1 (St 4) is 1.21 wt%, which is 1.5 times higher than background level; Al-Hamriya St 2 (St 5) showed level of 1.8 times higher, whereas Al-Hamriya St 3 (St 6) showed value of 7.4 times higher than unpolluted value. The maximum value is about 37 times higher than the minimum, while Al-Hamriya St 3 represents approximately half (46%) of TOC values in the study area.

Table 4.2 demonstrates a comparison between the data obtained by several researchers of organic carbon contents in sediments from different areas of UAE coasts with present study. Evidently TOC values, which, recorded in Dubai sediments, are higher than the

values provided by Abu Hilal and Khordagui (1992) of UAE coasts. Al-Hamriya St 3 showed level of 2.2 times higher than the earlier value reported by Abu Hilal and Khordagui (1992) at the same environment. Shriadah (1998a) performed study on the organic carbon content in sediments from the Arabian Gulf coast of UAE. These values were at the background levels, but the values, which were obtained from Dubai sediments in this study showed higher levels in comparison with Ras Al-Khaimah (0.12–0.89 wt%), Umm Al-Quwain (0.15–0.38 wt%), Sharjah (0.49–1.2 wt%) and Abu Dhabi (0.45–0.77 wt%). El-Sammak (1998) assessment of organic carbon in Dubai Creek was in a range from 0.0052 to 0.445 wt% but the present study provided a range from 0.16–5.9 wt%. The concentration of TOC at Al-Hamriya St 3 is about 13 times higher than the previous value. The TOC in Dubai sediments from Al-Qubaisi (2001) study was in a range from 0.06–0.27 wt%, which represents significant lower range compared with present range. The level of TOC at Al-Hamriya is about 22 times higher than the previous range. The variation between these values and the present value mainly attributed to the variation in the sites of collection.

In contrast the value of TOC in Al-Hamriya St 3 (5.9 wt%) is comparable with the value recorded by Deshgooni (2002) at Dubai Creek (5.8 wt%). Worldwide TOC value showed also quantifiable level with the value obtained from muddy sediments of Baltic Sea (5.71 wt%), in case of there is no effect of textural class in accumulation of organic matter.

Based on previous reports one heavily polluted (5.9 wt%) region could be recognized in the northeastern part of the study area at Al-Hamriya St 3 (St 6). It is observed that the northeastern parts of the study area contain higher TOC contents than southwestern parts. In the present study, the high level of TOC mainly related with high TPH. Which suggested anthropogenic (man-made) source of pollution.

Significant positive correlation (r = 0.98) has been found between TOC and TPH concentrations (Figure 4.1). Based on this result, it may be suggested that organic carbon concentration could be considered as an indicator of petroleum pollution in the area, a conclusion that is in agreement with the earlier observations of Emara (1998) and Shriadah (1998a) in case of heavily oiled sediments.

Table 4.2 : *Organic carbon contents (wt%) in sediments from the UAE coasts*

Reference	Area	Range	Average ± S.D
Abu Hilal & Khordagui (1992)	Dubai	0.14–2.65	1.02 ± 1.15
Abu Hilal & Khordagui (1992)	Sharjah	0.44–1.36	0.78 ± 0.35
Abu Hilal & Khordagui (1992)	Ajman	0.24–1.42	0.7 ± 0.5
Shriadah (1998a)	Ras Al-Khaimah,	0.12–0.89	0.34 ± 0.29
Shriadah (1998a)	Umm Al-Quwain	0.15–0.38	0.27 ± 0.22
Shriadah (1998a)	Sharjah	0.49–1.2	0.57 ± 0.43
Shriadah (1998a)	Abu Dhabi	0.45–0.77	0.61 ± 0.4
El-Sammak (1998)	Dubai Creek	0.0052–0.445	0.153
Al-Qubaisi (2001)	Dubai	0.06–0.27	0.1 ± 0.08
Deshgooni (2002)	Dubai Creek	0.3–5.8	2.7 ± 1.6
Present study	Dubai offshore	0.16–5.9	0.86 ± 1.44

TPH vs. TOC
TOC = .45324 + .00011 * TPH
Correlation: r = .98105
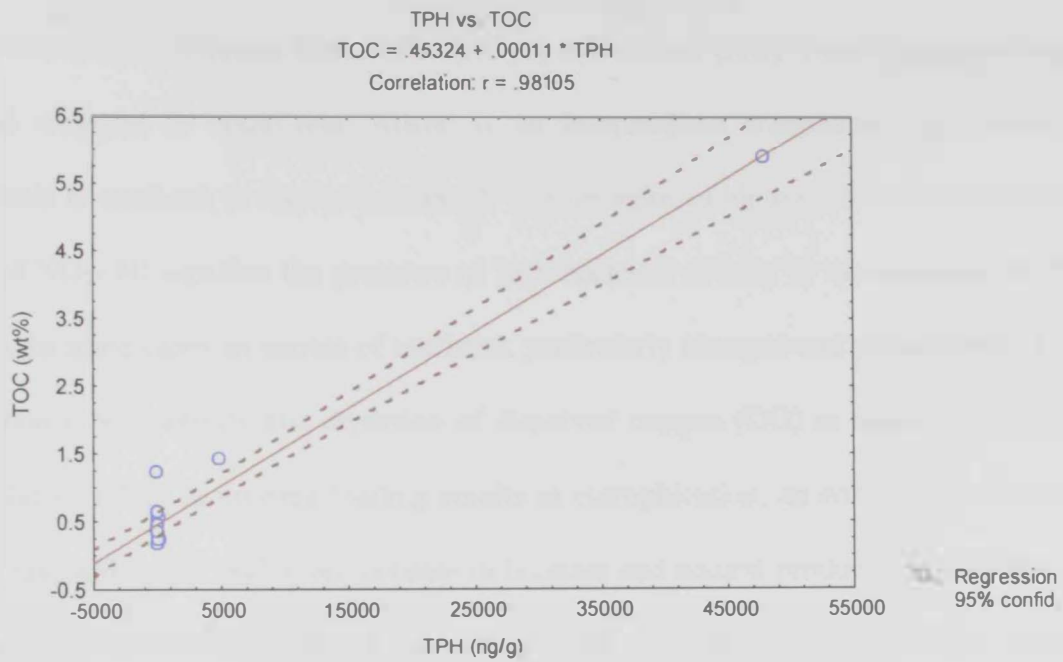
Figure 4.1 : *Scatter plot showing the relationship between TPH and TOC*

4.2.3 Total Kjeldahl Nitrogen (TKN)

Nitrogen is essential in producing amino acids, the building blocks of proteins (Thurman and Trujillo, 1999). Ammonia is a nutrient compound, which rapidly undergoes biological conversion, i.e., oxidation into nitrite (NO_2^-) and nitrate (NO_3^-) and fixation as amino-bound nitrogen in organisms. Nitrite is an intermediate compound, which occurs if ammonia is oxidized or nitrate is reduced. The presence of higher amounts of nitrite (<0.1 µg/l of NO_2- N) signifies the presence of high bacterial activity in the seawater (ROPME, 1999). In some cases an excess of nutrients, particularly nitrogen and phosphorus, can lead to enhance productivity and depletion of dissolved oxygen (DO) in aquatic systems. The cumulative effect of nutrient loading results in eutrophication, an enrichment of water by nutrients, which can lead to an increase in biomass and natural productivity within a given aquatic community structure (Wilson *et al.*, 1993). This can cause major ecological changes, e.g. algal blooms, reduction in species diversity and major changes in community structure. Thus, assessing nutrient concentrations is of paramount importance for providing insight into the relative health of aqueous environments.

The obtained data of TKN in Dubai sediments showed higher concentrations compared to the maximum value (300 µg/g) suggested by Alloway (1993). Only Al-Mamzar mouth (St 1) and Dubal (St 10) have been achieved the previous level. Al-Hamriya stations showed higher levels range from 814 to 2222 µg/g, which represent from 2.7 to 7.4 times higher than the suggested level. Another high value (2457 µg/g) was found at Dewa (St 9), which represents 8.2 times enrichment than the suggested level. The maximum value is about 11 times higher than the minimum value.

The high concentrations of TKN at Al-Hamriya St 3 (St 6) and Dewa (St 9) probably originated from run-off of fertilizers, livestock and human wastes and municipal sewage-

treatment facilities. Another interpretation of high value of TKN may be attributed to high level of TPH (48018 μg/g), which increases the mortality rate among the aquatic organisms such as phytoplankton and zooplankton. That enhances the bacterial decomposition activity, which increase the rate of nitrite.

It is important here to mention the Redfield ratio in marine sediments (carbon:nitrogen: phosphorus). That represents the average atomic ration of C:N:P (106:16:1 respectively) in marine phytoplankton (El-Sabrouti *et al.*, 1990). the ratio of C:N is about 6.625. Table 4.3 illustrates the ratio of C:N in the study area, it is obvious that all the stations showed deviation by increase from the Redfield ratio except for Dewa (St 9) with ratio of 0.94, which showed sharp deviation by decrease. Only Ras Ghantoot (St 13) with ratio of 6.97 nearly achieved the Redfield ratio (6.625). Al-Hamriya St 3, St 2 with ratios of 26.55 and 17.32 respectively and Dubal (St 10) with ratio of 23.77, exhibited sharp deviation by increase from the Redfield ratio.

The sharp deviation from the Redfield ratio at Dewa (St 9), which has the highest value of TKN (2457 μg/g) and relatively low level of TOC (2300 μg/g) could be attributed to preferential oxidation of carbon than nitrogen (El-Sabrouti *et al.*, 1990). The sharp deviation at Al-Hamriya St 3 and Al-Hamriya St 2, which have the high values of TOC (59000 μg/g and 14100 μg/g) and high TKN value (2222 μg/g and 814 μg/g) lead to produce high ratio. The deviation from the Redfield ratio at Dubal (St 10), where TOC value is relatively low (6300 μg/g) and also the TKN value is low 265 μg/g, which produced high ratio. These ratios may be also attributed to variability in the elemental composition of phytoplankton and zooplankton and/or highly terrestrial input (El- Sabrouti *et al.*, 1990).

The distribution of TKN in Dubai sediments revealed two heavily and moderately (814–2222 µg/g) and heavily (2457 µg/g) contaminated regions. One heavily and moderately contaminated region is located in the far northeastern part at Al-Hamriya area (St 4–6); another heavily contaminated region is located in the near southwestern part of the study area at Dewa (St 9).

The high levels of TKN in Al-Hamriya stations and Dewa (Al-Hamriya St 3 and Dewa exhibit more than 1/5 [21% and 23% respectively] of TKN values) are related with land-based discharge. As it well known that the main source of nutrients enrichment are the fertilizers.

Figures 4.2 & 4.3 exhibit positive correlation between TKN and TPH ($r = 0.61$); TKN and TOC ($r = 0.61$). It is worthy to note that in the present study TPH, TOC and TKN have the same trend of an increase which is toward northeastern except for TKN which also has another trend of an increase toward southwestern (Figure 4.4A, B & C).

Table 4.3 : *The ratio of organic carbon:nitrogen in Dubai sediments*

Stations	Locality	TOC (µg/g)	TKN (µg/g)	C/N
1	Al-Mamzar mouth	1600	218	7.34
2	Al-Mamzar mid	4400	420	10.48
3	Al-Mamzar end	5200	410	12.68
4	Al-Hamriya St 1	12100	931	13
5	Al-Hamriya St 2	14100	814	17.32
6	Al-Hamriya St 3	59000	2222	26.55
7	Dry Docks	5500	523	10.5
8	Jumeirah Beach	2500	234	10.68
9	Dewa	2300	2457	0.94
10	Dubal	6300	265	23.77
11	Jebel Ali Hotel	3700	385	9.6
12	Ras Hisyan	2700	324	8.33
13	Ras Ghantoot	2300	330	6.97
14	Dubai approach	4400	507	8.68
15	Neptune Wreck	3400	402	8.46
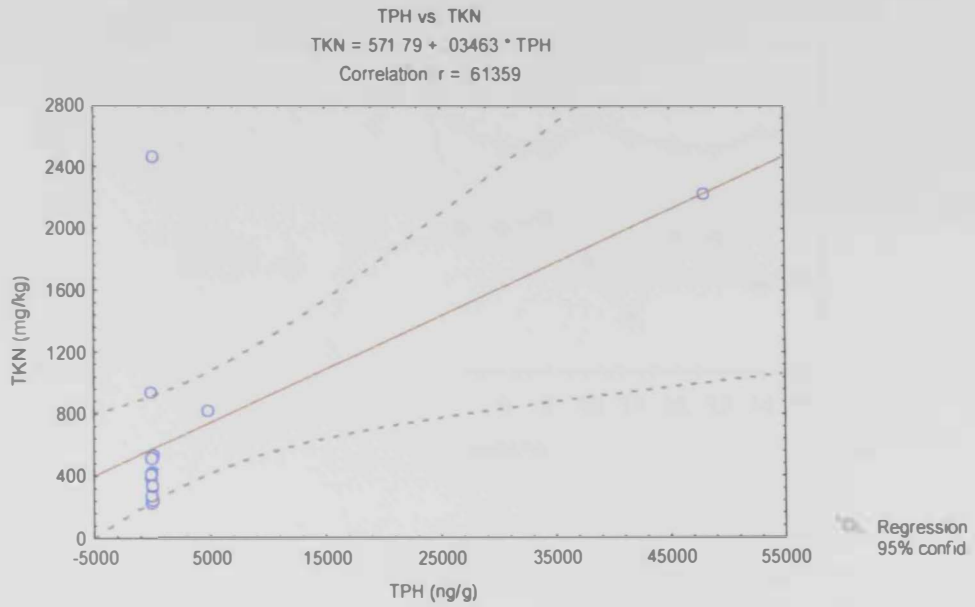
Figure 4.2 : *Scatter plot showing the relationship between TPH and TKN*
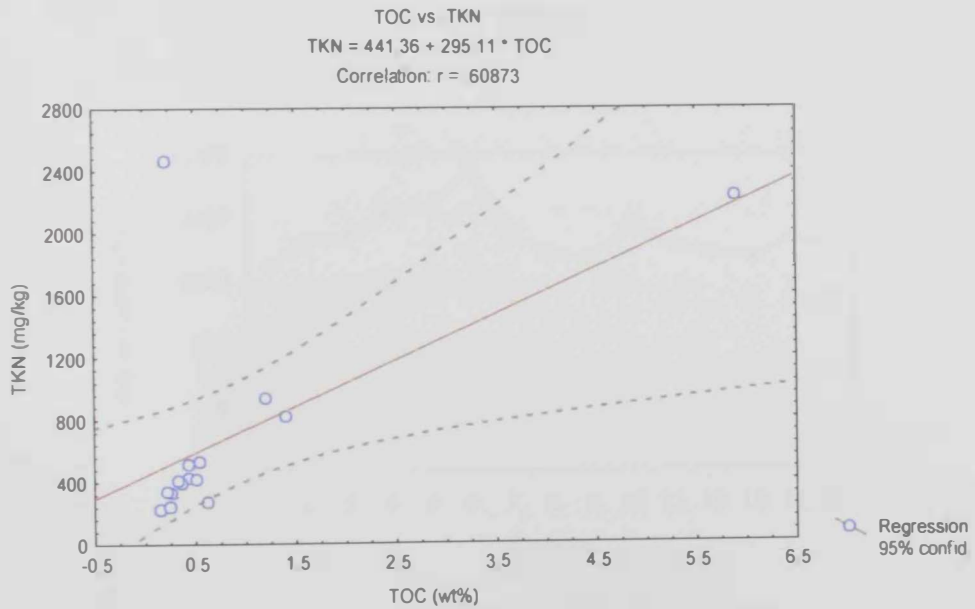
Figure 4.3 : *Scatter plot showing the relationship between TOC and TKN*

A.

B.

C.
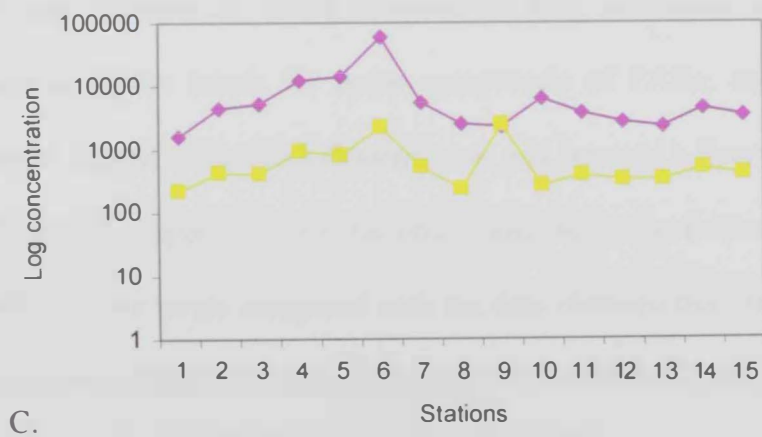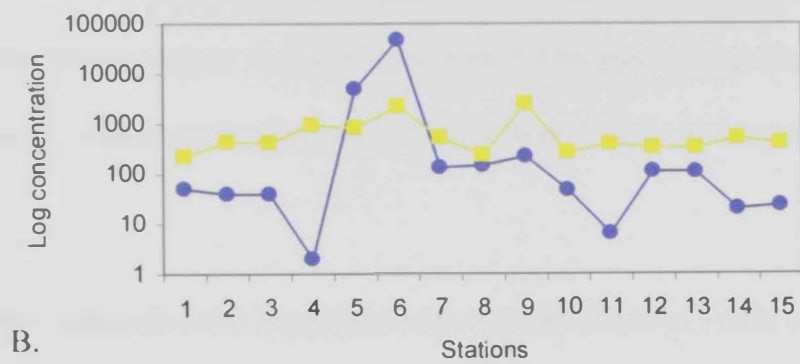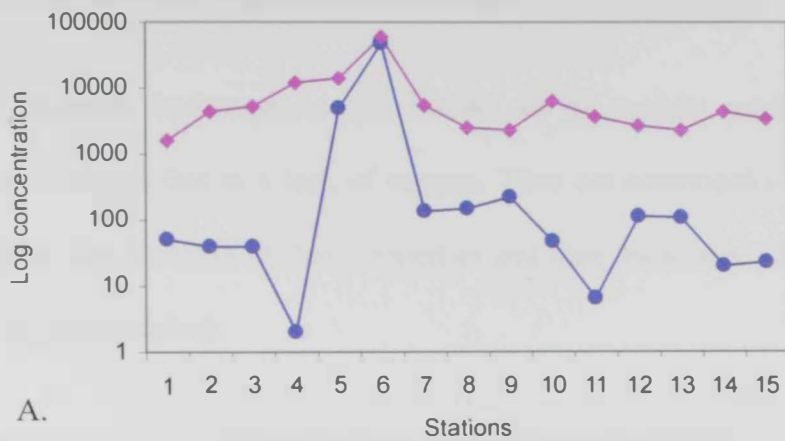
TPH   TOC   TKN

Figure 4.4 : *The relationship between log concentration (μg/g) of TPH, TOC and TKN*

4.2.4 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons are known to be mainly products of incomplete combustion processes due to a lack of oxygen. They are composed of two or more fused aromatic rings. On the basis of their properties and their molecular weight, two classes of PAHs can be distinguished:

1) The two and three ring aromatics from naphthalene to anthracene.

2) The four to six ring aromatics from fluoranthene to indeno(1,2,3-c,d)pyrene.

The lower-molecular-weight two and three ring PAHs have a significant acute toxicity, whereas some of higher-molecular-weight PAHs show a high carcinogenic potential (Witt, 1993).

Few published materials were found about the concentrations of PAHs in marine sediment. The value, which obtained from Victoria Harbour, estimated the concentration of TPAHs from 1.2 to 14 µg/g (Hong *et al.*, 1995). However the data, which was gathered from Dubai sediments, showed higher levels for some compounds of PAHs; especially of higher-molecular-weight. Chrysene, benzo(k)fluoranthene and benzo(g,h,i)perylene are measured 34.8, 43 and 46.1 µg/g respectively. On the other hand the concentration of PAHs in Dubai sediments showed lower levels compared with the data obtained from the Baltic Sea (Witt, 1993). Table 4.4 illustrates the minimum and maximum values of PAH compounds in two regions.

According to the provided data all PAH compounds in Dubai sediments are considered to be low. The possible explanation for PAHs enrichment in Baltic Sea sediments is attributed to seasonal variation. Due to high temperature of Gulf waters compared with Baltic Sea, which enhance the microbial degradation, the values of PAHs will be lowered in Dubai

sediments. Another reason for the low level of PAHs in Dubai sediments that the primary source of anthropogenic PAHs in the environment is thought to be atmospheric depositions (Witt, 1995). The use coal-fire power plants and combustion related to private heating sources in cold countries, which release large quantities of soot and that increase PAHs depositions.

The total PAHs (0.09–162 µg/g) in Dubai sediments found to be lower than the values recorded along Saudi Arabian coast (10–300 µg/g) one year after the Gulf War (Hayes *et al.*, 1993), although this range was in heavily oil contaminated sediments. In contrast the total PAHs in Dubai sediments showed higher levels than TPAH (2.9–61 µg/g) recorded in Xiamen Houbar (Hong *et al.*, 1995).

One contaminated region in the study area can be recognized located in the far northeastern part at Al-Hamriya St 3 (St 6). TPAHs in this station is more than 9/10 (92%) of an overall values. The maximum value is 1800 times higher than the minimum value, which exhibits a drastic variation.

The concentration of PAHs correlated positively with TOC. The highest concentrations of pyrene, chrysene, benzo(k)fluoranthene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene were recorded at Al-Hamriya St 3 (St 6). This confirms the earlier conclusion proposed by Evans *et al.* (1990) that the highest amount of PAHs almost associate in sediments with a high TOC. The distribution pattern appeared to be related to oil pollutant sources, such as discharge from vessels and port activities (Hong *et al.*, 1995).

Table 4.4 : *Comparison between the concentrations of PAHs (µg/g) in Dubai*

and the Baltic Sea sediments

Area Compounds	Dubai sediments	Baltic Sea (Sandy sediments) (Witt, 1993)	Ratio of PAHs in Baltic Sea: Dubai sea
Naphthalene	0.09–6.6	0.05–5.88	0.9
Acenaphthene	nd	0.69–26.95	–
Fluorene	0.24–0.78	0.15–5.36	6.9
Phenanthrene	0.02–0.32	1.4–47.88	149.6
Anthracene	nd	0.2–47.12	–
Fluoranthene	0.04–3.9	0.83–151	38.7
Pyrene	0.03–13.7	0.4–85.9	6.3
Benzo(a)anthracene	0.04–0.2	0.25–66.52	332.6
Chrysene	0.02–34.8	0.28–58.2	1.7
Benzo(b)fluoranthene	0.3–3.1	0.75–157.22	50.7
Benzo(k)fluoranthene	0.02–43	0.31–62.35	1.45
Benzo(a)pyrene	0.05–2.34	0.36–94.94	40.6
Dibenzo(a,h)anthracene	0.03–10.5	0.08–14.74	1.4
Benzo(g,h,i) perylene	0.03–46.1	0.4–116.69	2.5
Indeno(1,2,3-c,d)pyrene	0.02–0.3	0.03–144	480

nd (Not detected)

4.2.5 Polychlorinated Biphenyls (PCBs)

The well-known acronym PCBs stands for a group of industrial organochlorine chemicals that become a major environmental concern in the 1980s and 1990s. As a result of careless disposal practices, they have become a major environment contaminant in many areas of the world. In some locales, PCBs are destroyed by incineration which produce another chemical compounds may become more toxic to the environment than the parent compounds. PCBs are now widespread in the environment and can be detected in air, water, soil, sediments and organisms; the typical environmental concentration is 2–50 µg/kg in soil (Killops and Killops, 1993). PCBs are transported from application and depositional sites to the aquatic environment in overland flows and ground leachate following rainfalls (Clendening *et al.*, 1990). Poly chlorinated biphenyls can also enter the environment as contaminants contained in effluent discharges and in urban stormwater runoff. PCBs tend to adsorb to fine particulates or be bioaccumulated into lipids in aquatic biota (Olsen *et al.*, 1982).

Based on previous range (2–50 µg/kg), total PCBs in Al-Hamriya St 1 and 2 (St 4 & 5) values (34.9 and 34.6 µg/kg) approach the major term (50 µg/kg), whereas the value (93.3 µg/kg) in Al-Hamriya St 3 (St 6) was 1.9 times higher than the typical environmental concentration. Also Dry Dock (St 7) showed level (46 µg/kg) slightly lower than the major term of typical concentration. The other stations showed levels approach the minor term of previous range (2 µg/kg), only Al-Mamzar mid (St 2) displayed lower value (0.8 µg/kg). All PCB compounds were not detected in stations 9, 11, 12 and 13.

In comparison the concentration of TPCBs in Dubai sediments (0.8–93.3 µg/kg) with concentration of TPCBs in Victoria Harbour (320–1600 µg/kg). It was found that Dubai sediments showed very low level values of PCBs. The high values of TPCBs in Victoria

Harbour were from a sampling location situated where industrial wastes are discharged (Hong *et al.*, 1995). In contrast the average concentration of TPCBs in San Francisco Bay is 2.9 ± 1.0 µg/kg (Bothner *et al.*, 1998). This showed significant lower level than the values obtained from Dubai marine sediments with an average of 17.17 ± 25.7 µg/kg. This average is nearly 6 times higher than which in San Francisco Bay. The highest values (34.9, 34.6, 93.3 & 46 µg/kg) were recorded for Al-Hamriya stations and Dry Docks respectively. Al-Hamriya St 3 represents more than 1/3 (36%) of total PCBs values in Dubai sediments. The maximum value is about 117 times higher than the minimum with a wide variation between two values.

Two contaminated regions can be recognized in the study area, one is located in the far northeastern part at Al-Hamriya stations. The other one is located in the middle northeastern part at Dry Docks.

The high value of TPCBs in Al-Hamriya stations and Dry Docks may be related to the location, sediment grain size and organic carbon contents as reported by Fowler (1990). The expected source of PCBs in Dubai marine sediments is fallout or runoff because the primary method of disposal of the waste is by incineration. Another important source may be related to using chemicals in Al-Hamriya Port and Dry Docks. It is notable here that the high value of TPCBs in Al-Hamriya stations mainly attributed to PCB 180 (2,2', 3,4, 4', 5,5'-Heptachlorobiphenyl), present at 86.5 µg/kg at Al-Hamriya St 3 (St 6), 28.6 µg/kg in Al-Hamriya St 2 (St 5) and 19.5 µg/kg at Al-Hamriya St 1 (St 3), in addition to PCB 8 (2,4'-Dichlorobiphenyl), which contributes by 9 µg/kg at Al-Hamriya St 1(St 3). In Dry Docks (St 7) PCB 52 (2,2', 5,5'-Tetrachlorobiphenyl) adds 27 µg/kg to the total concentration.

However both PCBs and PAHs showed the maximum value at Al-Hamriya St 3 (St 6), but PCBs exhibit wider range of distribution in the study area. The highest values were at the stations from 4 to 7. The distribution of PAHs concentrated at station 6 (Figure 4.5), which exhibit very high level compared with other stations. Table 4.5 demonstrates comparison between the total PAHs and PCBs in the study area.

A.

B.
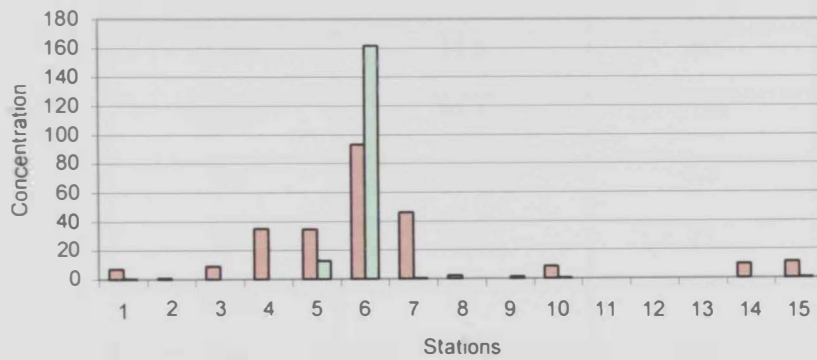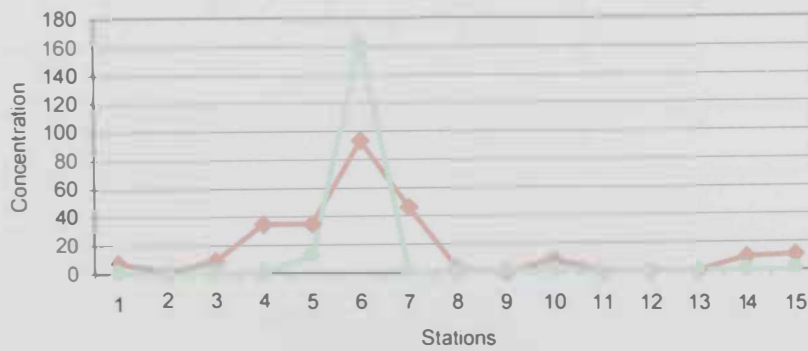
Figure 4.5 : *Comparison between the distribution of TPAHs and TPCBs in Dubai sediments*

Table 4.5 : *The ratio of TPAHs:TPCBs in Dubai sediments*

Station	TPAHs (µg/kg)	TPCBs (µg/kg)	TPAHs/TPCBs
1	260	7.21	36
2	nd	0.8	–
3	220	9.05	24
4	nd	34.9	–
5	12560	34.6	363
6	162000	93.3	1736
7	300	46	6.5
8	50	2.34	21
9	1500	nd	–
10	330	8.38	39
11	nd	nd	–
12	nd	nd	–
13	nd	nd	–
14	90	9.8	9
15	400	11.1	36

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4.2.6 Major Oxides and Trace Elements

Bottom sediments are known to act as a reservoir or sink for many trace metals and some other pollutants. Substantial quantities of major and trace elements are known to be transported annually by major rivers associated with suspended sediments. The airborne fallout from dust storms associated with *Shamal* winds may also be a significant source of trace metal input to local waters (Literathy & Foda, 1985).

Trace metals are natural constituents of all environments and are found in seawater, marine organisms and sediments (Bryan, 1976). Therefore, knowing their natural background levels, or at least their permanent concentrations in a marine environment, is essential for detecting and assessing trace metal pollution (Anderlini *et al.*, 1986).

The background levels suggested by some investigators for unpolluted marine sediments from different areas in the Arabian Gulf are given in Table 4.6. According to the background levels proposed by Fowler *et al.* (1993) of unpolluted areas of UAE; the mean value of Zn in Dubai sediments of the present study is 210.5 ppm. This value is about 84 times higher than the background level. The minimum value is still higher than the limited range of unpolluted areas. The highest three values 415, 145 and 132 ppm are encountered at Al-Hamriya St 3 and 2 (St 6 & 5) and Dry Docks (St 7), respectively, which may be regarded as chronically polluted areas. The mean value of Pb is 18 ppm, which is about 6 times higher than unpolluted level. The highest three values 35, 18 and 20 ppm are found at the same pervious stations, which suggest that these elements are closely associated and are derived from pollutant sources. The cadmium (0.1–0.4 ppm), Mn (8–145 ppm) and V (2–27 ppm) concentrations attained the natural background levels. This finding is in accordance with the previous conclusion of Al-Abdali *et al.* (1996) that Cd and Mn are natural constituents of the Gulf marine environment and not derived from pollutant source.

The mean value of Ni is 80.5 ppm, which is over 4 times higher than background level. The concentrations of Ni in Dubai sediments are within unpolluted range except for Dry Docks (St 7) and Dubal (St 10). The mean value of Fe is 9000 ppm, which is 2 times higher than background level. The high concentrations of Fe (> 6000 ppm) may be attributed to chronic or historical polluted levels in the region and were recorded at six of the studied stations. These values are 6200, 8500, 8600, 10300, 12000 and 17600 ppm and were represented at Al-Mamzar mid and end (St 2 & 3), Al-Hamriya St 2 and 3 (St 5 & 6), Dry Docks (St 7) and Dubal (St 10), respectively. The mean value of Cu is 79 ppm, which considered 19 times higher than the background level. Most stations fall within the limited range of unpolluted areas provided by Fowler *et al.* (1993) except for Al-Hamriya St 1, 2 and 3 (St 4, 5 & 6) and Dry Docks (St 7), which are considered highly polluted with values of 36, 72, 157 and 88 ppm, respectively.

According to the data obtained from marine sediment, which was collected from Canada and can be used as standard value (Table 4.7) the highest value of Si (669900 ppm) is lower than the level of Si in Canadian marine sediments (871000 ppm). Aluminum concentration in Canadian marine sediments is 54200 ppm, whereas in Dubai sediments is (400-24400 ppm). This value forming less than half of proposed value depends on the presence of clay minerals and the highest value was reported at Al-Mamzar end (St 3). However Fe level was high in the study area compared with unpolluted marine sediments but it is still in comparative level with the value of Canadian marine sediments (35500 ppm). Each of Si, Al and Fe are associated with clays, therefore the high level of these elements may be attributed to mineral composition. The highest value of Mg (30900 ppm) is 3 times higher than that is found in Canadian sediment and was reported at Dubal (St 10). However Mg is considered one of the common earth elements (Montgomery, 1995) and the common presence of dolomite (Table 3.11, Ch 3) as a major mineral causes such

relative high level of Mg. But also this high value may be related to polluted sources. Manganese values (8–145 ppm) in Dubai sediments show comparable level with Mn value (125 ppm) in Canadian marine sediment. Calcium is very high (251300–485500 ppm) compared with the Canadian marine sediment (8300 ppm). The maximum value is 58 times higher than that of the Canadian marine sediment. This may be attributed to the common presence of calcite and aragonite minerals in the sediment of Dubai as major minerals in all stations.

Sodium concentration (6800–19800 ppm) is 2 times higher than that recorded in the Canadian marine sediment. This is attributed to the high salinity of the Arabian Gulf as a result of high temperature and evaporation, which concentrate the salt in Gulf waters (al-Abdul-Razzed, 1984). Potassium concentrations in Dubai sediments ranged from (1000–7700 ppm), while Ba has a range of (11–95 ppm). Potassium and Ba attained unpolluted levels compared with the Canadian marine sediment values 11700 and 565 ppm respectively. Cadmium also has attained unpolluted levels comparing with values either from the region or with Canadian value, which confirms the previous conclusion that Cd and Mn are natural constituents of Gulf marine environment (Al-Abdali *et al*, 1996). Although the presence of any element in a marine sediments is natural. The important consideration is the concentration if it is below or above the background level.

Chromium concentration (5–173 ppm) is 3 times higher than that recorded for the Canadian marine sediment. The highest value was reported at Dubal (St 10). Copper concentration (2–157 ppm) is 5 times higher than the recorded value of the Canadian marine sediment. Nickel concentration (2–159 ppm) is 5.5 times higher and lead concentration (1–35 ppm) is 3.5 times higher. This suggests that Cr, Cu, Ni and Pb may be related to polluted sources.

Table 4.6 : *Comparison between mean and range values of trace metal concentrations (µg/g) in unpolluted marine*

sediments from different areas in the Arabian Gulf and study area

Reference (Area)	Zn	Pb	Cd	Ni	Mn	Fe	V	Cu
Qatar/Bahrain	26.3			6.5	50	8	5.1	3.9
Basaham& Al-lihaibi, 1993	(20.4–32.2)	—	—	(0.2–12.8)	(42.8–57.2)	(6–10)	(2.7–7.4)	(3.8–4)
Bahrain	3.1	12.3	0.4	15	57	4600	23	9.6
Basaham& Al-lihaibi, 1993	(2.3–3.8)	(0.5–24)	(0.01–0.8)	(9–20)	(17–97)	(3200–6000)	(9–36.6)	(1.5–17.6)
UAE	2.5	2.9	0.96	18.9	237	4800	20.7	4.2
Fowler *et al.*, 1993	(1.6–3.4)	(0.5–5.2)	(0.02–1.9)	(12.8–25)	(231)	(3600–6000)	(7.3–36)	(1.3–7.0)
Oman	8.8	4.11	0.38	26	200	8000	29.2	7.9
Fowler *et al.*, 1993	(7.7–9.8)	(1.2–7.2)	(0.06–0.7)	(9.9–46)	(89–310)	(5000–11000)	(10.4–48)	(1.7–14)
Dubai offshore, UAE	210.5	18	0.25	80.5	76.5	9000	14.5	79
Present study	(6–415)	(1–35)	(0.1–0.4)	(2–159)	(8–145)	(400–17600)	(2–27)	(1–157)

µg/g = ppm

Table 4.7 : *Comparisons between the concentration of major and trace elements in Dubai sediments and standard Canadian marine sediments*

Major & trace elements	Canadian marine sediments	Dubai sediments		Factor of an increase
		Max.	Locality	
Major oxides (wt %)				
SiO_2	87.1	66.99	Jumeirah Beach	0.8
Al_2O_3	5.42	2.44	Mamzar end	0.5
Fe_2O_3	3.55	1.76	Dubal	0.5
MgO	0.9	3.09	Dubal	3.4
CaO	0.83	48.55	Jebel Ali Hotel	58.5
Na_2O	1.02	1.98	Dry Dock	1.9
K_2O	1.17	0.77	Mamzar end	0.66
Trace elements (ppm)				
Ba	565	95	Dubal	0.16
Cd	0.6	0.4	Hamriya St 3	0.67
Cr	62	173	Dubal	2.8
Cu	31	157	Hamriya St 3	5
Mn	125	145	Dubal	1.16
Ni	29	159	Dubal	5.5
Pb	10	35	Hamriya St 3	3.5
Sr	53	5201	Jebel Ali Hotel	98
V	142	27	Dubal	0.2
Zn	86	415	Hamriya St 3	4.8

(Source: present study)

Strontium exhibits very high levels (1212-5201 ppm) compared with the Canadian marine sediment. This related to the textural characteristics of the sediment because most of the studied stations are covered by carbonate gravel sands and sands. It is well known that the sandy-size deposits are restricted to the western area off of Bahrain, Qatar and UAE off of Bahrain, Qatar and UAE (Al-Ghadban *et al.*, 1996). Strontium is known to be closely associated with Ca in recent aragonite rich sediments, because they are similar in both size and charge. Vanadium concentration (2-27 ppm) is lower than the value obtained from Canadian marine sediment (53 ppm), which confirms the previous reached conclusion that V has attained unpolluted levels. Zinc concentration (6-415 ppm) is 5 times higher than that of the Canadian marine sediment (86 ppm), which also confirms pervious reached conclusion that Zn high level is related to chronic or historical pollution.

On the other hand, the present data of Dubai sediments provided evidence of high levels of some of major and trace metals compared with unpolluted areas in Qatar and Bahrain (Basaham and Al-lihaibi, 1993); Bahrain (Basaham and Al-lihaibi, 1993) and Oman (Fowler *et al.*, 1993). Except for Kuwait sediments in the Arabian Gulf, with their high levels of Ni, Mn, Fe and V, due to oil pollution after Gulf war (Basaham and Al-lihaibi, 1993). In spite of this Dubai sediments generally show higher levels of Zn and Cu.

The data provided by Shriadah (1998b) indicate that Dubai offshore sediments have higher ranges concentrations of heavy metals than those of Abu-Dhabi, Umm Al-Quwain and Ras Al-Khaimah. For example Cu in Abu-Dhabi ranged (7.6–29.4 ppm), Umm Al-Quwain (10.36–57.4 ppm) and Ras Al-Khaimah (11.1–58.7 ppm), while the range in Dubai is (1–157 ppm). Also Ni showed the ranges (10.1–25.1 ppm) in Abu-Dhabi, (11.6–25.1 ppm) in Umm Al-Quwain and (10.1–25.1 ppm) Ras Al-Khaimah, while in Dubai varies from 2–159 ppm. Zinc exhibited the range from (6.7–21.4 ppm) in Abu-Dhabi, (8.56–31 ppm) in

Umm Al-Quwain and (7.98–31 ppm) Ras Al-Khaimah, while in Dubai shows the range from 2–159 ppm.

In an agreement to the present data, earlier study proposed by Abu Hilal and Khordgui (1992) obtained equivalent or higher levels of Zn (3.01–534 ppm), Pb (9.03–57 ppm), Cd (4.32–9.55 ppm) and Ni (8.01–214.5 ppm) in creeks nearshore sediments of UAE.

The concentrations of major and trace metals in Dubai sediments used to determine the regional distribution and pollution levels in Dubai offshore. Three contaminated regions are delineated; one is located in the far northern part of studied area represented by Al-Hamriya stations contaminated by Fe, Cu, Pb and Zn. The second is located in the middle northeastern part at Dry Docks contaminated by Cu, Ni, Pb and Zn and, finally the third is located in the middle southwestern part at Dubal contaminated by Fe, Mg, Cr, Ni and Zn.

The high concentrations of Zn, Pb and Cu found at Al-Hamriya St 3 (St 6) give direct evidence that this station is highly influenced by the presence of Al-Hamriya port as navigation road. The staining of wooden ship may be the source for these high levels of these heavy metals. Dry Docks (St 7) also exhibited high values of Zn, Pb, Ni and Cu, which may be attributed to chemical substances used in repairing and painting different kind of ships. The relative high concentrations of Pb in the same areas may also be due to high traffic activity in these parts (Guvenç et al., 2003). Dubal (St 10) shows high levels of Fe, Mg, Cr and Ni, which mostly attributed to the presence of Dubal Company in the area. In additional, this station covered mainly by mud, which has high adsorption capacity to pollutant particles (Massoud et al., 1996).

On the other hand the concentrations of major oxides and trace elements in the fine fractions show various trends. The concentrations of K, Ba, Cd, Cr, Mn, Ni, Pb and V

show regular trend of increase in the fine fractions compared to the bulk. The calcium and strontium contents decreased in the fine fractions. The concentrations of Si, Al, Fe, Mg, Na, Cu and Zn are higher in some stations and lower in the others. In general, the concentrations of major and trace metals are higher in fine fractions than the corresponding values in the bulk samples except for Ca and Sr. This suggests a negative correlation between grain size and accumulation of metal particles (the concentration of the elements increase by decrease the grain size). The lower concentrations of Ca and Sr in the fine fraction confirm that these metals are related to the coarse carbonate fragments in the sediments and not to polluted source. The minimum values of both of Ca and Sr were found at Dubal (St 10), which covered by mud.

4.3 Multivariate Statistics

The statistica program was used to look for a linear correlations (r) between the variables of each set of data as well as factor and regression analyses.

4.3.1 Correlation Matrix

The statistical correlation matrices are multivariate analyses used to correlate the relationships between variables such as major and trace metals, TOC, TKN and TPH (Table 4.8). Silicon, Al, Fe and Mg have a strong positive correlation with K, Ba, Cd, Cr, Mn, Ni and V. This indicates the clay and dolomite mineralogy and terrigenous fraction associations. Calcium is significantly positive correlated with Sr. Besides; Ca shows a strong negative correlation with Si, Al, Fe, Mg, K, Ba, Cd, Cr, Mn, Ni and V. This indicates the carbonate mineralogy association (the high values of Ca and Sr not related to pollution factor).

Table 4.8 : *Correlation matrix between major oxides, trace elements, TOC, TKN and TPH (P< .05*

	SiO₂ (wt%)	Al₂O₃ (wt%)	Fe₂O₃ (wt%)	MgO (wt%)	CaO (wt%)	Na₂O (wt%)	K₂O (wt%)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Sr (ppm)	V (ppm)	Zn (ppm)	TOC (wt%)	TKN (mg/kg)	TPH (mg/kg)
SiO₂ (wt%)	1.00	.64	.70	.56	-.98	.08	.66	.70	.43	.73	.11	.80	.60	.14	-.75	.71	.08	.02	-.28	-.05
Al₂O₃ (wt%)		1.00	.74	.49	-.76	.39	.99	.87	.56	.50	.22	.93	.42	.26	-.87	.79	.17	.11	-.13	.03
Fe₂O₃ (wt%)			1.00	.80	-.80	.09	.77	.96	.87	.80	.52	.85	.79	.55	-.78	.98	.48	.37	.04	.29
MgO (wt%)				1.00	-.65	-.02	.52	.69	.49	.92	.07	.65	.96	.09	-.73	.83	.06	.02	-.12	-.05
CaO (wt%)					1.00	-.18	-.79	-.82	-.53	-.78	-.16	-.89	-.66	-.20	.86	-.82	-.12	-.04	.27	.05
Na₂O (wt%)						1.00	.44	.23	.03	-.15	-.06	.31	-.18	-.03	-.44	.13	-.20	-.36	-.31	-.38
K₂O (wt%)							1.00	.90	.57	.53	.21	.95	.47	.26	-.89	.82	.13	.04	-.17	-.05
Ba (ppm)								1.00	.84	.68	.49	.90	.66	.53	-.85	.95	.43	.32	-.01	.22
Cd (ppm)									1.00	.46	.83	.58	.49	.87	-.49	.78	.82	.72	.33	.63
Cr (ppm)										1.00	.03	.72	.97	.04	-.69	.83	.03	.00	-.19	-.05
Cu (ppm)											1.00	.20	.05	1.00	-.12	.42	.97	.87	.53	.83
Mn (ppm)												1.00	.62	.24	-.93	.91	.14	.04	-.20	-.02
Ni (ppm)													1.00	.07	-.62	.81	.06	.03	-.15	-.02
Pb (ppm)														1.00	-.16	.45	.97	.86	.50	.81
Sr (ppm)															1.00	-.85	-.04	.07	.34	.14
V (ppm)																1.00	.37	.26	-.05	.19
Zn (ppm)																	1.00	.96	.57	.93
TOC (wt%)																		1.00	.61	.98
TKN(mg/kg)																			1.00	.61
TPH (mg/kg)																				1.00

Red colour indicates significant correlation

Sodium has moderate positive correlation with K and negative correlation with Sr. Potassium has a strong positive correlation with Ba, Mn and V, also it has significant positive correlation with Cd and Cr. Potassium shows a significant negative correlation with Ca and Sr. Barium and Cd have significant positive correlation with V, Mn and Pb. On the other hand, Ba is significantly positive correlated with Cr and Ni. Cadmium shows significant positive correlation with Cu and Zn. Both of these elements show negative correlation with Ca and Sr. This indicates the terrigenous input of these elements (Literathy & Foda, 1985). Chromium has significant positive correlation with Mn, Ni and V and negative correlation with Ca and Sr. This can be proved the terrigenous source of these elements. Copper has a strong positive correlation with Pb and Zn. This suggests anthropogenic input of this element (Al-Abdali *et al*, 1996). On the other hand Cu correlates positively with Cd and Fe. Nickel correlates positively with V and Mn. Nickel is significantly positive correlated with Cr and Mg. This indicates terrigenous input of this element (Literathy & Foda, 1985). Lead is highly positive correlated with Cu and Zn, and has positive correlation with Fe, Ba and Cd.

The organic compounds such as TOC, TKN and TPH show significant positive correlation with Cu, Pb and Zn. The association of these elements with organic compounds in absence of V and Ni disproves the presence of natural seepage or crude oil source (as mentioned before) and at the same time prove the anthropogenic source of these pollutants. Another thing worth to be noted, that the regression analysis exhibits negative correlation between Na and each of: TOC, TKN, TPH, Pb, Zn and Cu (Figure 4.6), which may be attributed to presence of fresh water inflow (anthropogenic discharge).

Consequently, the correlation matrix reveals the following elements and organic compounds associations, which is summarized in Table 4.9.

Table 4.9 : *Different types of association of major and trace elements and organic compounds*

No.	Elements association	Type of association
1.	*Silicon* correlates with Al, Fe, Mg, K, Ba, Cd, Cr, Mn, Ni & V	Clay mineralogy
2.	*Aluminum* correlates with Si, Fe, K, Ba, Cd, Cr, Mn & V	Clay mineralogy
3.	*Iron* correlates with Si, Al, Mg, K, Ba, Cd, Cr, Cu, Ni, Pb & V	Terrigenous fraction
4.	*Magnesium* correlates with Si, Fe, Mn, K, Ba, Cd, Cr, Ni & V	Dolomite mineralogy
5.	*Calcium* correlates with Sr	Carbonate mineralogy
6.	*Potassium* correlates with Si, Al, Fe, Mg, Ba, Cd, Cr, Mn & V	Clay mineralogy
7.	*Barium* correlates with Si, Al, Fe, Mg, K, Cd, Cr, Mn, Ni, Pb & V	Terrigenous fraction
8.	*Cadmium* correlates with Si, Al, Fe, K, Ba, Cu, Mn, Pb, V & Zn.	Terrigenous fraction
9.	*Chromium* correlates with Si, Fe, Mg, K, Ba, Cd, Mn, Ni & V	Terrigenous fraction
10.	*Copper* correlates with Fe, Cd, Pb, Zn, TOC, TKN & TPH	Organic matter and heavy metals association
11.	*Manganese* correlates with Si, Al, Fe, Mg, K, Ba, Cd, Cr, Ni & V	Iron- Mn adsorption
12.	*Nickel* correlates with Si, Fe, Mg, Ba, Cr, Mn & V	Terrigenous fraction
13.	*Lead* correlates with Fe, Ba, Cd, Cu, Zn, TOC, TKN & TPH	Organic matter and heavy metals association
14.	*Strontium* correlates with Ca	Carbonate mineralogy
15.	*Vanadium* correlates with Si, Al, Fe, Mg, K, Ba, Cd, Cr, Mn & Ni	Clay and iron oxides
16.	*TOC* correlates with Cu, Pb, Zn, TKN & TPH	Organic matter and heavy metals association
17.	*TKN* correlates with Cu, Pb, Zn, TOC & TPH	Organic matter and heavy metals association
18.	*TPH* correlates with Cu, Pb, Zn, TOC & TKN	Organic matter and heavy metals association
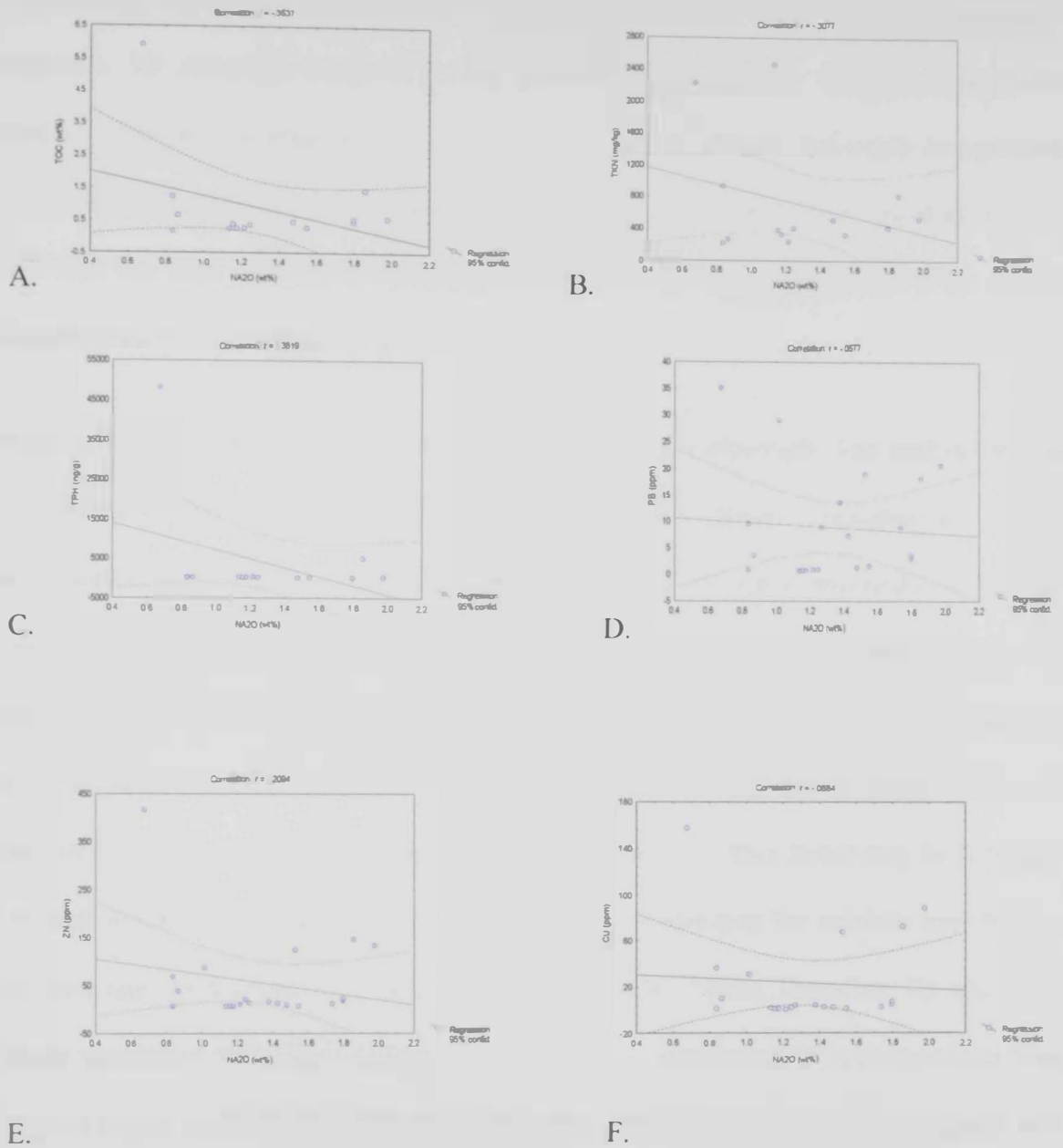
Figure 4.6: *Scatter plots of Na vs. TOC (A), Na vs. TKN (B), Na vs. TPH (C). Na vs. Pb (D), Na vs. Zn (E) and Na vs. Cu (F)*

4.3.2 Factor Analysis

The principal component factor analysis, at its simplest, can be regarded as an ordination technique, for reducing multivariate data into fewer dimensions. Principle component analysis transform an original set of N variables into a net of N principle components. Although there are as many as principle components as variables, the transformation is such that the first and second components almost invariably account for a far greater proportion of the total value (Rock, 1988).

Factor analysis is applied for some selected elements and compounds. The analysis reveals two factors solution (Table 4.10 & Figure 4.7). Chemical elements including most of the heavy metals (Ba, Cu, Pb, V, and Zn) together with other organic compounds (TOC, TPH and TKN) are positively loaded on factor 1. This association could be related to pollution and transfer of heavy metals to be adsorbed by organic matter, this factor may be termed pollution factor. Factor 2 is a bipolar factor. Calcium oxide and Sr are positively loaded, whereas Cr, Ni, Ba and V are negatively loaded on Factor 2. This factor may be lithology. It is well known that aragonite structure favors the substitution for calcium ions by ions that have radii greater than that of Ca^{+2}, particularly Sr^{+2} ions. Therefore, Ca and Sr are closely associated in recent carbonate sediments. This conclusion is in concordance with previous report of El-Sammak and Aboul-Kassim (1999) that Ca and Sr incorporate with each other in form of aragonite.

Figure 4.8 illustrates the association of Cu, Zn and Pb with TPH and TOC in absence of V and Ni. TPH correlated significantly positively with Cu (r = 0.82), Zn (r = 0.93) and Pb (r = 0.80), whereas TPH correlated weakly positively with V (r = 0.19) and weakly negatively with Ni (r = -.02). TOC correlated significantly positively with Cu (r = 0.87), Zn (r = 0.95) and Pb (r = 0.86), whereas TOC correlated weakly positively with V (r =

0.26) and Ni (r = .03). This indicates that these pollutants are not related with crude oil, or natural seepage, which suggests the anthropogenic source. The highest concentrations of Cu, Pb and Zn were associated with highest TOC content indicates that TOC is an important metal-sorption phase in sediments (Luoma, 1990).

Table 4.10 : *Factor loadings of major and trace elements and organic compounds*

Variable	Factor 1	Factor 2
CaO	− .448315	.792077
Ba	.722114	− .620831
Cr	.369955	− .834739
Cu	.914862	.313002
Ni	.377105	− .775701
Pb	.923149	.279919
Sr	− .389276	.816142
V	.687470	− .706066
Zn	.921691	.371222
TOC	.858379	.439207
TKN	.448258	.546227
TPH	.796820	.494868
Expl. Var.	6.046708	4.82614
Prp. Totl	.465131	.371242

Marked loadings are > .700000

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Factor Loadings, Factor 1 vs. Factor 2
Rotation: Unrotated
Extraction: Principal components
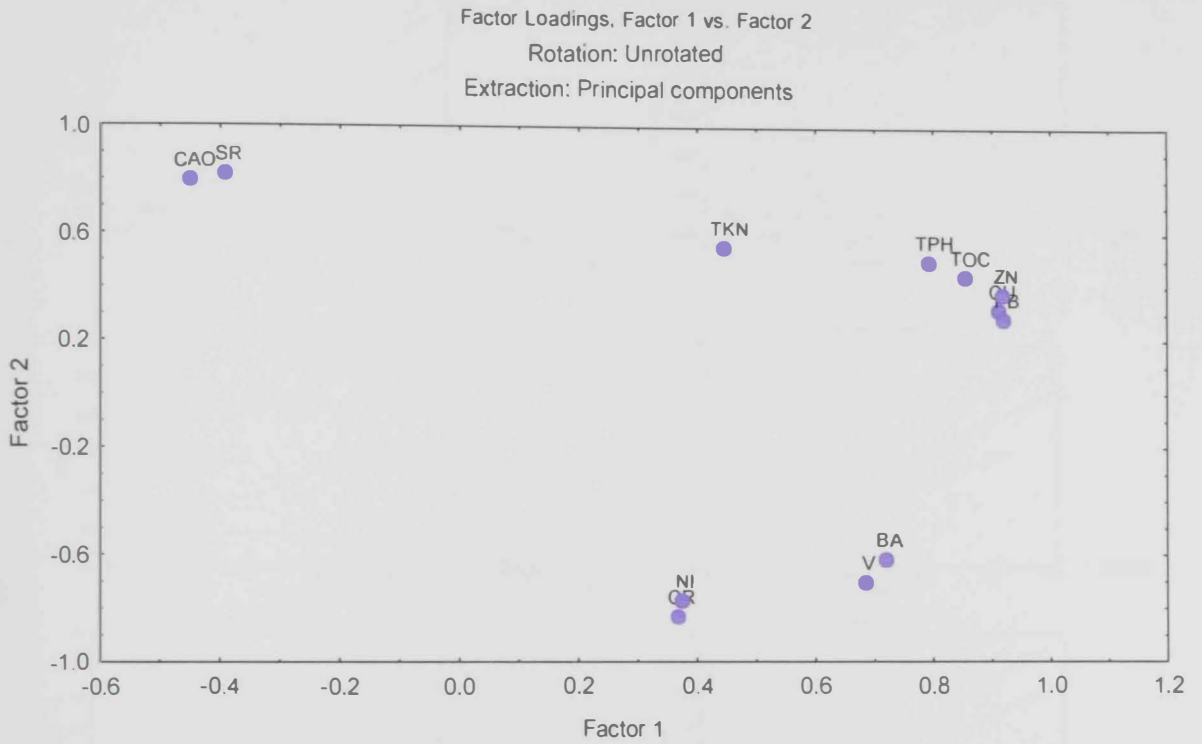
Figure 4.7 : *Factor analysis of major elements, trace elements and organic compounds*
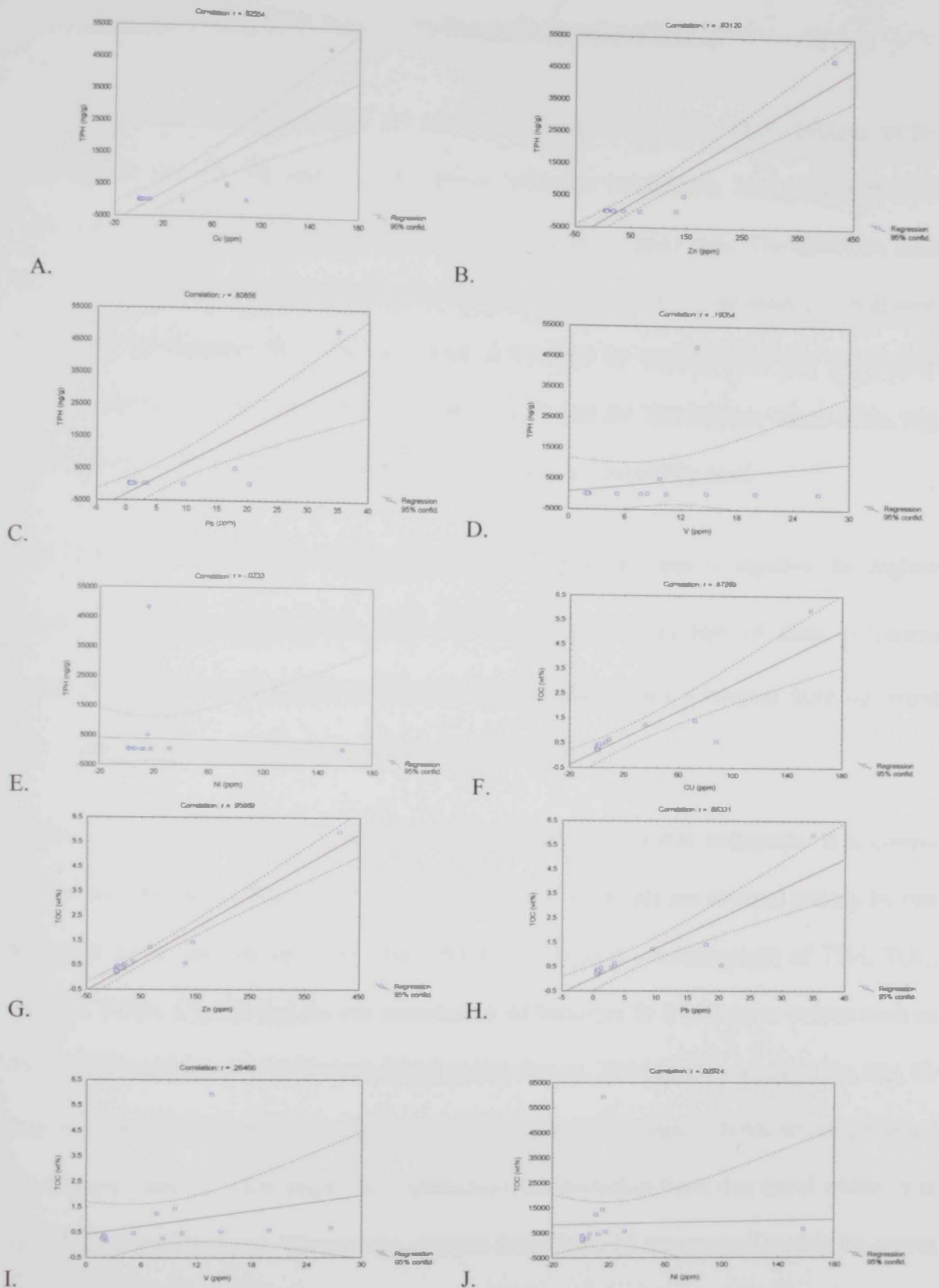
Figure 4.8 : *Scatter plots of Cu vs. TPH (A), Zn vs. TPH (B), Pb vs. TPH (C), V vs. TPH (D), Ni vs. TPH (E), Cu vs. TOC (F), Zn vs. TOC (G), Pb vs. TOC (H), V vs. TOC (I) and Ni vs. TOC (J)*

4.4 Effect of Textural Class in Pollutants Accumulation

Tables 4.11 and 4.12 demonstrate the relation between TPH, TOC, TKN, TPAHs, PCBs, Fe, Mg, Cr, Cu, Ni, Pb, and Zn and various grain-size parameters. It is notable that the concentrations of these pollutants increase by decrease the grain size. The deviation from this trend attributed to geographical position and the distance from the source of pollution. Therefore Al-Hamriya St 3 (St 6), which is covered by muddy sand has the highest concentrations of TPH, TOC, TPAHs, PCBs, Cu, Pb and Zn. The highest values of Fe, Mg, Ba, Cr, and Ni were reported at Dubal (St 10), which is covered by mud.

The correlation between the values of M_z and the sand size class is negative; the highest values of M_z indicate very fine sand. However the concentration of these pollutants increases by decreases the sand size but there is deviation in some samples from this trend due to geographical position or sediments composition.

Figure 4.9 reflects the mean grain-size (φ) distribution in Dubai sediments. It is clearly noted that the stations from 2 to 10 (Al-Mamzar mid to Dubal) are covered mainly by fine sand and some parts by very fine sand. Where the highest concentrations of TPH, TOC, TPAHs, PCBs, Cu, Pb and Zn are recorded at Al-Hamriya St 3 and some values such as TPH, PCBs and heavy metals were found at Dry Docks. The highest values of Fe, Mg, Cr and Ni were recorded at Dubal, which is covered by very fine sand. Dewa, which provided the highest value of TKN might be, represented the deviation from this trend where, it is covered by medium sand. Whereas the stations from 11 to 15 are covered mainly by coarse sand and medium sand in some parts provided the minimal levels of pollutants or unpolluted levels.

Figure 4.10 shows the sorting of Dubai sediments at different stations. The highest values indicate more poorly sorted, which was found at Al-Hamriya St 3 (St 6), Dry Docks (St 7) and Dubai approach (St 14). Al-Hamriya St 3 and Dry Docks have high concentrations of organic compounds and heavy metals, whereas Dubai approach has low concentrations of these pollutants due to the farness from the coast activities (geographical position). These give evidence that finer and poorly sorted sediments tend to accumulate pollutants particles. This mostly attributed to large surface area of the fine poorly sorted sediments.

Table 4.11 : *Concentrations of organic compounds and various grain-size parameters*

Station	Textural class	Sorting (φ)	Mean – size (φ)	TPH (µg/g)	TOC (wt%)	TKN (mg/kg)	TPAHs (ppm)	PCBs (ppb)
1	G.S.	Poorly sorted	Coarse Sand	50	0.16	218	0.26	7.21
2	S	Moderately sorted	Fine Sand	39	0.44	420	nd	0.8
3	G.M.S.	Poorly sorted	Very Fine S	39	0.52	410	0.22	9.05
4	M.S.	Poorly sorted	Fine Sand	2	1.21	931	nd	34.9
5	S	Moderately sorted	Fine Sand	4888	1.41	814	12.56	34.6
6	M.S.	Poorly sorted	Fine Sand	48018	5.9	2222	161.72	93.3
7	G.S.	Poorly sorted	Fine Sand	134	0.55	523	0.3	46
8	G.M.S.	Moderately well sorted	Fine Sand	146	0.25	234	0.05	2.34
9	S	Moderately sorted	Medium S	223	0.23	2457	1.5	nd
10	M.	Moderately sorted	Very Fine S	47	0.63	265	0.33	8.38
11	S.	Poorly sorted	Coarse Sand	6.44	0.37	385	nd	nd
12	G.S.	Poorly sorted	Coarse Sand	113	0.27	324	nd	nd
13	S	Moderately well sorted	Medium S.	108	0.23	330	nd	nd
14	G.S.	Poorly sorted	Medium S.	20	0.44	507	0.09	9.3
15	G.S.	Poorly sorted	Coarse Sand	23	0.34	402	0.4	11.1
Average		1.15	1.85	3590.43	0.86	696	11.83	17.17
S.D		0.45	1.15	12353	1.44	697	41.6	25.7

G. S. (Gravel Sand)   S. (Sand)   G.M.S. (Gravel Muddy Sand)   M.S. (Muddy Sand)   M.(Mud)

Red colour indicates maximum value

$\mu g/g = wt \% \times 10^4 = mg/kg = ppm = ppb \times 10^{-3} = \mu g/kg \times 10^{-3}$

Table 4.12 : *Concentrations of major, trace elements and various grain-size parameters*

Stations	Textural class	Sorting (φ)	Mean –size (φ)	Fe_2O_3 (wt%)	MgO (wt%)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
1	G.S.	Poorly sorted	Coarse Sand	0.07	0.49	6	1	2	1	6
2	S	Moderately sorted	Fine Sand	0.62	0.79	24	5	13	3	18
3	G.M.S.	Poorly sorted	Very Fine S.	0.85	1.19	31	7	18	4	22
4	M.S.	Poorly sorted	Fine Sand	0.52	0.82	20	36	12	10	67
5	S.	Moderately sorted	Fine Sand	0.86	0.88	22	72	16	18	145
6	M.S.	Poorly sorted	Fine Sand	1.03	0.87	23	157	17	35	415
7	G.S.	Poorly sorted	Fine Sand	1.2	1.37	45	88	32	20	132
8	G.M.S.	Moderately well sorted	Fine Sand	0.4	0.56	48	0	6	1	9
9	S.	Moderately sorted	Medium S.	0.05	0.49	7	2	2	1	6
10	M.	Moderately sorted	Very Fine S.	1.76	3.09	173	10	159	4	38
11	S.	Poorly sorted	Coarse Sand	0.04	0.52	5	1	2	1	6
12	G.S.	Poorly sorted	Coarse Sand	0.05	0.94	6	1	2	2	6
13	S.	Moderately well sorted	Medium S.	0.04	0.53	5	1	2	1	6
14	G.S.	Poorly sorted	Medium S.	0.18	1.07	16	2	7	1	8
15	G.S.	Poorly sorted	Coarse Sand	0.07	0.87	5	2	2	1	20
Average		1.15	1.85	0.52	0.97	29	26	19	7	60
S.D		0.45	1.15	0.53	0.65	42	46	39	10	108

G. S. (Gravel Sand)   S. (Sand)   G.M.S. (Gravel Muddy Sand)   M.S. (Muddy Sand)   M.(Mud)

Red colour indicates maximum value

Wt % x 10^4 = ppm
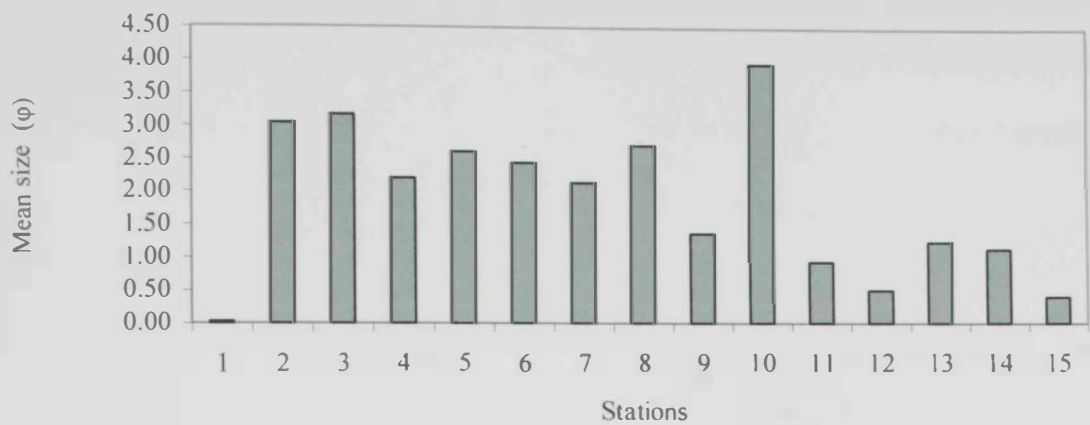
Figure 4.9 : *Mean grain-size (φ) Distribution in Dubai sediments*
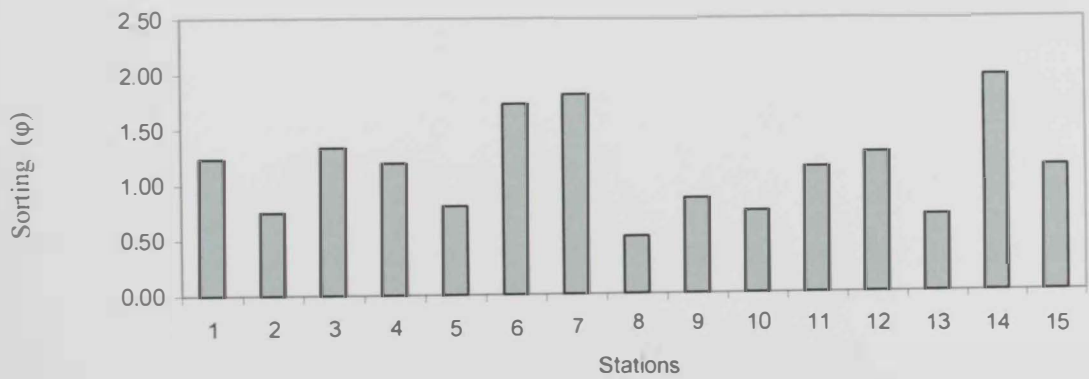
Figure 4.10 : *Sorting (φ) of Dubai sediments*

4.5 Areal Distribution of Contaminants

The organic compounds and heavy metals exhibited wide range of distribution in the study area. Organochlorines compounds, PAHs and heavy metals tend to partition to sediments, and as a consequence, marine sediments are usually regarded as a major repository for persistent pollutants released to the aquatic environment from various sources (Gibbs, 1973). A majority of studies carried out to determine pollutant concentrations in sediments have been initiated in response to port and harbour developments or dredging of shipping channels. The effect of Al-Hamriya Port, followed by Rashid Port and Dry Docks were obvious in the present study.

Very recent research proposed by Guvenç *et al.* (2003) stated that the concentrations of elements that have anthropogenic sources is expected to be highly variable from one sampling point to another, because their concentrations in the study area depend on the distance between sampling point and the source. Owing to such strong variability in their concentrations, these elements should have high relative standard deviations. Furthermore the elements that are derived from anthropogenic activities in the city are also expected to have higher concentrations in urban stations than their corresponding concentrations in rural stations, which are mentioned above.

This finding showed a good agreement with the present study, which confirm the suggestion of anthropogenic source of some assessed substances. The values of TPH vary widely even at one area; the maximum and minimum values reported at Al-Hamriya stations 3 and 1 respectively within a range of 2–48018 μg/g and relatively high S.D of 12353. The concentrations of TOC also vary from station to another within a range of 0.16–5.9 wt% and S.D 1.44. The concentration of TKN also supported the idea of anthropogenic source, because some stations showed high concentration and other stations

showed normal levels with a range from 218–2457 mg/kg and high relative S.D of 697. The values of TPAHs showed also wide variation in the study area; when Al-Hamriya St 3 exhibited the highest value (162 ppm), the recorded concentration at Al-Hamriya St 2 was 12.56 ppm, with an average of 11.83 ppm and high S.D of 41.6. In the same context the distributions of PCBs in Dubai sediments, however it is low but also followed the previous trend with an average of 17.17 ppb and high S.D of 25.7. The iron concentrations showed also variability in distribution even at the same area. The reported value in Al-Mamzar mouth was 0.07 wt%, while the value in Al-Mamzar end was 0.86 wt%. The iron values ranged from 0.04–1.76 wt% and high S.D of 0.53. The magnesium distributions vary from 0.49–3.09 wt% with relatively high S.D of 0.65. The chromium exhibited frequency distributions between increase and decrease within a range of 5–173 ppm and high relative S.D of 42. The copper concentrations changed from station to another within a range of 1–157 ppm and S.D of 46. The nickel concentrations showed frequency distributions ranged from 2-159 ppm with high relative S.D of 39. The lead concentrations frequency changed among stations within a range of 1–35 ppm and high S.D of 10. The concentrations of Zn showed fluctuation in distribution, The recorded value in Al-Hamriya St 1 was 67 ppm, while the value in Al-Hamriya St 3 was 415 ppm, within a range of 6– 415 ppm and high S.D of 108.

Table 4.13 summarizes the areal distributions of contaminants. Most of pollutants concentrated in the northeastern parts of the study area, where these ports are located. In addition to population centers (with population more than 860000 and the number increases to more than 1.5 at tourism seasons), which are presenting a risk of inputs from recreational and urban activities.

On the other hand the southwestern parts, which are rural area and unaffected by urbanization and industrial activities, have minimal concentrations. Al-Hamriya area represents a hot spot of contamination, where most of contaminants reflected their maximum values at this part. Jebel Ali Sanctuary (Jebel Ali Hotel, Ras Hisyan & Ras Ghantoot) at the middle and far southwestern part of the study area, which has nearly negligible industrial impact, reflected uncontaminated area except for TPH, which mainly referred to the nature of the Gulf countries. On the other hand the distance from the coast also considered to be controlling factor of pollutant concentrations and distribution, which appear in Dubai approach and Neptune Wreck (St 14 & 15 respectively), which have low level of contamination or uncontaminated. These stations are far from coastal activities and urban runoff so any pollutants reach these stations will be diluted.

Table 4.13 : *Areal distribution of contaminants in Dubai sediments*

	NW (St 14 &15)	Far NE (St 1-6)	Middle NE (St 7)	Near NE (St 8)	Near SW (St 9 &10)	Middle SW (St 11)	Far SW (St 12 &13)
TPH	___	Heavily polluted (Al-Hamriya St 2&3)	Moderately Polluted (Dry Docks)	Moderately polluted (Jumeirah beach)	Moderately polluted (Dewa)	___	Moderately polluted (Ras Hisyan & Ras Ghantoot)
TOC	___	Heavily contaminated (Al-Hamriya St 3)	___	___	___	___	___
TKN	___	Heavily& moderately contaminated (Al-Hamriya St 1- 3)	___	___	Heavily contaminated (Dewa)	___	___
TPAHs	___	Moderately contaminated (Al-Hamriya St 1- 3)	___	___	___	___	___
PCBs	___	Moderately contaminated (Al-Hamriya St 1- 3)	Moderately contaminated (Dry Docks)	___	___	___	___
Major and Trace Metals	___	Heavily & moderately contaminated (Al-Hamriya St 1- 3 and contaminated by Fe, Cu, Pb & Zn)	Heavily & moderately contaminated (Dry Docks and contaminated by Cu, Ni, Pb & Zn)	___	Heavily & moderately contaminated (Dubal and contaminated by Fe, Mg, Cr, Ni & Zn)	___	___

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CHAPTER V

SUMMARY AND CONCLUSION

SUMMARY AND CONCLUSION

The investigated area extends along Dubai offshore on the Arabian Gulf. Dubai coastline is approximately 70 km long. Human activities are often concentrated in coastal regions which are often least able to tolerate those activities, and where adverse effects are most apparent. The rapid development of the Emirate and the highly usage of the coastal region either for industrial or private and public has led to obvious changes in sediments quality of the marine environment.

The present study aims to provide appropriate measurements of organic pollutants such as TOC, TKN, TPH, PAHs and PCBs and inorganic pollutants such as major and trace elements. The comprehensive perspective about the level of these pollutants is expected to be useful in management the discharges into the marine environment and solving many related problems. Also it can be used to monitor any future improvement in sediments quality.

Fifteen stations were chosen to cover most fragments of Dubai offshore, starting from Al-Mamzar and ending by Ras Ghantoot. The texture analysis was carried out through standard sieving and pipette method. The TOC contents were determined by using Walkey-Black Method. TKN was measured by the Kjeldahl method, while TPH was analyzed by using Infrared Spectrophotometric. The HPLC was used to determine the PAHs, and the GC-ECD was used to determine the total and individual PCBs. The ICP was used to carry out the concentrations of major oxides and trace elements (for major oxides the obtained values were multiplied by factor oxides); the mineral analysis was done to identify the major, subordinate and minor minerals by using X-ray diffraction. The

Statistica ™ was used to apply statistical analysis, whereas the Surfer 7.01™ was used to provide the areal distribution of organic pollutants.

The grain-size analysis showed that about 67% of the studied stations are covered by gravel sand and sand. There is clear trend of increasing the organic and inorganic pollutants by decreasing grain-size .The samples, which deviate from this trend, could be attributed to the geographic location (far from coastal activities or from the source of anthropogenic discharge). The TOC content varies within limited range at all stations except for Al-Hamriya stations. The maximum value was recorded at Al-Hamriya St 3 (St 6) with a wide variation about 37 higher than the minimum value, which was reported at Al-Mamzar mouth (St 1). Al-Hamriya St 3 represents approximately half (46%) of total percentage of TOC values. The TKN content showed fluctuation among stations. The maximum value exists at Dewa (St 9), whereas the minimum value was found at Al-Mamzar mouth (St 1). The maximum value is about 11 times higher than the minimum. Also Al-Hamriya St 3 (St 6) exhibited high TKN content, which is about 10 times higher than minimum value. This station forms more than 1/5 (21%) of TKN values in the study area. The highest ratio of (C/N) was recorded at Al-Hamriya St 3 (St 6) and this phenomenon known as deviation by increase from Redfield ratio. The lowest ratio was reported at Dewa (St 9) and this also exhibits deviation by decrease. Al-Hamriya St 3 (St 6) shows high TPH content, whereas Al-Hamriya St 1(St 4) shows very low concentration. The percentage of TPH in Al-Hamriya St 3 is 90%, which represents 9/10 from total values. The concentrations of TPH show drastic variation from the minimum to the maximum value. The maximum value is 24009 times higher than the minimum value.

Evidently, TOC correlated significantly positively with TPH ($r = 0.98$) and moderately positively with TKN ($r = 0.6$). On the other hand TPH correlated moderately positively

with TKN (r = 0.61). The distribution maps of TOC and TPH show trend of an increasing toward the northeastern part of the study area, whereas TKN shows two trends of an increasing one toward the southwest and another toward northeast of the study area.

The concentrations of PAH compounds vary widely among stations. Al-Hamriya St 3 (St 6) exhibits the maximum values of naphthalene, fluorene, fluoranthene, pyrene, chrysene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a.h)anthracene and benzo(g.h,i)perylene. The maximum value of TPAHs is 1800 times higher than the minimum value. Al-Hamriya St 3 constitutes more than 9/10 (92%) of total values. The distribution maps display a northeastern trend of increasing. The TPCBs values show a wide variation from the minimum to the maximum. The maximum value was recorded at Al-Hamriya St 3 and it is nearly 117 times higher than the minimum value, which was found at Al-Mamzar mid (St 2). The percentage of total PCBs in Al-Hamriya St 3 is 36%, which represents more than 1/3 from total values. On the other hand the maximum values of each of individual PCBs (PCB 105, PCB 118, PCB 138, PCB 153 & PCB 180) were reported at Al-Hamriya St 3. Whereas the maximum value of PCB 8 was found at Al-Hamriya St 1 (St 4) and of PCB 52 at Dry Docks (St 7). The distribution maps also show northeastern trend of increasing.

On the other hand the major and trace metals show various trends of an increasing. The highest concentrations of the studied major oxides including, SiO_2 was found at Jumeirah Beach (St 8), Al_2O_3 and K_2O at Al-Mamzar end (St 3), Fe_2O_3 and MgO at Dubal (St 10), CaO at Jebel Ali Hotel (St 11) and Na_2O at Dry Docks (St 7). The highest concentrations of trace elements were recorded at Dubal (St 10) for Ba, Cr, Ni and V, whereas Al-Hamriya St 3 shows the maximum values of Cu, Pb and Zn and the maximum value of Sr was found at Jebel Ali Hotel. The mineral analysis revealed that calcite is the most abundant mineral in Dubai sediments; the aragonite follows calcite in abundance.

Based on the overall estimation it can be concluded that:

1. Two distinct geochemical features can characterize Dubai offshore sediments. One in the northeastern parts and can be described as heavily or moderately polluted region. Another one in the southwestern and northwestern parts and can be described by moderately, slightly or unpolluted region.

2. Most of the study area is covered by unpolluted sediments, containing natural background levels of organic and inorganic compounds. Only TPH showed wide distribution in the study area and that mainly attributed to the nature of the region and the production and transport of petroleum. The other pollutants are concentrated at Al-Hamriya stations and Dry Docks.

3. Al-Hamriya St 3 (St 6) represents the most contaminated part in the study area and the major source of contamination is attributed to anthropogenic source (man-made).

4. The presence of Al-Hamriya Port and Dry Docks in the northeastern part of the study area provide reasonable source of the high level of contamination, taking into consideration that the contaminant gradients may occur with distance from a source, as concentrations change over time.

5. Fine and poorly sorted sand tend to have high values of organic substance and heavy metals. The adsorption onto fine-grained sediments is probably due to the larger surface area.

6. Al-Hamriya St 3 exhibits the maximum values of TOC, TPH, C/N, naphthalene, fluorene, pyrene, chrysene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(a,h) anthracene, benzo(g,h,i)perylene, TPCBs (PCBs 105, 118, 138 & 180), Cu, Pb and Zn.

7. The level of TOC in Al-Hamriya St 3 is nearly 7 times higher than unpolluted region in the Arabian Gulf as be recorded by some investigators.

8. TPH in Al-Hamriya St 3 shows higher value compared with other heavily polluted areas in the Arabian Gulf.

9. TOC can be considered as an indicator of hydrocarbon contamination when TPH are present in high concentration.

10. The level of TKN in Al-Hamriya St 3 is about 7 times higher than the value, which was suggested as a natural background level.

11. There is significant positive correlation between TPH and TOC ($r = 0.98$); moderately positive correlation is found between TPH and TKN ($r = 0.6$) and TOC and TKN ($r = 0.6$), which show the same trend of increasing in the study area.

12. The mean values in Dubai sediments of Zn is about 84, Pb is about 6, Cu is 19 and of Ni is about 4 times higher than the values, which obtained from unpolluted areas in UAE as be recorded by some investigators.

13. Vanadium, Cd and Mn have been achieved the natural background levels. Both of Cd and Mn considered as natural constituents of the Gulf environment.

14. The high values of Ca and Sr are mainly attributed to carbonate mineralogy. The minimum values of both Ca and Sr, which reported at Dubal (covered by mud) confirm this suggestion.

15. The factor analysis reveals the association of Zn, Cu and Pb with TPH and TOC , which concluded that these metals are related to polluted source.

16. The high correlations between TOC and each of Cu ($r = 0.87$), Zn ($r = 0.95$) and Pb ($r = 0.86$) indicate that the organic matter play an important role in accumulation of these metals.

17. The presence of Zn, Cu and Pb with TPH in absence of V and Ni suggested that

the source of these pollutants are not related to crude oil (natural seepage or damages in oil pipelines), because V and Ni the largest trace metal constituents of crude oil.

18. The negative correlation of Na with TOC, TKN, TPH, Pb, Zn and Cu may be suggested, the source of these pollutants related to fresh water discharge (anthropogenic input).

20. The variation in concentrations from station to another and the high relative S.D of most studied pollutants raise the suggestion of anthropogenic source .

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تركيزات مرتفعة من المحتوى الكلي للنيتروجين و الحديد و الكروميوم والنيكل و الفناديوم في المحطة رقم ٩ (ديوا).

كما أظهرت الدراسة وجود علاقة موجبة قوية بين المحتوى الكلي للهيدروكربونات البترولية و المحتوى الكلي للكربون العضوي، مما يُرجح استخدام المحتوى الكلي للكربون العضوي كدليل على التلوث البترولي. يدّل الانتشار المتغير لهذه المواد من محطة إلى أخرى بمعدل انحراف معياري مرتفع نوعياً على وجود مصدر تلوث من تدخل الإنسان. كما أن تواجد كل من النحاس والرصاص والخارصين مع المواد البترولية و عدم تواجد الفناديوم و النيكل يُرجح مصدر التلوث البترولي من تدخل الإنسان و ليس من تسرب طبيعي للنفط. كذلك العلاقة السالبة بين الصوديوم و كل من المحتوى الكلي للهيدروكربونات البترولية و المحتوى الكلي للكربون العضوي و المحتوى الكلي للنيتروجين و النحاس والرصاص والخارصين يؤكد الاقتراح السابق.

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الملخص باللغة العربية

تناولت الدراسة الحالية تقدير الملوثات العضوية و غير العضوية في رواسب المياه العميقة لإمارة دبي بدولة الإمارات العربية المتحدة . وقد تم جمع العينات من خمس عشرة محطة موزعة على معظم المنطقة الساحلية ، ابتداء من مدخل الممزر حتى رأس غنتوت .

خضعت العينات للعديد من التحاليل و التي تشمل : تحليل حجمي للحبيبات ، وتحليل التركيب المعدني ، و تحديد الملوثات العضوية مُمثلة بتعيين المحتوى الكلي للكربون العضوي و المحتوى الكلي للنيتروجين و المحتوى الكلي للهيدروكربونات البترولية و الهيدروكربونات متعددة الحلقات ومركبات ثنائي الفينيل متعدد الكلورة . كذلك تم حساب الملوثات غير العضوية من خلال تعيين تركيز المعادن الثقيلة سواء الأكاسيد الرئيسية (أكسيد السيليكون، أكسيد الألمنيوم، أكسيد الحديد، أكسيد الماغنسيوم، أكسيد الكالسيوم، أكسيد الصوديوم ، أكسيد البوتاسيوم) أو العناصر الشحيحة (الباريوم، الكاد يوم،الكروميوم ، النحاس، المنجنيز، النيكل، الرصاص، الإسترانشيوم، الفناديوم،الخارصين).

و قد دلت الدراسة على أن معظم المنطقة قيد الدراسة خالية من وجود الملوثات السابقة، ماعدا الجزء الشمالي الشرقي من المنطقة قيد الدراسة حول المحطة رقم ٦ (الحمرية ٣) إذ أظهرت الدراسة وجود نسب مرتفعة من حيث تراكيز المحتوى الكلي للكربون العضوي و المحتوى الكلي للنيتروجين و المحتوى الكلي للهيدروكربونات البترولية و الهيدروكربونات متعددة الحلقات ومركبات ثنائي الفينيل متعدد الكلورة بالإضافة إلى النحاس والرصاص والخارصين. كذلك وُجدت

عمادة الدراسات العليا

برنامج ماجستير علوم البيئة

تقدير الملوثات العضوية و غير العضوية في رواسب المياه العميقة لإمارة دبي بدولة الإمارات العربية المتحدة

رسالة مقدمة من الطالبة

هـــــــــيفاء درويش أحـــــــمد آل درويش

إلى

جامعة الإمارات العربية المتحدة

استكمالاً لمتطلبات الحصول على درجة الماجستير في علوم البيئة

بإشراف

د. فتحي حسن محمد	د. عصام أحمد عبد الجواد
أستاذ مساعد في علم الجيوكيمياء	أستاذ مساعد في علم الجيوكيمياء البترولية
قسم الجيولوجيا	قسم الجيولوجيا
كلية العلوم	كلية العلوم
جامعة الإمارات العربية المتحدة	جامعة الإمارات العربية المتحدة

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