2007

Assessment of Marine and Coastal Pollution a long the Eastern Coast, United Arab Emirates (UAE)

Shaheera Ali Juma Ali Bahwan

Recommended Citation

Ali Bahwan, Shaheera Ali Juma, "Assessment of Marine and Coastal Pollution a long the Eastern Coast, United Arab Emirates (UAE)" (2007). *Theses*. 201.
https://scholarworks.uaeu.ac.ae/all_theses/201

United Arab Emirates University
Deanship of Graduate Studies
M.Sc. Program in Environmental Sciences

Assessment of Marine and Coastal Pollution a long the Eastern Coast, United Arab Emirates (UAE)

By

Shaheera Ali Juma Ali Bahwan

A thesis submitted to

United Arab Emirates University
In Partial Fulfillment of the Requirements
For the Degree of M.Sc. in Environmental Sciences

2007

United Arab Emirates University
Deanship of Graduate Studies
M.Sc. Program in Environmental Sciences

Assessment of Marine and Coastal Pollution along the Eastern Coast, United Arab Emirates (UAE)

By

Shaheera Ali Juma Ali Bahwan

A thesis Submitted to

United Arab Emirates University
In Partial Fulfillment of the Requirements
For the Degree of M.Sc. in Environmental Sciences

Supervisors

Esam A. Abd El-Gawad **Associate Professor of petroleum Geochemistry** **Department of Geology** **college of Science** **UAE University**	**Fadhil N. Sadooni** **Professor of Petroleum Geology** **Department of Geology** **college of Science** **UAE University**

2007

The Thesis of Ms. Shaheera Ali Bahwan for the Degree of Master of Science in Environmental is approved.

Examining Committee Member, Dr. Esam Abd El Gawad

m. alomar

Examining Committee Member, Dr. Muthanna Al-Omar

Examining Committee Member, Dr. Ahmed Murad

Director of the Program, Dr. Tarek Youssef

James E. Fletcher

Dean of the Graduate Studies, Prof. James Fletcher

United Arab Emirates University
2006/2007

ACKNOWLEDGEMENTS

I would like to extend my sincere thanks and gratitude to my country and the great university that I have studied in for several years under the leadership of Sheikh Nahayan Bin Mubarak Al- Nahayan.

I would like to thank my thesis supervisor Dr. Esam A.Abd El-Gawad and Dr. Fadhil N.Sadooni from Geology Department for their supervision, and support throughout my study.

My thanks would be also to Dr. Mostafa Lotfy for his valuable suggestions and help throughout the study.

My thanks would be also for Dr. Ali Kablawy from biology department for helping in statistic programs during my study.

My thanks are also extended to Dr. Rao, Director of the CLU at United Arab Emirates University. As well as Mr. Omar Al-Basher and Mr.Wajeeh Kettana for their help in the mechanical and chemical analyses.

Finally, I would like to express my deep thanks to my family for their invaluable advice and continuous encouragement. My special thanks also to all my friends for her helping (Salama Al- Swadi, Raja Al- Meskari, Naeema Al- Shamsi and Hind Al- Nuaimi).

List of contents

CHAPTER I …… INTRODUCITON

CHAPTER II …… LITERATURE REVIEW

CHAPTER III…… MATERIALS AND METHODS

CHAPTER IV...... RESUTLS & DISCASSION

CHAPTER V...... SUNMMARY & CONCLUSION

List of Figures

List of Tables

Abstract

The present study aims to quantifying and assessing the organic and inorganic pollutants extents along eastern side of the United Arab Emirates UAE offshore on the Gulf of Oman, which consist of Fujairah, Khor Fakkan and Kalba. Rapid development and the highly usage of the coastal region for industrial activities, sewage disposal and marine transportation has led to obvious changes in sediments quality of the marine environment. Twelve coastal sampling stations were selected to cover the maximum area of the eastern side, three sampling stations were selected from marine sediments and six sampling collected from spilled oil near investigated area.

Sediments samples were subjected to a variety of analyses including mechanical, total organic carbon (TOC), total petroleum hydrocarbon (TPH), total kjeldahl nitrogen (TKN), twenty congeners of polychlorinated biphenyl's (PCBs), sixteen different polycyclic aromatic hydrocarbons (PAHs) and heavy metals analyses

The grain size analysis showed that about 42 % of the studied stations are covered by medium sand and 33% covered by fine sand, which reflected trend of increasing the organic and inorganic pollutants by decreasing grain size. The average TOC % analyzed in the study area is 0.6 % which higher value than other regional studies. The average TPH in study area is around 156 mg/kg. The total concentration of TKN in ranged between 83.8 mg/kg to 1443 mg/kg. This study indicates positive correlation between TKN and TOC, which may be related to land pollution such as industrial areas and agricultural pollution. The distribution maps of TOC and TPH shows trend of an increasing toward the northern part of study area whereas, TKN showed a trend of increasing toward the southern part of study area.

The total concentration of PCBs in the study area was found to range between 0.06 mg/kg to 0.145 mg/kg. The distribution maps of TPCBs show increasing toward the northern part of study area KhorFakkan.

The total PAHs concentration in sediment samples ranges between 0.07 mg/kg to 0.28 mg/kg, in contrast the total concentration of PAHs from oil sample was between 44.28 mg/kg to 299.3 mg/kg. The distribution maps for each of compounds show two trend of increasing, in which one toward the southern and another toward northeast of study area.

Nine heavy metals elements have been analyzed in this study i.e. Cd, Cr, Cu, Co, Mn, Ni, Pb, V, and Zn. The highest detected concentrations are Ni and Mn with average of 398.4 mg/kg and 191.4 mg/kg respectively. The lowest determined concentration is Cd with average of 0.24 mg/kg. In general, the heavy metals concentrations in the study area are low compared to previous studies in the region.

CHAPTER 1

INTRODUCTION

INTRODUTION

1.1 General

The sources of pollution in the Gulf region have undergone considerable development and consequently urbanization, industrialization. Port areas and refineries have become major sources of pollution to the marine environment .Also, combination of tanker traffic and either accidental or international spills have prevailed (Tolosa et al., 2005). Agriculture has been expanding in the region, with the commensurate increase in use and emission of pesticides and other agrochemicals. Nevertheless, the current database for agrochemical residues in the marine environment of the Gulf remains rather limited, and even more so with respect to the Gulf of Oman. Ongoing industrial development in the region, even though geographically variable, continues to cause concern (De Mora et al., 2005).

Due to these sources, coastal and marine sediments can be contaminated by several chemical compounds each years, organic compounds (contain carbon atoms) and other inorganic pollutants such as heavy metals. Some are carcinogenic and have harmful effects to humans, other organism and the water become more heavily utilized, especially with respect to oil tanker traffic and especially in these areas because its semi-closed areas. Also the disadvantage of some of these chemical compounds can accumulate in organisms, humans and sediments, and can be converting to other toxic compounds in both humans and organisms.

Oil spill are impotents sources of organic pollution in marine ecosystem for the Arabian Gulf area that has been exposed to hydrocarbon inputs for many years. Tanker and ship traffic, discharges from the oil and petrochemical industry and natural seepage of oil are among the main contributor to these inputs. The environmental conditions of the area (oil degrading bacteria, high temperatures and intense solar radiation) are very favorable for the degradation of the hydrocarbons thus allowing the marine ecosystem to better cope with this chronic exposure. During the 1991 Gulf war, marine environment in the Arabian Gulf was subjected to estimated six million barrels of crude oil making it the largest oil spill ever recorded. In the comparison, the much publicized 1989 Exxon

Valdes tanker spill in Alaska released only 258000 barrels of crude oil (Vazquez et al., 1999).

1.2 Geography of the United Arab Emirates.

The United Arab Emirates (UAE), a federation of seven independent states since 1971, is located in the southeastern corner of the Arabian Peninsula. It is bordered by the Arabian Gulf to the north, Saudi Arabia to the south and west, and Oman and the Gulf of Oman to the east. The United Arab Emirates (Fig. 1.1) lies between latitudes 22° 50' and 26° North and longitudes 51° and 56° 25' East.

The UAE stretches for more than 650 Km along the southern shore of the Arabian Gulf. Most of the coastal areas consist of salt pans that extend far inland. Numerous islands and shallow inlets and mangrove trees are found in the Gulf. The UAE also extents for about 100 Km along the Gulf of Oman, an area known as the Al-Batinah coast. The Al-Hajar Al-Gharbi Mountains, rising in places to 2500 meters, separate the Al-Batinah coast form the rest of the UAE. The mountain slopes tend to run right to the shore. Nevertheless, there are small harbors at Diba Al-Hisn, Kalba and Khorfakkan on the Gulf of Oman. In the vicinity o Fujairah, where the mountains do not approach the coast, there are sandy beaches.

The eastern coast is essentially a fertile plain where rainfall and subterraneous water have allowed agriculture to develop thousands of years ago. The coastal zone is commonly referred to as the transition space between two environmental domains, the land and the sea. It has been defined as “the part of the land affected by its proximity to the sea and that part of the ocean affected by its proximity to the land” (Sorensen and McCreary, 1990).

1.2.1 History of oil spill in the UAE.

The eastern part of the U.A.E is an area of environmental interest not only because of incidents tourism, but also because of the presence of the industrial activities and marine transportation. There are several oil spills in the Arabian Gulf and Gulf of Oman that physically damage the coastal line and the aquatic life. Table1.2 shows the oil spill history in the UAE.

Table 1.2: History of oil spill in the UAE

Date/years	**Oil spill(events)**
December 19-1972	After a collision with Brazilian tanker Horta Barbosa the South Korean tanker Sea Star spilled about 840,000 barrels of crude into the Gulf of Oman.
January 26- 1991	An estimated 240 million gallons of oil were spilled from terminals, tankers and oil wells during the final phase of the Iraqi invasion of Kuwait.
March 31 -1994	15,900 tons of crude oil leaked into the Arabian Sea after the Panamanian-flagged supertanker Seki spilled the crude (16 km) off the UAE port of Fujairah, just outside the Gulf, when it collided with the UAE tanker Baynunah, which was in ballast. Oil reached the UAE coast north of Khor Fakkan close to the Strait of Hormuz. The oil slick severely polluted several beaches and threatened more than (40 km) of coastline.
January 24-2000	The Honduran-flagged cargo vessel Al Jazya 1 sank 4 miles east of Abu Dhabi's coast, laden with 980 tons of fuel oil. The tanker sank in bad weather, leaving an oil spill of around 2000 feet. The Federal Environmental Agency said it is still too early to assess the extent of damage caused by the slick on marine life and birds.
April 6 -2001	The spill was caused by the Iraqi fuel tanker Zainab, suspected of smuggling around 1,300 tons of fuel oil from Iraq, as it ran into trouble on its way to a holding area in international waters. The Emirate of Sharjah said it had temporarily shut down a desalination plant as a precautionary measure, after the spill neared pumping stations. The spill is said to be the emirate's worst environmental disaster in years.

Fig. 1.1: Location map of the United Arab Emirates showing the Arabian Gulf and the Gulf of Oman.

1.3 Aim of study

The present work aims at initiating and conducting a baseline field assessment of the pollutants effecting the marine and coastal environment. The particular target is to assess organic and inorganic pollutants in bottom sediments in the coastal line and offshore of eastern side of the UAE and also sample of the oil spill. The specific aims of this study are:

- Providing appropriate measurements of TOC, TPH, TKN, PAHs, PCBs, and heavy metals values in bottom sediments and coastal line.
- Comparing the present values with standard values in order to identify areas of impacted areas or at increased risk.
- Using some ratio to identify the sources of pollution from petrogenic or pyrogenic.
- Providing input to management questions in order to find new methods of waste disposal.

This study focuses on the determination of composition, concentration and origin of hydrocarbons based on examination of the following geochemical markers: N-Alkanes, isoprenoid alkanes, and petroleum biomarkers. Accumulations of petroleum hydrocarbons and heavy metals have been observed in organisms found in contaminated sediments, and this resulting change in food chain. Known the percentage of petroleum and heavy metals can help to use many techniques or plants to reduce this concentration such as bioremediation techniques by plants and microorganisms have widely applied in cleaning up petroleum hydrocarbon and heavy metals polluted sediments.

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

1.4 Thesis Organization

Chapter two reviews previous published work on the organic and inorganic pollutants in the world as well as in the region. Chapter three presents the materials and analytical

CHAPTER 2

LITERATURES REVIEW

LITERATURE REVIEW

2.1 Geomorphology of the Arabian Gulf and Gulf of Oman.

The Arabian Peninsula lies between latitudes 13° and 32° N and longitudes 35° and 60° E. it forms apart of the great desert belt which stretches from the Atlantic ocean, near the coast of northwestern Africa, to the desert of northwestern India. It has an area of approximately three million square kilometers which is about 10.5 % of the earth's surface and supports a population of about 49 million. The Arabian Peninsula includes small states of Kuwait, Bahrain, Qatar and the United Arab Emirates as well as the proportionality larger ones of Oman, Yemen and Saudi Arabia.

Geologically, the Arabian Peninsula is bounded by the Owen fracture zone and the Gulf of Aden rifting to the south, the rift system of the Red Sea / Gulf of Aqaba to the west and the Oman Mountains to the east. The Arabian Peninsula is divided geologically into the western Arabian shied, part of the Precambrian crustal plate and the Arabian shelf which consists of an eastward thickening sedimentary wedge separated into an interior homocline and interior platform. The source of the sediments is the peneplaned Arabian shield, which has been subjected to mild epeirogenic uplift. The sediments through the Phanerozoic were deposited in shallow to deep shelf seas, giving an alternation of continental and marine deposits, punctuated by evaporitic events. The total thickness of the Phanerozoic deposits increases from 5,500 m in central Arabia to about 7,500 m along the Arabian Gulf.

The flat desert landscape which characterizes the coastal regions of the Arabian Gulf and stretches from Kuwait to Oman has few distinctive features. There are some positive topographic features, such as the Dammam some, and the Abqaiq and Dulhan anticlines interpreted a developing over salt plugs, though they rise only a few tens of meters above the desert surface. The most marked feature is the presence of inland and coastal sabkhas, particularly in the United Arab Emirates and Saudi Arabia and the presence of a large number of collapse structures at Qatar and in parts of Saudi Arabia in the vicinity of Riyadh.

The shoreline of the Arabian Gulf is irregular and dominated by supratidal Sabkhas, sand spits and carbonate sands. Bordering this zone to the south is a 30 to 120 km wide zone of active dunes, often resting directly on a gravel surface. Tidal flats along the Arabian Gulf coast of the United Arab Emirates, as far as Kuwait are made up of sandy, silt-sized carbonate sediments with anhydrite and halite resting on calcareous beds. Sabkha Matti in western United Arab Emirates is thought to be the largest coastal Sabkha in the Arabian Gulf. It extends 40-60 km east- west and reaches to 120 km north- south. Most of the sabkha consists of partly cemented sand dune, and is undergoing slow deflation. On the eastern coast of the United Arab Emirates, the sand flats and wadi fans coalesce to an almost continuous littoral strip between the mountain and the sea, and they retain some often fresh water draining form the main wades. On the other hand, the northern slopes of the mountains do not receive much rain and remain dry and arid.

The Gulf has a rough complicated bottom, which varies considerably form area to area. Thus, there are scattered small islands and coral reefs, rock and shallows, which are the main characteristics dominating the Gulf seabed. The Gulf is divided into four main areas depending on variations in depth of water and these are:

(1) The coastal area: this extends from the seashore to a depth of 15-20 meters, and 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. The northern, where the depth ranges between 50-65 meters, the seabed is flat and covered by river deposits, although there are certain areas of coral reefs. The southern zone ranges from 70 to 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 seedbed (Abdul-Razzak, 1984).

The coastal sector of UAE is a low – lying area with extensive tidal flats, lagoons and sand dunes (M.Sc thesis 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.

(3) Tidal action.

The energy of each process depends on several variables, which are wave velocity, configuration of the coastline, relief, lithology and structure of the coastal area and the nature of marine sediments (Embbabi & Sharkawi, 1989).

2.2 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are among the major components in crude oil, and defined as a group of organic compounds with two, or more than two fused benzene rings (Fig. 2.2) (Baird, 1999). PAHs have been contaminates of the environment ever since human life first evolved. However, the growing industrialization of human society has involved an increase in their environmental pollution management issue.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants that are formed by the incomplete burning of organic components, such as fossil fuel (coal, oil, and gas) and other organic materials like wood, garbage and tobacco during natural, and other human activities such as oil spills form different sources i.e. offshore production platforms, oil transportation and combustion which pose serous and significant threats to all coastal habitats components mangroves (Teresa et al, 2002). According to the Wang and Fingas, (2003) they divided the sources of PAHs to the marine environment to pyrogenic sources derived from combustion and petrogenic sources derived from petroleum inputs such as oil spill. These substances have been shown to be widely distributed in aquatic sediments, water, air, plants and animals. The interest in this group is derived from their wide occurrence and the possible induction of cancer in organisms as a result (ATSDR, 1990). PAHs are relatively insoluble in water.

Some of PAHs are present at ambient temperatures in air, both as gases and associated with particles. The lighter PAHs, such as Phenanthrene, are found almost exclusively in the gas phase; the heavier PAHs, such as B (a) P, are almost totally adsorbed onto particles (Baird, 1999). There are common parents PAHs that occur throughout the environment and may have highest toxicity, some of which are listed in Table 2.1.

Many studies have been conducted on determination of PAHs in the sediments of the Arabian Gulf. Because of the Gulf crisis especially during the Kuwait oil fires, the concentration of particulate and associate pollutants increased. Levels of PAHs were measured extensively during 1991 in Kuwait and found with the ranged form 7 to 387 ng/m^3 in ambient air particulate. The level in sediment from Kuwait in 1991 found 30.4ppb; in Saudi Arabia was 36.4-761 ppb; in Bahrain was 47.5-97.5 ppb; in the UAE was in the range of 10.9-21.8 ppb; in Oman was in the range of 4.5-36.5 ppb, and marine sediments from the Iranian coast was found to contain 1.63-6.48 ppb PAHs (UNEP, 2002). Table 2.2 summarizes the data conducted by (Witt et al., 1995) of Baltic Sea. Few published materials were found about the concentration of PAHs in marine sediments. The value, which obtained from Olbia harbor, estimated the concentration of TPAHs from 0.16 μg/g to 0.77 μg/g (De Luca et al., 2005),

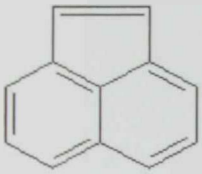
Table 2.1: Individual PAHs compounds (ATSDR, 1990).

1.Naphthalene	**9.Benzo(a)Anthracene**
2.Acenaphthylene	**10.Chrycene**
3.Acenaphthene	**11.Benzo(b)Fluoranthene**
4.Fluorene	**12.Benzo(k)Fluoranthene**
5.Phenanthrene	**13.Benzo(a)Pyrene**
6.Anthracene	**14.Dibenzo(a,h)Anthracene**
7.Fluoranthene	**15.Benzo(g,h,i)Perylene**
8.Pyrene	**16.Indeno(1,2,3-cd)Pyrene**

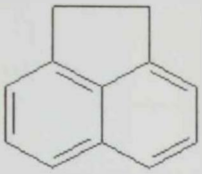
Naphthalene

Fluorene

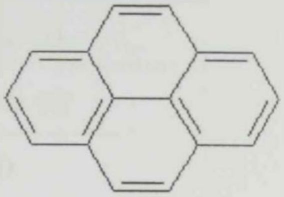
Anthracene



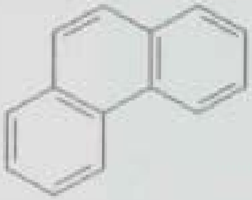
Acenaphtylene



Acenaphtene



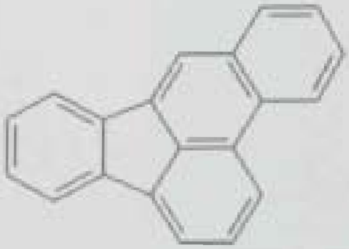
Pyrene =
Benzo(d,e,f)phenanthrene



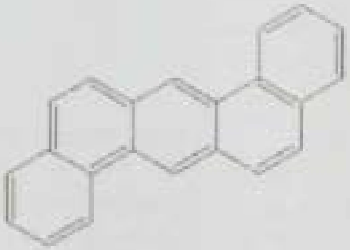
Phenanthrene

Fluoranthene =
1,2 Benzacenaphtene

Chrysene =
1,2-Benzophenanthrene



Benzo(b)fluoranthene =
3,4-Benzofluoranthene



Benzo (a) anthracene

Fig. 2.1: Structural formula of Polycyclic Aromatic Hydrocarbons (PAHs) compounds (ATSDR, 1990).

Table 2.2: Concentration of PAHs in the Baltic Sea sediments (Witt et al., 1995).

PAHs Compounds	Concentration
Naphthalene	0.05-5.88
Acenaphthene	0.69-26.95
Acenaphthylene	ND
Fluorene	0.15-5.36
Phenanthrene	1.4-48.88
Anthracene	0.2-47.12
Fluoranthene	0.83-151
Pyrene	0.4-85.9
Benzo(a)anthracene	0.25-66.52
Chrysene	0.28-58.2
Benxo(b)fluoranthene	0.75-157.22
Benzo(k)fluoranthenbe	0.31-62.35
benzo(a)pyrene	0.36-94.94
Dibenzo(a,h)anthracene	0.08-14.74
Benzo(g,h,i)perylene	0.4-116.69
Indeno(1,2,3-cd)pyrene	0.03-144

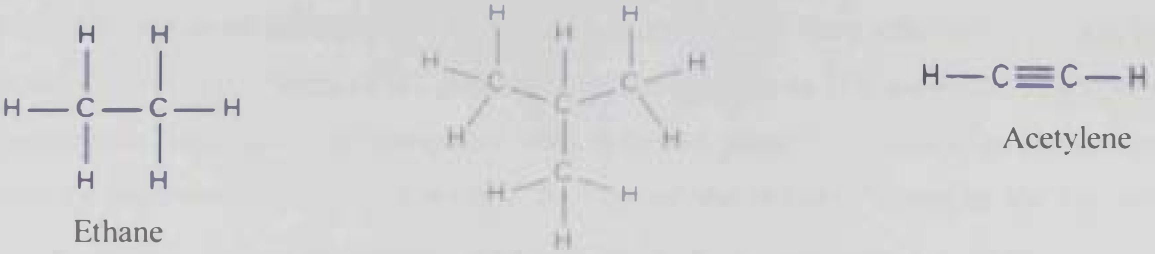
ND (Not Detected)

2.3 Aliphatic Hydrocarbon

Aliphatic compounds are organic compounds in which carbon atoms are joined together in straight or branched chains. The simplest aliphatic compound is methane (CH_4). Aliphatics include not only the fatty acids and other derivatives of paraffin hydrocarbons (alkanes), but also unsaturated compounds, such as ethylene (the alkenes) and acetylene (the alkynes).Aliphatic hydrocarbons and other lipid compounds in coastal environments have been studied to as certain their terrestrial, marine or anthropogenic origins. Aliphatic hydrocarbon analysis can be used as fingerprint spilled oils and to provide additional information on the source of hydrocarbon contamination and the extent of degradation of the spilled oil. Chemical fingerprinting defined as the application of analytical chemistry to identify the source of complex environmental pollutants, including petroleum. Chemical fingerprinting provides information about the sources of pollution, biodegradation, correlation among pollution components, and consequently it can be applied for environmental quality control purposes (Pena-Mendez et al., 2001). The origins of aliphatic hydrocarbons were often identified by diagnostic concentration indicates together with molecular markers and multivariate methods.

According to the (Sauer et al., 1998) was reported the degree or stages of oil in sediments after the Gulf war oil spill by using some ratio for saturated hydrocarbons defined as n -Alkanes from C_{10}-C_{32} and Isoprenoids and polycyclic aromatic hydrocarbons PAHs. This was to determine the effect of different geomorphic habitats from exposed to shelter on the extent of weathering of these oil sediments.

Table 2.3 summarizes the data conducted by Tolosa et al. (2005) about the total n-alkanes in the Arabian Gulf coast and Gulf of Oman.



Ethane

Isobutane

Acetylene

Fig. 2.2: Structural formula of Aliphatic compounds.

Table 2.3: Concentration of total n- alkanes (μg/g) in the Arabian Gulf and Gulf of Oman Tolosa et al. (2005).

Countries	**Location**	**Total n- alkanes (μg/g)**
UAE	**Akkah Head**	**1.1**
	Akkah beach	**0.45**
Qatar	**Dukhan**	**1.8**
	Ras Al Nouf	**3.3**
Bahrain	**Jasra**	**3.9**
	BAPCO refinery	**4.3**
Oman	**Al-Sawadi**	**0.2**
	Mina al Fahal	**0.11**

2.4 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls compounds are a class of synthetic chemicals which do not occur naturally in the environment. They consist of the biphenyl structure of two linked benzene rings in which some or all of hydrogen atoms have been substituted by chlorine atoms (Fig. 2.2) (O'Neill, 1993). PCBs are mixtures of up to 209 individual chlorinated compounds and it's called congeners with different physical chemical properties and toxicity depending on the number and position of the chlorine atoms in the biphenyl molecule (Fig. 2.3). The chemical formula of PCBs is ($C_{12}H_{10}$-nCl_n), where n ranges from (mono- to deca – PCBs) with different numbers of isomers. PCBs have been produced commercially since 1929. Polychlorinated biphenyls PCBs are colorless to light yellow oils or resins even at low temperatures. The more highly chlorinated PCB congeners adsorb strongly to soil and sediment and are generally persistent in the environment. These properties led to use PCBs in many of industrial and commercial application. The presence of PCBs is a reflection of industrial contamination; unfortunately these properties may damage the organisms and human by accumulation in the liver, adipose tissue, brain and skin (Ahlborg et al., 1992). Other sources of contamination are recent leaks and fires in transformers or capacitors (Faroon et al., 2003). Table 2.3 illustrates the chemical names of individual PCBs based on the number and position of chlorine atom on the biphenyl aromatic structure.

As mentioned earlier, PCBs are mainly imported and used as dielectric fluids especially with electrical transformers. The occurrence of PCBs in electric power stations and in scrapped electrical equipment and transformers in the Gulf represents one of the pollution problems. As a result of the war activities, the environment was exposed to different pollutants such as industrial hazardous wastes form war damaged industries and disposal sites, including PCBs from destroyed transformers (Literathy, 1993). However, during preliminary assessment of the impact of draining of Iraqi marshes on Kuwait's northern marine environment PCBs were not detected in any of the samples (Saeed, 1999). The limited data available on the subject indicate relatively low levels of contamination by PCBs compounds in the Arabian Gulf compared to other regional sea. The levels of PCBs in the northwest part of the region were generally below 5 ppb. Levels comparable to these ranges have been reported from Bahrain, Oman, Qatar and UAE (UNEP, 1999).

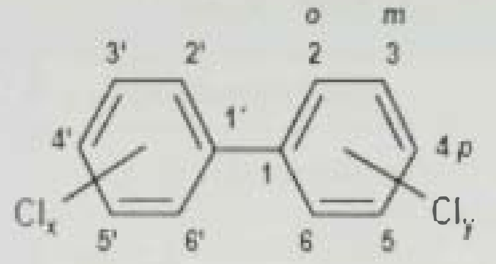


Fig. 2.3: Structure of polychlorinated biphenyl (PCB) Molecule, Baird (1999).

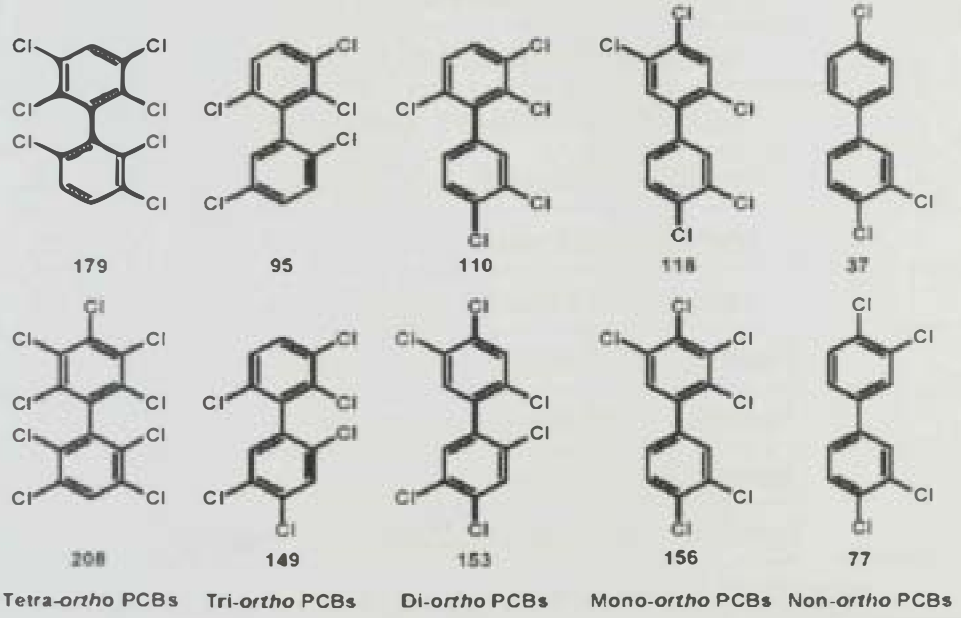


Fig. 2.4: Structural formula of PCBs and PCB homologues, Ahlborg et al., (1992).

Table 2.4: Chemical names of individual polychlorinated biphenyls (PCBs).

Commercial Name	Chemical Name & Structure
PCB8	2,4'- Dichlorobiphenyl
PCB18	2,2',5- Trichlorobiphenyl
PCB28	2,4,4'- Trichlorobiphenyl
PCB44	2,2', 3,5'- Tetrachlorobiphenyl
PCB52	2,2', 5,5'- Tetrachlorobiphenyl
PCB66	2,3', 4,4'- Tetrachlorobiphenyl
PCB77	3,3', 4,4'- Tetrachlorobiphenyl
PCB101	2,2', 4,5,5'- Pentachlorobiphenyl
PCB105	2,3,3', 4,4'- Pentachlorobiphenyl
PCB118	2,3', 4,4', 5- Pentachlorobiphenyl
PCB126	3,3', 4,4', 5- Pentachlorobiphenyl
PCB128	2,2', 3,3', 4,4'- Hexachlorobiphenyl
PCB138	2,2', 3,4,4',5'- Hexachlorobiphenyl
PCB153	2,2',4,4',5,5'- Hexachlorobiphenyl
PCB170	2,2',3,3',4,4',5- Heptachlorobiphenyl
PCB180	2,2',3,4,4',5,5'- Heptachlorobiphenyl
PCB187	2,2',3,4',5,5',6- Heptachlorobiphenyl
PCB195	2,2',3,3',4,4',5,6- Octachlorobiphenyl
PCB206	2,2',3,3',4,4',5,5',6- Nonachlorobiphenyl
PCB209	2,2',3,3',4,4',5,5',6,6'- Decachlorobiphenyl

2.5 Total Petroleum Hydrocarbon (TPH)

Total petroleum hydrocarbons are defined as a group of chemical compounds that came from crude oil. TPH is an estimate of the amount of hydrocarbons present between the carbons ranges from C_8 to C_{40}. This range of carbon extends from the volatile hydrocarbons compounds with the lower boiling to the non- volatile compounds found at the higher boiling point range. These different compounds can expose from many sources, including petroleum extraction, transportation refining and consumption (Huang et al., 2005). The amount and types of compounds in a petroleum hydrocarbon release differ widely depending on the product spilled and how it weathered (Azam khan and Ahmed khan, 2003).

Total petroleum hydrocarbon inputs to the gulf are estimated to be 47 times higher on an average basis than the global average. Inputs are mainly attributed to chronic spills form heavy tanker transport activities in the Gulf and form major spills such as those that occurred during the Iran -Iraq war in 1983 and the gulf war. Although the gulf has shown a large capacity for short term self- cleaning after spills, long- term effects are still unknown(Al-Ghadban et al., 1994). In the Arabian Gulf, sediments impacted by the Gulf war were restricted to an area within approximately 400km of the source of the spill in Kuwait. Surface sediments in this area surveyed soon after the war contained 62-1440 ppm of TPH. However, off the immediate coast of the UAE concentration ranged form only 0.1 to 7 ppm (Fowler et al., 1993).

Massoud et al. (1998) indicated that the comparison of TPH between sub sediment samples collected in 1992 and 1993. Despite the increase of the TPH content in sediments (Bahrain, Qatar, and UAE) polluted by the Kuwait oil slick. Both sets of sample contain intermediates TPH concentration, indicating that the increase was not high enough to change the moderate oil pollution level in the area. The study Tolosa et al. (2005) reported that the levels of TPH in sediments were relatively low compared to world wide location reported to be chronically contaminated by oil. Some evidence of oil contamination was apparent in sediments around Akkah head and Abu Dhabi in the UAE and Oman.

Shridadah (1998) 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 the levels and distribution of petroleum hydrocarbon 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 level. Al-Darwish, 2004 reported that the average of TPH in coastal sediments of Dubai was 3590.43 mg/kg which reflected high pollutants of TPH due to marine transportation and discharge form industrial activities.

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 areas

Table 2.4 summarizes the data conducted by Shriadah (1988) about the petroleum hydrocarbons pollutants along the Arabian Gulf coast.

Table 2.5 Levels of TPH along the UAE coast, Shriadah (1988).

Emirate	**TPH mg/kg**
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

2.6 Total organic carbon (TOC wt %)

The total organic carbon value indicates the sum of organic carbon and represents a measure for all organic substance in sediments. These substances can be of natural organic like humic acids, mineral oils, pesticides, polycyclic aromatic hydrocarbon or chlorinated organic compounds. Industrial waste effluents may contain carbon containing compounds with various toxicity levels (Dell'Anno et al., 2002). Organic matter is present in water as individual particulate or as adsorbed matter. Different factors may control the availability of the organic matters and the heavy metal pollutants. These factors include various sediment characteristics, such as grain size distribution, mineral composition and organic content. The TOC concentration can be considered as an indicator of hydrocarbon pollution only when the TPH content is high (Al Ghadban et al., 1994). Only limited work has been done on the organic matter in the sediments of the Arabian Gulf. Evans (1966), in his study of the recent sedimentary faces of the Arabian gulf indicated that the sediments of the northeastern parts contain 0.83-1.51 % organic carbon, whole the sediments of the northwestern part of the gulf show lower organic carbon. Al- Ghadban (1994), conducted a study on the total organic carbon in the sediments of the Arabian Gulf and the need for biological productivity investigations, reported tat the TOC of the Arabian gulf ranged form 0.46 % to 2.8 % in the bottom sediments samples if the Gulf. The contamination screening survey conducted in 2000 and 2001 revealed TOC concentration in sediment from UAE found low content (0.10 % to 0.39 %). In contrast sediment from Bahrain exhibited the highest levels of TOC with values from (3.25 % to 5.08 %). Qatar and Oman showed intermediate vales of TOC ranging from 0.56% to 2.21 %) (Tolosa et al., 2005). (Shriadah et al., 1998) performed study on the organic carbon content in sediments from the Arabian Gulf coast of UAE. These values were at the background levels, 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 %). Al-Darwish, 2004 found the average of TOC % was 0.86 % in coastal sediments of Dubai emirates.

2.7 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, called ammonification (nitrogen fixation); while other organisms nitrify the (NH_4) to (NO_3) is process called nitrification. Both nitrification and ammonification convert gaseous nitrogen into bioavailable chemical forms (Wilson et al., 1993). Al-Darwish, 2004 recorded the average of TKN was 696 mg/kg in coastal sediments of Dubai emirates.

2.8 Heavy metals distribution

Elements divided to the major, minor, and trace elements. heavy metals, refer to any metallic chemicals elements that has a relatively high density and poisonous at low concentrations like mercury, cadmium, arsenic, chromium, thallium, and lead (Nriagu et al., 1989). The heavy metals are natural components of the earths crust; they cannot be degraded or destroyed. Small extents enter to the air, water and soil as trace elements and some heavy are essential to maintain the metabolism of the human body. Heavy metals are dangerous because they tend to bioaccumulation that means the concentration of a chemical in a biological organism over time, compared to the chemicals concentration in the environment (Haynes and Johnson, 2000). There are two types of sources can enter the metals into the marine environment; natural sources and anthropogenic sources. Natural sources such as atmospheric deposition of particles emitted from natural sources such as acidic rain, anthropogenic sources of heavy metals include industrial, consumer wastes agriculture and other human activities can also result increasing of metal content (Bloemen et al., 1995). Several studies have been conducted on the concentration of trace metals in different location of the Arabian Gulf region. Fowler (1988) conducted a baseline study on pollutants i.e. beach tar, petroleum hydrocarbons, chlorinated hydrocarbons and heavy metals in Bahrain, UAE and Oman. He concluded that Cd, Cu, Pb and V concentration in both oysters and sediments were generally low. The fate of the Kuwait oil slick to the bottom sediments of the Arabian Gulf indicates the content of trace metals (Fe, V, Pb, and Ni) was recorded in the northern part of the Arabian Gulf due to the diversified of natural and anthropogenic inputs and positive correlation is found between increasing trace metal concentrations and decreasing carbonate content and grain size, verifying that adsorption into muds is the primary mechanism of the trace metals concentration in marine sediments. Correlation with TOC contents indicates that organic matter is a significant concentrator only in the case of Pb and Cu. In general, the oil slick had minima effect on the state of pollution by trace metals in the Arabian Gulf (Al-Abdali et al., 1996). Folwer, et al (1993) studied the petroleum hydrocarbons and trace metal in near shore Gulf sediments and biota before and after the 1991 war. This study was planned to determine the extent and degree of contamination by petroleum hydrocarbon and trace metals that entered the Gulf form the massive oil spill and oil field fires in Kuwait. They concluded that concentrations of the oil- related metals Ni and V were slightly elevated in oil- contaminated sediments form Saudi Arabia but elsewhere in the Gulf, they were similar to their previous levels. Table 2.5 summarizes the background levels of trace elements in coastal and marine from different areas in the Arabian Gulf.

Table 2.6: Comparison between average and range values of trace metal concentrations in marine sediments from different countries.

(area)reference	Cd	Co	Cr	Cu	Mn	Ni	Pb	V	Zn
Bahrain **Fowler et al.,1993**	0.2 0.19-0.210	1.325 0.99-1.66	7.87 3.84-11.9	2.29 1.16-3.43	28.6 17.3-39.9	17.8 16-19.6	5.82 0.64-11	15.85 12.7-19	3.065 2.34-3.79
U.A.E **Fowler et al.,1993**	0.96 0.02-1.9	2.54 1.79-3.3	76.85 71.9-81.8	4.2 1.3-7	237 231	18.9 12.8-25	2.9 0.5-5.2	20.7 7.3-36	2.5 1.6-3.4
Oman **Fowler et al.,1993**	0.38 0.06-0.7	12.04 1.98-22.1	211.5 66-357	7.9 1.7-14	200 89-310	26 9.9-46	4.11 1.2-7.2	29.2 10.4-48	8.8 7.7-9.8
Dubai offshore ,U.A.E **Al-Darwish,2004**	0.25 0.1-0.4	-- --	-- --	79 1-157	76.5 8-145	80.5 2-159	18 1-35	14.5 27-2	210.5 6-415

CHAPTER 3

MATERIALS & METHODS

MATERIALS AND METHODS

3.1 Sediments Collection and Preparation

The collected samples (21) include 12 sample sediments from coastal, 3 sample sediments from marine and 6 samples from spilled oil near study area. KH1 to KH4 were collected from Khor Fakkan coastal sediments. from KH5 to Kh8 were collected from Kalba coastal sediments and were sample from KH9 to KH12 were collected from Fujairah coastal sediments (Fig. 2.1 & Table 2.1). A Van Veen grab sampler made from stainless steel was used to obtain bottom sediments. 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 until required for future use. Figure 2.2 shows the distribution of industrial activities and location of ports in the same investigates area.

3.2 Analytical Methods

3.2.1 Grain Size analysis

The collected samples were dried in oven under moderate temperature about 70 C^{o} in order to remove any humidity 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 in which 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 1φ intervals were selected. The sample was placed into the top sieve after arranged the sieves based on mesh number. The sieves were place in mechanical shaker and sieved for 15 minutes. Each sieve was emptied onto a large sheet of paper and 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 contain more than 20% mud, pipette analysis is the most common method used for determining the grain-size distribution of sediments > 4φ. Sediment samples should be air-dried and 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 meshes. 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 Anderson Sedimentation Cylinder. Distilled eater was added to bring the volume too exactly to 500 ml and stirred for 2-3 minutes. After 20 seconds of stirring, the pipette was inserted to depth of 20 cm and 10 ml exactly were withdrawn. This first withdrawal is very important step, as it represents the total fraction finer than 4 φ. The pipette was removed and the suspension was expelled into a weighing beaker of 30 ml. distilled water of 10ml 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 place 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. This method was detailed by ROPME (Manual of Oceanographic Observation and Pollutant Analysis Method, 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 "$\mathbf{M_z}$", Inclusive Graphic Standard Deviation "σ_I ", Inclusive Graphic Skewness "$\mathbf{SK_I}$", and Graphic Kurtosis "$\mathbf{K_G}$" were calculated according to the equations described by ROPME (1999).

3.2.2 Extraction and Clean up.

Fifty gram of dry sediment samples were taken soxholet - extracted for 8 h in 250 ml of the extraction solvent (1:1 hexane: acetone). Aanhydrous sodium sulfate removal procedure was performed using activated elemental copper in order to avoid sulphur interferences when using gas chromatography. The solvent extract was concentrated on a rotary evaporator to a volume of approximately 2 ml.

Table 3.1: Sampling locations

Stations	Location	Stations	Location
KH1	Coastal –Khorfakkan	KH 9	Coastal-Fujairah
KH 2	Coastal–Khorfakkan	KH 10	Coastal- Fujairah
KH 3	Coastal–Khorfakkan	KH 11	Coastal- Fujairah
KH 4	Coastal–Khorfakkan	KH 12	Coastal- Fujairah
KH 5	Coastal-Kalba	S1	Marine
KH 6	Coastal- Kalba	S2	Marine
KH 7	Coastal- Kalba	S3	Marine
KH 8	Coastal- Kalba		

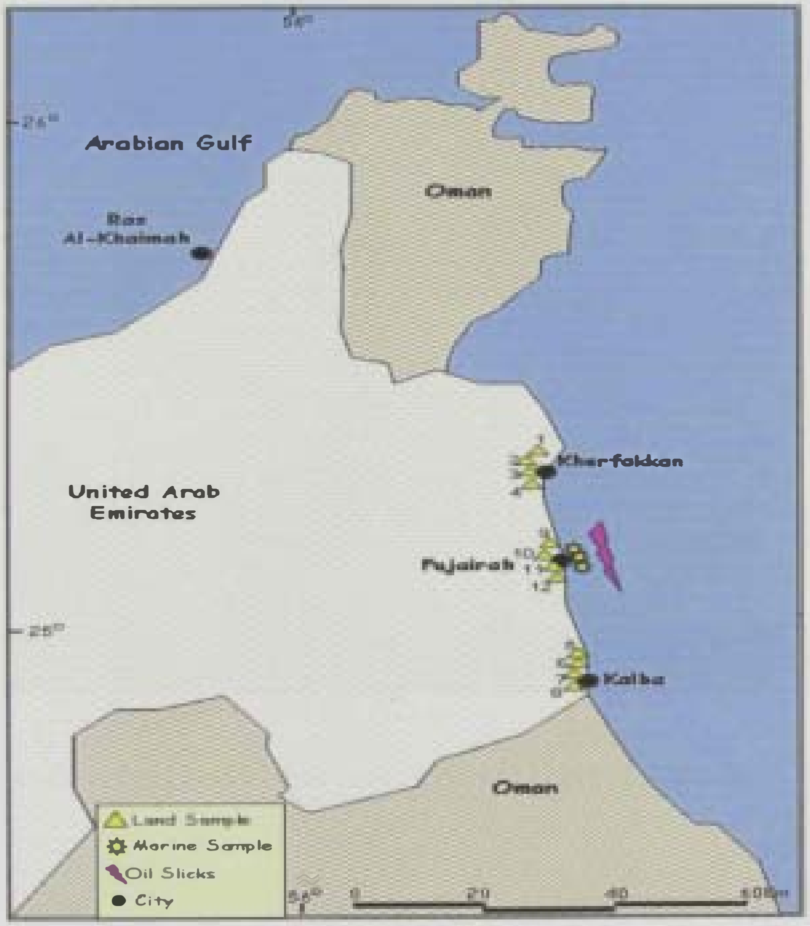


Fig. 3.1: Map showing sampling site along eastern side of the UAE.

Fig. 3.2: Map showing industrial areas and ports area along eastern side of the UAE.

3.2.3 Column chromatography (oil spill).

Crude oil is defined as petroleum that is removed from the earth, many types of compounds presents in petroleum such as saturates, aromatics, NSO compounds, and asphaltens. Actually the saturated and aromatic defined as hydrocarbons and the asphaltens and NSO compound defined as non hydrocarbon substances. Column chromatography using to separates this compounds by taking one gram of crude oil in beaker and adding N-pentane to separated asphaltens by precipitation operation then calculate the percentage of asphaltenes. Then the reaming petroleum was taken and add it to the top of the glass column and added it to run through by gravity flow. Using different elutants in a glass column containing silica gel after activation of it. Then put the n-hexane to separate saturates, evaporate of the solvent and weight the saturate. After that can add the petroleum eather 60-80 to separate the aromatic substance and evaporates the solvents and weight the aromatic. Finally can adding mixture of ethanol and benzene (1:2) to separates resins then evaporate the solvents and weight the resins. Then calculate the percentage of saturates, aromatic and resins and take the saturate and injected in GC instruments.

3.2.4 Determination of Polycyclic Aromatic Hydrocarbons (PAHs) by HPLC

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds with structures consisting of 2-7 aromatic rings. Environmental contamination (soil, sediments and water) with PAHs occurs from tar, burning of organic wastes and due to oil spills. These compounds are highly toxic and carcinogenic to humans as well as other living organisms. The method is applicable for the determination of PAHs in soil, sediment, as per the modivied EPA-8310 procedure. Specifically this method is recommended to determine the first highly 16 pollutant are Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrycene, Benzo(b)fluroanthene, Benzo(k)fluroanthene, Benzo(a)pyrene, Dibenzo(a,h)anthracene, Benzo(g,h,i)perylene, Indeno(1,2,3-cd)pyrene.

Five grams of the sediments were placed in an extraction thimble (hexane: acetone, 50:50) by using soxhlet extraction. The solvent was carefully removed by evaporation under nitrogen a residue which was dissolved in acetonitrile. Sample extracted was cleaned, when necessary, using solid phase extraction using PAH SPE columns. A 20 μl aliquot of the extract was injected into an HPLC, and the above listed compounds are detected by ultraviolet (UV) and fluorescence detectors simultaneously. The condition of the apparatus and materials is given below:

- Analytical balance- capable of weighing to 0.0001g
- Automatic soxhlet extraction with appropriate extraction thimble.
- Concentrator tube - 10 ml graduated.
- HPLC apparatus: a gradient HPLC with auto sampler, fluorescence detector and UV detector.
- HPLC column: chromospher 3 PAH column (100 mm*4.6 mmID, 3 MM)

Five grams of the solid sample was accurate weighed and blend it with equal quantity of anhydrous sodium sulfate and place it in an extraction thimble. Place approximately 70 ml of the extraction solvent (hexane: acetone 50:50), extract the sample in an continuous soxhlet extraction apparatus for 2 hours (boiling 1 hr and rinsing 1 hr) and transfer the extract to a 10 ml volumetric flask. Pipette 2ml into a concentrator and evaporate under nitrogen to reduce solvent to about 0.5 ml. Add acetonitrile and evaporate again. If required, make up to 2 ml mark on the concentrator with acetonitrile.

3.2.5 Determination of Aliphatic Hydrocarbon by GC- FID.

Gas chromatography is a separation of compounds in the gas phase based on the same types of interactions as in HPLC. The compounds are separated due to differences in their ability to partition or transfer between the stationary and mobile phases. Usually this partition is based on polarity when doing GC analysis. The analysis is done at a specific high temperature, usually higher than the highest boiling point in the mixture. FID is flame ionization detector, it's as the effluent (carrier gas and any organic compounds) comes of out of the column and they are ignited in a flame made of hydrogen and air. The compounds produce ions as they burn and these ions conduct electricity. Changes in current within the flame are measured and sent to the computer to be seen as peaks on the chromatogram.

One µl of extraction was taken and analyze it with a Varian Model 3400 gas chromatograph equipped with flame ionization detector (GC-FID) fitted with a quadrex 50 meter fused silica capillary column. The GC is programmed from 40°C to 340°C at 10°C/ minute with a 2 minute hold at 40°C and a 20 minute hold at 340°C. Analytical data are processed with a nelson analytical model 3000 chromatographic data system and IBM computer hardware.

This software system facilitates data processing and graphic display as well as electronic data transmittal.

3.2.6 Determination of Polychlorinated Biphenyls (PCBs) by GC- ECD

The analysis of PCBs was held in the Central laboratory unit (CLU) at the United Arab Emirates University, Al Ain, UAE. The central laboratory unit has NAMAS accreditation and is accredited to ISO 9001.

Gas chromatography with electron captures detector 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/CH4 at flow rate recommended by the manufacturer (between 30 to 60ml/min).

-Injector temperature: 225 °C.

-Detector temperature: 300°C.

-Initial temperature: 100°C hold 2 minutes.

GC with electron capture detector can determine PCBs in soils, sediments and wastes. Specifically this method is recommended for the determination of 20 PCBs congeners which are propriety pollutants. Samples can be prepared by blend 5g ± 0.5 g of the solid sediments with 5g ± 0.5g of anhydrous sodium sulfate and place in an extraction thimble. Place approximately 70 ml of the extraction solvent (1:1 hexane: acetone) and extract the sample for 2 hours (boiling 1 hr and rinsing 1 hr), after extraction, the sample is carefully evaporated. When all but 2-5 ml of solvent have been collected, open the system and remove the cups.

The extract is quantitatively transferred to a 10 ml measuring cylinder. Rinse the cups using hexane and add the rinsates to the measuring cylinder at a fixed volume of 10 ml, transfer apportion to a 2 ml GC autosamapler vial and inject 1 µl in GC-ECD (EPA, 1999).

3.2.7 Determination of Total Petroleum Hydrocarbons (TPH)

Determination of total petroleum hydrocarbons provides information on the contamination of water, soil and sediments with petroleum products .TPH is an estimated of the amount of hydrocarbons present between the carbon ranges C_8 to C_{40}. This range of carbon extends from the volatile hydrocarbons compounds with the lower boiling to the non volatile compounds found at the higher boiling point range (ROPME, 1999). The method is applicable for the determination of TPH either by gravimetry or Nicolet Fourier Transform Infrared Manma IR560 FTIR. The method is not applicable to light hydrocarbons that volatilize below 70 °C. Also some crude oils and heavy fuel oils that is partially soluble which give low recovery. Five grams of sample take and placed in a 50 ml beaker, acidify the sample to PH i.e. 2 by adding 0.1ml concentrated HCL and add five grams of prepared $MgSO_4$ to the acidified sample and stir to create a smooth paste. Then spreader the paste on the sides of the beaker leaves it for about 15-30 minuts at room temperature until the material is solidified. Transfer the solid to a mortar and grind to a fine powder. After that add the powder to paper extraction thimble .Wipe both the beaker and the mortar with pieces of filter paper moistened with solvent and add the paper to the thimble. Place the thimble in a soxhlet apparatus and extract using n- hexane. The rate and time of extraction in the soxhlet apparatus should be strictly controlled to extract greases having varying solubilities. Then remove the solvent, cool and remove the extraction cup which contains the residue (TPH). Dissolve the residue in the cup in fluorocarbon -113; quantitatively transfer into 25 ml volumetric flask a make up to volume. Then place the solution in a suitable FTIR cuvette. Select appropriates working standards and cell path length. The results of the analysis calculated by this formula:

Total petroleum hydrocarbons (mg/kg) = X*Y*D*1000/W

Where:

X=instrument reading (mg/L)

Y=volume made up from the sample

D=dilution factor

W=wet weight of sediments extracted in

3.2.8 Determination of Total Organic Carbon (TOC)

Five grams of powdered sediment sample was dried and place in the beaker. After that, 10 % HCl was added to remove all the inorganic carbon and heat to complete removal of inorganic carbon. Then take 0.25 gram of sample after HCl and analyze by Leco- carbon analyzer (CS-200) by ignition the sample in the presence of O_2. All CO_2 released from the ignition of organic carbon will be collected by CO_2 trap, then detected by CO_2 detector and recorded by digital voltammeter record.

3.2.9 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 samples 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 $Cu SO_4 \times {}_5H_2O$) 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 = $[(T\text{-}B) \times N \times 14.007 \times 100]$/ weight of sample in mg

% protein= $\%N \times F$

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

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

Mg N/100ml = $[(T\text{-}B) \times N \times 14.007 \times 100]$ / 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.

3.2.10 Determination of heavy metals by (ICP-AES)

0.5 gram of the samples was Weighted in to a beaker and moister the sample with about 5ml of distilled water. Add 3 ml of HCL and 9 ml of HNO_3 and digest the mixture in hotplate for 30 minutes. Then cool the sample and filtrate the solution .After that, quantitatively transfer the contents and make up to 50 ml in a volumetric flask with deinoized water. Blank must be prepared at the same time under the same conditions (ROPME, 1999). The equipment and operating conditions as follows:

Equipment:

Inductively coupled argon plasma-atomic emission spectrometer (ICP-AES), Varian, vista-MPX-CCD, simultaneous, with background correction, auto-fit multi-calibration curve fitting, signal to background ratio signal to root background ratio (Fig2.12& Fig2.13).

-Computer personal and printer.

-Analytical balance capacity 200 gram and sensitivity ± 0.0001 g.

-Hotplate.

Operating condition

-Power = 1.2 KW

-Plasma flow= 15 L/min

-Aux. flow= 1.5 L/min

-Neb. flow= 0.75 L/min

-Replicate time(S) = 10 Sec.

-Sample uptake time= 20 Sec.

-Rinse time = 10 S

-Pump rate= 15 rpm

3.3 Statistical analysis

Microsoft office **EXCEL** ^{TM} **XP** software was also used for plotting histogram and pie charts of total organic carbon, total petroleum hydrocarbon, total nitrogen, polychlorinated biphenyl, individual polychlorinated biphenyl and polycyclic aromatic hydrocarbon compounds either in coastal and marine sediments or stations.

SURFER7.01^{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.

SYSTAT^{10} program was used to carry out univariate, biavariate and multivariate statistical analyses for the obtained geochemical data such as histogram, factor analysis, and regression analysis, correlation matrix and cluster analyses.

****

CHAPTER 4

RESULTS & DISCASSION

RESUTLS AND DISCUSSION

4.1 Grain –Size Distribution

Grain size analysis was carried out to construct histograms and cumulative curves (Fig. 4.1, Fig. 4.2, and Fig. 4.3) and interpret the grain-size frequency distribution in the studied sediments. Moreover, cumulative curves were used to calculate the grain-size statistical parameters (M_Z, σ_I, Sk_I and K_G) through applying the equations of Folk and Ward, (1957).

The grain-size analysis of the present work revealed the size of sediment in the study area. The sample obtained from Khorfakkan, Fujairah and Kalba coastline were divided into four groups based on their M_Z. Table 4.2 demonstrates frequency distribution of the statistical grain size parameter in the coastal sediments of studied areas.

Most of the samples are classified as medium sand and fine sand, which cover about 75% of the study area. The parameter reflects the overall average size of the sediments which is influenced by sediments mixture, mode of transportation and environment of deposition (Udden, 1914 & Folk, 1966).

The data obtained from sieving analysis were used to chart cumulative curves on probability paper. The percentiles, which obtained from the curves, were used to calculate grain-size statistical parameters (Table 4.1) by using the equations adopted by Folk and Ward, (1957).

The histograms were constructed (Fig. 4.1) to show the variation in grain-size distribution at different stations in the study area.

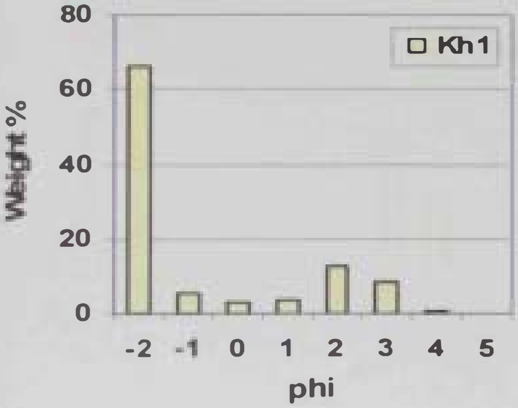
Values of graphic mean **M_Z** (a description of size class) occupy the range from – 4.63 Ø to 2.53 O with an average value of 1.49 O. Station KH1 showed the minimum value, whereas the maximum value was found at station KH2. Depending on the M_Z values, the samples were classified into: **1)** Medium sand, samples collected from Khorfakkan KH3, Kalba KH6, KH8 and Fujairah KH9, KH12. **2)** Fine sand, samples collected from Khorfakkan KH2, Kalba KH5 and Fujairah KH10, KH11. 3) Course sand, samples collected from Khorfakkan KH4 and Kalba KH7. 4) Pebble, sample collected from Khorfakkan KH1, which showed in Fig 4.1 & Table 4.1.

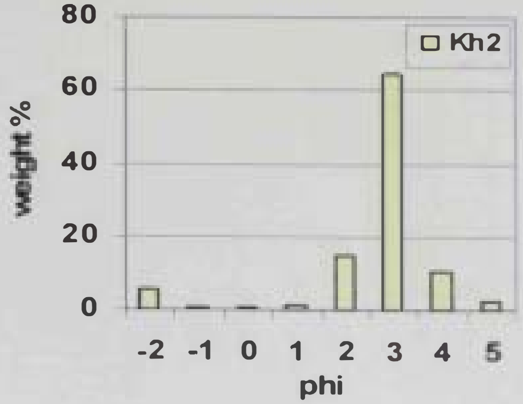
The inclusive standard deviation σ_I is a measure of the uniformity of grain-size distribution within the sediments. It depends on the size range in the source rock, extent of weathering, distance of transportation and the energy variation of the depositing medium (Folk and Ward, 1957 & Amaral and Prayor, 1977).

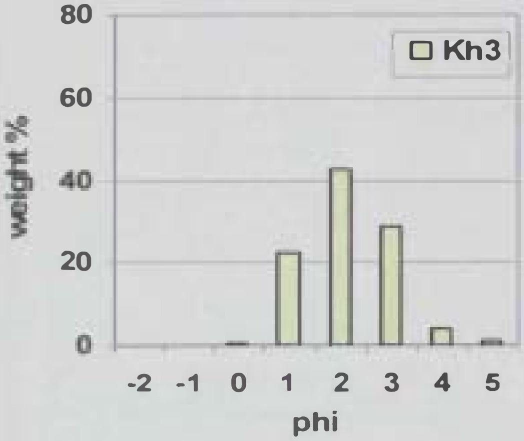
Values of inclusive graphic standard deviation of the coastal samples along the Gulf of Oman (Table 4.1) range between 0.66 (moderately well sorted) to 5.92 (extremely poorly sorted). The average value of σ_I is 1.50 Ø. The frequency distribution of the Gulf of Oman coastal sediments among the sorting classes (Table 4.2 & Fig. 4.3) reveals that the moderately and poorly sorted sediments are equally distributed (33.33 %) and higher than the moderately well sorted sediments (16.66%). On the other hand, the very poorly and extremely poorly sorted classes are equal and less abundant (8.33 %).

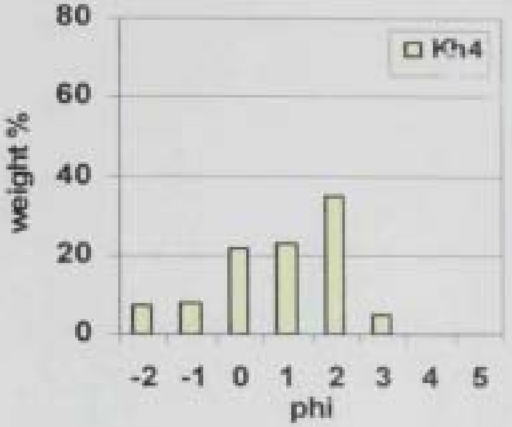
Values of inclusive graphic skewness **Sk_I** (a measure of symmetrical degree of the distribution curve) vary from -0.46 to 0.1 with an average value of Sk_I - 0.15. Table 4.2 and Fig.4.3 show that the coarse skewned sediments are the most dominant (41.66 %). Meanwhile, the near symmetrical and strongly coarse skewed sediments are equally abundant 25% for each. The less abundant skewness class is the fine skewed (8.33 %).

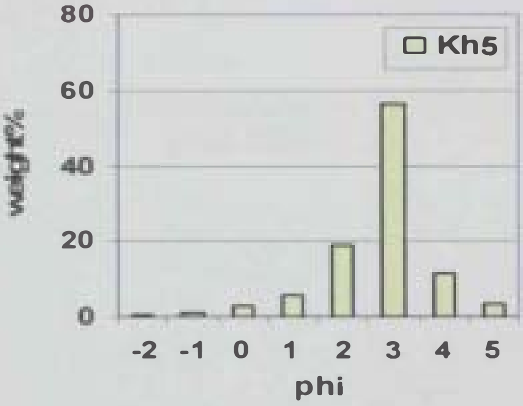
Values of graphic kurtosis **K_G**; measure the normality of grain size distribution using the ratio of sorting in the central part of the curve to that in its extremities (Folk, 1966). The Gulf of Oman coastal samples show kurtosis values ranging from 0.75 (platy kurtic) to 3.68 (extremely leptokurtic) with an average value of 1.36, which represents leptokurtic class. According to the kurtosis scale, 33.33 % of the samples have leptokurtic curves of distribution and 25 % of the samples have mesokurtic curves. The very leptokurtic and platy kurtic samples are equally abundant (16.6 %). The rest of the samples have extremely leptokurtic curves (Table 4.2 & Fig. 4.3).

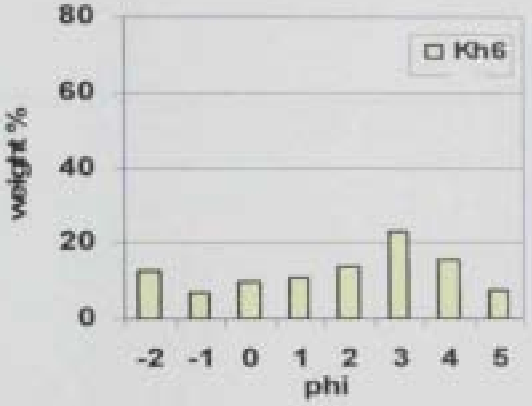

Kh1
Weight %
80
60
40
20
0
-2 -1 0 1 2 3 4 5
phi

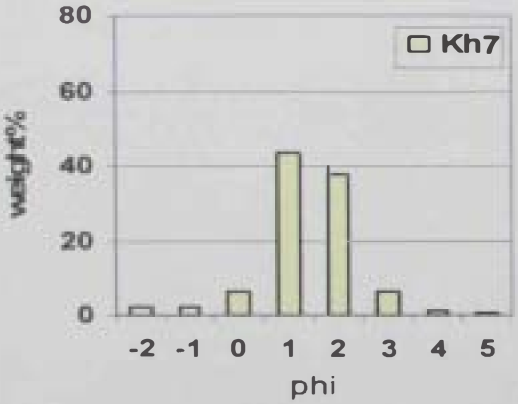

Kh2
weight %
80
60
40
20
0
-2 -1 0 1 2 3 4 5
phi

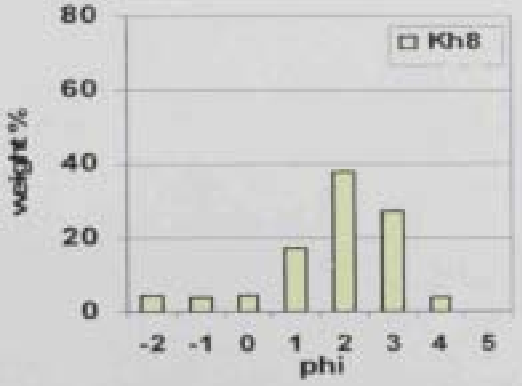

Kh3
weight %
80
60
40
20
0
-2 -1 0 1 2 3 4 5
phi


Kh4
weight %
80
60
40
20
0
-2 -1 0 1 2 3 4 5
phi


Kh5
weight%
80
60
40
20
0
-2 -1 0 1 2 3 4 5
phi


Kh6
weight %
80
60
40
20
0
-2 -1 0 1 2 3 4 5
phi


Kh7
weight%
80
60
40
20
0
-2 -1 0 1 2 3 4 5
phi


Kh8
weight %
80
60
40
20
0
-2 -1 0 1 2 3 4 5
phi

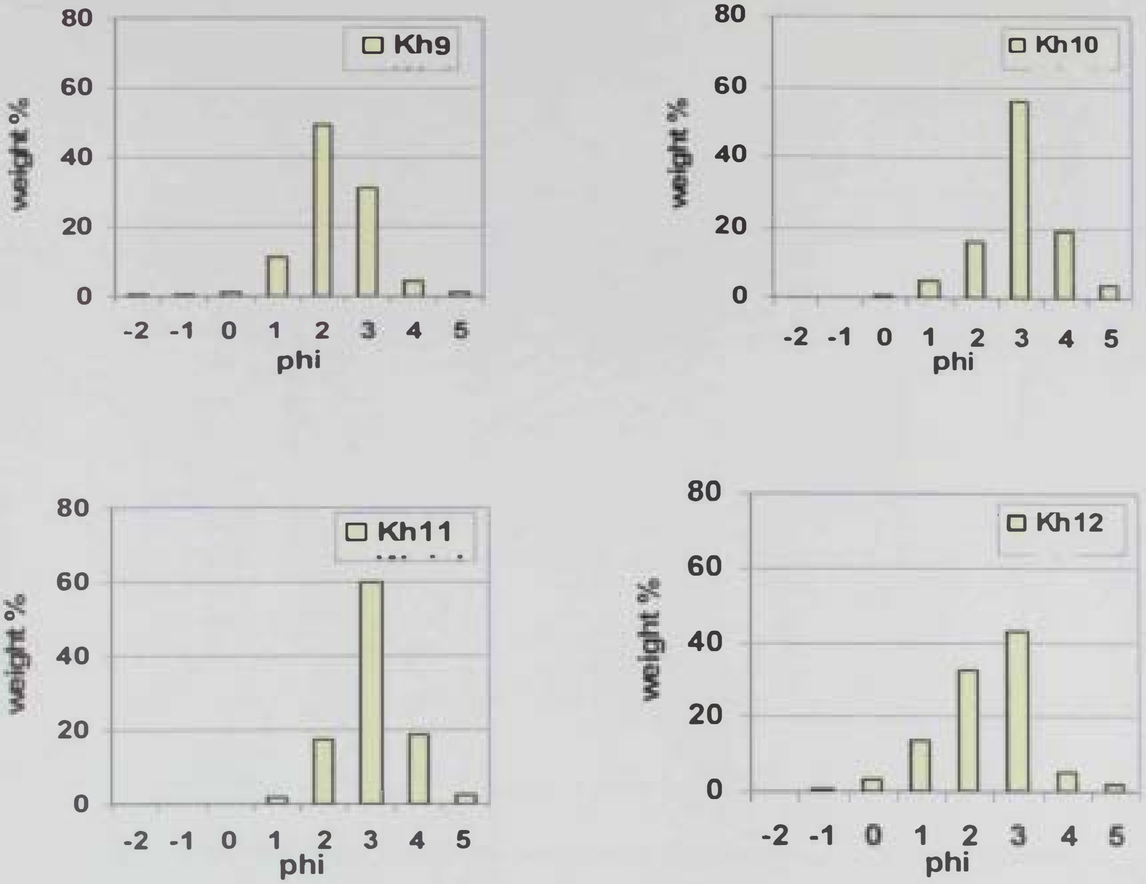


Fig. 4.1: Histograms Bar Chart of grain-size distribution of sediments along the coastal area of the Gulf of Oman.

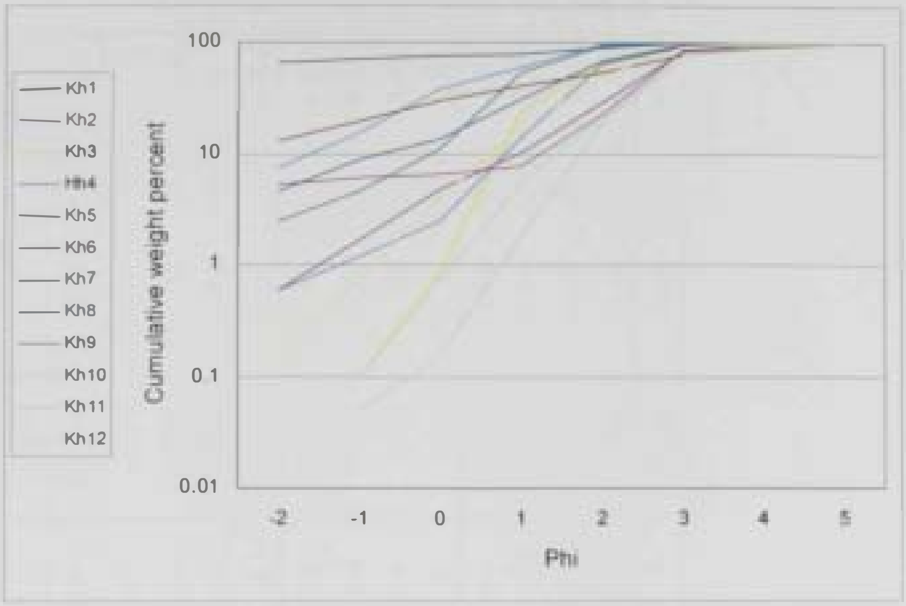


Fig. 4.2: Cumulative curves of sediments along the coastal area of the Gulf of Oman.

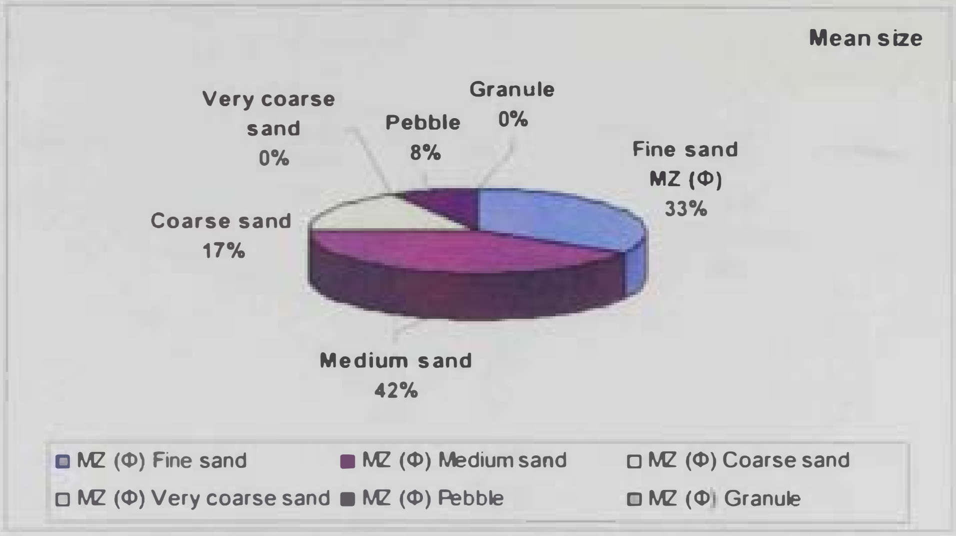
Table 4.1: Values of Phi percentiles and statistical parameters for the analyzed samples from the Gulf of Oman Coast.

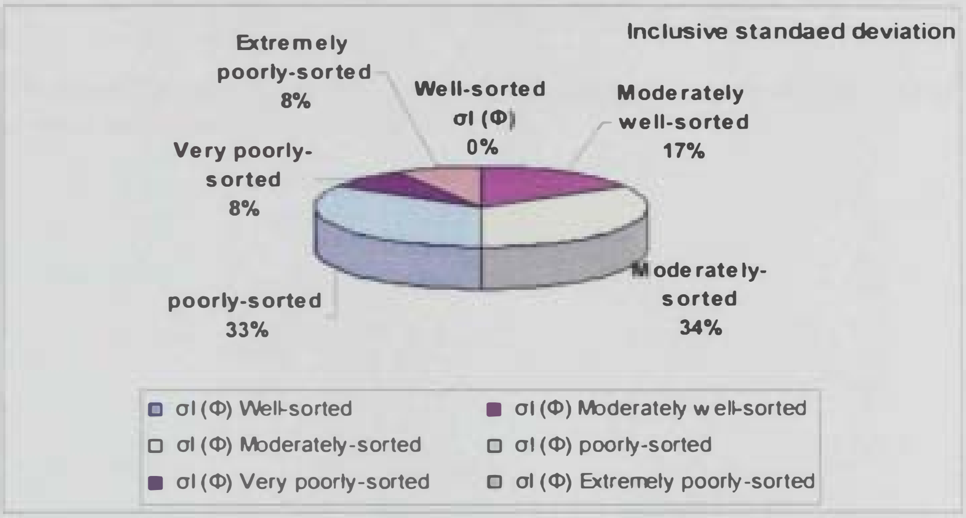
Station	**Sites**	**Phi Percentiles**							**Statistical Parameters**			
		Φ5	**Φ16**	**Φ25**	**Φ50**	**Φ75**	**Φ84**	**Φ95**	**$M_z(\Phi)$***	**$\sigma_I(\Phi)$**	**SK_I**	**K_G**
Khor Fakkan	**Kh1**	-15	-11.2	-9.4	-4.7	0	2	2.3	-4.63	5.92	0.1	0.75
	Kh2	-2	1.8	2.1	2.4	2.7	2.9	3.4	2.37	1.09	-0.36	3.68
	Kh3	0.4	0.8	1.1	1.7	2.2	2.5	3.1	1.66	0.83	-0.01	1
	Kh4	-2.1	-1.1	-0.6	0.5	1.4	1.6	2	0.33	1.2	-0.22	0.84
Kalba	**Kh5**	0.1	1.6	1.9	2.4	2.8	3	3.7	2.33	0.89	-0.19	1.63
	Kh6	-3.3	-1.5	-0.5	1.5	2.9	3.4	4.4	1.13	2.39	-0.45	0.92
	Kh7	-1.1	-0.1	0.2	0.8	1.3	1.6	2.2	0.77	0.93	-0.1	1.22
	Kh8	-2.1	0.4	0.8	1.5	2.1	2.4	3	1.43	1.7	-0.46	1.6
Fujairah	**Kh9**	0.7	1.1	1.3	1.7	2.1	2.3	3.1	1.7	0.66	0.08	1.2
	Kh10	0.9	1.7	2.1	2.6	3.1	3.3	3.8	2.53	0.83	-0.14	1.18
	Kh11	1.4	1.8	2.1	2.5	2.9	3.2	3.7	2.5	0.69	0.02	1.17
	Kh12	0.2	1	1.3	1.9	2.5	2.7	3.4	1.86	0.9	-0.06	1.09
Average									**1.49**	**1.5**	**-0.15**	**1.36**

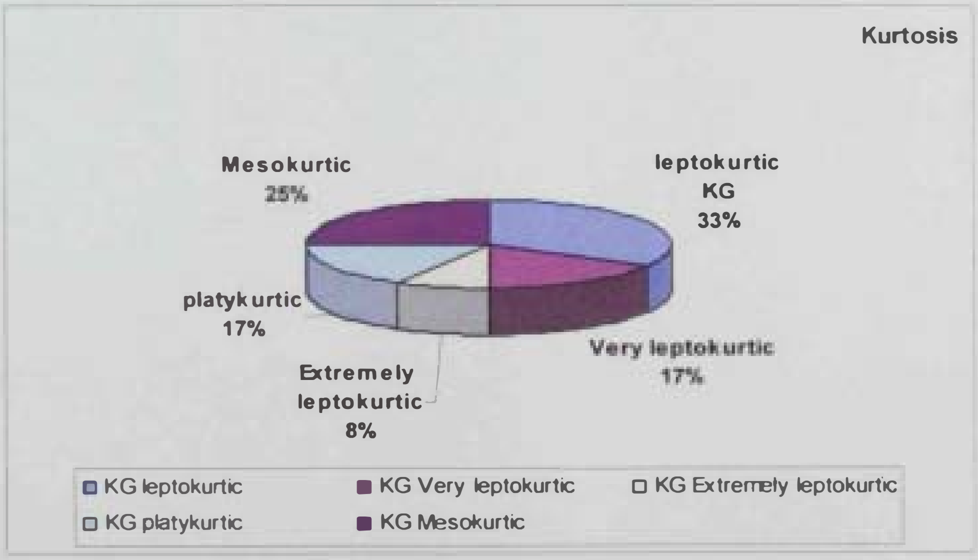
Mz: Mean size; **σ_I:** Sorting; **SK_I**: Skeweness; **K_G**: Kurtosis.

Table 4.2: Frequency distribution of the statistical grain-size parameters in the coastal sediments along the Gulf of Oman.

Parameter	Description	Percentage of samples
M_Z (Φ)	Fine sand	33.33%
	Medium sand	41.66%
	Coarse sand	16.66%
	Very coarse sand	0.00%
	Pebble	8.33%
	Granule	0.00%
σ_I (Φ)	Well-sorted	0.00%
	Moderately well-sorted	16.66%
	Moderately-sorted	33.33%
	poorly-sorted	33.33%
	Very poorly-sorted	8.33%
	Extremely poorly-sorted	8.33%
SK_I	Fine-skewed	8.33%
	Near-symmetrical	25%
	Coarse-skewed	41.66%
	Strongly coarse-skewed	25%
K_G	leptokurtic	33.33%
	Very leptokurtic	16.66%
	Extremely leptokurtic	8.33%
	platykurtic	16.66%
	Mesokurtic	25%


Mean size
Very coarse sand 0%
Pebble 8%
Granule 0%
Fine sand MZ (Φ) 33%
Coarse sand 17%
Medium sand 42%
MZ (Φ) Fine sand
MZ (Φ) Medium sand
MZ (Φ) Coarse sand
MZ (Φ) Very coarse sand
MZ (Φ) Pebble
MZ (Φ) Granule


Inclusive standaed deviation
Extremely poorly-sorted 8%
Well-sorted σI (Φ) 0%
Moderately well-sorted 17%
Very poorly-sorted 8%
poorly-sorted 33%
Moderately-sorted 34%
σI (Φ) Well-sorted
σI (Φ) Moderately well-sorted
σI (Φ) Moderately-sorted
σI (Φ) poorly-sorted
σI (Φ) Very poorly-sorted
σI (Φ) Extremely poorly-sorted


Kurtosis
Mesokurtic 25%
leptokurtic KG 33%
platykurtic 17%
Very leptokurtic 17%
Extremely leptokurtic 8%
KG leptokurtic
KG Very leptokurtic
KG Extremely leptokurtic
KG platykurtic
KG Mesokurtic

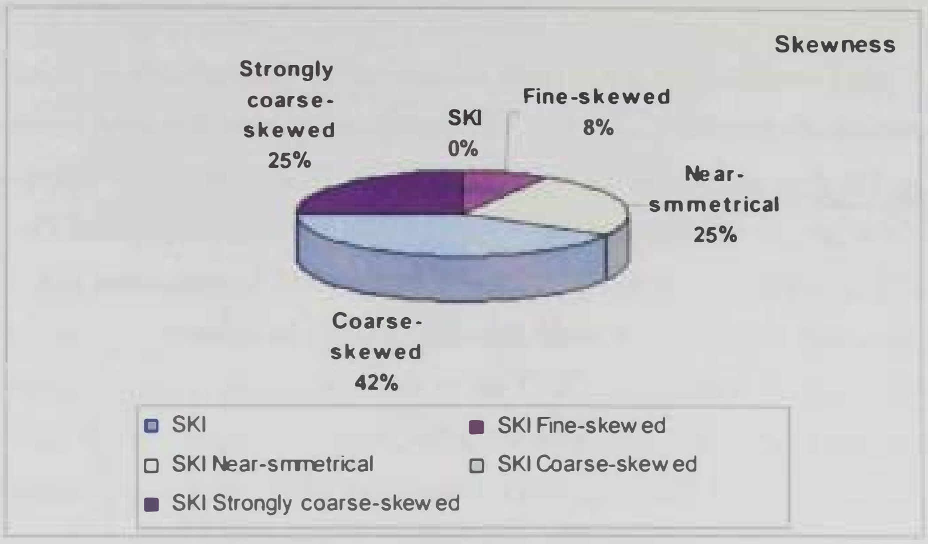


Fig. 4.3: Pie diagrams showing the frequency distributions of the grain-size parameters in the coastal sediments along the Gulf of Oman.

4.2 Polycyclic Aromatic Hydrocarbons (PAHs)

Table 4.3 illustrates that TPAHs values range between 0.07 mg/kg to 0. 28 mg/kg. Variation in the reported values can be observed among stations (Fig. 4.4). The minimum value was recorded at station KH5, and KH12, whereas the maximum value was provided by station KH2, KH7 and KH9, with an average of 0.187 mg/kg and S.D of 0.066. High percentage of TPAHs was 10 % occurs at KH7, and KH9 stations, while low percentage of TPAHs was 2 % where detected at KH12 (Fig. 4.5). Fig 4.6 shows the concentration of PAHs compounds in each station from marine and coastal sediments collected from eastern side of the UAE (Khorfakkan, Fujairah, and Kalba). Also this figure can give good comparing between each station for coastal and marine sediments. Fig. 4.8 shows the distribution map of TPAHs which increasing towards northern part of Khorfakkan and southern part of Fujairah stations.

3.2.1 Naphthalene

It is a polycyclic aromatic hydrocarbon PAHs with two aromatic rings ($C_{10}H_8$) and it is also called white tar or tar camphor. Exposure to naphthalene can cause systemic reactions including nausea, headache, diaphoresis, hematuria, fever, anemia, liver damage, vomiting, convulsions and coma (Rowat Sc., 1998). Naphthalene was detected at twelve stations (KH1, KH2, KH3, KH6, KH7, KH8, KH9, KH10, KH11, S1, S2, and S3) with concentrations vary within a range from 0.079 mg/kg to 0.01 mg/kg. The maximum value was reported at station S1 and the minimum value at station KH8 (Table 4.3 & Fig. 4.6 A). The map of naphthalene showed a trend of increasing towards the northern and southern part, of the study areas around all stations (Fig. 4.9).

3.2.2 Acenaphthylene

Acenaphthylene is one of polycyclic aromatic hydrocarbons PAHs. Its formula is ($C_{12}H_8$) and molecular weight of 152.20. Acenaphthylene reach the environment from natural sources such as forest fires and man made sources including burning of wood, automobile and truck emissions. Acenaphthylene can affect on the kidneys, liver, blood and a lungs (Faust, 1994) .This compound was detected at twelve stations at marine and coastal sediments. The values ranged from 0.012 mg/kg to 0.041 mg/kg. Low concentration (0.012 mg/kg) occurs at KH1, KH2, KH3, KH4, KH5, KH6, and

KH7, while the high concentration (0.041 mg/kg) occurs at KH8, KH9, KH10, KH11, S2, and S3 (Table 4.3 & Fig. 4.6 B). The map of acenaphthylene showing a trend of increasing towards the southern part of the study area (Fujairah and Kalba) (Fig. 4.10).

3.2.3 Acenaphthene

It is a polycyclic aromatic hydrocarbon PAHs consisting of the two ringed naphthalene with a (C_2H_4) bridge between positions 1 and 8. Its formula is ($C_{12}H_{10}$) and it does not appear to be carcinogenic. Acenaphthene has second names naphthyleneethylene and 1, 2- dihydrocenaphthylene (ATSDR, 1990).Acenaphthene was detected at four stations (KH1, KH2, KH7, and KH9) with concentrations vary within a range from 0.001 mg/kg to 0.02 mg/kg. The maximum value was reported at station KH1 and the minimum value recorded at reminder three stations (Table 4.3 & Fig. 4.6 C). The map of Acenaphthene showing a trend of increasing towards the southern part of the study area (Fig. 4.11).

3.2.4 Flourane

Fluorene is one of a group of polycyclic aromatic hydrocarbons PAHs with one five – membered and two six - membered rings. Fluorene was detected in all stations (KH1 to S3) of the study area .The highest concentration was recorded 0.037 mg/kg at station KH1, whereas the minimum concentration 0.006 mg/kg & 0.007 mg/kg was provided by stations KH3 & KH12 respectively (Table 4.3 & Fig. 4.6 D). The distribution map demonstrates that its values increased towards the northern part particularly around KH2, KH3, and KH4 stations and southern part around KH5, KH6, KH7, and KH8 (Fig. 4.12).

3.2.5 Phenanthrene

It is a tricyclic aromatic hydrocarbon derived from coal tar. Phenanthrene is non carcinogenic PAH, but also toxic to some organisms and its formula is ($C_{14}H_{10}$) (ATSDR, 1990). Phenanthrene was recorded at all stations which ranged from 0.006 mg/kg at S1 to 0.139 mg/kg at KH2. High concentration occurs at KH1, KH2, KH3, KH4, KH7, and KH9. Low concentration occurs at KH5, KH11, KH10, and KH12 (Table 4.3 & Fig. 4.6 E). The map of Phenanthrene showing a trend of increasing towards the northern part of the study areas (KH1 to KH4 stations) Khorfakkan (Fig. 4.13).

3.2.6 Anthracene

It is one of the polycyclic aromatic hydrocarbon PAHs with three rings and the molecular weight is 178. This compound was detected only at one station KH7 of the study area with concentration at 0.005 mg/kg (Table 4.3 & Fig. 4.6 F).

3.2.7 Fluoranthene

It is a type of polycyclic aromatic hydrocarbon PAHs with one five – membered and three six – membered rings. Its formula is ($C_{16}H_{10}$) and its non carcinogenic PAH, but also toxic to some organisms. This compound ranged from 0.007 mg/kg to 0.066 mg/kg. A high level of Fluoranthene was detected at all stations of coastal sediments, while the low concentration occurs at marine sediments (Table 4.3 & Fig. 4.6 G). The map of Fluoranthene showing a trend of increasing towards the northern part of the study area (Fig. 4.14). Table 4.4 and Fig. 4.7 illustrate the TPAHs values range between 44.2 to 299.3 mg/kg at oil samples. The minimum value was recorded at oil-4 sample and the maximum vale was provided by oil-1 sample.

3.2.8 Pyrene

It is a polycyclic aromatic hydrocarbon PAHs with four aromatic rings. Pyrene is non carcinogenic PAH but also toxic to some organisms. Pyrene values ranged from 0.01 mg/kg to 0.05 mg/kg. High concentration occurs at KH7, and KH11 and low concentration occurs only at stations KH1, KH10, and S3 (Table 4.3 & Fig. 4.6 H). The distribution map of Pyrene exhibits an increasing trend towards the northern parts of the study area. The highest values were concentrated for Khorfakkan (Fig. 4.15).

3.2.9 Benzo (a) Anthracene

It is a polycyclic aromatic hydrocarbon PAHs with four aromatic rings. This compound ranged from 0.002 mg/kg to 0.015 mg/kg. High concentration of benzo (a) anthracene was detected only at KH2, and KH3, while the low concentration was detected at KH8 (Table 4.3 & Fig. 4.6 I). The map of Benzo (a) anthracene showing a trend of increasing towards the northern part of the study area Khorfakkan (Fig. 4.16).

3.2.10 Chrysene

It is a polycyclic aromatic hydrocarbon PAHs with four aromatic rings. Its formula is ($C_{18}H_{12}$) and the molecular weight is 228.3. It's present to the environment due to anthropogenic activities; Chrysene is a probable carcinogen on human and animals (ATSDR, 1990). This compound was 0.01 mg/kg which recorded at all stations marine and coastal sediment excepted KH9, and KH12 (Table 4.3 & Fig. 4.6 J). The distribution map of Chrysene exhibits an increasing trend towards the southern part of the study area. The highest values were concentrated in Fujairah Emirate and Kalba (Fig. 4.17).

3.2.11 Benzo (b) Fluoranthene

It is a polycyclic aromatic hydrocarbon PAHs with one five –membered and four six-membered rings. This compound was detected only at three stations KH8, KH10, and S2 of the study area with concentrations were 0.02 mg/kg (Table 4.3 & Fig. 4.6 K). The map of Benzo (b) Fluoranthene showing a trend of increasing towards the southern part of the study area Fujairah and Kalba (Fig. 4.18).

3.2.12 Benzo (K) Fluoranthene

It is a polycyclic aromatic hydrocarbon PAHs with one five-membered and four six-membered rings. Benzo (k) Fluoranthene is found in fossil fuels and in products of incomplete combustion (ATSDR, 1990). Benzo (k) Fluoranthene was detected at two stations KH7, and S2 of the study area with the same concentrations 0.01 mg/kg for coastal and marine sediments (Table 4.3 & Fig. 4.6 L). The mapping of survey also shows an increase towards the southern part of the study area (Fig. 4.19).

3.2.13 Benzo (a) Pyrene

It is a polycyclic aromatic hydrocarbon with five aromatic rings. Benzo (a)pyrene is carcinogenic , causing tumors in animals and are acutely toxic to some organisms. This compound was found only at four stations KH7, KH9, KH11, and S3 of the study area, with the same values 0.01 mg/kg for coastal and marine sediments (Table 4.3 & Fig. 4.6 M).The map of Benzo (a) Pyrene showing a trend of increasing towards the southern part of the study area (Fujairah and Kalba) (Fig. 4.20).

3.2.14 Benzo (g,h,i) Perylene

It is a polycyclic aromatic hydrocarbon PAHs with six aromatic rings. This compound was detected just at three stations KH8, KH9, and KH11 of the study area with varying concentrations from 0.02 mg/kg to 0.03 mg/kg (Table 4.3 & Fig. 4.6 N). The map of Benzo (g,h,i)Perylene showing a trend of increasing towards the southern part of the study area (Fujairah and Kalba) (Fig. 4.21).

3.2.15 Indeno (1,2,3-cd) Pyrene

It is one of the polycyclic aromatic hydrocarbon PAHs with one five- membered and four six-membered rings. This compound was detected only at one station KH9 of the study area with concentration 0.005 mg/kg (Table 4.3 & Fig. 4.6 O).

3.3 Polycyclic Aromatic Hydrocarbon Ratios

Kot-Waisk et al. (2004) divided PAHs in to three groups: (1) **Low Molecular Weight** 128-178 g/mol (2-3 rings) Napththalene, Acenaphthylene, Acenaphthtene, Flourane, Phenanthrene, and Anthracene; (2) **Medium Molecular Weight** 202-228 g/mol (4 rings) Fluoranthene, pyrene, Benzo (a) Anthracene, and chrycene, (3) and **High Molecular Weight** 252-278 g/mol (5-6 rings), Benzo (b) Fluoranthene, Benzo (K) Fluoranthene, Benzo (a) Pyrene, Dibenzo(a,h) Anthracene, Benzo (g,h,i)perylene, and Indeno(1,2,3-c,d)pyrene. Table 4.5 & Fig. 4.22 C showed the distribution of PAHs molecular weight at all stations was low molecular weight rather than the medium and high molecular weight, which reflected the sources of pollution which, is spilled oil. According to the Fang et al. (2003) & Ma et al. (2005) petrogenic PAHs are characterized by a predominance of PAHs with low molecular weights **(2-3 ring PAHs)**, which detected at all the studied station (Fig. 4.23). This value indicated the sources of pollution are mainly from spilled oil. On the other hand, some PAHs, such as perylene, largely come from digenesis processes of biogenic precursors. Absence of perylene at all stations reflected the source of pollution was not from biogenic sources.

A method of using the ratio P/A <10 and Fluoranthene/Pyrene>1 to identify contamination sources of combustion processes (pyrogenic PAHs) is disscused by Wang et al. (2004). There are another ratio can identify the pyrogenic PAHs which including: Benz(a) anthracene/chrysene (BaA/Ch), P/(P+A), and indeno(1,2,,3-cd)pyrene/(indeno(1,2,3-cd)pyrene+benzo-(ghi)perylene). Certain diagnostic ratios have been widely used in identifying sources of PAHs. In contrast to pyrogenic sources, petrogenic are characterized by high ratios of Phenanthrene/Anthracene ($P/A > 15$) in association with lower ratios of Fluoranthene/Pyrene ($Flu/P < 1$) and Benzo (a) Anthracene / (Benzo (a) Anthracene + Chrycene) ($(BaA / (BaA + Chry) < 0.4)$). These ratios should be used in combination to avoid erroneous conclusion reading origins of PAHs (Wang and Fingas, 2003).

3.3.1 ($\sum PAH_{CARC}$): The Total Carcinogenic Polycyclic Aromatic Hydrocarbons which defined as sum of = Benzo (a) Anthracene + Benzo (b) Fluoranthene + Benzo (k)Fluoranthene+benzo(a)Pyrene+indeno(1,2,3_c,d)Pyrene+dibenzo(a,h)Anthracene. Dahle et, al (2003) & Cao et al. (2005), were defined pyrene, phenanthrene and anthracen as non carcinogenic compound, while the benzo(a) anthracene, acenaphthylene, naphthalene benzo(a)pyrene, fluorine, chrysene, fluoranthene and benzo(b)fluoranthene were reported as carcinogenic compounds. Within the study area, marine sediments attain high $\sum PAH_{CARC}$ ranging from 0 at (S1) to 0.024 at (S2). The coastal sediment from 0.004 at (KH4) to 0.021 at (KH8), which reflected sources of pollution mainly from oil spill (Table 4.5 & Fig. 4.22 A).

3.3.2 $\sum$ Pyro (%): defined as sum of PAHs with MW >178/total PAHs (perylene accepted). PAHs in either fossil fuels or uncombusted fossil fuel residues are characterized by higher proportions of lower molecular weight PAHs (two to three rings) and a greater abundance of alkylated homologues. This ratio was used to account for PAH derived from combustion/pyrolysis processes (Medeiros et al., 2005). Within the study area, the value was ranging from 0.06 % at (KH1) to 0.66 % at (KH11) for the coastal sediment samples, while the values ranging from 0.047 % at (S1) to 0.37 % at (S3) for marine sediments samples (Table 4.5). So, all the studied sediments have low concentration of $\sum$ Pyro which indicates that the sources of pollution are not from pyrolysis or combustion of fossil fuels, but absolutely from petrogenic sources (Fig. 4.22 B).

3.3.3 Phenanthrene/Anthracene (P/A) (Fang et al., 2003). This ratio is equal to 1 for both coastal and marine sediments samples within the study area, except for station KH7 (0.9), which reflect pyrogenic sources of PAHs (Table 4.5).

3.3.4 Benzo (a) Anthracene/ (Benzo (a) Anthracene +Chrycene): Stations KH4, KH7, KH8, KH9, KH10, S1, S2, and S3 have values of BaA / (BaA+Chry) ≤ 0.4 which reflect petrogenic sources. While stations KH1, KH2, KH3, KH5, KH6, KH11, and KH12 attain values of BaA/(BaA+Chry) ranging from 0.5 to 0.75 indicating pyrogenic sources (Table 4.4) (Fang et al., 2003).

3.3.5 Indeno(1,2,3-c,d)pyrene/(Indeno(1,2,3-c,d)pyrene +Benoz(ghi)perylene) Indeno/(indeno+BghiP) : the (indeno) and (BghiP) have been used by several researchers as a source identifier for aerosols from automobiles (Hartmann et al., 2004). In this study, this ratio equal to zero for all coastal and marine sediments except KH9 which recorded value of 0.17 (Table 4.5).Theses ratios are lower than the 0.33±0.06 observed for automobile emissions.

3.3.6 Fluoranthene/ (Fluoranthene+Pyrene): Flu/ (Flu + P)>1 which indicate pyrogenic sources while values < 1 indicate petrogenic sources of PAHs (Guinan et al., 2001). Within the study area, the Flu/ (Flu + P) ratio was ranging from 0 at KH1, KH6 and KH12 to 1 at KH2, KH3, and KH8 for coastal sediments samples. For marine sediment sample, the values were from 0 at S1 to 1 at S2. So, the concentration at most stations was less than 1 that indicates petrogenic sources PAHs (Table 4.5).

Based on all the above calculated ratios, it can be concluded that sources of pollution within the study area are predominantly of petrogenic origin (oil spill). In addition to minor contribution from pyrogenic sources (combustion of oil products and shipping activities at nearest harbor).

Table 4.3: Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs mg/kg) in sampling stations.

Stations	Napththalene	Acenaphthylene	Acenaphthene	Flourane	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo(a)anthracene	Chrysene	Benzo(b)flouranthene	Benzo(k)flouranthene	Benzo(a)pyrene	Benzo(g,h,i)perylene	Indeno(1,2,3-cd)pyrene	total- PAHs
KH1	0.035	0.012	0.02	0.037	0.138	ND	ND	0.01	0.006	0.01	ND	ND	ND	ND	ND	0.25
KH2	0.037	0.012	0.01	0.031	0.139	ND	0.029	ND	0.015	0.01	ND	ND	ND	ND	ND	0.27
KH3	0.02	0.012	ND	0.006	0.109	ND	0.025	ND	0.01	0.01	ND	ND	ND	ND	ND	0.19
KH4	ND	0.012	ND	0.017	0.082	ND	0.033	0.04	ND	0.01	ND	ND	ND	ND	ND	0.19
KH5	ND	ND	ND	0.007	0.039	ND	0.02	0.02	0.005	0.01	ND	ND	ND	ND	ND	0.09
KH6	0.011	0.012	ND	0.014	0.071	ND	ND	0.03	0.006	0.01	ND	ND	ND	ND	ND	0.15
KH7	0.02	0.012	0.01	0.027	0.091	0.005	0.04	0.05	ND	0.01	ND	0.01	0.01	ND	ND	0.28
KH8	0.01	0.038	ND	0.032	0.051	ND	0.019	ND	0.002	0.01	0.02	ND	ND	0.02	ND	0.2
KH9	0.029	0.041	0.01	0.024	0.096	ND	0.019	0.02	ND	ND	ND	ND	0.01	0.02	0.005	0.27
KH10	0.017	0.029	ND	0.012	0.049	ND	0.02	0.01	0.005	0.01	0.01	ND	ND	ND	ND	0.16
KH11	0.014	0.035	ND	0.019	0.01	ND	0.066	0.05	0.006	0.01	ND	ND	0.01	0.03	ND	0.24
KH12	ND	ND	ND	0.007	0.03	ND	ND	0.02	0.005	ND	ND	ND	ND	ND	ND	0.07
S1	0.079	ND	ND	0.015	0.006	ND	ND	ND	ND	0.01	ND	ND	ND	ND	ND	0.11
S2	0.047	0.02	ND	0.011	0.047	ND	0.02	ND	0.006	0.01	0.01	0.01	ND	ND	ND	0.18
S3	0.06	0.041	ND	0.01	0.038	ND	0.007	0.01	ND	0.01	ND	ND	0.01	ND	ND	0.18
															average± S.D	**0.187 ±0.066**

ND = Not Detected

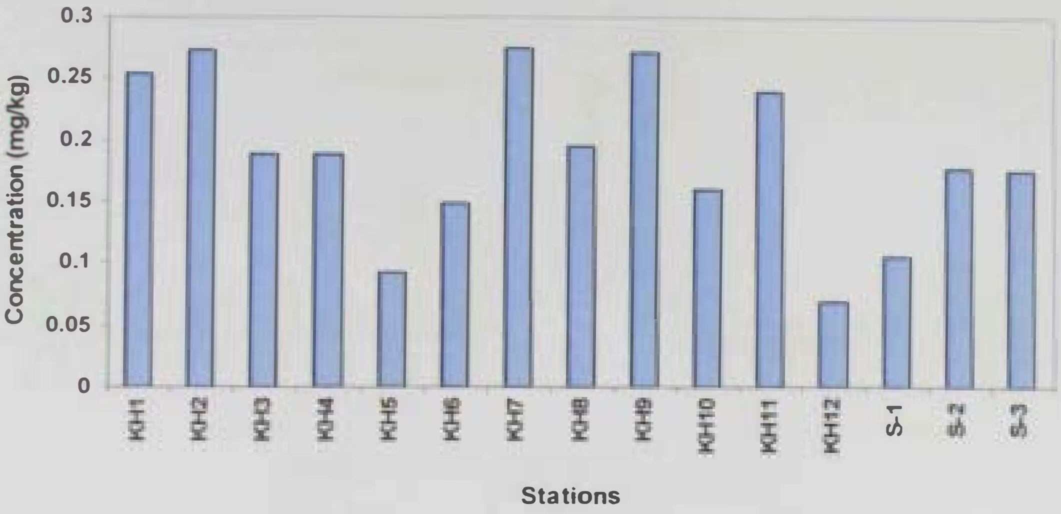


Fig. 4.4: Concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in studied stations.

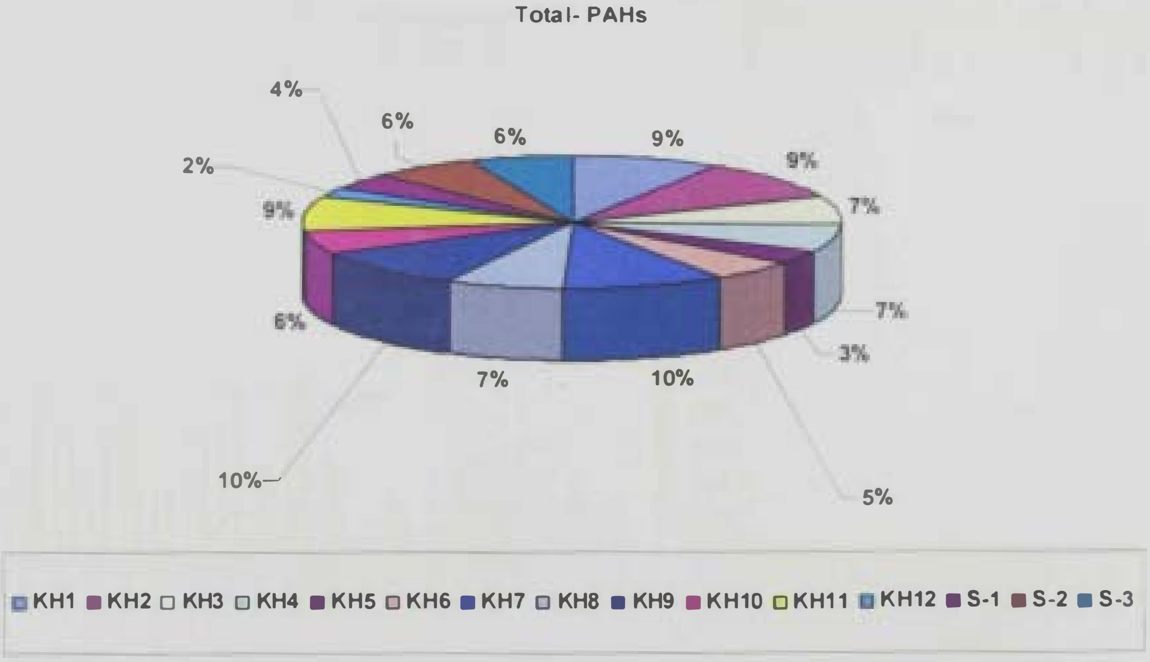
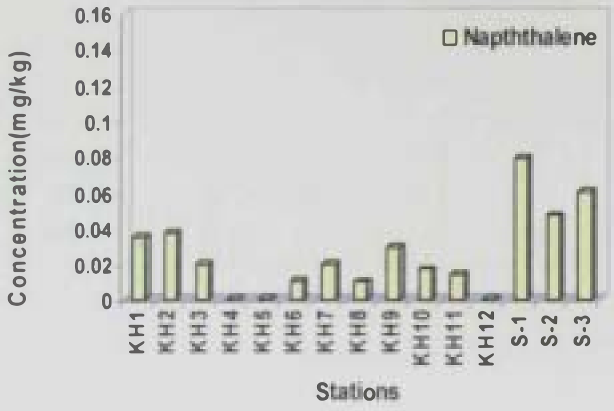
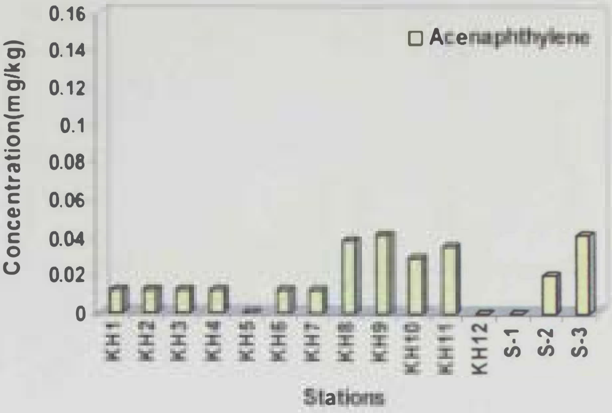


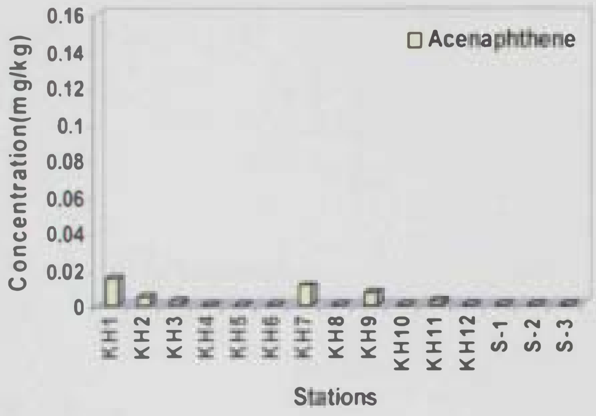
Fig. 4.5: Percentages of Total Polycyclic Aromatic Hydrocarbons (TPAHs) in studied stations.


Concentration(mg/kg)
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
☐ Napththalene
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
S-1
S-2
S-3
Stations

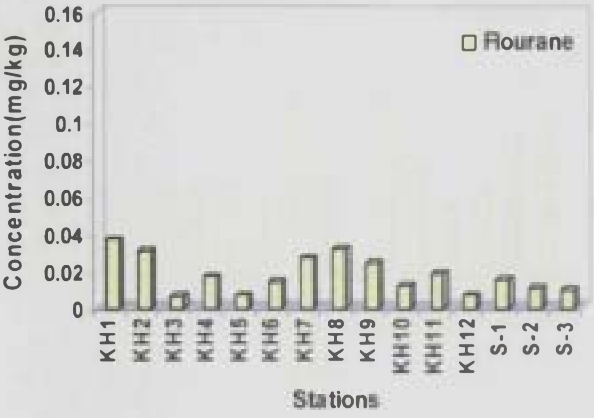
A.


Concentration(mg/kg)
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
☐ Acenaphthylene
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
S-1
S-2
S-3
Stations

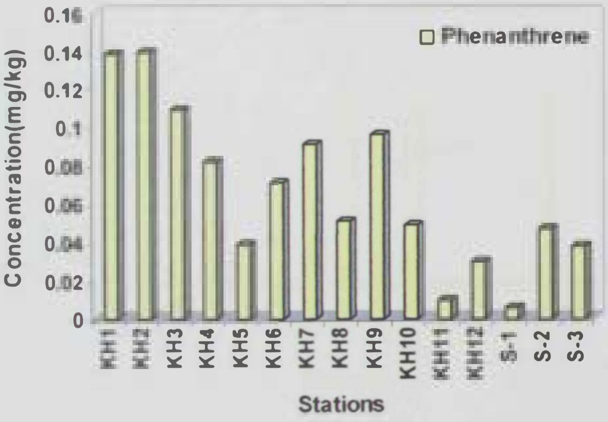
B.


Concentration(mg/kg)
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
☐ Acenaphthene
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
S-1
S-2
S-3
Stations

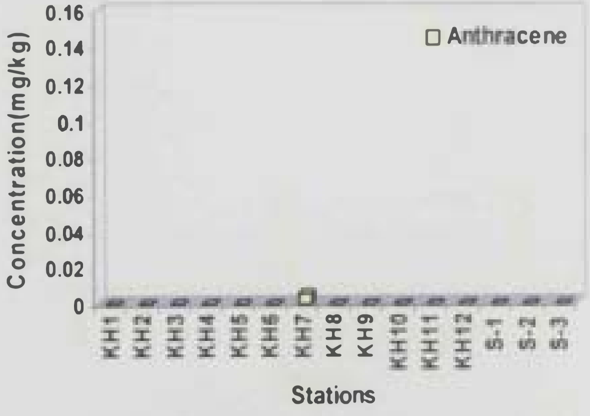
C.


Concentration(mg/kg)
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
☐ Flourane
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
S-1
S-2
S-3
Stations

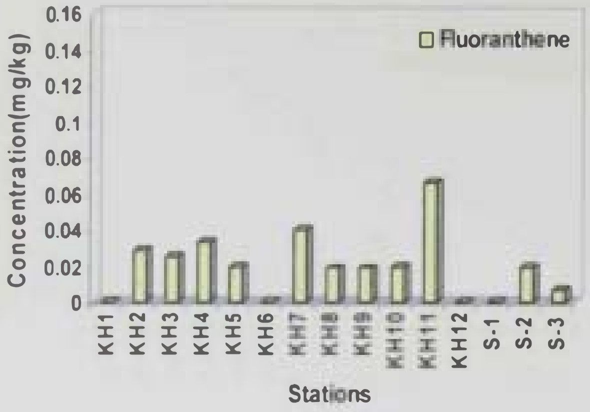
D.


Concentration(mg/kg)
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
☐ Phenanthrene
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
S-1
S-2
S-3
Stations

E.

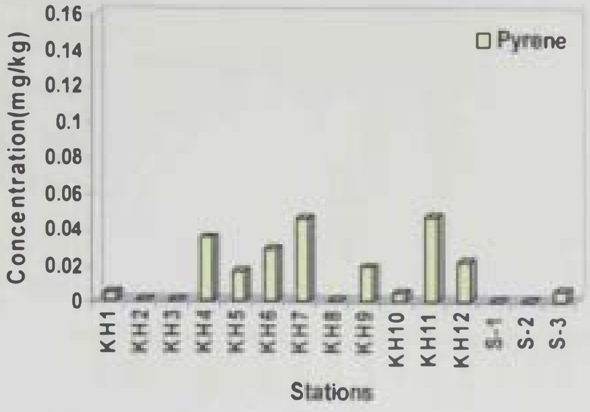

Concentration(mg/kg)
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
☐ Anthracene
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
S-1
S-2
S-3
Stations

F.



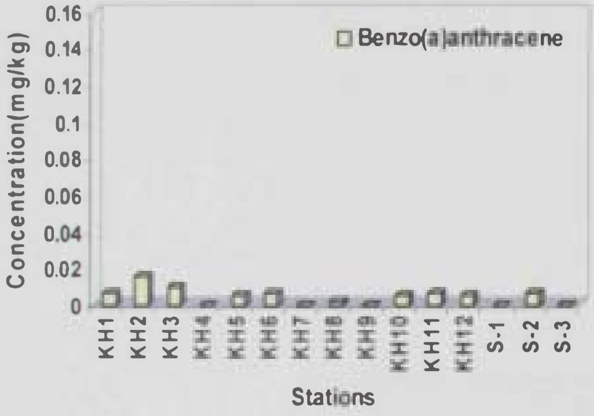
Concentration(mg/kg)
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
☐ Fluoranthene
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
S-1
S-2
S-3
Stations

G.



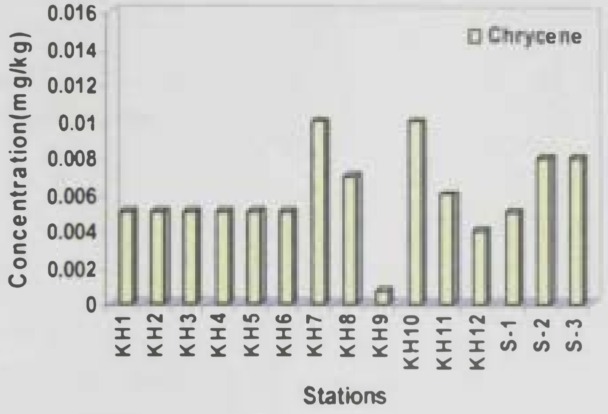
Concentration(mg/kg)
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
☐ Pyrene
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
S-1
S-2
S-3
Stations

H.



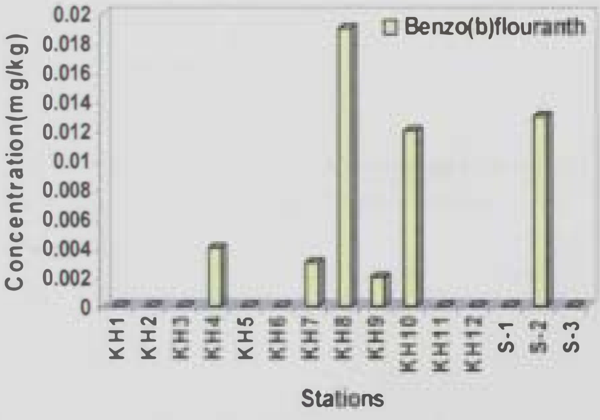
Concentration(mg/kg)
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
☐ Benzo(a)anthracene
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
S-1
S-2
S-3
Stations

I.



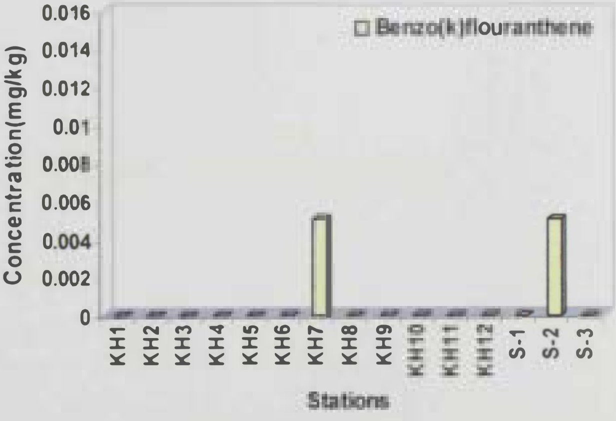
Concentration(mg/kg)
0
0.002
0.004
0.006
0.008
0.01
0.012
0.014
0.016
☐ Chrycene
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
S-1
S-2
S-3
Stations

J.



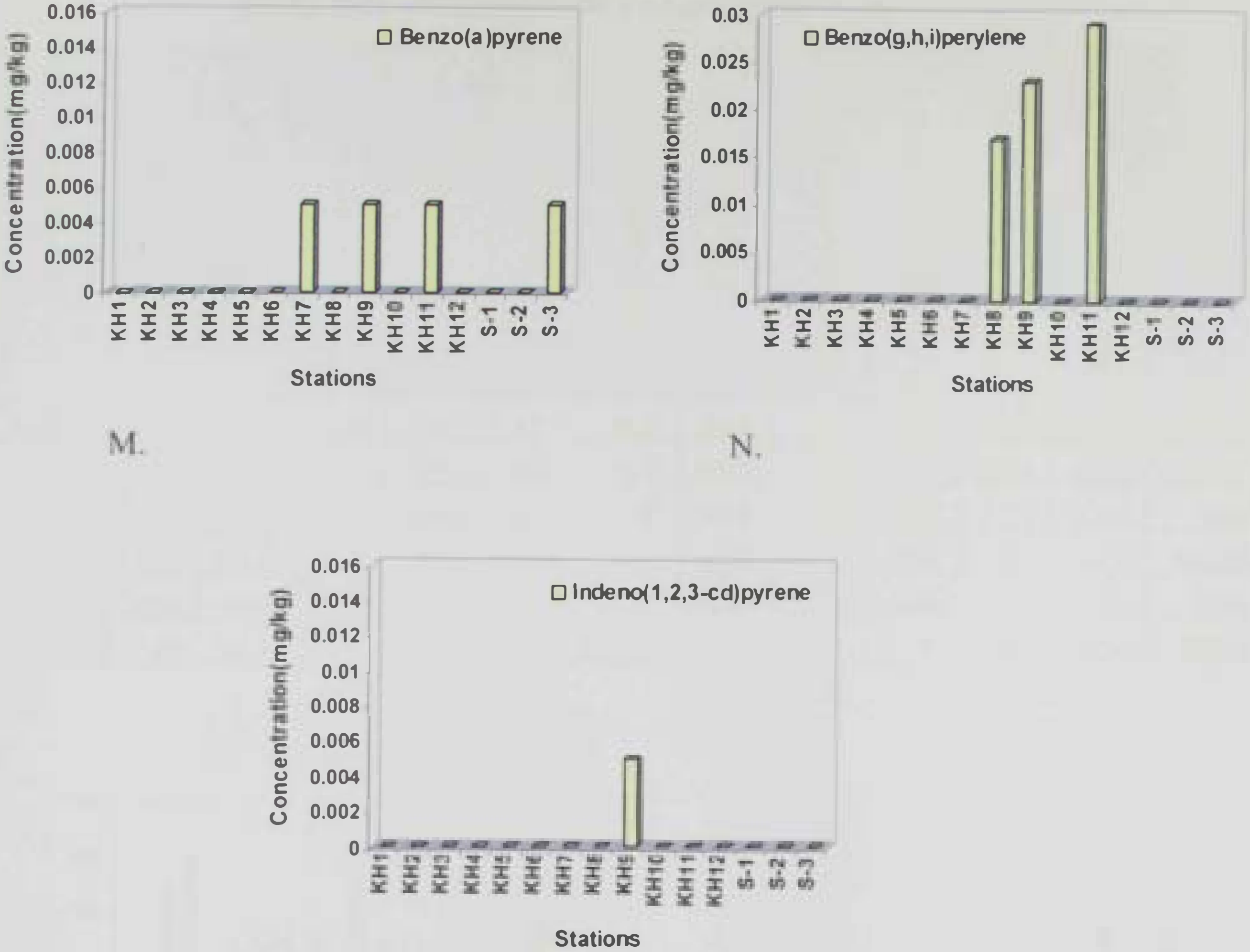
Concentration(mg/kg)
0
0.002
0.004
0.006
0.008
0.01
0.012
0.014
0.016
0.018
0.02
☐ Benzo(b)flouranth
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
S-1
S-2
S-3
Stations

K.



Concentration(mg/kg)
0
0.002
0.004
0.006
0.008
0.01
0.012
0.014
0.016
☐ Benzo(k)flouranthene
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
S-1
S-2
S-3
Stations

L.



M.

N.

O.

Fig. 4.6: Concentrations of Polycyclic Aromatic Hydrocarbon compounds (PAHs) mg/kg in each station.

Table 4.4: Concentrations of Polycyclic Aromatic Hydrocarbon compounds (PAHs mg/kg) in the oil samples collected from Gulf of Oman.

Stations	Flourane	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo(a)anthracene	Chrycene	Benzo(b)flouranthene	Benzo(k)flouranthene	Benzo(a)pyrene	Benzo(g,h,i)perylene	Total PAHs
Oil-1	7.96	91.8	0.38	101	47.1	26.9	11.3	3.6	2.02	1.59	5.64	299.3
Oil-2	10.4	113	ND	45.1	48.3	19.8	20.3	14.4	2.47	2.99	4.91	281.7
Oil-3	4.44	75.9	ND	34.2	32.2	9.98	25.5	4.39	1.64	1.39	4.34	194
Oil-4	ND	20.8	ND	7.12	6.28	2.57	4.98	1.34	ND	ND	1.19	44.28
Oil-5	4.56	41.9	ND	18.4	13.8	4.27	6,48	3.39	1.06	1.44	2.38	91.2
Oil-6	7.17	74.4	ND	33.1	30.4	4.33	22.9	2.7	1.78	1.21	1.51	179.5

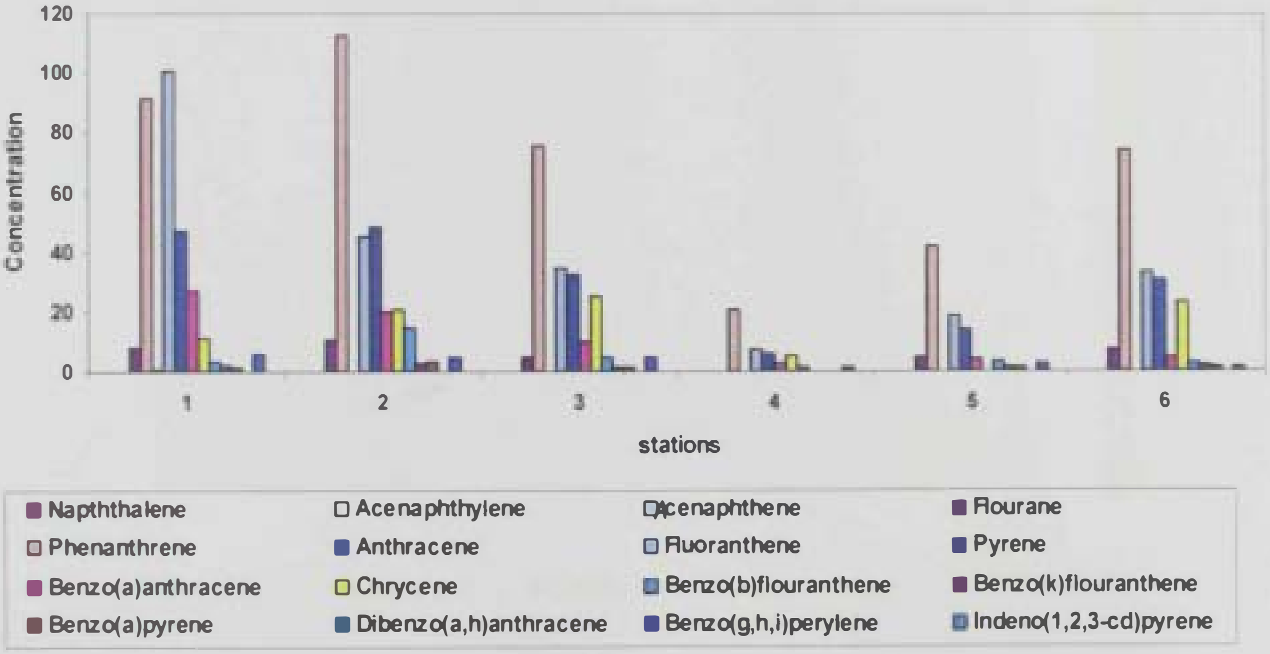


Fig. 4.7: Concentrations of Polycyclic Aromatic Hydrocarbon compounds (PAHs mg/kg) in the oil samples collected from Gulf of Oman.

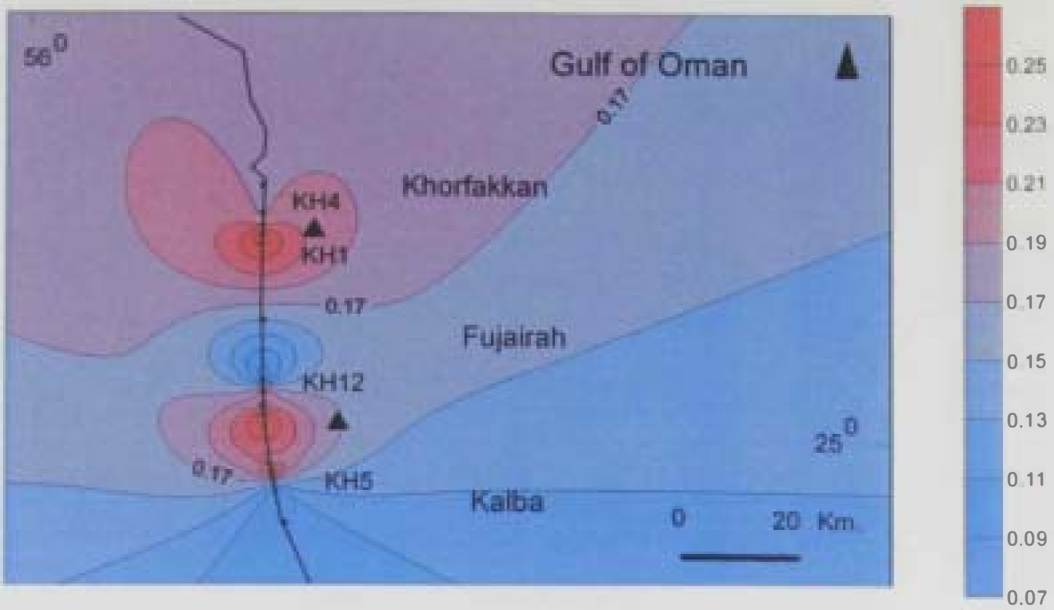


Fig. 4.8: Distribution map of TPAHs mg/kg in the investigated area.

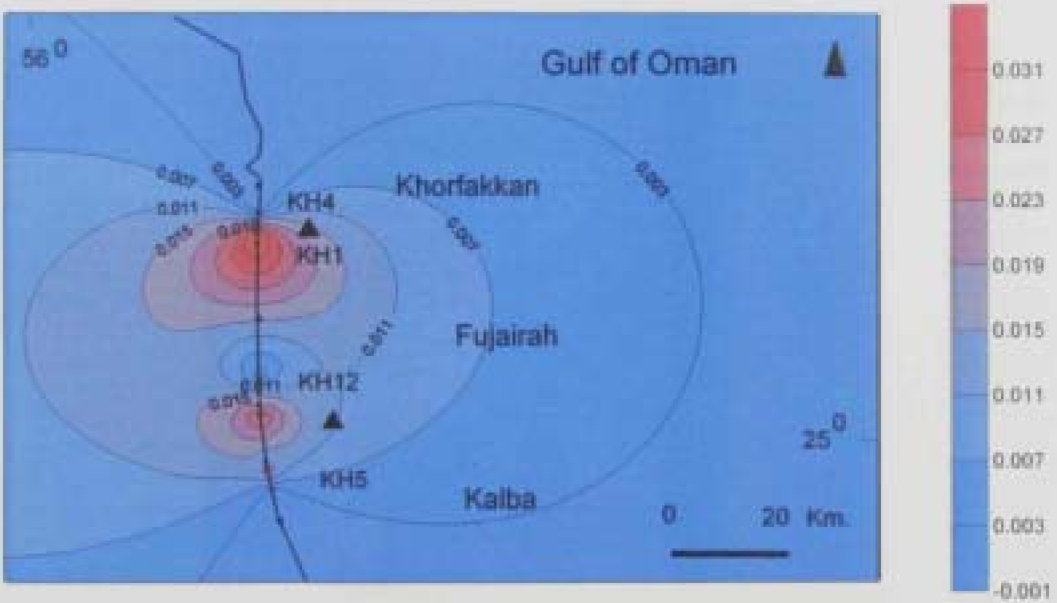


Fig. 4.9: Distribution map of Naphthalene (mg/kg) in eastern side of the UAE.

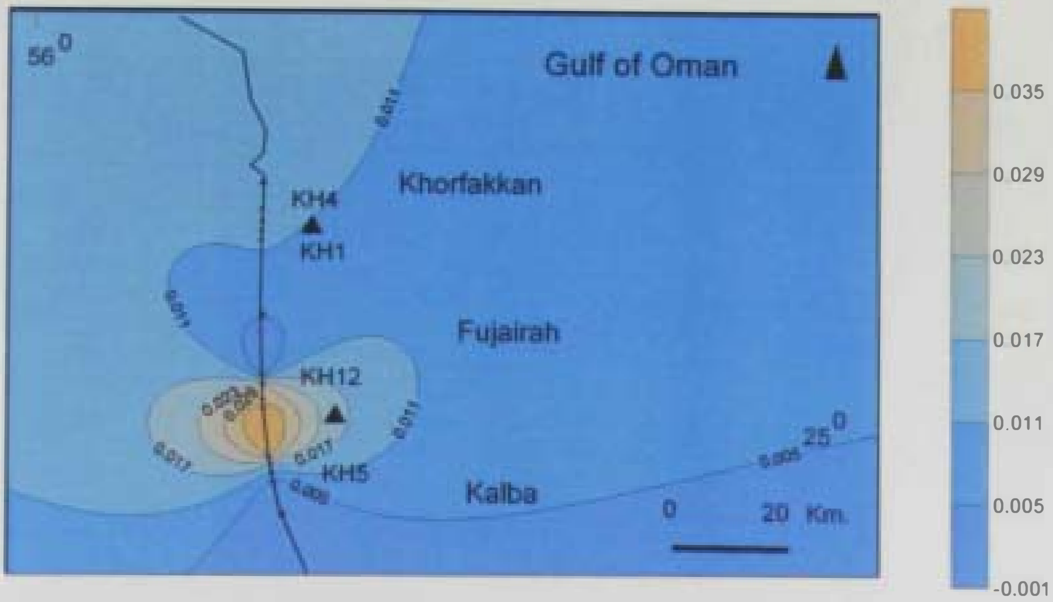


Fig. 4.10: Distribution map of Acenaphthylene (mg/kg) in eastern side of the UAE.

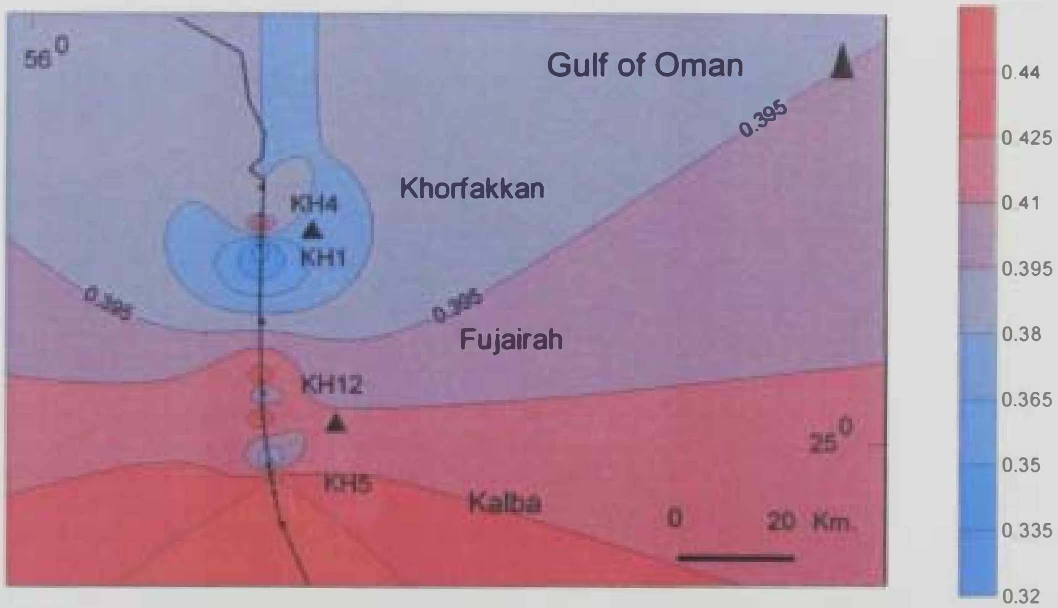


Fig. 4.11: Distribution map of Acenaphthene (mg/kg) in eastern side of the UAE.

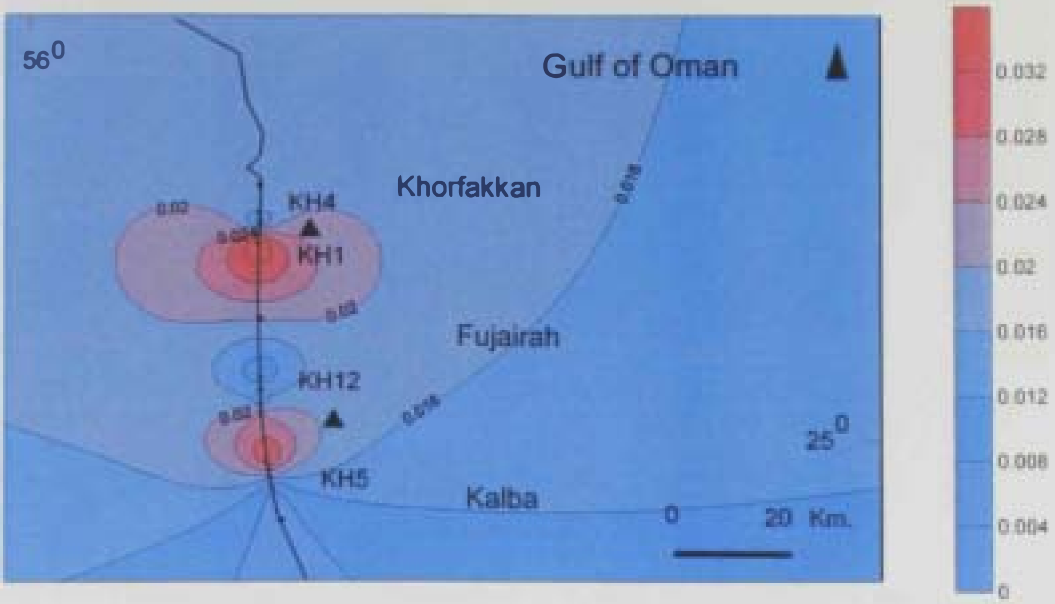


Fig. 4.12: Distribution map of Flourane (mg/kg) in eastern side of the UAE.

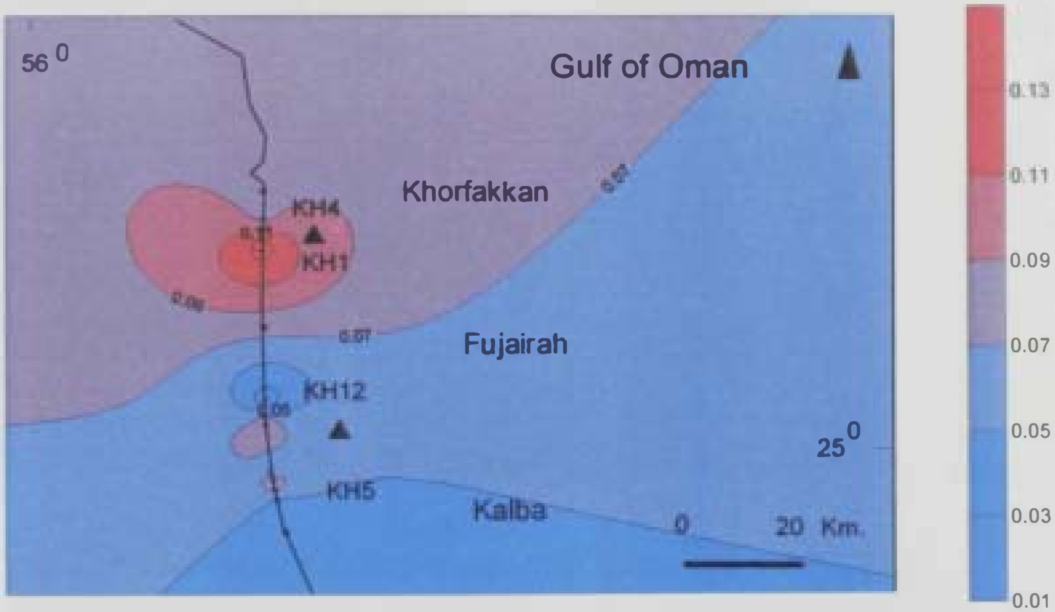


Fig. 4.13: Distribution map of Phenathrane (mg/kg) in eastern side of the UAE.

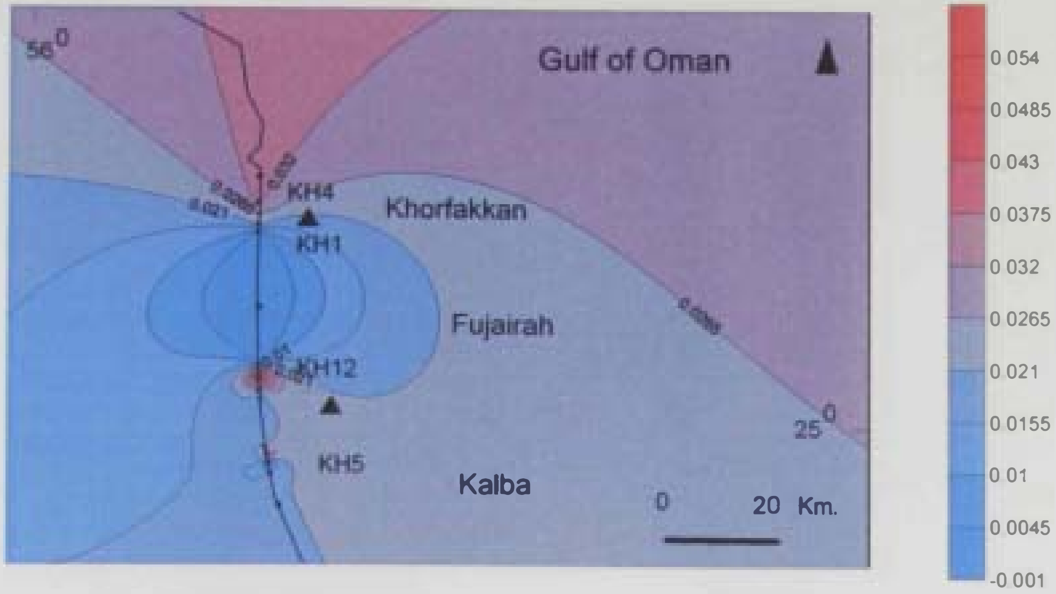


Fig. 4.14: Distribution map of Fluoranthene (mg/kg) in eastern side of the UAE.

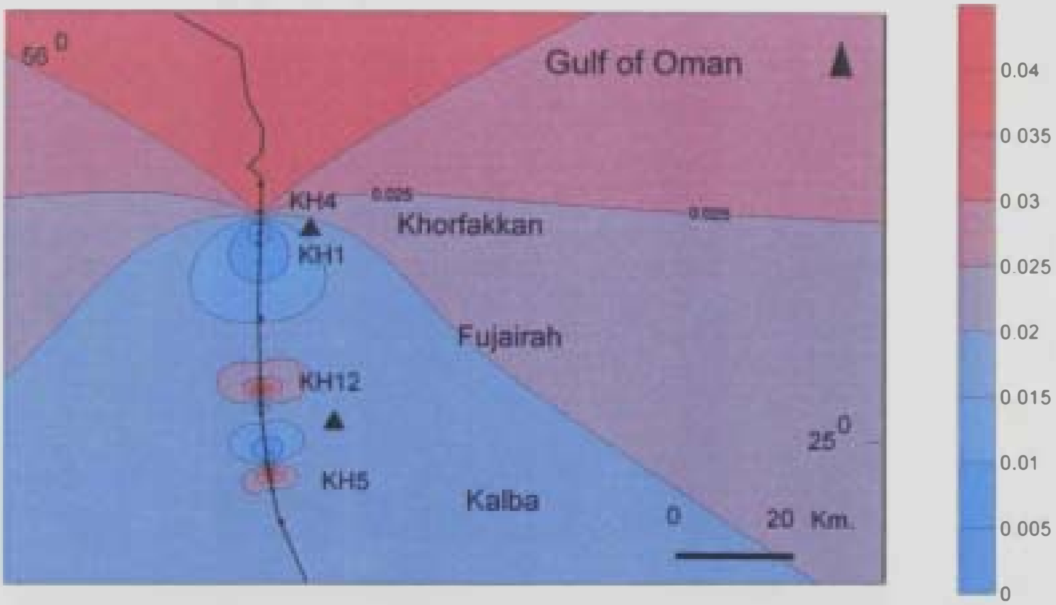


Fig. 4.15: Distribution map of Pyrene (mg/kg) in eastern side of the UAE.

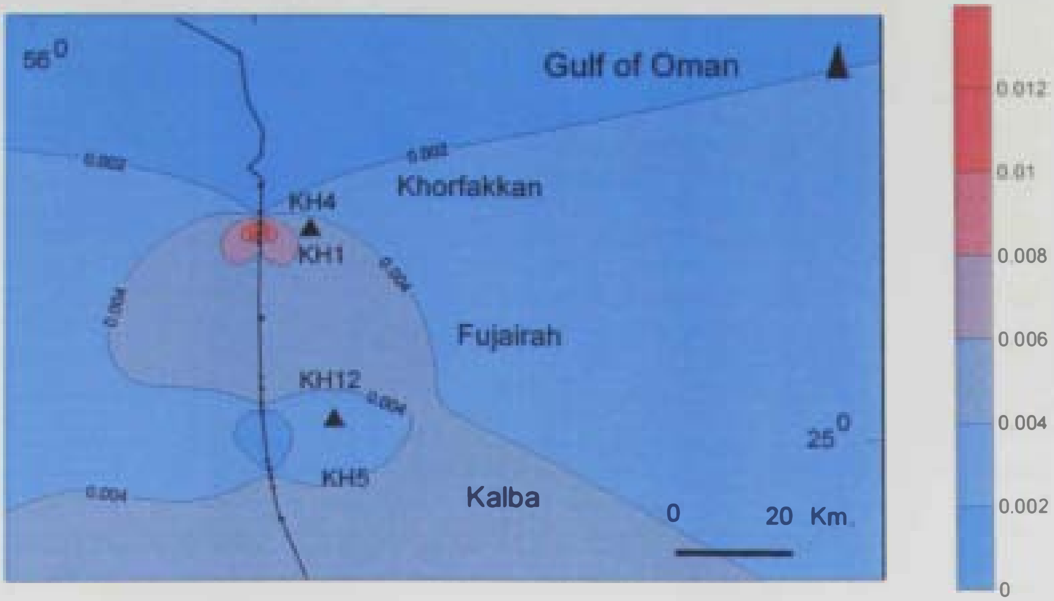


Fig. 4.16: Distribution map of Benzo (a) Anthracene (mg/kg) in eastern side of the UAE.

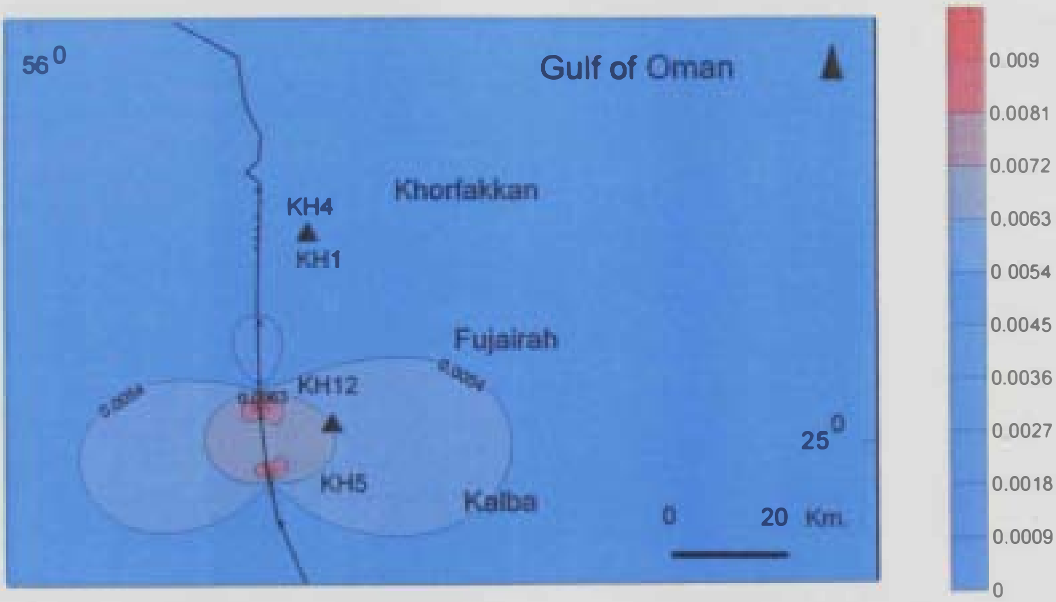


Fig. 4.17: Distribution map of Chrycene (mg/kg) in eastern side of the UAE.

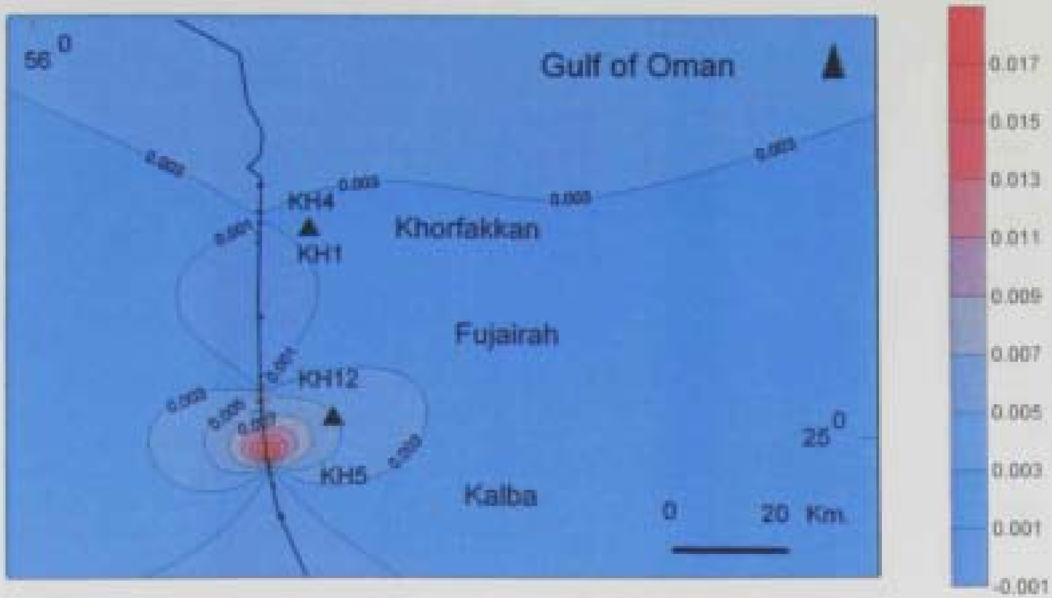


Fig. 4.18: Distribution map of Benzo (b) Fluoranthene (mg/kg) in eastern side of the UAE.

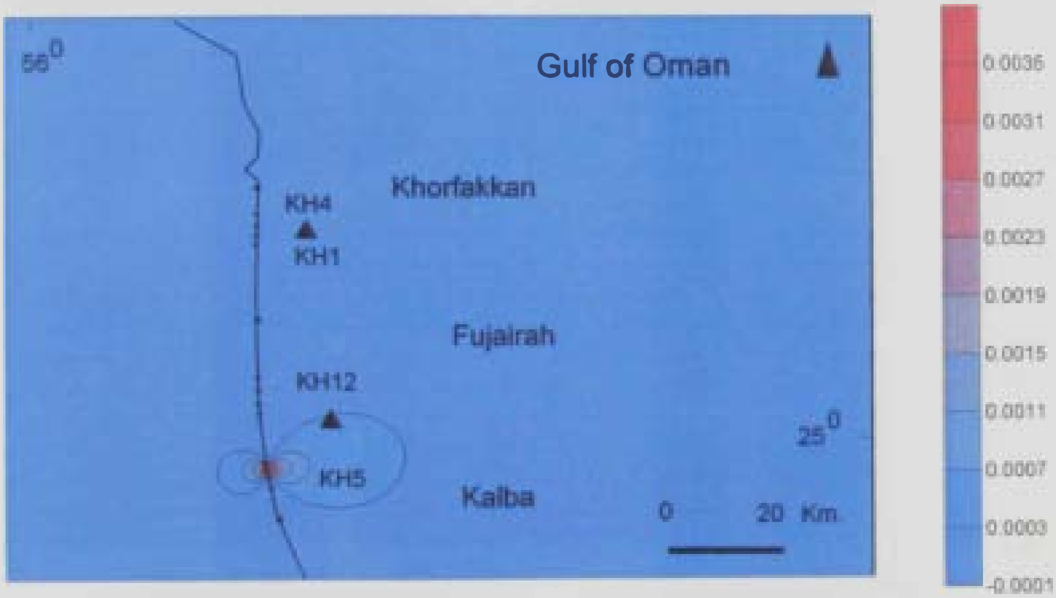


Fig. 4.19: Distribution map of Benzo (k)Flouranthene (mg/kg) in eastern side of the UAE.

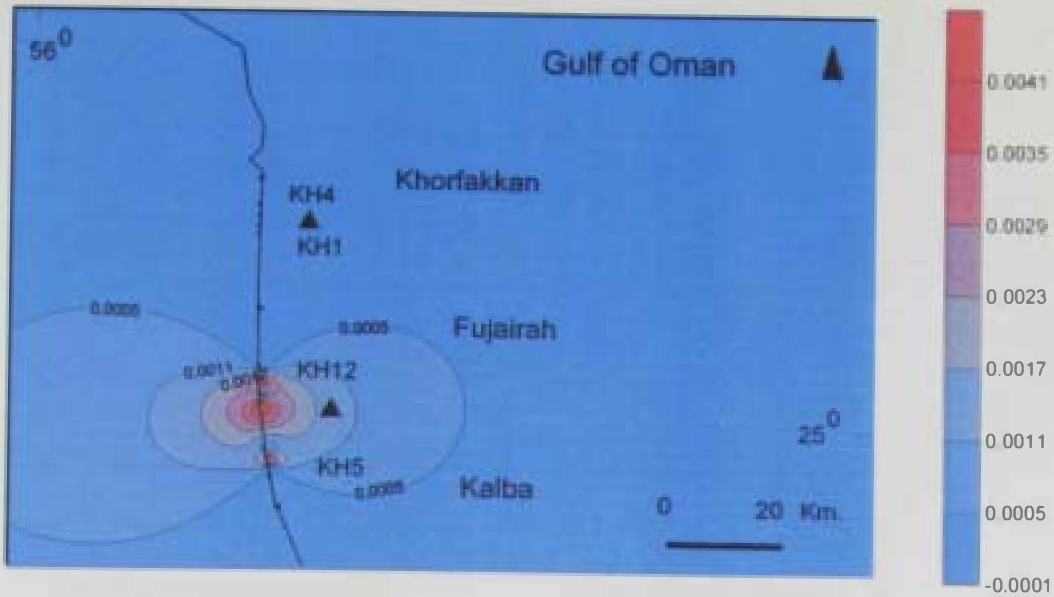


Fig. 4.20: Distribution map of Benzo (a) Pyrene (mg/kg) in eastern side of the UAE.

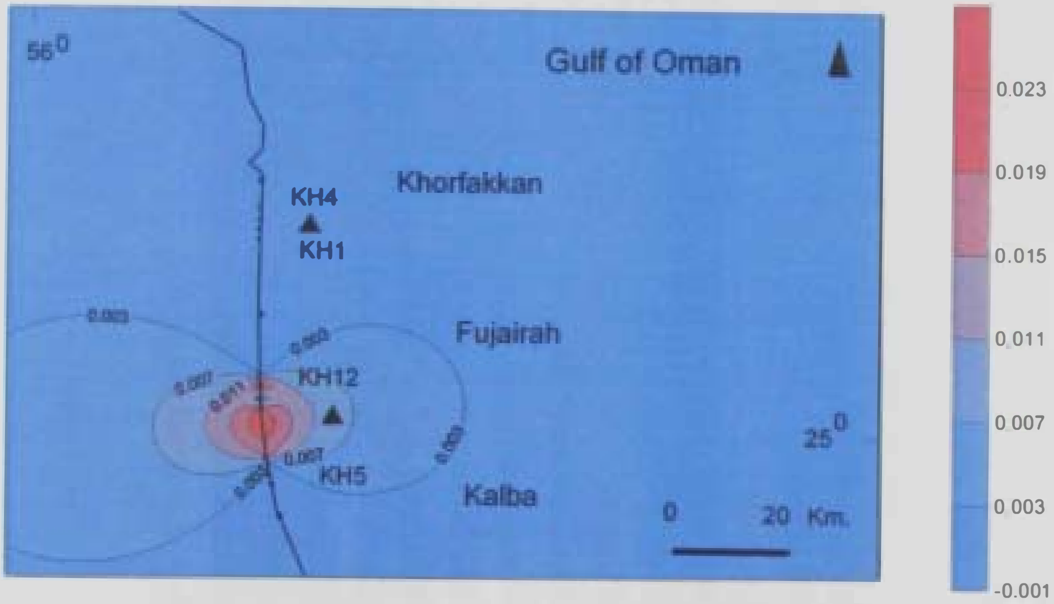


Fig. 4.21: Distribution map of Benzo (g,h,i)Perylene (mg/kg) in eastern side of the UAE.

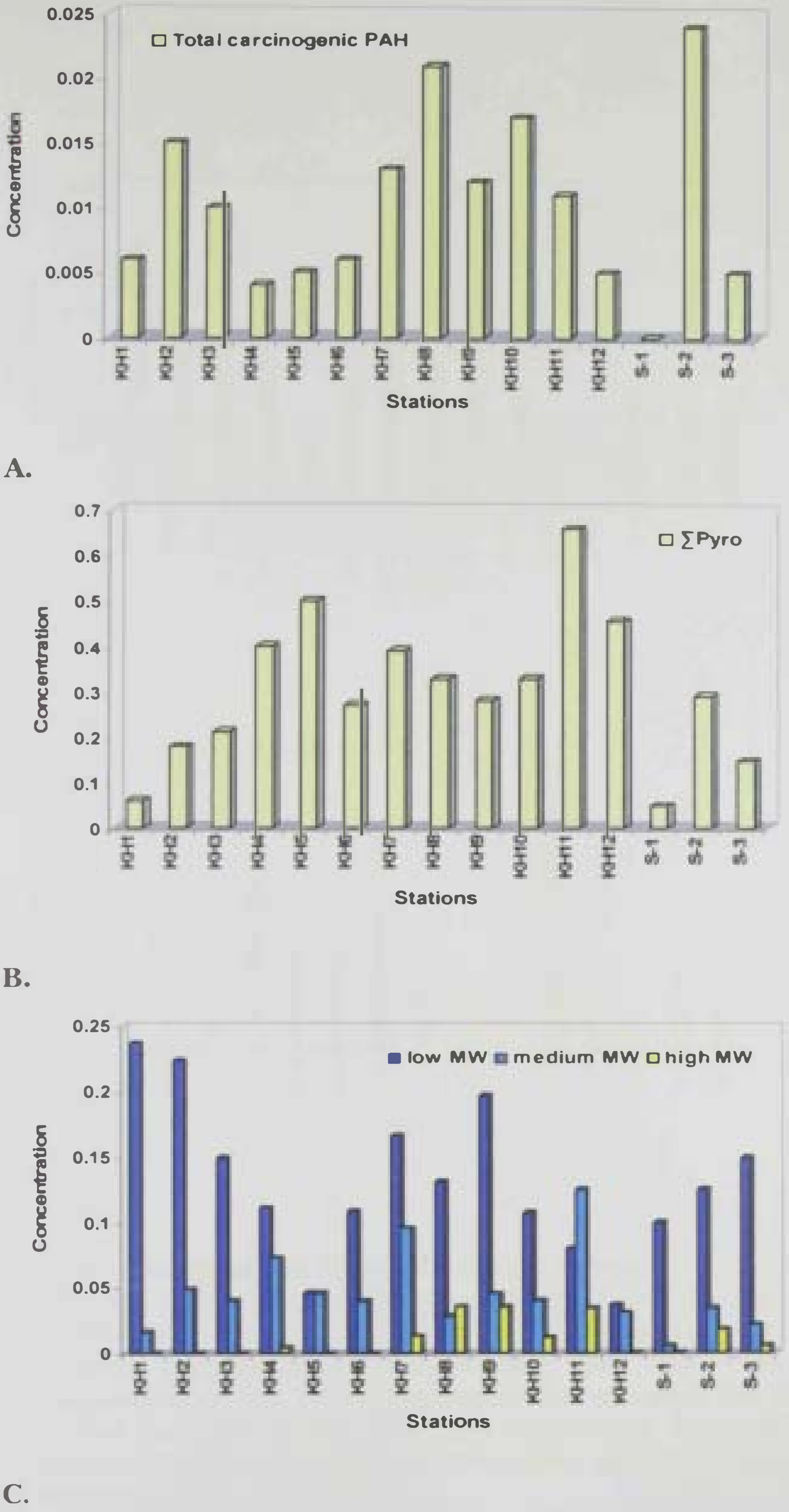


Fig. 4.22: distribution of some ratios, A. The total carcinogenic PAHs, B. ∑Pyro ratio And C. The low, medium and high molecules weight of PAHs in each stations of the study area.

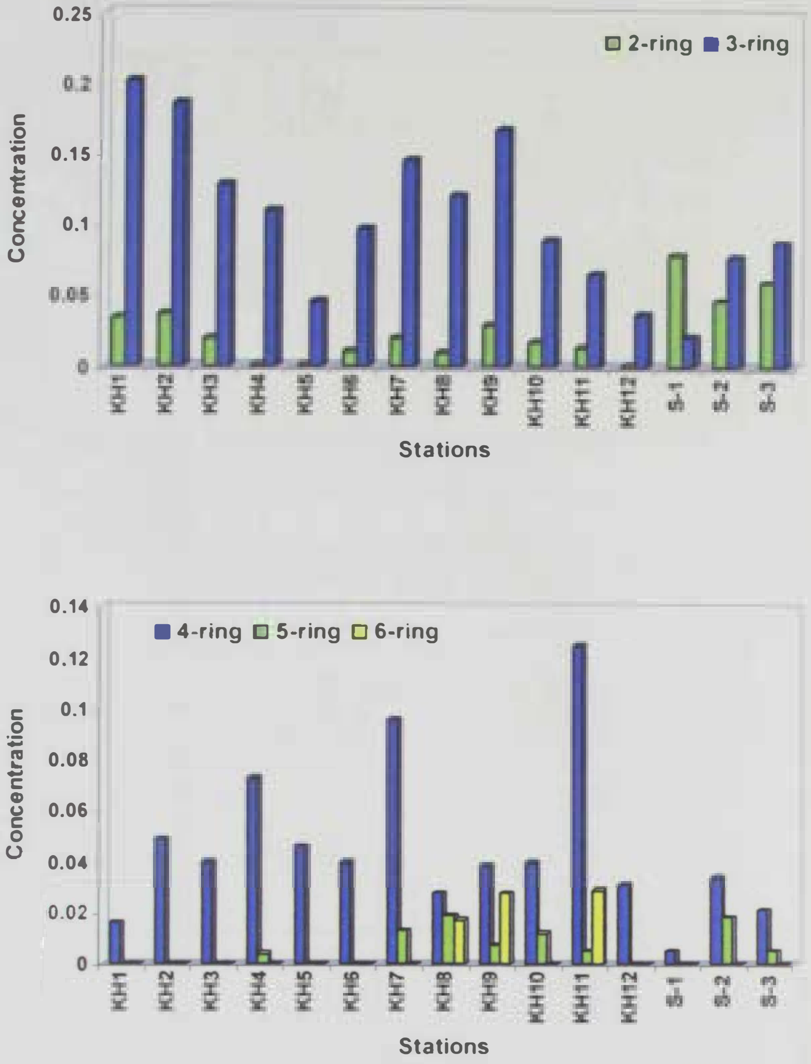


Fig. 4.23 : Concentrations of two, three ,four, five and six ring and total PAHs in the sampling stations of the eastern side of U.A.E. two ring PAHs include naphthalene; three ring PAHs include acenaphthylene, acenaphthene, fluorine, phenanthrene and anthracene; four ring PAHs include fluoranthene, pyrene, benzo(a)anthracene and chrysene; five ring PAHs include benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene and dibenzo(a,h)anthracene; six ring PAHs include indeno(1,2,3,cd)pyrnen and benzo(g,h,i)Perylene.

Table 4.5: Polycyclic Aromatic Hydrocarbons (PAHs) ratio for coastal and marine sediments samples in the eastern side of the UAE.

Stations	Location	Total- PAHs	Fluo/Fluo+P	BaA/(BaA+Chry)	P/(P+A)	Indeno/Indeno+BghiP)	∑PAHCARC	∑Pyro	low MW	medium MW	high MW
KH1	Coastal	0.253	0	0.5	1	0	0.006	0.06	0.237	0.016	0
KH2	Coastal	0.273	1	0.75	1	0	0.015	0.179	0.224	0.049	0
KH3	Coastal	0.189	1	0.6	1	0	0.01	0.21	0.149	0.04	0
KH4	Coastal	0.188	0.48	0	1	0	0.004	0.4	0.111	0.073	0.004
KH5	Coastal	0.092	0.5	0.5	1	0	0.005	0.5	0.046	0.046	0
KH6	Coastal	0.148	0	0.5	1	0	0.006	0.27	0.108	0.04	0
KH7	Coastal	0.275	0.46	0	0.9	0	0.013	0.39	0.166	0.096	0.013
KH8	Coastal	0.195	1	0.2	1	0	0.021	0.328	0.131	0.028	0.036
KH9	Coastal	0.277	0.5	0	1	0.17	0.012	0.28	0.197	0.045	0.035
KH10	Coastal	0.159	0.8	0.3	1	0	0.017	0.327	0.107	0.04	0.012
KH11	Coastal	0.239	0.58	0.5	1	0	0.011	0.66	0.08	0.125	0.034
KH12	Coastal	0.068	0	0.55	1	0	0.005	0.455	0.037	0.031	0
S1	Marine	0.105	0	0	1	0	0	0.047	0.1	0.005	0
S2	Marine	0.177	1	0.4	1	0	0.024	0.29	0.125	0.034	0.018
S3	Marine	0.175	0.5	0	1	0	0.005	0.148	0.149	0.021	0.005

Total PAHs=∑ PAHs, **Fluo/Fluo+P**= Fluoranthene/ (Fluoranthene+Pyrene), **BaA/(BaA+Chry)**= Benzo(a)Anthracene/(Benzo(a) Anthracene +Chrycene, **P/(P+A)**= Phenanthrene/ (Phenanthrene +Anthracene), Indeno/Indeno+BghiP)= Indeno(1,2,3-c,d)pyrene/(Indeno(1,2,3-c,d)pyrene +Benoz(ghi)perylene), **∑Pyro**= MW>178/total PAHs , **Low MW**= Napththalene, Acenaphthylene, Acenaphthtene, Flourane, Phenanthrene and Anthracene, **Medium MW**= Fluoranthene, pyrene, BaA, and chrycene, **High MW**= BbF,BkF,BaP,Di(a,h)A,B(ghi)P, In(1,2,3,cd)P.**∑PAH$_{CARC}$** = Benzo(a)Anthracene+benzo(b)Fluoranthene + indeno(1,2,3_c,d)Pyrene+dibenzo(a,h)Anthracene.

4.4 Aliphatic Hydrocarbon

The concentrations of the total aliphatic hydrocarbons for the studied stations vary from 1.0 µg/g at KH4 to 0.95 µg/g at KH2 for coastal samples. For marine sediments samples, the total aliphatic hydrocarbons are ranging from 2.5 µg/g to 4.1 µg/g, while they range from 0.3 µg/g to 1.4 µg/g for spilled oils (Table 4.6). These values are considered relatively equal to or less than other values recorded in similar areas in UAE and other Gulf countries (Table 2.3). For instance, the values for Akkah head and Akkah beach in eastern coast of UAE were ranging from 1.1 µg/g to 0.4 µg/g. In the Bahrain at PAPCO refinery, the value was 4.30 µg/g and in Qatar at Ras Al Nouf it was 3.30 µg/g indicating important anthropogenic inputs such as oil spill and marine transportation activities (Tolosa et al., 2005). The mapping shows total n-alkanes increasing toward the northern part of the investigated areas (around Khorfakkan and Fujairah) (Fig. 4.24). According to the Wang, (2003) the measured TPH in samples by GC-FID chromatograms can provide a distribution pattern of petroleum hydrocarbons (carbon range and profile of UCM), fingerprints of the major oil components (individual resolved n- alkanes and major isoprenoids), and information on the weathering extent of the spilled oil. Comparing biodegradation indicators such as n-C_{17} /pristine and n-C_{18} /phytane for the spilled oil with the source oil can be also used to monitor the effect of microbial degradation on the loss of hydrocarbons at the spill site. Crude oil compositions vary widely (n-alkane, aromatic and ashpaltenic compounds) depending on the sources of carbon, geologic environment, and reservoir. Fig 4.27, Fig.4.28 and Fig. 4.29 shows GC-FID chromatograms for six samples of oil spills and sixteen samples of coastal and marine sediments (Wang et al., 2004).Within all the studied GC fingerprints, the dominant peaks occurred mainly at C_{29} and C_{31} for most coastal stations. The dominant peaks for the marine sediments occurred at C_{30}, C_{28}, and C_{34}. The C_{30} and C_{32} are the most dominant peaks for the oil spill samples, which indicate marine oil spill sources (Medeiros et al., 2005).

4.4.1 < C_{24} *% ratio (∑C12-C_{23}/ total n-alkanes):* the short-chain (C< 24) n – alkanes profile is relatively low at all stations indicating petrogenic sources. In contrast, the long – chain (C>25) n-alkanes profiles occurred in variable concentrations at most coastal sediments from KH1 to KH12 (Table 4.6). These long chain compounds are characterized by dominant peaks at C_{31} and high odd to even carbon number preference CPI (Medeiros et al., 2005).

4.4.2 ***n- C_{16} ratio ($\sum$ total n-alkanes/n-C_{16}):*** this ratio tends to be small < 50 for petroleum contaminated samples, while it is > 50 for biogenically contaminated samples (Commendatore and Esteves, 2003). Within the study area, most stations indicate more petrogenic rather than biogenic contribution of hydrocarbons contaminants exception two stations were recorded more than (> 50), which indicted biogenic pollution at KH2 (68.44) for coastal sediment and S2 (209.9) for marine sediment (Table 4.6).

4.4.3 ***alk_{terr} % ratio {(C_{27}+C_{29}+C_{31}+C_{33}) / total n - alkanes}***. The percentage of the most abundant n - alkanes related to biogenic terrestrial sources are (C_{27}, C_{29}, C_{31}, and C_{33}) and referred here as **alk_{terr}** (Medeiros at el., 2005). Within the study area, **alk_{terr}** has low values at almost all coastal and marine stations. It ranges from 0.05 % to 0.45 % for marine and coastal sediments respectively (Table 4.6). This may indicate multi-source contaminants for the study area (the harbor of Fujairah and Khorfakkan).

4.4.4 ***Carbon preference index (CPI)***: the **CPI** has been a useful parameter for estimating biogenic or anthropogenic contributions since it was first put forward. The n - alkanes from higher plants waxes show a pronounced odd carbon number preference, while fossil fuel and microbial hydrocarbons exhibit CPI ≈ 1. The carbon number ranges used for calculations are different among different researchers. In the present study, the CPI for n - alkanes was calculated as follows: **CPI_1** (***Whole range for n-alkanes***) = **$\sum$ (C_{13}-C_{35})/$\sum$ (C_{14}-C_{36})**; **CPI_2** (***Petrogenic n-alkanes***) = **$\sum$ (C_{13}-C_{23})/$\sum$ (C_{14}-C_{24})** and **CPI_3** (***Higher plant wax n-alkanes***) =**$\sum$ (C_{25}-C_{35})/$\sum$ (C_{26}-C_{36})** (Zhu et al., 2004). Within the study area, the **CPI_1** of coastal sediments samples was ranging from 0.89 to 1.35, and it's vary from 0.5 to 1.06 for the marine sediments samples, reflecting similar petrogenic sources of pollution rather than biogenic. The **CPI_2** for the coastal sediments samples was ranging from 0 to 0.89, while for the marine sediments it was ranging from 0.6 to 0.9. Thus, most **CPI_2** values were closed to 1 that indicated petrogenic sources rather than biogenic sources. Finally **CPI_3** values varied between 0.8 to 1.4 for coastal sediments, while it is ranged from 0.3 to

1.3 for the marine sediments, suggesting higher plants waxes as the predominant sources for obtained n- alkane range of the studied samples (Table 4.6 & Fig. 4.26 A).

4.4.5 ***The petrogenic /biogenic ratio***: the values >1 indicate petrogenic hydrocarbon input, but the biogenic input show as <1 values (Colombo, et al, 2005a). The petrogenic /biogenic ratio has important role to explain the sources of n- alkanes from bio or petrogenic origin. At all the studied stations, this ratio is ≈ 1, which may reflect anthropogenic (petrogenic) rather than biogenic sources of n-alkanes. So, spilled oils near Fujairah and Khorfakkan harbors have more contribution of hydrocarbon contaminants rather than biogenic and land-based sources (Table 4.6 & Fig. 4.26 B). The mapping shows an increasing trend of petrogenic sources toward northern part of the investigated area (Fig. 3.25) which is coincident with the marine currents in that area (S-N).

4.4.6 ***C_{17}/Pr (n-C_{17}/pristine) and C_{18}/Ph (n-C_{18}/phytane)***: these ratios used to indicate microbial degradation. Biodegradation for n-alkane are faster than those of Pr and Ph, therefore the lower indices suggested the presence of degraded oil and the higher values indicate fresh oil input. All studied coastal and marine samples have zero values except KH1 (0.65) that may reflect the level of biodegradation and the natural climate at this region (high temperature and arid conditions most of the year) (Table 4.6).

4.4.7 ***(Pr/Ph) ratio*** **Pristane/Phytane:** values approaches close ≈ 1 indicate petroleum hydrocarbon sources while values from 1.4 to 6.7 indicate biogenic hydrocarbons. The ***(Pr/Ph)*** ratio has been proposed as a measure of the redox potential of sediments as well as a way to identify oil spill and tar balls (Pena-Mendez et al., 2001 & Zhu et al., 2005).

The ***(Pr/Ph)*** ratio for the studied samples ranged from 0 to 0.4 at KH2 for coastal sediment, while the value of marine sediment samples ranged from 0.1 to 0.8 (Table 4.6). This ratio shows that biodegradation was very high for coastal sediments, and was low for marine sediments due to elution of Pr and Ph from oil spill samples (Medeiros et al., 2005).

4.4.8 ***The (TAR$_{HC}$) ($C_{27}+C_{29}+C_{31}$)/ ($C_{15}+C_{17}+C_{19}$):*** the Tar$_{HC}$ ratio is the ratio between the concentration of long chain n - alkanes to short chain n - alkanes. The short chain is attributed to plankton or marine petrogenic sources, but the long chain indicates terrestrial sources. When aquatic sources predominate, the terrestrial to aquatic ratio **(TAR)** decreases to values of < 1 (Fabbri et al., 2005).

Within the study areas the TAR$_{HC}$ values reported at Table (4.6) and depicted at Fig. (4.26 C). This ratio is ranging from 0 to 59.83. The highest value occurs for the coastal sediment samples at KH1, KH2, and KH8. But for the marine sediment samples, the value of TAR$_{HC}$ is ranging from 3.9 to 5.1 at S1, S2, and S3. Also this ratio indicates higher concentration of long chain alkanes than short chain, which reflects terrestrial plant sources rather than plankton sources that derive from Fujairah and Khorfakkan harbors and other industrial activities.

4.4.9 ***LHC/SHC (long chain hydrocarbon $C_{27}+C_{29}+C_{31}$/ short chain hydrocarbon $C_{17}+C_{19}$):*** this ratio used to investigate macrophyte and phytoplankton dominated trends (Silliman and Schelske, 2003). In the study area, LHC/SHC ratios ranged from 0.0 at most coastal stations such as KH3, KH4, KH5, KH6, KH7, KH9, KH10, KH11, and KH12 to 59.83 at (KH1), 13.1 at (KH2), and 19.1 at (KH8), while for the marine sediment samples, the value was from 3.9 at (S3) to 6.7 at (S1). This indicates predominance of long chain n - alkanes rather than short chain n- alkanes. This may reflect petrogenic sources (oil spill) rather than biogenic sources (Table 4.6 & Fig. 4.26 D).

4.4.10 ***LHC/TOC and SHC/TOC ratio:*** the long chain n- alkanes are considered to be recalcitrant hydrocarbons that typically resist biodegradation, LHC to TOC. This ratio used to indicate the input of land derived organic matter. Short chain n-alkanes that stem from algae are more sensitive to biodegradation than long – chain n- alkanes. The ratio of SHC to TOC is used for this study to denote phytoplankton input and to evaluate the extent of microbial degradation of organic matter. It's represented as: SHC/TOC = ($C_{17}+C_{19}$)/TOC. (Silliman and Schelske, 2003). In the study area, LHC/TOC ratio was ranged from 0.1 at (KH2) to 6.8 at (KH7) for the coastal sediment samples, while the concentration for the marine sediments samples was ranging from 0.1 at (S2) to 0.5 at (S1). SHC/TOC ratios were ranged from 0.01 at

(KH2) to 0.22 at (KH8) for the coastal sediments samples. While the values for the marine sediment samples were ranging from 0.01 at (S2) to 0.06 at (S1).

4.4.11 ***C_{29}/C_{27}, C_{31}/C_{27}, C_{31}/C_{29} n -alkanes ratio***: these ratios are given in Table 4.6. It's used to identify sources of oil spill. Within the study area, this ratio is often dominated by the C_{31} and C_{29} that indicates higher plant waxes rather than algae (Liu and Hung, 2005).

Table 4.6: Total aliphatic hydrocarbon and n-alkane concentrations, and selected aliphatic diagnostic criteria for the sediments collected in the eastern side of UAE.

Stations	Location	total *n*-alkanes	T/C_{16}	alk-terr	TAR_{HC}	C<24	petrogenic/biogenic	CPI_1	CPI_2	CPI_3
KH1	Coastal	0.98	0	0.32	59.83	0.00486	6.311	1.35	0.898	1.43
KH2	Coastal	0.95	68.44	0.36	13.152	0.0029	2	0.938	0.7	0.98
KH3	Coastal	0.99	0	0.449	0	0	0	1.03	0	1.079
KH4	Coastal	1.016	0	0.38	0	0.001025	0	0.92	0.536	0.95
KH5	Coastal	0.99	0	0.45	0	0	0	1.06	0	1.069
KH6	Coastal	0.99	0	0.449	0	0	0	1.05	0	1.057
KH7	Coastal	0.99	0	0.44	0	0	0	1.04	0	1.04
KH8	Coastal	0.97	0	0.37	19.168	0.0078	4.53	0.95	0.87	0.969
KH9	Coastal	0.99	0	0.44	0	0	0	0.91	0	0.9
KH10	Coastal	0.99	0	0.42	0	0	0	0.89	0	0.8
KH11	Coastal	0.99	0	0.38	0	0.00036	1.008	0.95	0.4	0.99
KH12	Coastal	0.99	0	0.44	0	0	0	0.96	0	0.96
S1	Marine	3.861	40.6	0.29	5.105	0.24	4.1	1.06	0.68	1.27
S2	Marine	4.198	209.9	0.056	5.13	0.0446	4.08	1.06	0.68	1.2757
S3	Marine	2.506	0	0.18	3.97	0.16	2.175	0.5	0.9	0.414

Total n- alkanes= $\sum$ *n*-alkanes ,**T/C_{16}**= ($\sum$ total *n* –alkanes/ *n*-C_{16}), **alk-$_{terr}$**= ($C_{27}+C_{29}+C_{31}+C_{33}$)/ total *n*-alkanes, **$TAR_{HC}$**= ($C_{27}+C_{29}+C_{31}$)/ ($C_{15}+C_{17}+C_{19}$), **C< 24**= ($\sum$C12-$C_{23}$/ total n-alkanes), **petrogenic/biogenic=** , **CPI_1** = $\sum$ (C_{13}-C_{35})/$\sum$ (C_{14}-C_{36}), **CPI_2** = $\sum$ (C_{13}-C_{23})/$\sum$ (C_{14}-C_{24}), **CPI_3** =$\sum$ (C_{25}-C_{35})/$\sum$ (C_{26}-C_{36})

Cont.

Stations	Location	C_{17}/Pr	C_{18}/Ph	Pr/Ph	dominant peak	LHC/SHC	LHC/TOC	SHC/TOC	C_{31}/C_{29}	C_{31}/C27	C_{29}/C_{27}
KH1	Coastal	0	1.538	0	C_{31},C_{30}	59.83	1.538	0.0257	21.98	23.8	1.08
KH2	Coastal	0	0	0.489	C_{29},C_{30}	13.152	0.138	0.01	0.8	2.314	2.736
KH3	Coastal	0	0	0	C_{31},C_{30}	0	1.732	0	1.13	1.6	1.424
KH4	Coastal	0	0	0	C_{31},C_{30}	0	2.238	0	1.055	3.519	3.33
KH5	Coastal	0	0	0	C_{31},C_{30}	0	5.157	0	1.171	1.58	1.35
KH6	Coastal	0	0	0	C_{31},C_{30}	0	0.945	0	1.11	1.489	1.34
KH7	Coastal	0	0	0	C_{31},C_{30}	0	6.839	0	1.08	1.466	1.35
KH8	Coastal	0	0	0	C_{31},C_{30}	19.168	4.282	0.223	1.007	2.208	2.19
KH9	Coastal	0	0	0	C_{32},C_{31}	0	4	0	1.45	2.05	1.408
KH10	Coastal	0	0	0	C_{32},C_{31}	0	1	0	1.175	1.7	1.448
KH11	Coastal	0	0	0	C_{31},C_{30}	0	1.4	0	1.027	1.407	1.36
KH12	Coastal	0	0	0	C_{31},C_{30}	0	4.437	0	1.077	1.624	1.507
S1	Marine	4.12	0.88	0.128	C_{29},C_{30},C_{31}	6.716	0.5	0.06	0.056	0.057	1.009
S2	Marine	4.2	0.857	0.125	C_{42},C_{43}	6.25	0.109	0.0127	0.056	0.0566	1.009
S3	Marine	0	0	0.87	C_{28}	3.97	0.28	0.03	0.75	0.758	1.006

C_{17}/Pr= C_{17}/pristine, **C_{18}/Ph=** C_{18}/phytane, **Pr/Ph=** Prastane/ Phytane, **dominant peak, LHC/SHC=** $(C_{27}+C_{29}+C_{31})$ / $(C_{17}+C_{19})$, **LHC/TOC=** $(C_{27}+C_{29}+C_{31})$/TOC, **SHC/TOC=** $(C_{17}+C_{19})$/TOC, **C_{31}/C_{29}, C_{31}/C_{27}, C_{29}/C_{27}.**

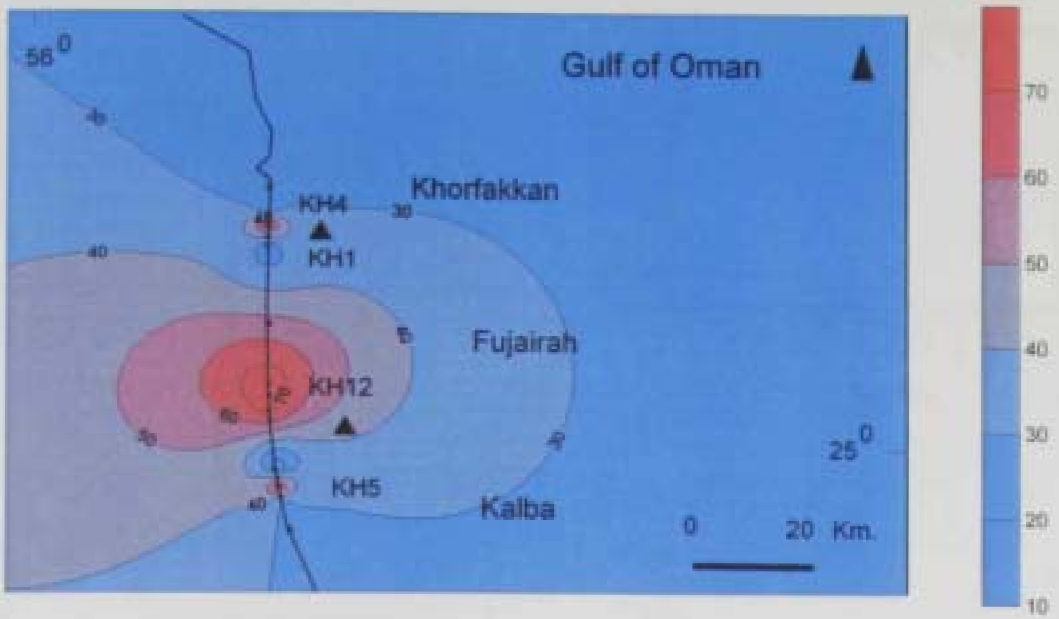


Fig. 4.24: Distribution of Total n- alkanes in the investigated area.

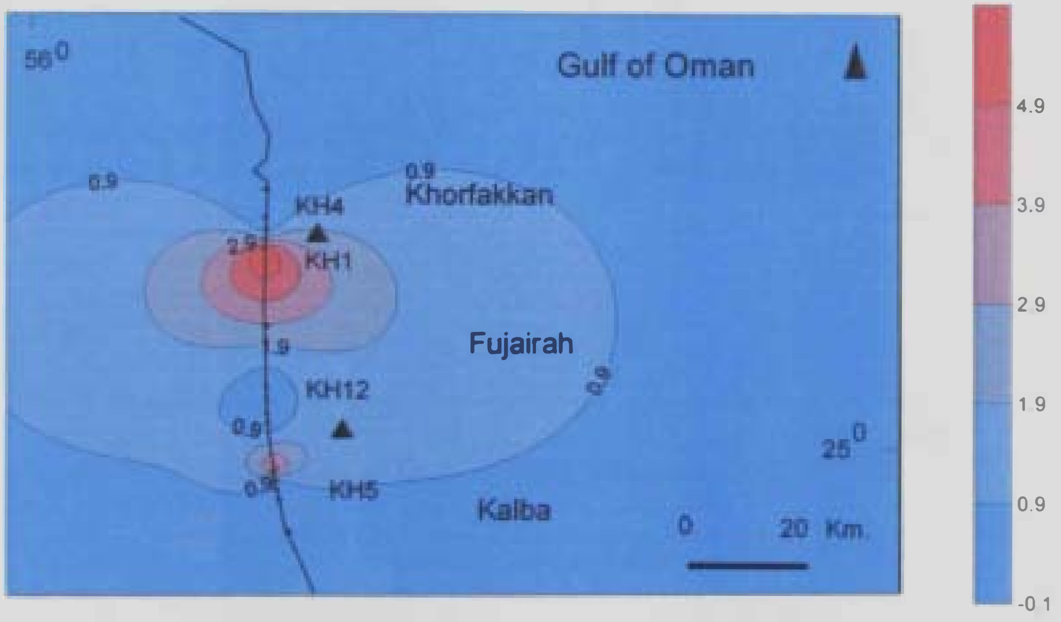
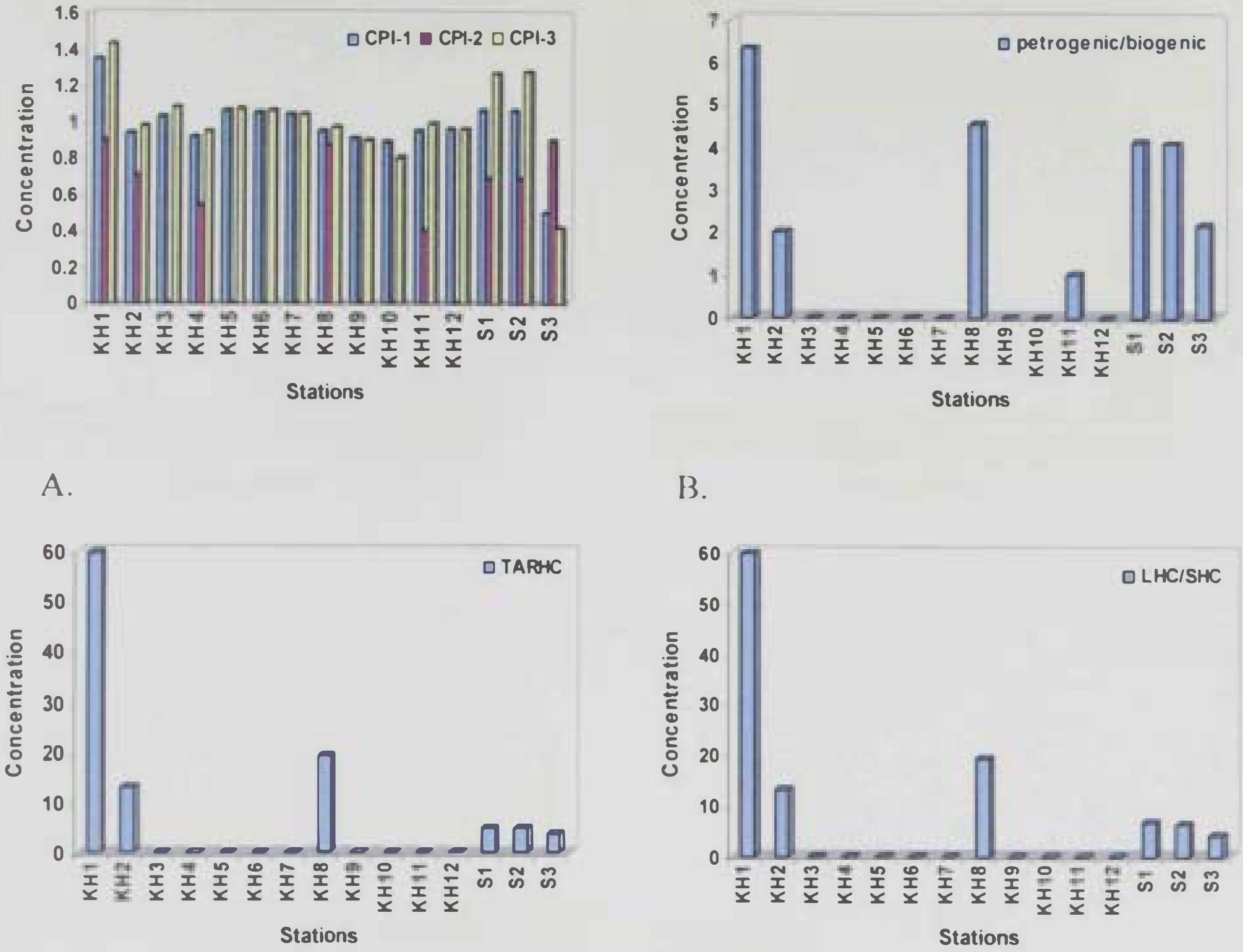


Fig. 4.25: Distribution of petrogenic ratio in the investigated area.



A.

B.

C.

D.

Fig. 4.26: A. Concentration of carbon preference index CPI in investigated areas. B. Concentration of petrogenic/ biogenic ratio. C. Concentration of TARHC ratio. D. concentration of LHC/SHC ratio in the study area.

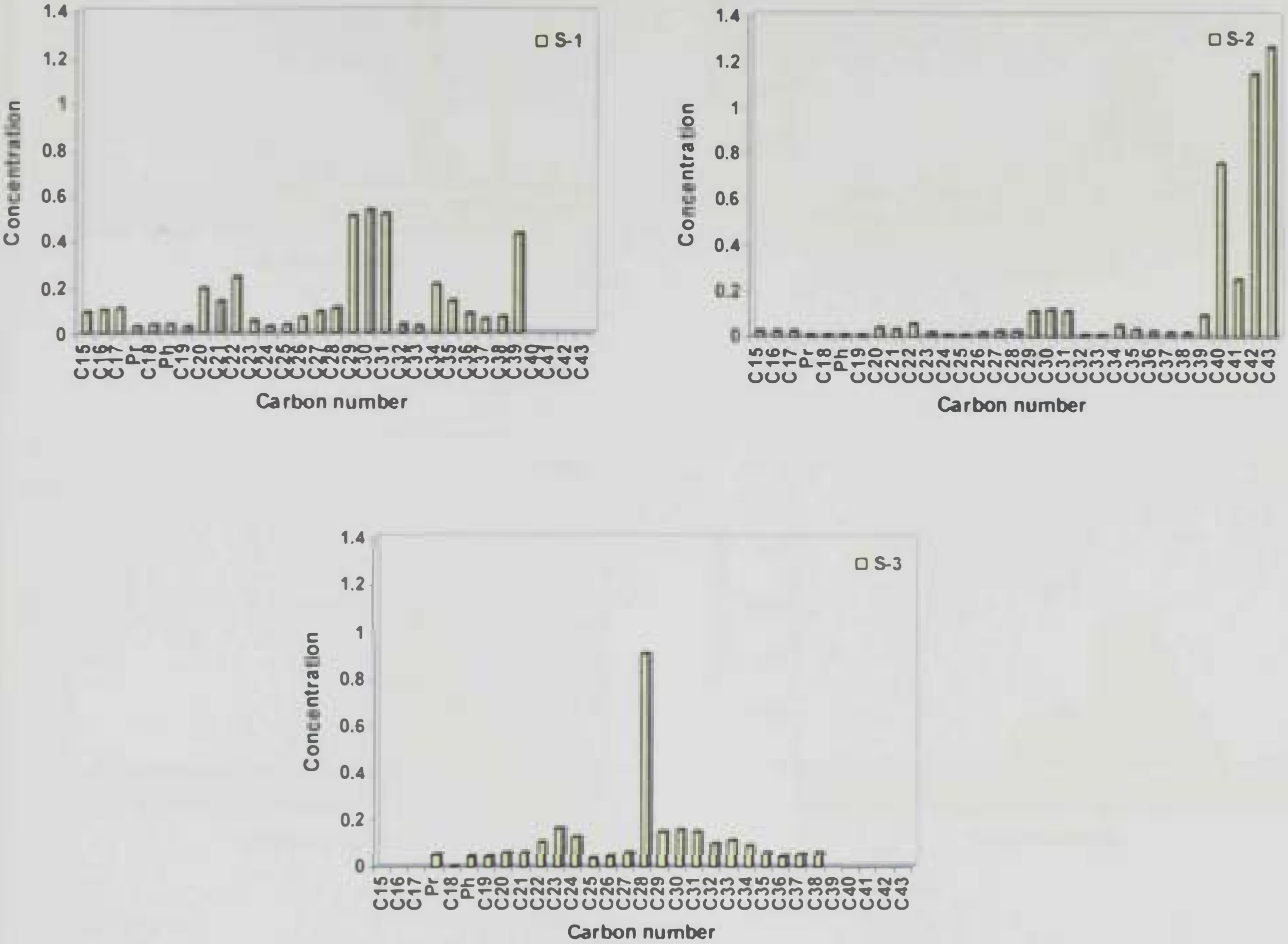
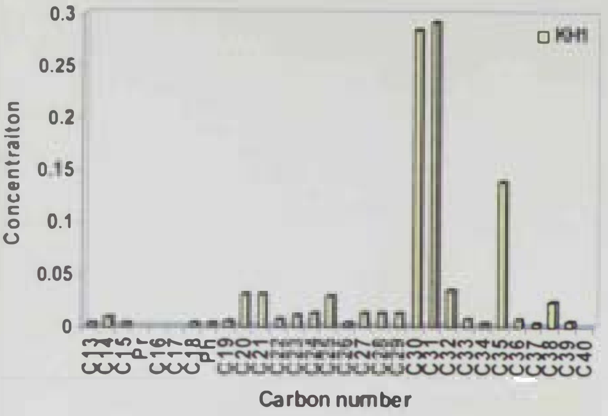
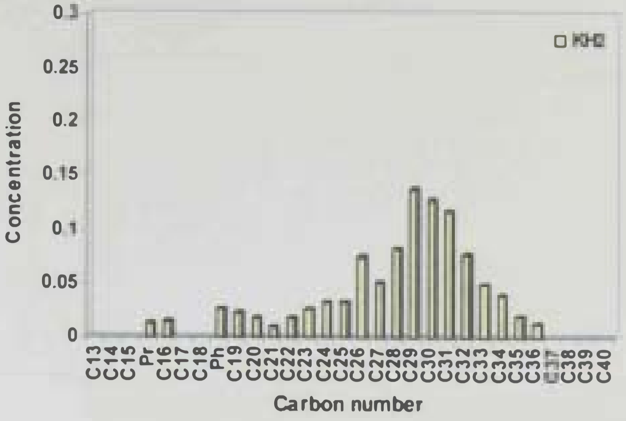
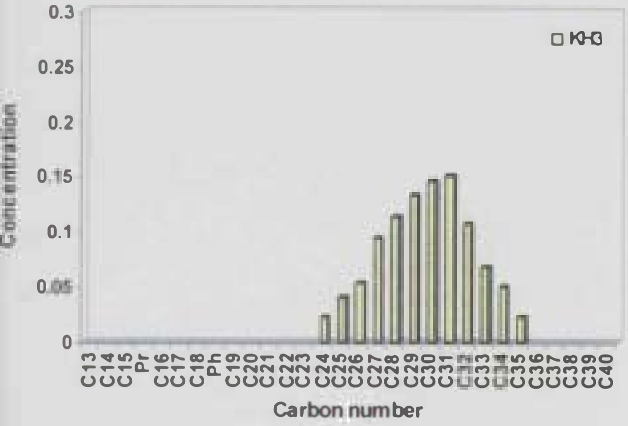
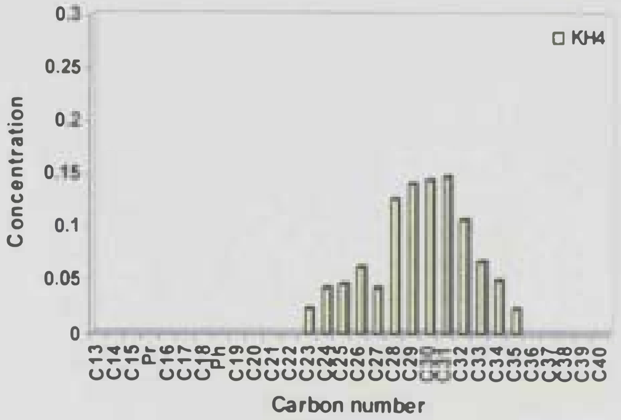


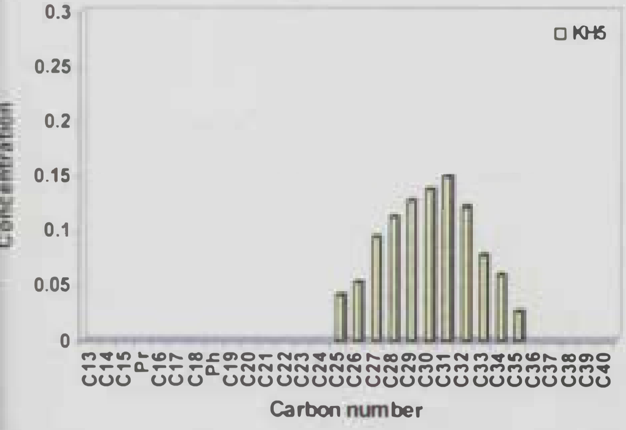
Fig. 4.27: Distribution of individual n-alkanes in marine sediment samples of eastern side of the UAE.

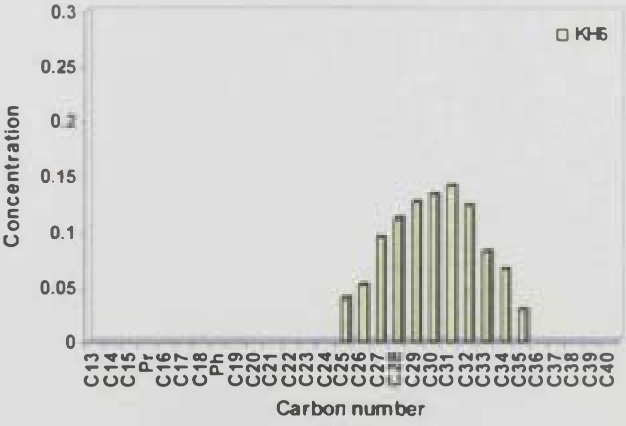

Concentralton
0.3
0.25
0.2
0.15
0.1
0.05
0
☐ KH1
C13 C14 C15 Pr C16 C17 C18 Ph C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36 C37 C38 C39 C40
Carbon number


Concentration
0.3
0.25
0.2
0.15
0.1
0.05
0
☐ KH2
C13 C14 C15 Pr C16 C17 C18 Ph C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36 C37 C38 C39 C40
Carbon number


Concentration
0.3
0.25
0.2
0.15
0.1
0.05
0
☐ KH3
C13 C14 C15 Pr C16 C17 C18 Ph C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36 C37 C38 C39 C40
Carbon number


Concentration
0.3
0.25
0.2
0.15
0.1
0.05
0
☐ KH4
C13 C14 C15 Pr C16 C17 C18 Ph C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36 C37 C38 C39 C40
Carbon number


Concentration
0.3
0.25
0.2
0.15
0.1
0.05
0
☐ KH5
C13 C14 C15 Pr C16 C17 C18 Ph C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36 C37 C38 C39 C40
Carbon number


Concentration
0.3
0.25
0.2
0.15
0.1
0.05
0
☐ KH6
C13 C14 C15 Pr C16 C17 C18 Ph C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36 C37 C38 C39 C40
Carbon number

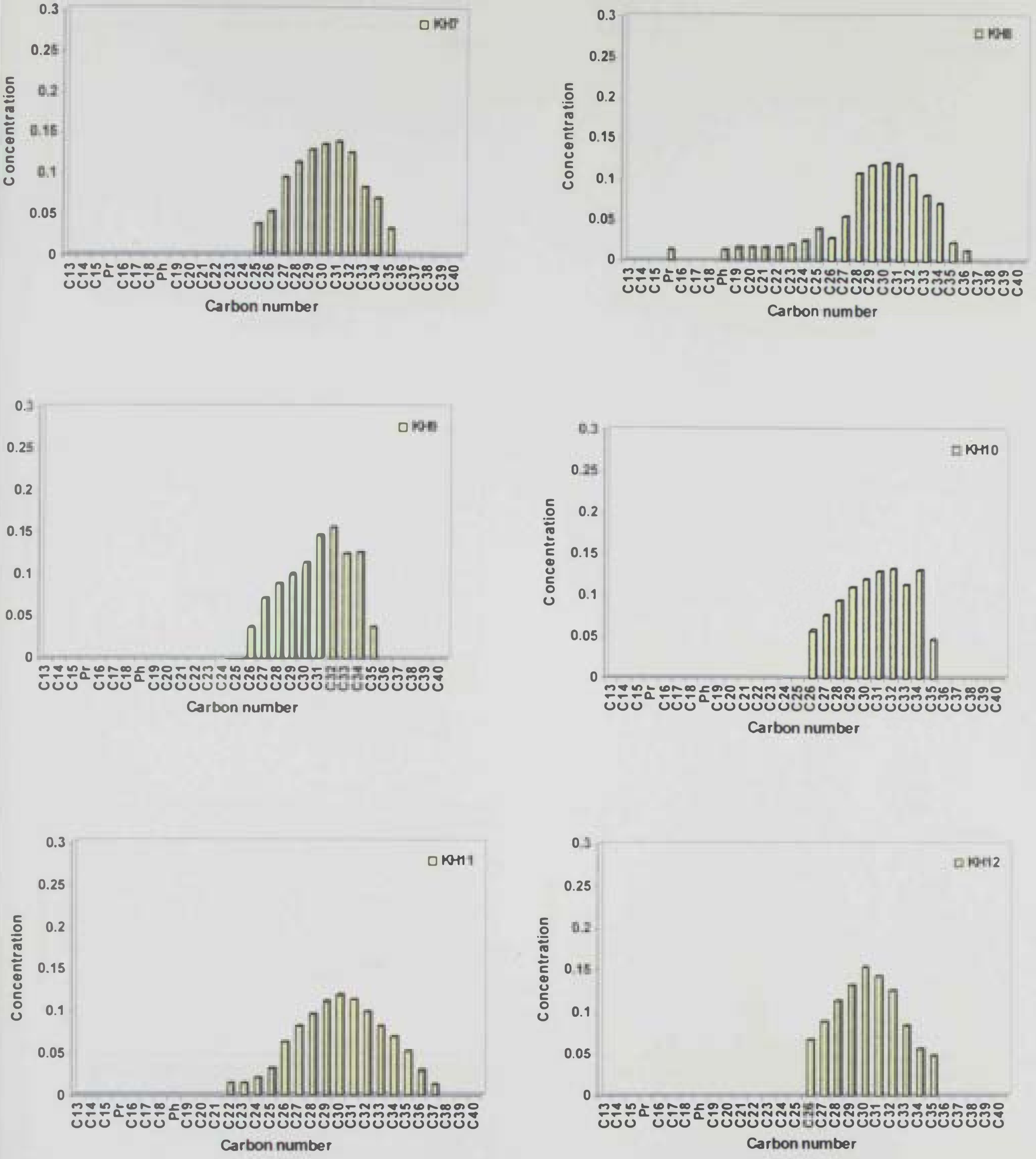


Fig. 4.28: Distribution of individual n-alkanes in coastal sediments samples of eastern side of the UAE.

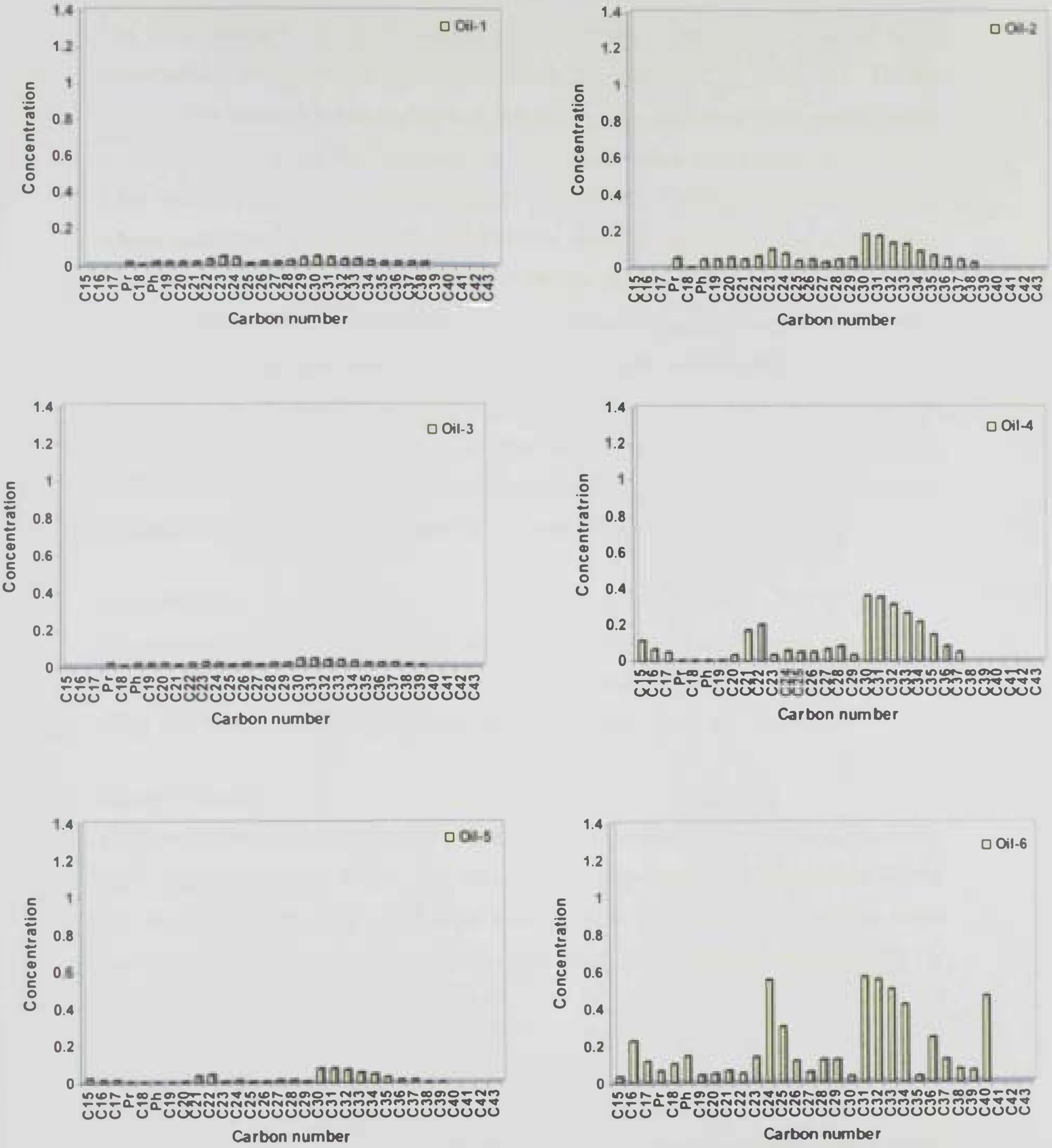


Fig. 4.29: Distribution of individual n-alkanes for oil spill samples.

4.5 Polychlorinated biphenyls (PCBs)

The data obtained for determination of total PCBs in the eastern side of UAE (Khorfakkan, Fujairah and Kalba) sediments are illustrates in Table 4.7. TPCBs values range between 0.060 mg/kg to 0.145 mg/kg. The minimum value was recorded at station KH9, and KH12, whereas the maximum value was provided by station KH4, with an average of 0.104 mg/kg and S.D of 0.03. The percentage of TPCBs in station constitutes 13% from an overall PCBs value in sediments (Fig. 3.31), while Fig. 3.30 demonstrates the distribution of TPCBs in the study area. The distribution map of total Polychlorinated biphenyls showed that increases towards northeastern part of the study area around KH1, KH2, KH3, and KH4 stations (Fig .3.32).General observation on the detected individual PCBs in eastern side of the U.A.E (Table 4.8) showed that PCB195 provided the highest values of PCBs congeners, except for PCBs 209,206,180, and 128 showed limited distribution in eastern side and the detected compounds also were found in limited stations.

4.5.1 PCB8

The concentration of PCB8 was 20 µg/kg. This substance was detected only in nine stations which are KH1, KH2, KH3, KH5, KH6, KH8, KH9, KH10, and KH11 of the study area. The value was the same in all station (Table 4.8 & Fig. 4.33 A).

4.5.2 PCB 18

This compound was detected just in eight stations which are KH 1, KH2, KH3, KH5, KH6, KH8, KH11, and KH12. The value of 20 µg/kg reported in all stations (Table 4.8 & Fig. 4.33 B). The distribution map of PCB 18 shows an increasing trend towards the southern and northern parts of the study area around KH8, KH10, KH11, and KH12 stations (Fig.4.34).

4.5.3 PCB28

This compound was found only in two stations (Kh5, and KH 6) in Fujairah of the study area. This concentration was 0.15 µg/kg recorded at all stations (Table 4.8 & Fig. 4.33 C).

4.5.4 PCB 52

This compound was detected just in six stations which are KH1, KH2, KH3, KH4, KH10, and KH11 in Khorfakkan and Kalba. The value of 15µg/kg; reported in all stations (Table 4.8 & Fig. 4.33 D). The distribution map of PCB52 shows an increasing trend towards the northern part of the study area around KH1, KH2, KH3, KH4, and KH10 stations (Fig.4.35).

4.5.5 PCB44

This compound was detected just in two stations (KH4, and KH7) in Khorfakkan and Fujairah. The value of 15 mg/kg; reported in these two stations (Table 4.8 & Fig. 4.33 E).

4.5.6 PCB66

This compound was recorded only in eleven stations which are KH1, KH2, KH3, KH 4, KH5, KH6, KH8, KH9, KH10, KH11, and KH12. The value of 10 µg/kg reported at all stations (Table 4.8 & Fig. 4.33 F). The distribution map of PCB66 shows an increasing trend towards the northern and southern parts of the study area (Fig.4.36).

4.5.7 PCB101

This compound was recorded only in nine stations which are KH1, KH2, KH3, KH 4, KH7, KH9, KH10, KH11, and KH12. The concentration was 15 µg/kg at all stations (Table 4.8 & Fig. 4.33 G). The distribution map of PCB101 shows an increasing trend towards the northern part of the study area around KH1, KH2, KH11, and KH12 stations (Fig.4.37).

4.5.8 PCB77

This compound was recorded only in four stations which are KH1, KH4, KH7, and KH10. The detected concentration was 20 µg/kg (Table 4.8 & Fig. 3.30 H).

4.5.9 PCB118

This compound was recorded only in four stations (KH1, KH4, KH7, and KH10) with very low concentration of 15 µg/kg (Table 4.8 & Fig. 4.33 I).

4.5.10 PCB105

This compound was recorded only in six stations (KH4, KH5, KH6, KH8, KH9, and KH10) with very low concentration of 15µg/kg (Table 4.8 and Fig. 4.33 J).

4.5.11 PCB 138

This compound was found only in seven stations which are KH2, KH4, KH6, KH7, KH8, KH10, and KH12. The concentration was 15 µg/kg at all stations (Table 4.8 & Fig. 4.33 K).

4.5.12 PCB187

This compound was found only in one station KH3 in Khor Fakkan with very low concentration of 15 µg/kg (Table 4.8 & Fig. 4.33 L).

4.5.13 PCB170

This substance was recorded in two stations (KH3 and KH6) in Khorfakkan and Fujairah. The value was 20 µg/kg at all station (Table 4.8 & Fig. 4.33 M).

4.5.14 PCB195

This compound was found in five stations (KH3, KH4, KH6, KH8, and KH11) with very high concentration of 25 µg/kg (Table 4.8 & Fig. 4.33 N). The distribution map of PCB195 shows an increasing trend towards the northern part of the study area around KH3 and KH4 stations (Fig.4.38).

Table 4.7: Concentrations of total polychlorinated biphenyls (TPCBs mg/kg) in eastern side of U.A.E.

Stations	TPCBs (mg/kg)
KH1	0.115
KH2	0.095
KH3	0.140
KH4	0.145
KH5	0.080
KH6	0.140
KH7	0.080
KH8	0.105
KH9	0.060
KH10	0.125
KH11	0.105
KH12	0.060
Average ± S.D	**0.104 ± 0.03**

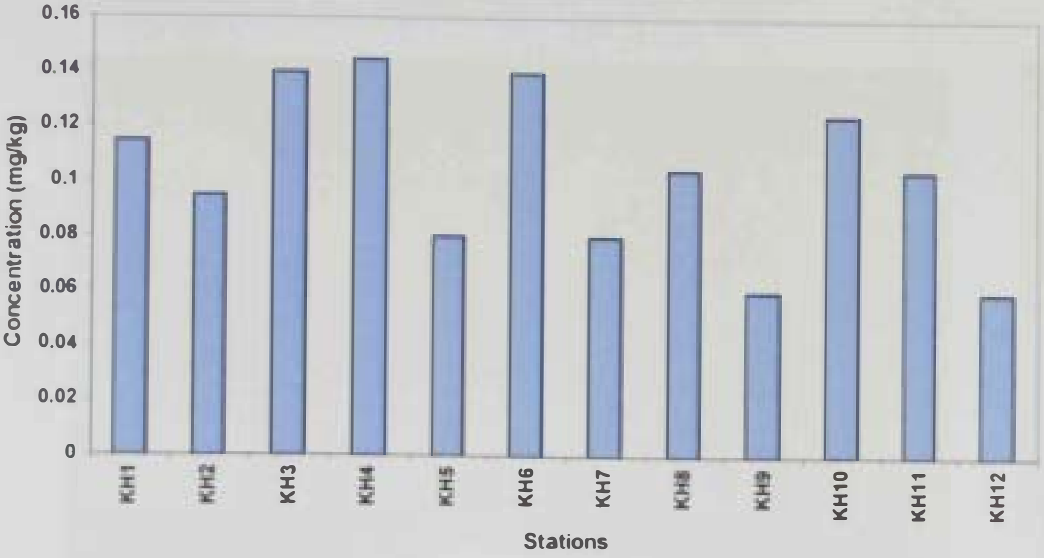


Fig. 4.30: Concentrations of Polychlorinated Biphenyls (PCBs) mg/kg in the studied stations.

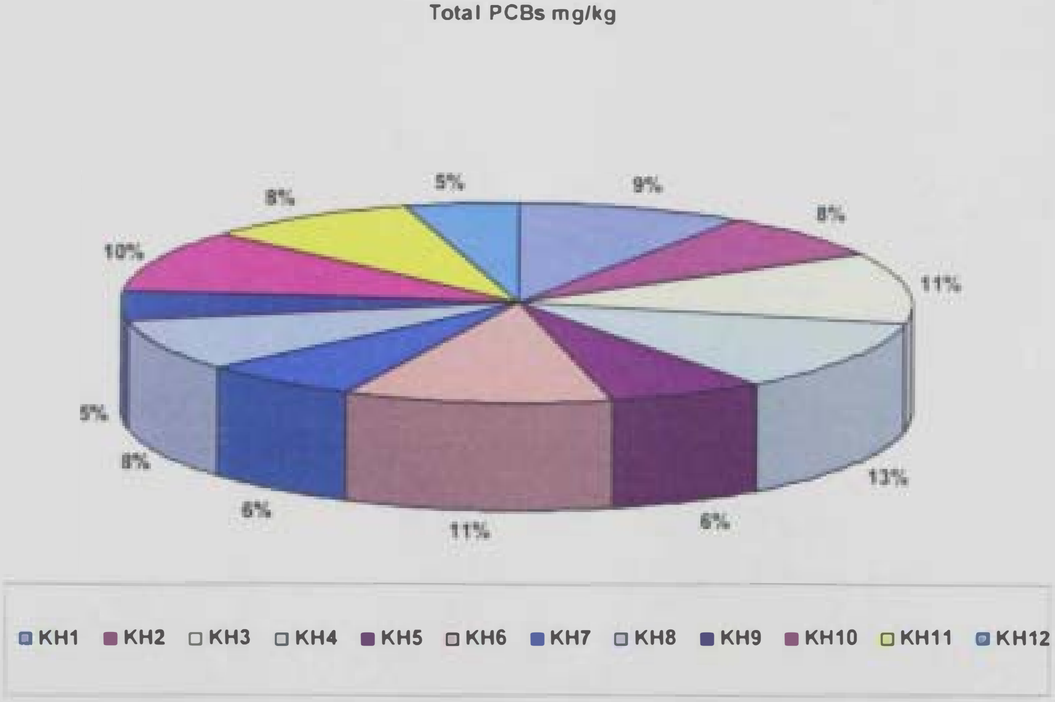


Fig. 4.31: Pie Diagram of Polychlorinated Biphenyls (PCBs) in the studied stations.

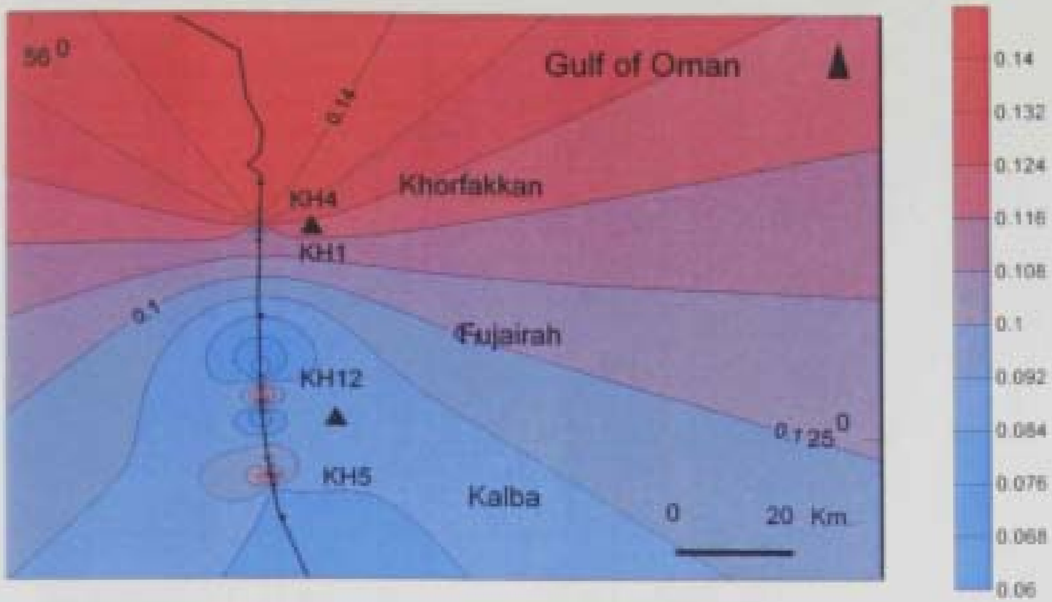
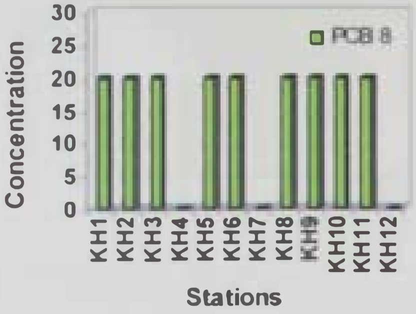


Fig. 4.32: Distribution map of total polychlorinated biphenyls TPCBs (mg/kg) in the studied stations.

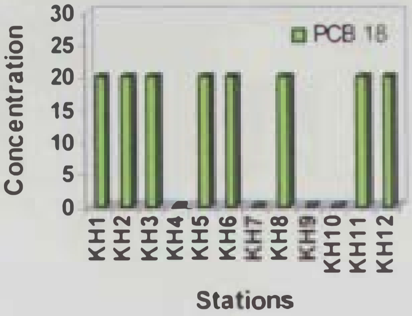
Table 4.8: Concentrations of individual Polychlorinated Biphenyls (PCBs μg/kg) in the eastern side of the U.A.E.

Stations	PCB 8	PCB 18	PCB 28	PCB 52	PCB44	PCB66	PCB 101	PCB 77	PCB 118	PCB 105	PCB 138	PCB 187	PCB 170	PCB 195	Total PCBs
KH1	20	20	ND	15	ND	10	15	20	15	ND	ND	ND	ND	ND	115
KH2	20	20	ND	15	ND	10	15	ND	ND	ND	15	ND	ND	ND	95
KH3	20	20	ND	15	ND	10	15	ND	ND	ND	ND	15	20	25	140
KH4	ND	ND	ND	15	15	10	15	20	15	15	15	ND	ND	25	145
KH5	20	20	15	ND	ND	10	ND	ND	ND	15	ND	ND	ND	ND	80
KH6	20	20	15	ND	ND	10	ND	ND	ND	15	15	ND	20	25	140
KH7	ND	ND	ND	ND	15	ND	15	20	15	ND	15	ND	ND	ND	80
KH8	20	20	ND	ND	ND	10	ND	ND	ND	15	15	ND	ND	25	105
KH9	20	ND	ND	ND	ND	10	15	ND	ND	15	ND	ND	ND	ND	60
KH10	20	ND	ND	15	ND	10	15	20	15	15	15	ND	ND	ND	125
KH11	20	20	ND	15	ND	10	15	ND	ND	ND	ND	ND	ND	25	105
KH12	ND	20	ND	ND	ND	10	15	ND	ND	ND	15	ND	ND	ND	60
														average	**104.16**
														S.D	**30.06**

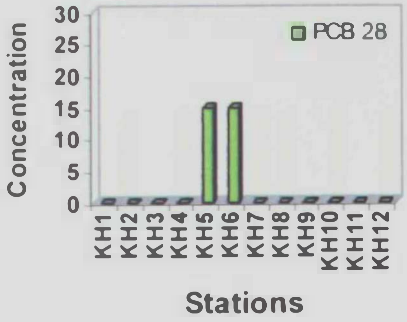
ND= Not Detected


PCB 8
Concentration
0
5
10
15
20
25
30
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
Stations

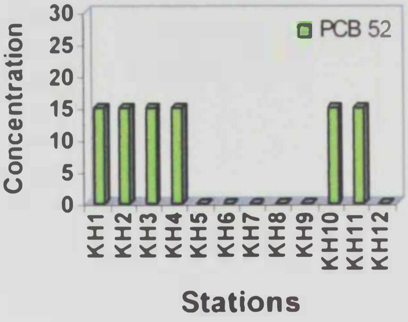
A.


PCB 18
Concentration
0
5
10
15
20
25
30
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
Stations

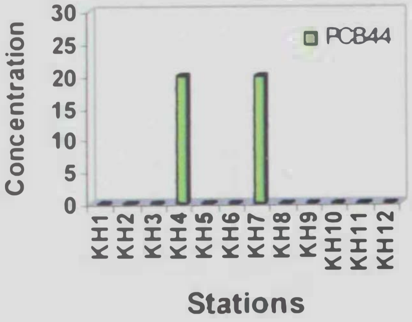
B.


PCB 28
Concentration
0
5
10
15
20
25
30
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
Stations

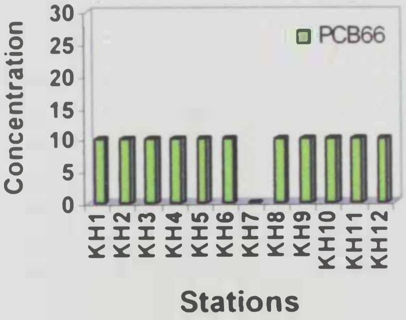
C.


PCB 52
Concentration
0
5
10
15
20
25
30
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
Stations

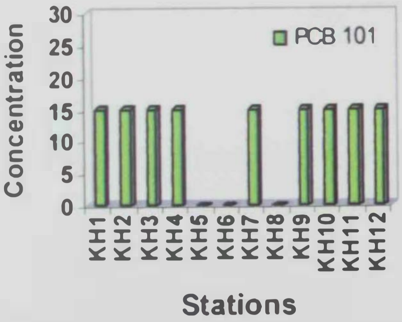
D.


PCB44
Concentration
0
5
10
15
20
25
30
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
Stations

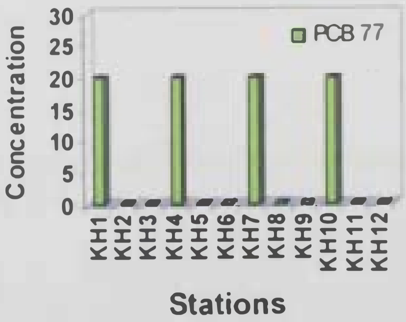
E.


PCB66
Concentration
0
5
10
15
20
25
30
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
Stations

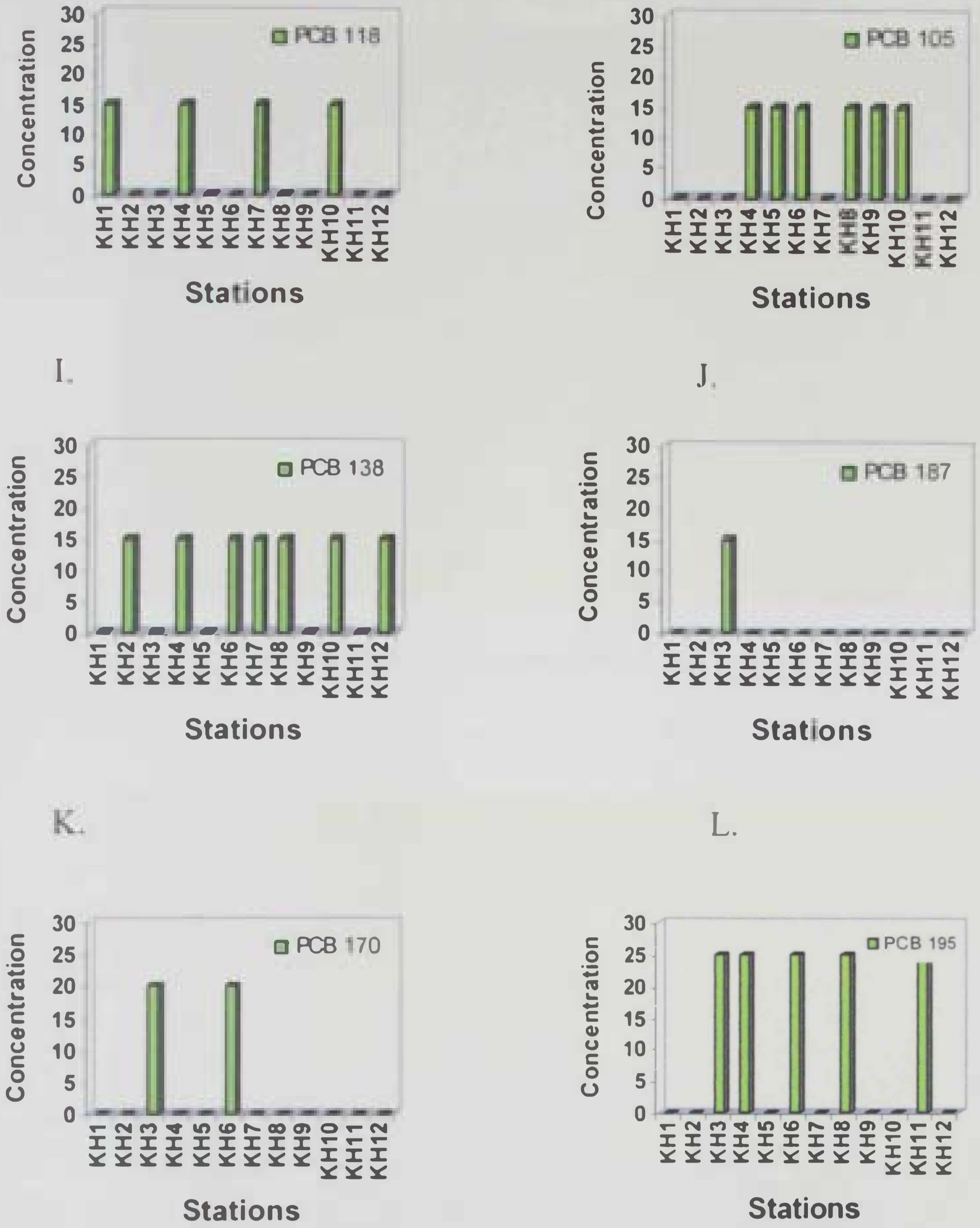
F.


PCB 101
Concentration
0
5
10
15
20
25
30
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
Stations

G.


PCB 77
Concentration
0
5
10
15
20
25
30
KH1
KH2
KH3
KH4
KH5
KH6
KH7
KH8
KH9
KH10
KH11
KH12
Stations

H.



I. J.

K. L.

M. N.

Fig. 4.33: Histograms representing concentrations of individual Polychlorinated Biphenyl compounds (PCBs) µg/kg in eastern side of U.A.E.

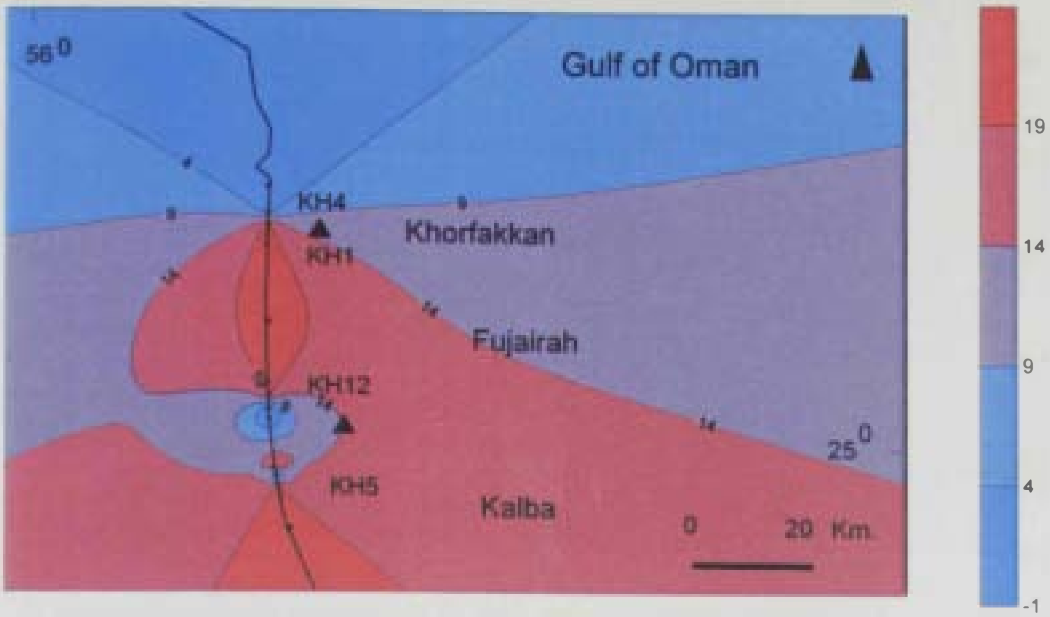


Fig. 4.34: Distribution map of PCB18 µg/kg in eastern side of UAE.

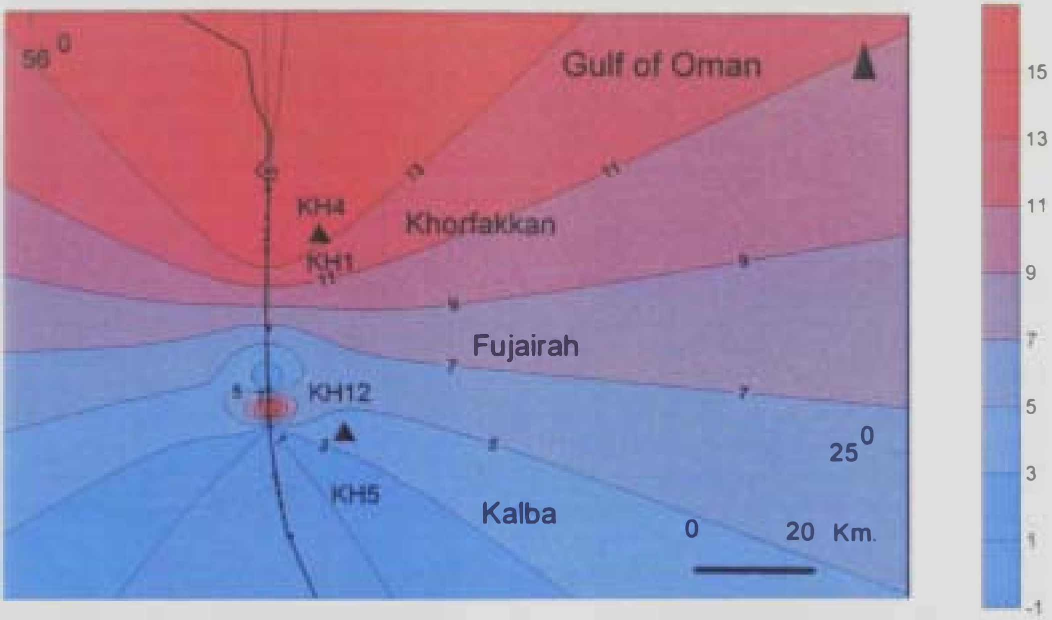


Fig. 4.35: Distribution map of PCB52 µg/kg in eastern side of UAE.

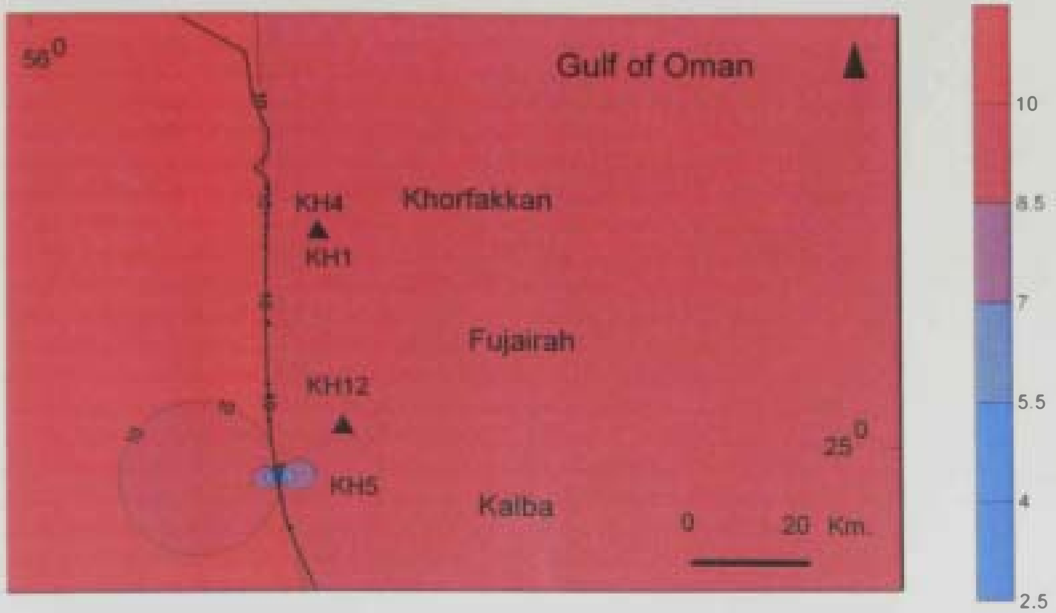


Fig. 4.36: Distribution map of PCB66 μg/kg in eastern side of UAE.

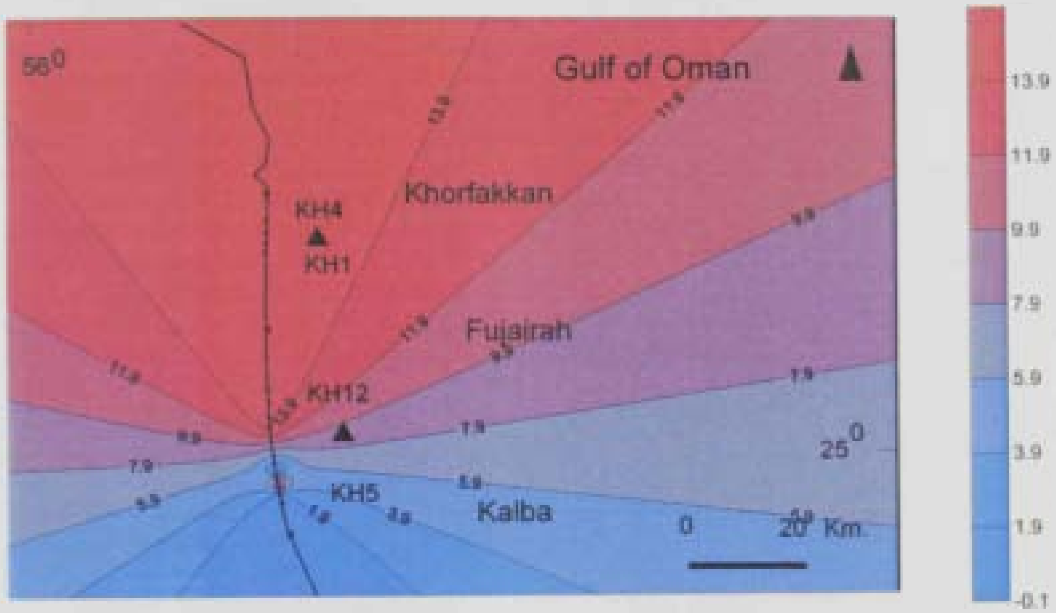


Fig. 4.37: Distribution map of PCB101 μg/kg in eastern side of UAE.

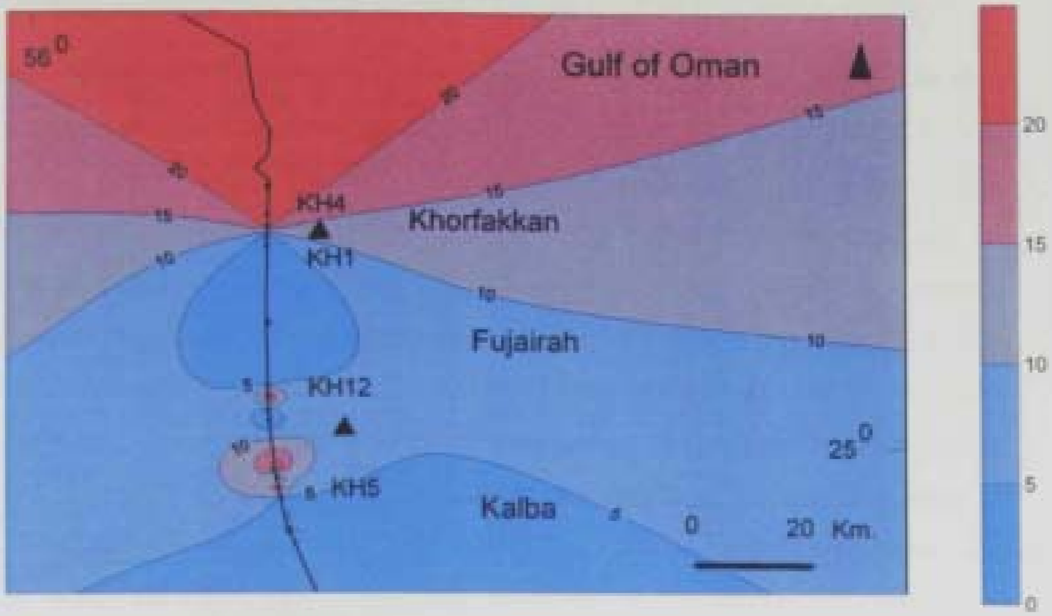


Fig. 4.38: Distribution map of PCB195 µg/kg in eastern side of UAE.

4.6 Total Petroleum Hydrocarbons (TPH)

Total petroleum hydrocarbons are defined as a group of chemical compounds that came from crude oil. The spectrophotmetirc measurement of eastern side of U.A.E (Table 4.9) demonstrated that the concentrations of total petroleum hydrocarbons (TPH) vary widely among the different stations. The values of TPH range from 91 mg/kg to 282 mg/kg, with an average of 156.06 mg/kg and S.D of 57.55. It is worthy to note that station KH7 showed a very high level of TPH (Fig. 4.39), whereas a very low level was recorded at station KH1 and other stations showed moderate to highly levels of TPH. The percentage of TPH for eastern side of U.A.E is demonstrated at KH7 (11 %) and at KH4 (10 %) of TPH value, but the low percentage can occur at KH1, KH6, and KH8 (4 %) of the TPH value (Fig. 4.40). For marine sediments, the highest value of TPH was 129 mg/kg recorded at S3 station in which low concentration was 111 mg/kg recorded at S2 station. The distribution map showed that TPH in eastern side sediment is concentrated in the northern part of the study area, which may reflect a heavily polluted area around KH1, KH2, KH3, and KH4 stations of Khorfakkan (Fig. 4.41).

According the Massoud et al., 1996 classification the present data of TPH recorded heavily to moderately pollutant areas. For instant only KH4 (Khorfakkan), KH7 (Fujairah) and KH9 (Kalba) have been attained the heavily pollutant areas. The rest of coastal sediments are described as moderately polluted areas. Marine sediments (S1, S2 and S3) also described as moderately polluted areas. Although, the present data of TPH in eastern coast of UAE recorded higher vales than western cost done by Shridah et al., (1988). The average TPH is 156.06 mg/kg, which is low than previous studies in coastal sediments of Dubai done by Al- Darwish, 2004.

Table 4.9: Concentrations of Total Petroleum Hydrocarbons TPH (mg/kg) in coastal and marine sediments.

Stations	locality	TPH mg/kg
KH1	coastal	91
KH2	Coastal	177
KH3	Coastal	191
KH4	Coastal	227
KH5	Coastal	155
KH6	coastal	93
KH7	Coastal	282
KH8	Coastal	93
KH9	Coastal	235
KH10	Coastal	168
KH11	Coastal	146
KH12	Coastal	123
S1	Marine	120
S2	Marine	111
S3	Marine	129
	average ± S.D	**156.06 ± 57.55**

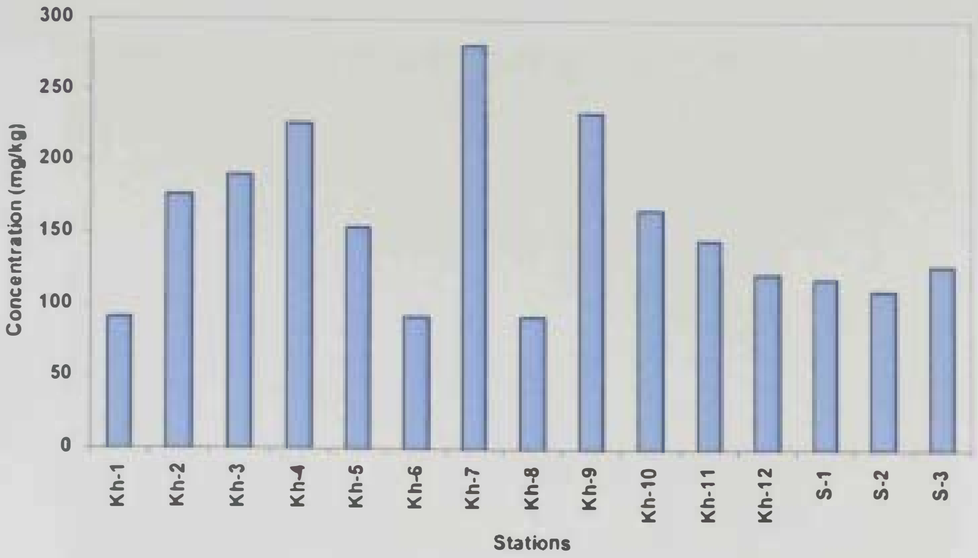


Fig. 4.39: Concentrations of Total Petroleum Hydrocarbons (TPH) mg/kg at different stations.

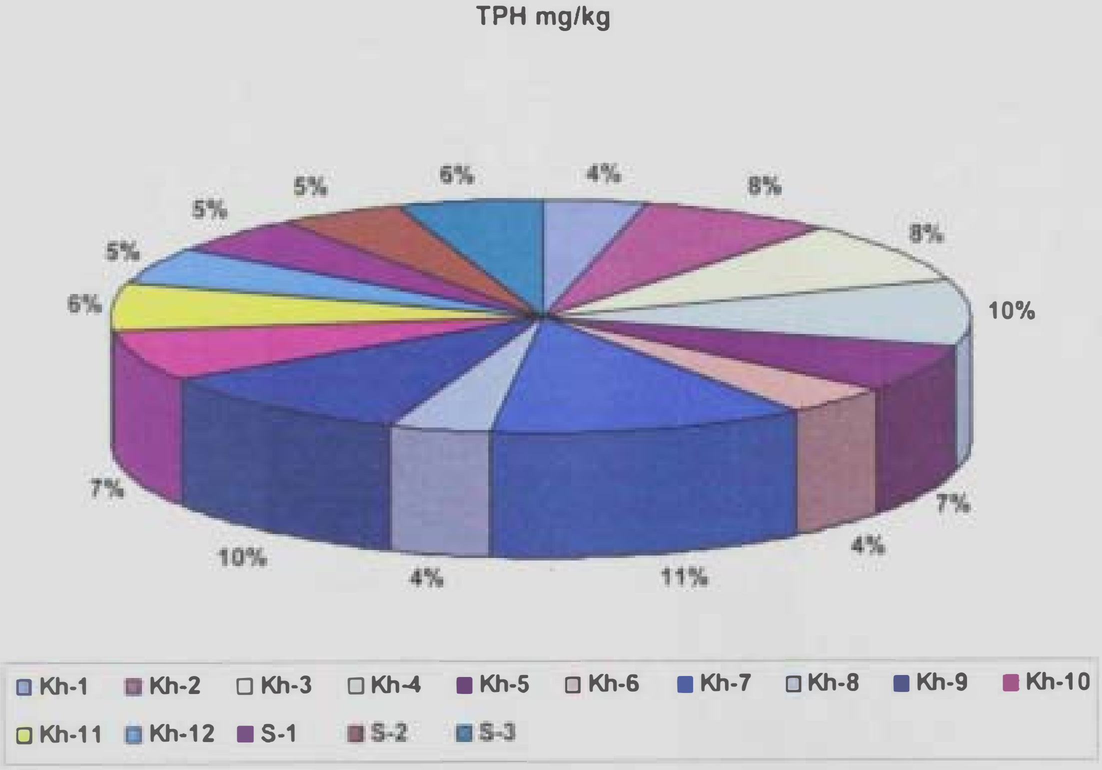


Fig. 4.40: Pie Diagram of Total Petroleum Hydrocarbons (TPH) in the studied stations.

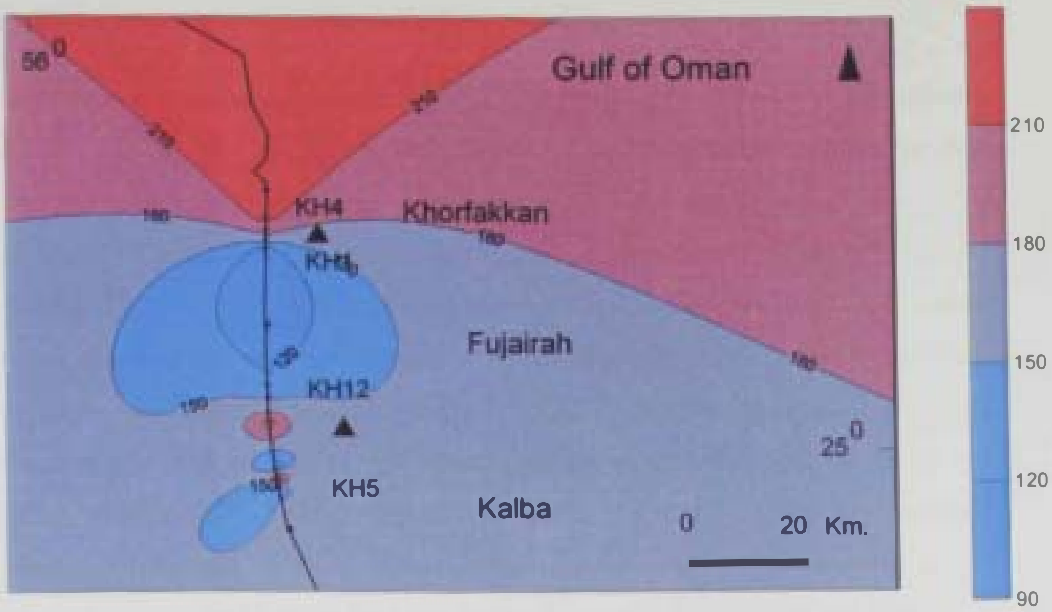


Fig. 4.41: The distribution map of Total Petroleum Hydrocarbons TPH (mg/kg) in the eastern side of UAE.

4.7 Total Organic Carbon (TOC wt %)

The total organic carbon value indicates the sum of organic carbon and represents a measure for all organic substance in sediments. Table 4.10 illustrates the data obtained from determination of organic carbon in investigation area. The concentrations of TOC vary between 0.028 % to 0.71 % with an average of 0.63, and standard deviation of 0.83. Most stations showed low concentration of TOC values excepted KH2, S1, S2, and S3 stations. The variation in TOC concentration was plotted in Fig. (4.42), while the percentage of TOC at different stations of the study areas is demonstrated in Fig. (4.43). The mapping survey was used to show the distribution of TOC in sampling stations sediments (Fig. 4.44), which most stations show few concentration of TOC whereas the increasing of TOC observed in the northern part around KH2 (Khorfakkan). These increases may reflect the sources of pollution such as agriculture activities and fertilizers.

The average TOC % was 0.6 % which is moderates value than previous studies in the region (Al Ghadban, 1994). The present data show higher values of TOC % (0.10 % to 0.39 %) than previous studies done by Tolosa et al, (2005). Although the present study of TOC % in eastern coast indicate high value than western coast inducing Ras Al-Khaimah, Umm Al-Quwain, Sharjah and Abu Dhabi (Shriadah et al., 1998). The average TOC is 0.63 %, which is low than previous studies in coastal sediments of Dubai done by Al- Darwish, 2004.

Table 4.10: Concentrations of Total Organic Carbon (TOC wt %) in each station of eastern side of U.A.E.

Stations	locality	TOC wt %
KH1	coastal	0.20
KH2	coastal	2.18
KH3	coastal	0.22
KH4	coastal	0.15
KH5	coastal	0.07
KH6	coastal	0.38
KH7	coastal	0.05
KH8	coastal	0.06
KH9	coastal	0.07
KH10	coastal	0.31
KH11	coastal	0.21
KH12	coastal	0.08
S1	marine	2.16
S2	marine	2.11
S3	marine	1.22
	Average ± S.D	**0.635 ± 0.837**

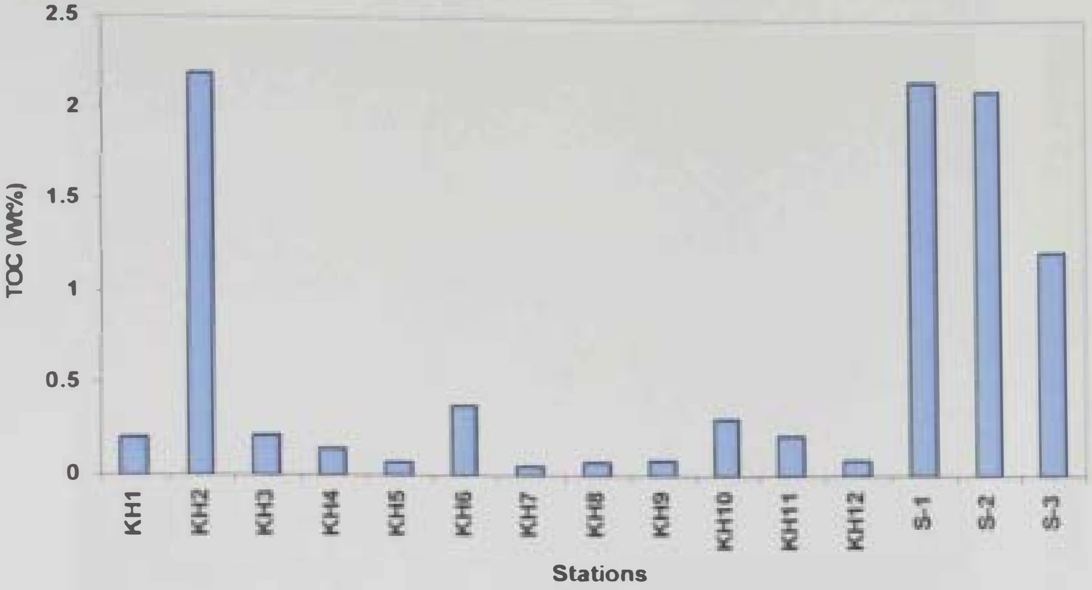


Fig. 4.42: Concentrations of Total Organic Carbon (TOC %) in the studied stations.

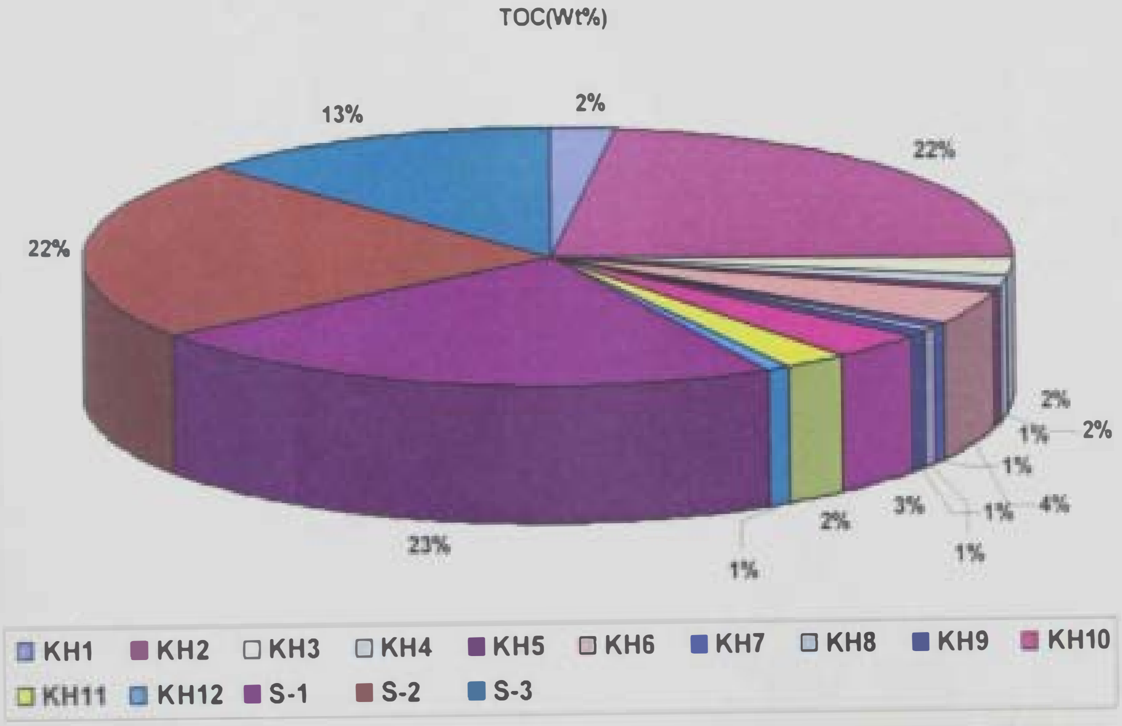


Fig. 4.43: Pie Diagram of Total Organic Carbon (TOC wt %) in the studied stations.

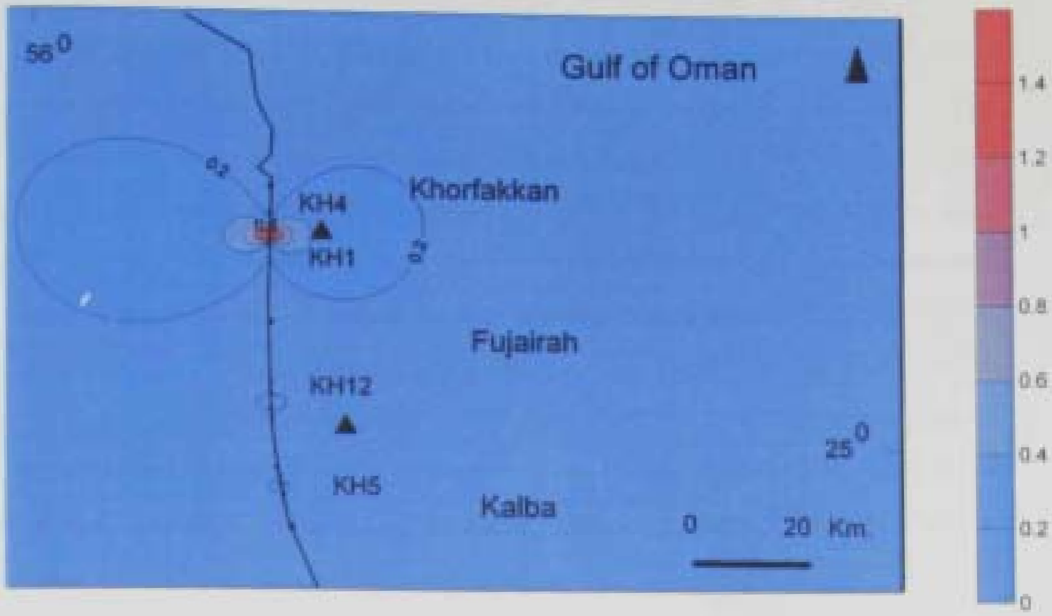


Fig. 4.44: Distribution map of total organic hydrocarbon (TOC wt %) in the eastern side of UAE.

4.8 Total Kjeldahl Nitrogen (TKN)

TKN stands for total kjeldahl nitrogen, which is the sum of ammonia (NH_3) and organic nitrogen. According to measurement of TKN in sampling sediments (Table 4.11) the values showed drastic fluctuation within a range from 83.8 mg/kg to 1,443 mg/kg. The maximum value was reported at station KH6, whereas station KH2 provided as second highest concentration with 825 mg/kg. The minimum concentration was recorded at station KH8 with an overall average of 357.05 mg/kg, and S.D of 437.393. The variation in TKN values was illustrated in Fig. (4.45), while Fig. 4.46 demonstrates the percentage of TKN in each station. High percentage of TKN recorded at KH6 with 28 %, but the low percentage reported at KH8, KH9, KH10, KH11, and KH12 with 2 %. The distribution map showed that the TKN for eastern side of UAE sediments is concentrated in the southern part of the study area around KH5, KH6, and KH8, which reflected anthropogenic sources such as industrial activities and agriculture activities (fertilizer) (Fig. 4.47).

TKN data for the studied sediments showed higher concentration compared to the maximum value (300 µg/g) suggested by alloway et al. (1993). Only six coastal sediment stations (KH7 to KH12) have been achieved the previous level. Sediments of KH6 and KH2 stations attained the highest levels 1,443 and 825 µg/g respectively, which represent 4.80 - 2.75 times higher than the upper permissible level. Marine sediments stations were ranged from 722 µg/g at S3 to 782 µg/g at S2, which represent from 2.4 to 2.6 times higher than background value. High concentration of TKN for coastal and marine stations reflected important anthropogenic sources that discharge to these areas such as human wastes, livestock, runoff of fertilizers and municipal sewage treatment facilities, In addition to the total petroleum hydrocarbons. It is important here to mention the Redfield ratio in marine sediments (carbon: nitrogen: phosphorus). That represents the average atomic ratios of C: N: P (106:16:1 respectively) in marine phytoplankton (El-Sabrouti et at., 1990). The ratio of C: N in the study area shows that all studied sediments have positive deviation from the Redfield ratio except for KH6, KH7, and KH9 with ratio of 2.6, 1.89 and 5.38 respectively, which reflected sharp negative deviation. The KH2, KH10, S1, and S2 with ratios of 26.4, 24.6, 28.9, and 26.9 respectively which KH11, and S3 have ratio of 16.15, and 16.8, exhibited sharp positive deviation from the Red field.

The sharp deviation from the Redfield ratio at KH6, which has the highest value of TKN (1443 µg/g) and relatively low level of TOC (3800 µg/g) could be attributed to preferential oxidation of carbon than nitrogen (El-Sabrouti et at., 1990). The sharp deviation at KH2, S1, S2, and S3, which have the high values of TOC (21800 µg/g, 21600 µg/g, 21100 µg/g, and 12200 µg/g respectively) and high TKN value (825 µg/g, 747 µg/g, 782 µg/g, and 722 µg/g respectively) lead to produce high ratio. The deviation from the Redfield ratio at KH8, KH10, KH11, and KH12, where TOC value is relatively low (600 µg/g, 3100 µg/g, 2100 µg/g, and 800 µg/g) and also the TKN value is low (83.8 µg/g, 126 µg/g, 130 µg/g, and 103 µg/g), which produced high ratio (Table 4.12). These ratios may be also attributed to the variability in the elemental composition of phytoplankton and zooplankton and /or highly terrestrial input (El-Sabrouti et at., 1990). High levels of TKN at KH2, KH6, S1, S2, and S3 are related with land based discharge. As it`s well known that the main sources of nutrients enrichment are the fertilizers. The average TKN is 357 mg/kg, which is low than pervious studies in coastal sediments of Dubai done by Al- Darwish, 2004.

Figure 4.48 exhibit negative correlation between TKN and TPH ($r = -0.36$); and positive correlation between TKN and TOC ($r = 0.6$). It is worthy to note that in the present study TPH and TOC have the same trend of increase toward the northern parts except for TKN has another trend of increase toward the southern parts of the studied area (fig. 4.49).

Table 4.11: Concentrations of Total Kjeldahl Nitrogen (TKN mg/kg) in the studied stations.

Stations	**Locality**	**TKN (mg/kg)**
Kh1	coastal	ND
Kh2	Coastal	825
Kh3	Coastal	ND
Kh4	Coastal	ND
Kh5	Coastal	ND
Kh6	Coastal	1443
Kh7	Coastal	264
Kh8	Coastal	83.8
Kh9	Coastal	130
Kh10	Coastal	126
Kh11	Coastal	130
Kh12	coastal	103
S1	Marine	747
S2	marine	782
S3	marine	722
	average± S.D	**357·05 ± 437·393**

ND= Not Detected

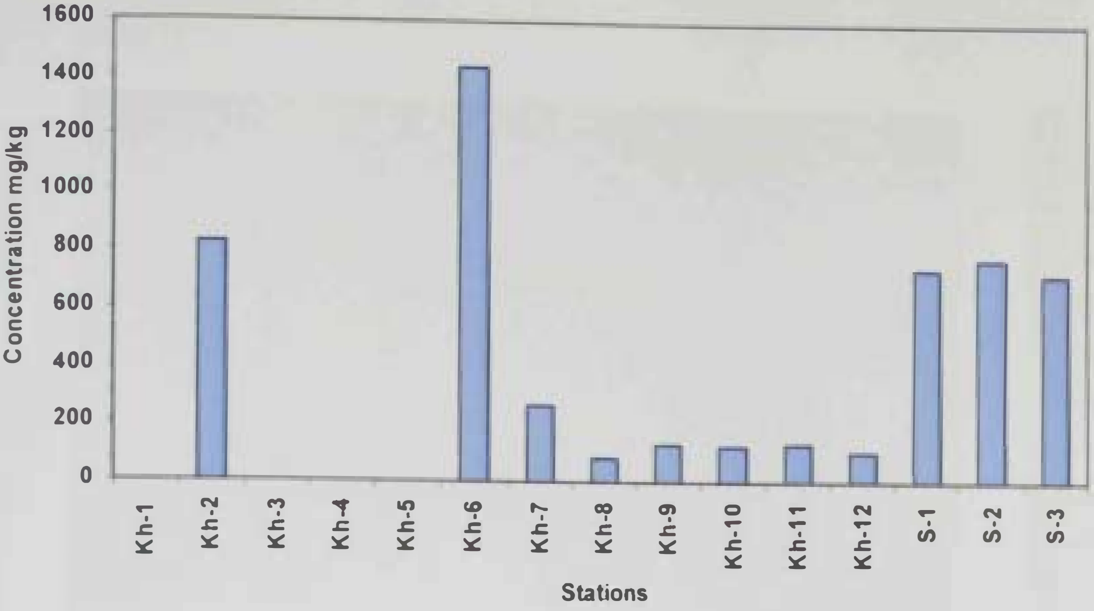


Fig. 4.45: Concentrations of Total Kjeldahl Nitrogen (TKN) mg/kg in sample sediments.

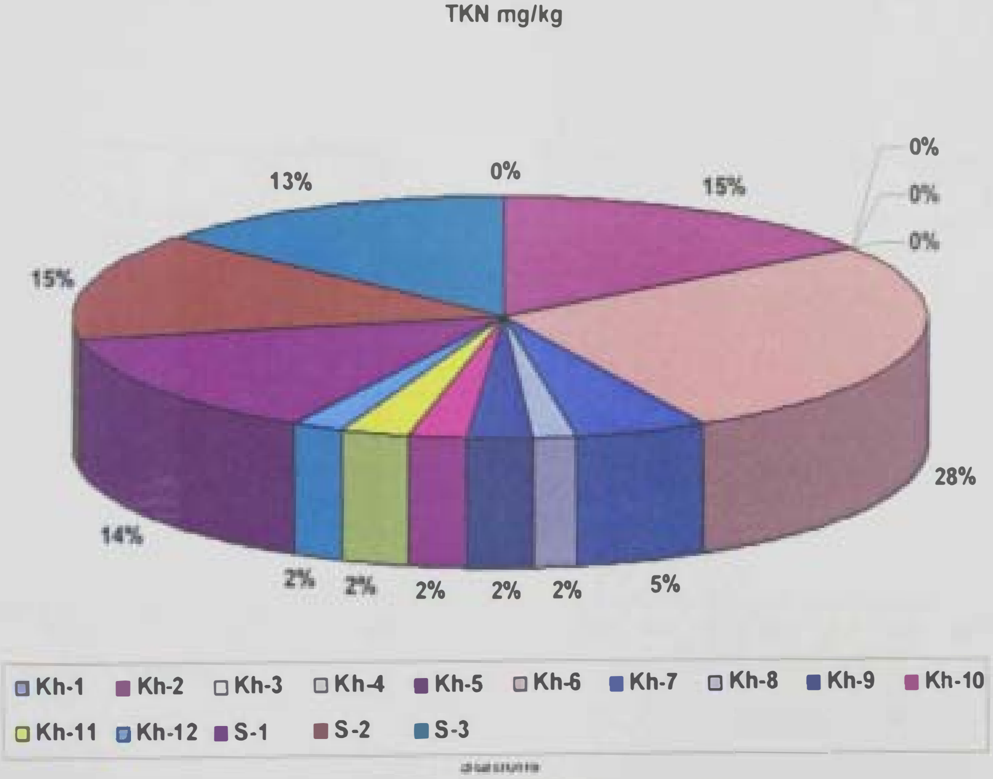


Fig. 4.46: Pie Diagram of Total Kjeldahl Nitrogen in the studied stations.

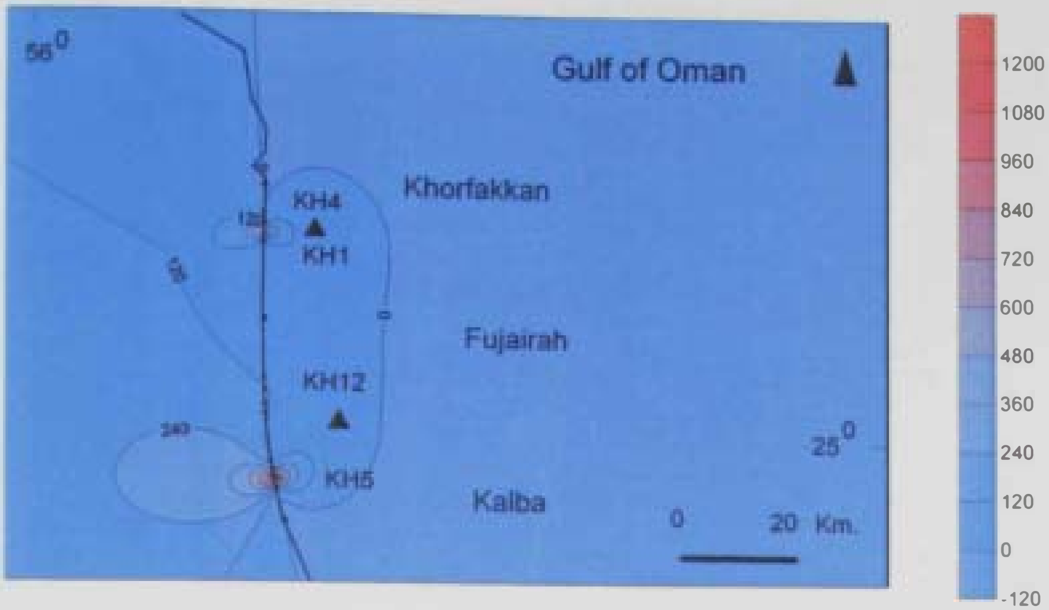


Fig. 4.47: Distribution map of Total Kjeldahl Nitrogen (TKN mg/kg) in the eastern side of UAE.

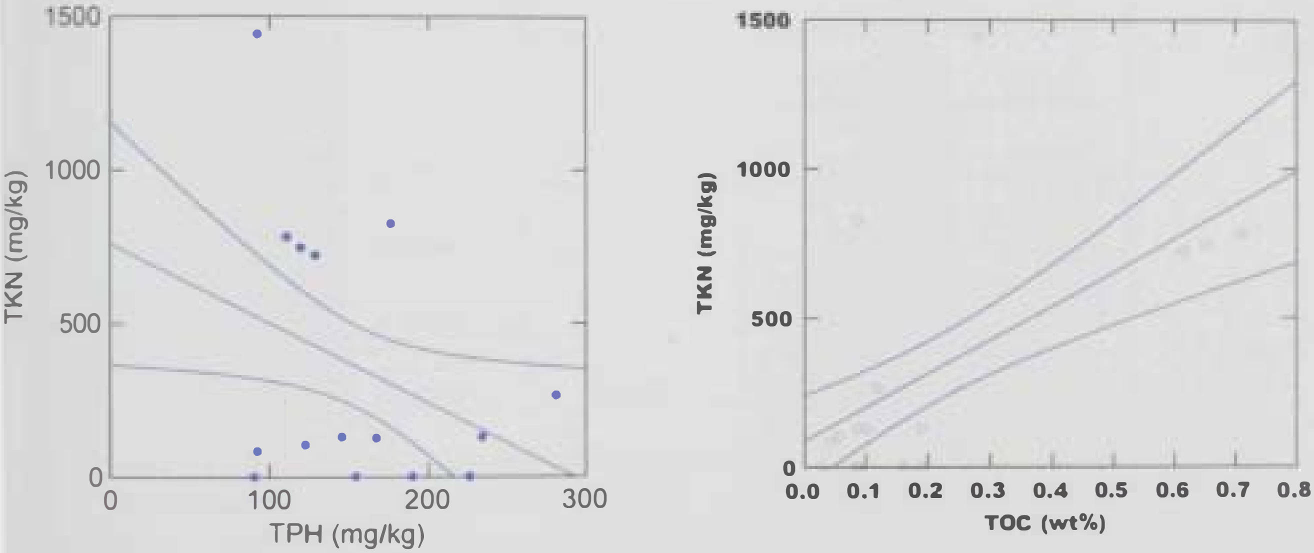


Fig. 4.48: Scatter plot showing the relationship between TOC and TKN and TPH with TKN in the study area.

Table 4.12: Ratios of carbon to nitrogen for the studied samples.

Stations	**Locality**	**TOC (mg/kg)**	**TKN (mg/kg)**	**C/N**
KH1	Coastal	2100	Nd	-
KH2	Coastal	21800	825	26.4
KH3	Coastal	2200	Nd	-
KH4	Coastal	1500	Nd	-
KH5	Coastal	700	Nd	-
KH6	Coastal	3800	1443	2.6
KH7	Coastal	500	264	1.89
KH8	Coastal	600	83.8	7.15
KH9	Coastal	700	130	5.38
KH10	Coastal	3100	126	24.6
KH11	Coastal	2100	130	16.15
KH12	Coastal	800	103	7.76
S-1	Marine	21600	747	28.9
S-2	Marine	21100	782	26.9
S-3	Marine	12200	722	16.89

TOC (mg/kg) = total organic carbon, **TKN (mg/kg)** = total Kjeldahl Nitrogen, **C/N**= total organic carbon / total Kjeldahl Nitrogen
µg/g = mg/kg

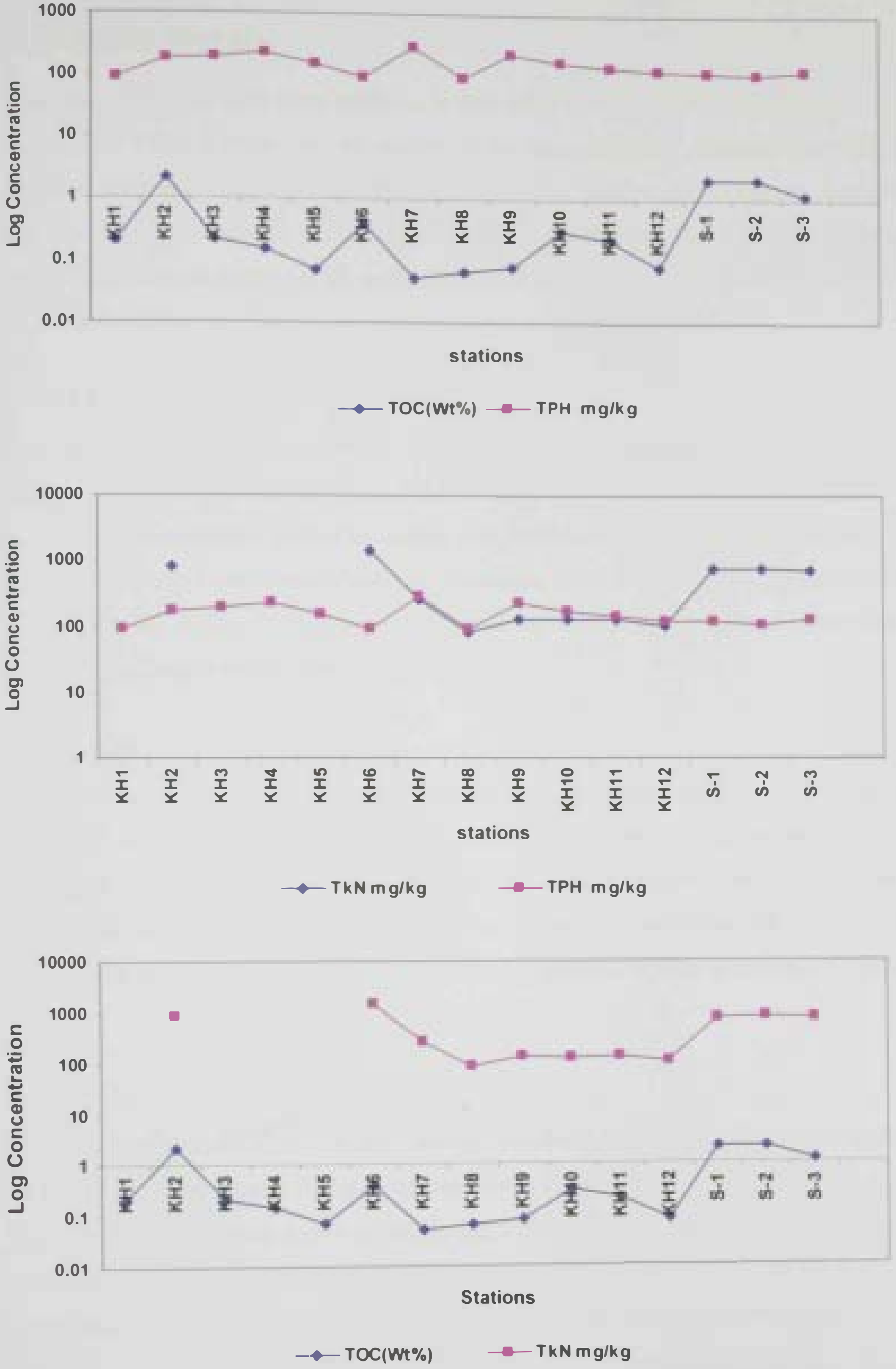


Fig. 4.49: Relationship between log concentration of TPH, TOC and TKN in the study area.

4.9 Heavy Metals

Nine trace elements have been analyses in this study i.e. Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn. Table 4.13 shows the results of the trace elements concentration which obtained form the study area sampling stations. The highest concentration detected was for Ni and Mn with an average amount of 398.4 mg/kg and 191.4 mg/kg respectively, which reflected oil contaminates of the study area sediments. On the other hand, Cd has the lowest concentration with an average of 0.24 mg/kg.

4.9.1 Cd

The value of cadmium showed very low concentration; ranged from 0.09 mg/kg at KH2 to 0.42 mg/kg at KH9 and a average value of 0.24 mg/kg and S.D 0.1 (Fig. 4.50 A). Therefore, cadmium values in eastern side sediment coastal and marine could be ignored. The distribution map shows an increasing trend towards southern part of the study area (Fig. 4.51). The Cd average in the study area is low compared to previous studies in the region (Table 2.6).

4.9.2 Co

The values of coupled vary moderate among stations, within a range from 9.6 mg/kg at S3 and S1 to 28.7 mg/kg at KH8 and a average value of 21.4 mg/kg and S.D 7.9 (Fig. 4.50 B). The distribution map shows an increasing trend towards southern part of the study area around KH5 to KH12 stations (Fujairah and Kalba) (Fig. 4.52). The Co average in the study area is high compared to previous studies in the region (Table 2.6).

4.9.3 Cr

The values of chromium vary widely among stations; within a range from 30.2 mg/kg at KH2 to 127 mg/kg at KH8 with average value 79.4 mg/kg and S.D 40.5 (Fig. 4.50 C). The distribution map shows an increasing trend towards southern part of the study area around KH5 to KH12 stations (Fujairah and Kalba) (Fig. 4.53). The Cr average in the study area is high compared to previous studies in the region (Table 2.6).

4.9.4 Cu

Copper values show low abundance, within a range from 2.18 mg/kg to10.7 mg/kg. The maximum value was recorded at stations KH6, and KH7 in Fujairah, whereas station KH4 for Khorfakkan has the minimum values with average value 6.8 mg/kg and S.D 2.8 (Fig. 4.50 D). The distribution map shows an increasing trend towards southern part of the study area around KH5 to KH12 stations (Fujairah and Kalba) (Fig. 4.54). The Cu average in the study area is high compared to previous studies in the region (Table 2.6).

4.9.5 Mn

The Manganese values ranged from 107 mg/kg to 289 mg/kg. The maximum value of Mn found at station KH8 for Fujairah and the minimum value found at KH2 station with average value 191.4 mg/kg and S.D 68.08 (Fig. 4.50 E). The distribution map shows an increasing trend towards southern part of the study area around KH5 to KH12 stations (Fujairah and Kalba) (Fig. 4.55). The Mn average in the study area is low compared to previous studies in the region (Table 2.6).

4.9.6 Ni

Nickel values vary widely among stations, within a range from 170 mg/kg to 591 mg/kg with average value 398.4 mg/kg and S.D 156.14 (Fig. 4.50 F). The maximum value was recorded at coastal stations KH8 for Fujairah. The minimum values were reported at marine sediments S1, S2, and S3. The distribution map shows an increasing trend toward southern and northern parts of the study area (Fig. 4.56). The Ni average in the study area is high compared to previous studies in the region (Table 2.6).

4.9.7 Pb

Lead values ranged from 0.7mg/kg to 6.65 mg/kg with average 2.4 mg/kg and S.D 1.4(Fig. 4.50 G). The maximum value was found at station KH12, whereas the minimum values were reported at KH3, and KH4. The distribution map shows an increasing trend around KH8 to KH12 stations (Fujairah and Kalba) (Fig. 4.57). The Pb average in the study area is high compared to previous studies in the region (Table 2.6).

4.9.8 V

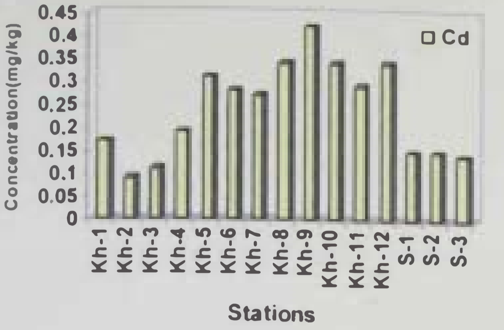
Vanadium values ranged from 6.92 mg/kg to 36.3 mg/kg with average value 18.29 mg/kg and S.D 8.8 (Fig. 4.50 H). The maximum value was recorded at station KH5, whereas the minimum values are found at KH4. The distribution map shows an increasing trend toward southern part of the study area (Fujairah and Kalba) (Fig. 4.58). The V average in the study area is low compared to previous studies in the region (Table 2.6).

4.9.9 Zn

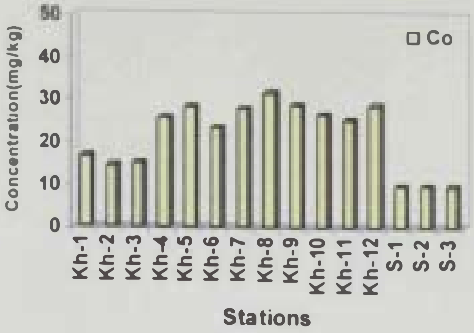
Zinc values ranged from 7.7 mg/kg to 23.5 mg/kg with average value 115.8 mg/kg and S.D 4.9 (Fig. 4.50 I). The maximum value was reported at station KH6, whereas the minimum values were found at KH2. The distribution map shows an increasing trend toward northern part of the study area (Khorfakkan) (Fig. 4.59). The Zn average in the study area is high compared to previous studies in the region (Table 2.6).

Table 4.13: Concentrations of heavy metals (mg/kg) in the studied stations.

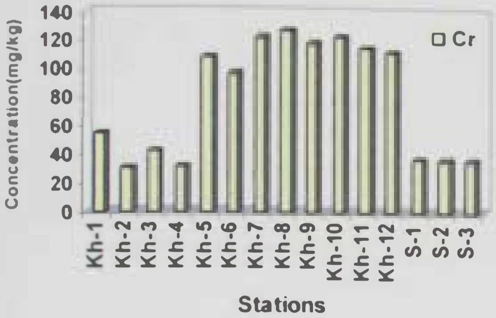
Stations	Cd	Co	Cr	Cu	Mn	Ni	Pb	V	Zn
KH1	0.17	16.7	54.9	4.71	128	296	3.34	18.3	11.7
KH2	0.09	14.4	30.2	2.96	107	246	2.87	15.5	7.74
KH3	0.11	15.1	42.9	3.6	114	285	0.73	7.56	8.48
KH4	0.19	25.7	31.7	2.18	178	517	0.78	6.92	12.7
KH5	0.31	28.2	108	9.61	250	502	2.1	36.3	20.3
KH6	0.28	23.4	97	10.7	231	413	2.53	29.1	23.5
KH7	0.27	27.9	122	10	246	482	3.66	27.4	18.1
KH8	0.34	31.6	127	9.24	289	591	1.78	24.1	20.4
KH9	0.42	28.7	118	8.3	255	556	2.56	19.5	19.2
KH10	0.34	26.6	123	8.74	246	523	1.7	21.6	19.6
KH11	0.29	25.1	115	8.42	235	510	2.14	19.8	20.9
KH12	0.34	28.5	112	8.96	249	538	6.65	21.3	18.5
S-1	0.15	9.67	36.8	5.14	113	171	1.95	9.23	12.2
S-2	0.15	9.84	36.4	5.2	115	176	1.98	8.73	12.7
S-3	0.14	9.64	36.7	4.88	115	170	1.89	9.05	12
average	0.24	21.4	79.44	6.843	191.4	398.4	2.4	18.29	15.87
S.D	0.1	7.927	40.57	2.832	68.08	156.14	1.41	8.835	4.98


Concentration(mg/kg)
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
☐ Cd
Kh-1
Kh-2
Kh-3
Kh-4
Kh-5
Kh-6
Kh-7
Kh-8
Kh-9
Kh-10
Kh-11
Kh-12
S-1
S-2
S-3
Stations

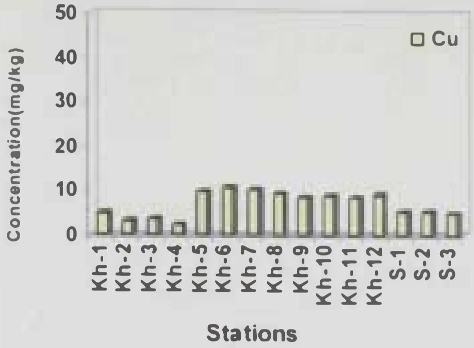
A.


Concentration(mg/kg)
0
10
20
30
40
50
☐ Co
Kh-1
Kh-2
Kh-3
Kh-4
Kh-5
Kh-6
Kh-7
Kh-8
Kh-9
Kh-10
Kh-11
Kh-12
S-1
S-2
S-3
Stations

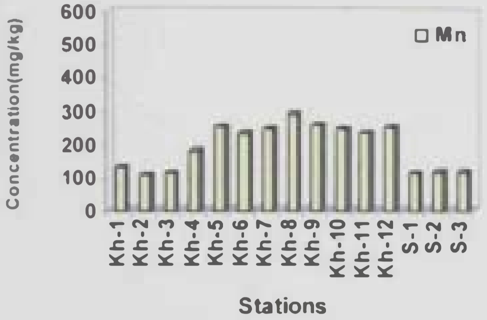
B.


Concentration(mg/kg)
0
20
40
60
80
100
120
140
☐ Cr
Kh-1
Kh-2
Kh-3
Kh-4
Kh-5
Kh-6
Kh-7
Kh-8
Kh-9
Kh-10
Kh-11
Kh-12
S-1
S-2
S-3
Stations

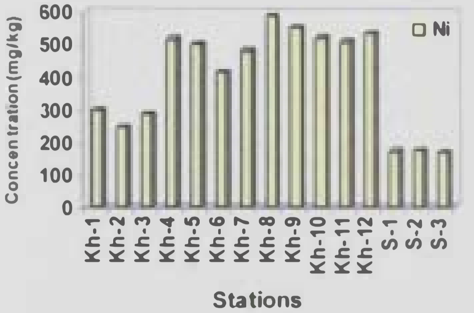
C.


Concentration(mg/kg)
0
10
20
30
40
50
☐ Cu
Kh-1
Kh-2
Kh-3
Kh-4
Kh-5
Kh-6
Kh-7
Kh-8
Kh-9
Kh-10
Kh-11
Kh-12
S-1
S-2
S-3
Stations

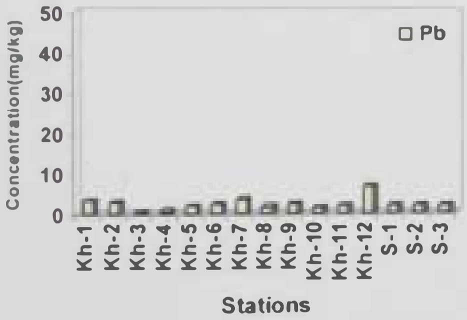
D.


Concentration(mg/kg)
0
100
200
300
400
500
600
☐ Mn
Kh-1
Kh-2
Kh-3
Kh-4
Kh-5
Kh-6
Kh-7
Kh-8
Kh-9
Kh-10
Kh-11
Kh-12
S-1
S-2
S-3
Stations

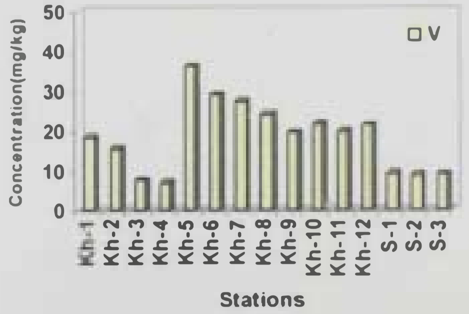
E.


Concen tration (mg/kg)
0
100
200
300
400
500
600
☐ Ni
Kh-1
Kh-2
Kh-3
Kh-4
Kh-5
Kh-6
Kh-7
Kh-8
Kh-9
Kh-10
Kh-11
Kh-12
S-1
S-2
S-3
Stations

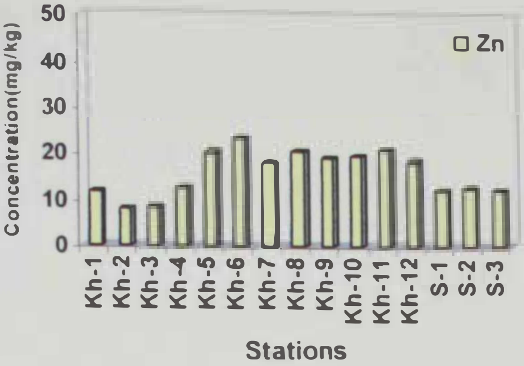
F.


Concentration(mg/kg)
0
10
20
30
40
50
☐ Pb
Kh-1
Kh-2
Kh-3
Kh-4
Kh-5
Kh-6
Kh-7
Kh-8
Kh-9
Kh-10
Kh-11
Kh-12
S-1
S-2
S-3
Stations

G.


Concentration(mg/kg)
0
10
20
30
40
50
☐ V
Kh-1
Kh-2
Kh-3
Kh-4
Kh-5
Kh-6
Kh-7
Kh-8
Kh-9
Kh-10
Kh-11
Kh-12
S-1
S-2
S-3
Stations

H.



I.

Fig. 4.50: Histograms representing concentrations of trace elements (mg/kg) in eastern side of UAE.

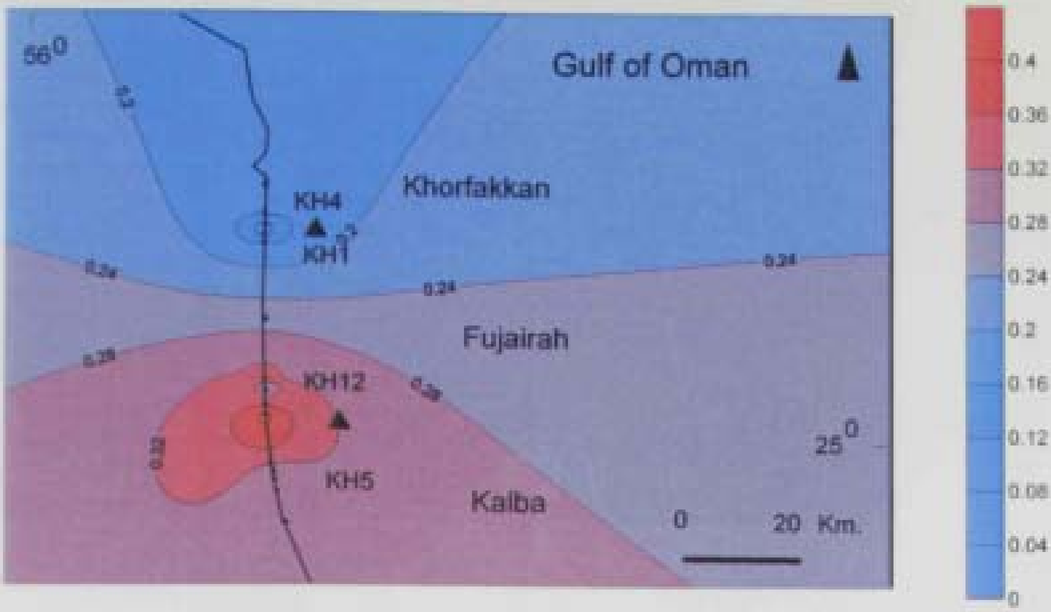


Fig. 4.51: Distribution map of Cd (mg/kg) in eastern side of UAE.

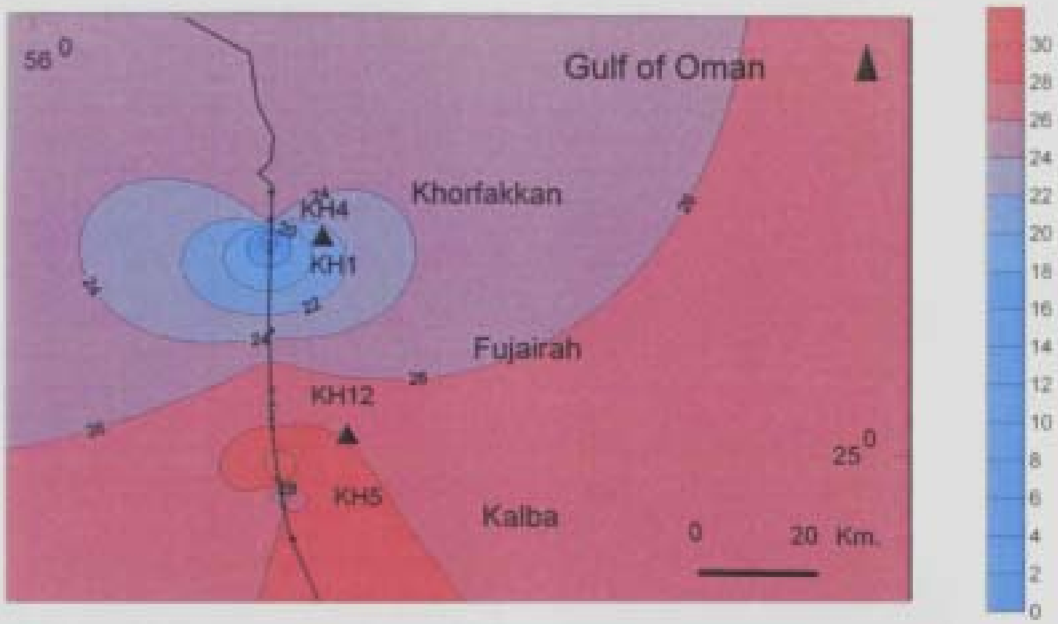


Fig. 4.52: Distribution map of Co (mg/kg) in eastern side of UAE.

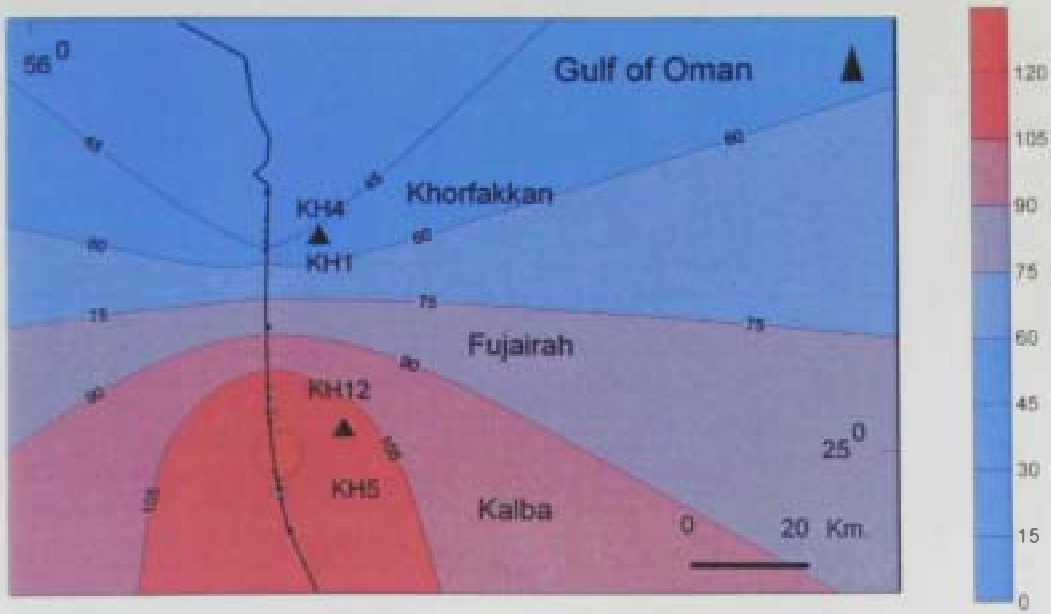


Fig. 4.53: Distribution map of Cr (mg/kg) in eastern side of UAE.

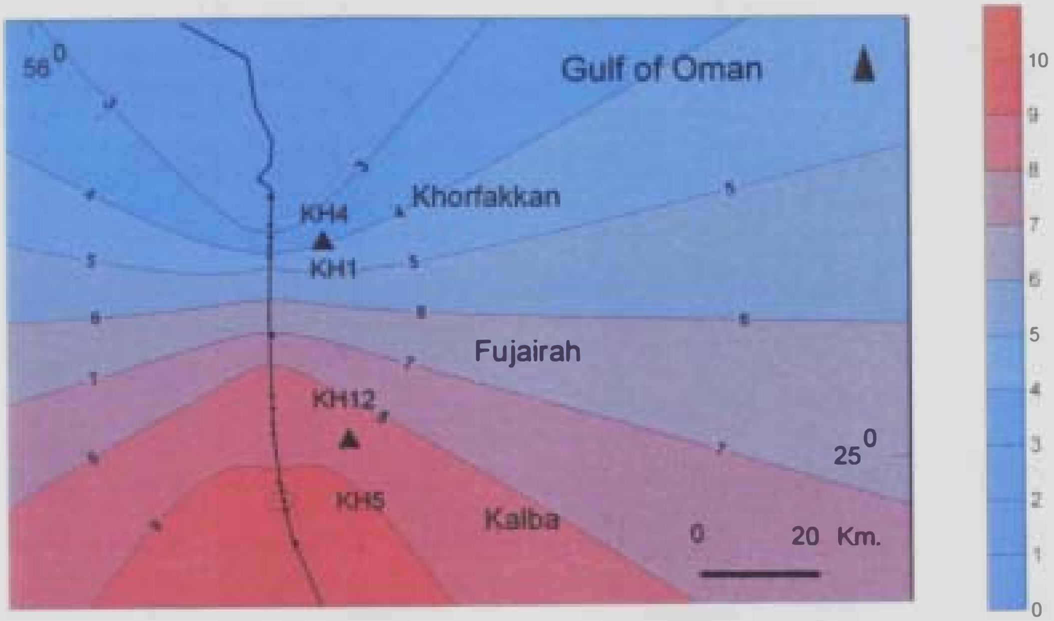


Fig. 4.54: Distribution map of Cu (mg/kg) in eastern side of UAE.

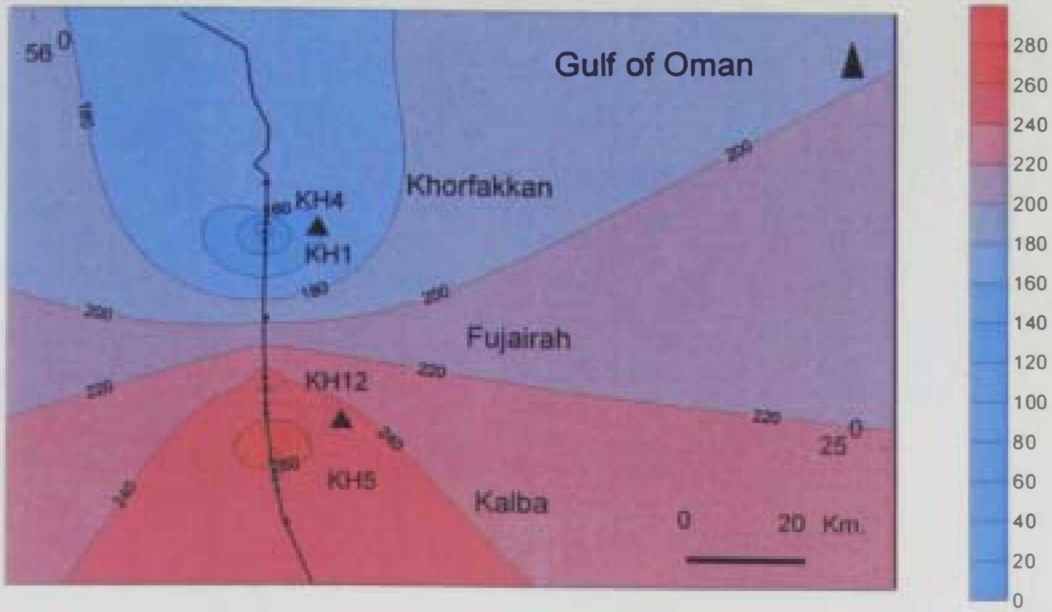


Fig. 4.55: Distribution map of Mn (mg/kg) in eastern side of UAE.

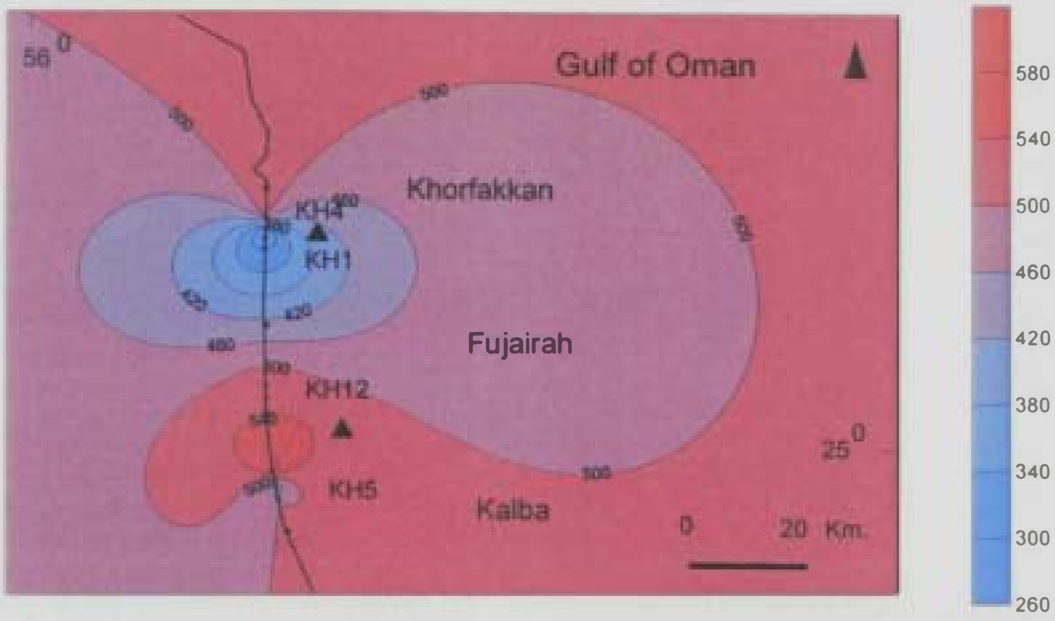


Fig. 4.56: Distribution map of Ni (mg/kg) in eastern side of UAE.

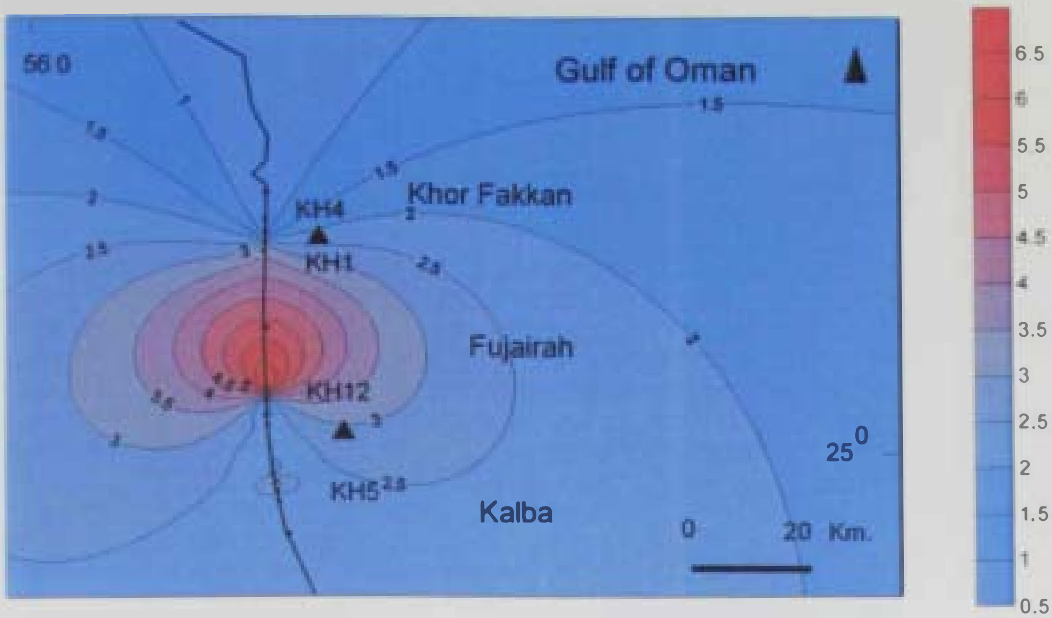


Fig. 4.57: Distribution map of Pb (mg/kg) in eastern side of UAE.

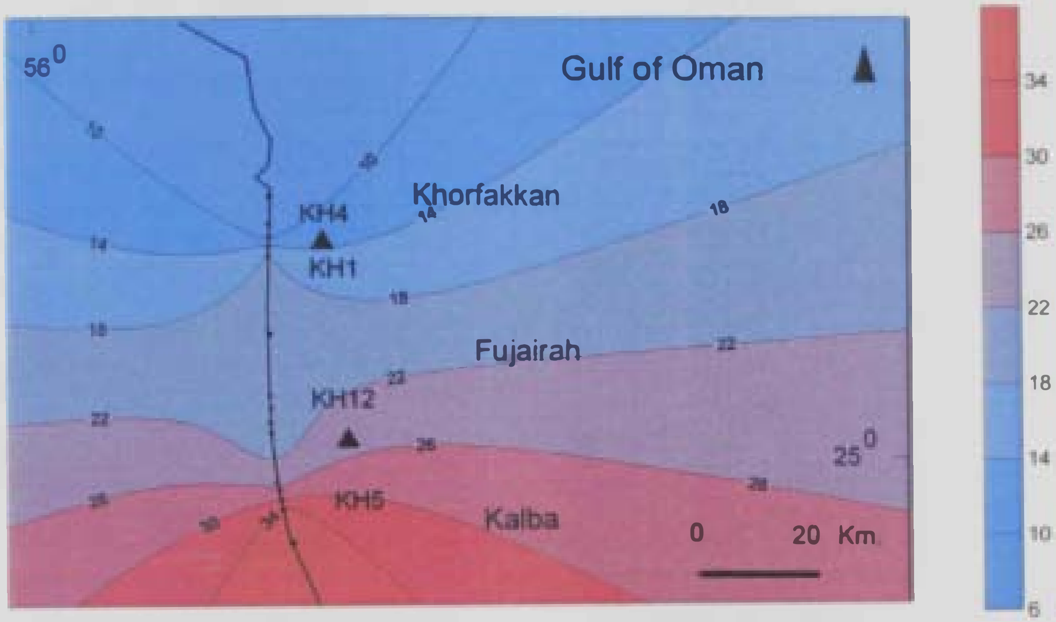


Fig. 4.58: Distribution map of V (mg/kg) in eastern side of UAE.

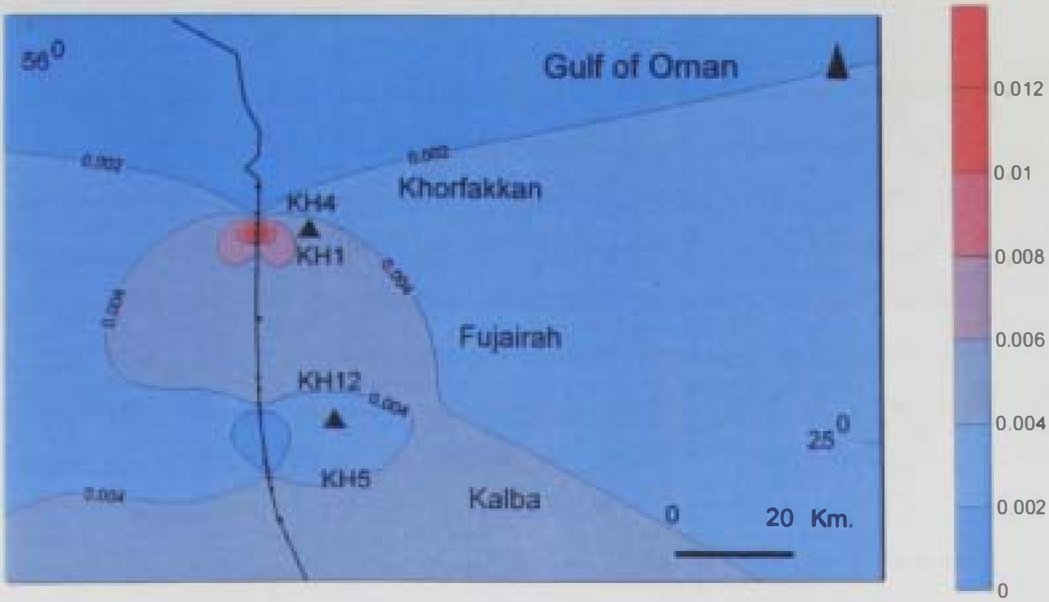


Fig. 4.59: Distribution map of Zn (mg/kg) in eastern side of UAE.

4.10 Statistical analysis

Dendrogram is an appealing method of displaying relationships between multivariate objects. The closest relationships are between nearest objects. Linkage refers to how the distance between an object and a cluster, or between two clusters (as opposed to two individual objects) is measured. Single linkage reflects the similarity of the two similarity measure and linkage method affect the appearance of the resulting dendrogram. The most-widely used parameters for measuring distance are the correlation coefficient and Euclidean distance (equals the sum of squares of differences of the N variable values between the two points).

The chemical associations of the various metals and pollutants can also be assessed using multivariate statistical analysis. The cluster analysis i.e. single linkage and euclidean distance were performed on the data matrix comprising 15 variables. The obtained dendrogram (Fig. 4.60) shows three major clusters, six heavy metals i.e. Co, V, and Zn, Cu, Pb and Cd with TOC distribution as one cluster. This reflected the positive relationship between these metals with TOC, which indicates the sources of these metals and TOC may can from industrial activities. Second clustered between TPCBs, TPH, TPAHs, Co, and Cr which indicated the second sources of pollution were from oil spilled, harbor and airplane and atmospheric deposition of PCBs from different industry. Final groups were TKN with Mn and Ni and these illustrate the relationship between TKN with these elements, which reflected the agriculture sources (fertilizer).

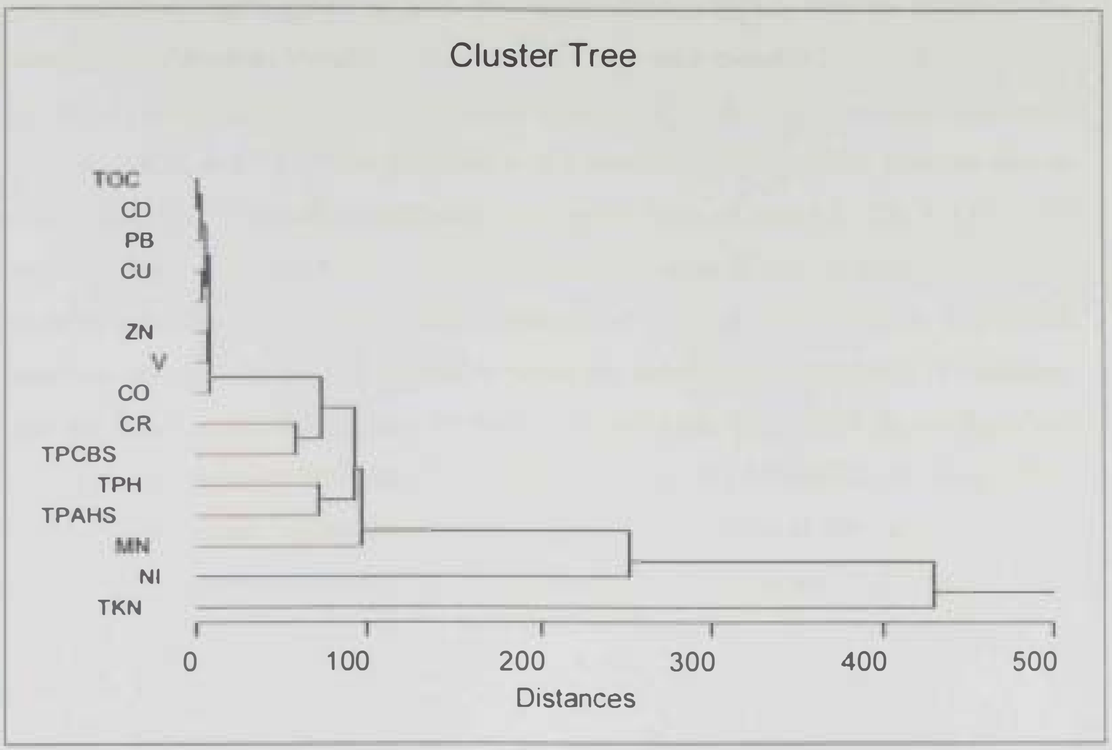


Fig. 4.60: Cluster analysis dendrogram for all sampling stations.

4.10.1 Correlation matrix

The statistical correlation matrices are multivariate analyses used to correlate the relationships between variables such as major and trace metals (Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn), TOC, TKN, and TPH (Table 4.14). The organic compounds such as TOC, TKN, and TPH. The correlation is a measure of the relation between two or more variables. Correlation coefficients can range from -1.0 to 1.0. The value o -1.0 represents a perfect negative correlation while a value of 1.0 represents a perfect positive correlation. A value of zero represents a lock of correlation. A correlation matrix is always a symmetric matrix to locate the correlation for any pair of variables, find the value in the intersection for those two variables. Table 4.14 shows that there are positive correlation between TOC and TKN, V and Zn, Ni and Zn, Ni, Zn and Mn. There are 78 unique correlations by using the follow l formula that tells how many pairs (e.g., correlation variables: $\frac{N*(N-1))}{2}$ where N is the number of variables.

Table 4.14: Correlation matrix between trace elements, TPH, TKN and TOC (P<.05) for study area.

	TPH	TKN	TOC	CD	CO	CR	CU	MN	NI	Pb	V	ZN
TPH	1											
TKN	-0.363	1										
TOC	-0.277	0.641	1									
CD	-0.039	-0.137	-0.569	1								
CO	0.086	-0.237	-0.609	0.883*	1							
CR	-0.074	-0.08	-0.519	0.899**	0.808	1						
CU	-0.188	0.198	-0.451	0.799*	0.702	0.931	1					
MN	-0.045	-0.077	-0.565	0.930**	0.957	0.926	0.861	1				
NI	0.093	-0.316	-0.621	0.873*	0.975	0.756	0.601	0.917	1			
Pb	-0.177	0.089	0.007	0.256	0.168	0.293	0.344	0.2	0.086	1		
V	-0.247	0.25	-0.21	0.561	0.512	0.704	0.854	0.651	0.355	0.309	1	
ZN	-0.227	0.173	-0.527	0.862*	0.8	0.88	0.92	0.916	0.758	0.171	0.738	1

Pearson correlation matrix

*: the r^2 values are significant at probability level = 0.05

**: the r^2 values are significant at probability level = 0.01

4.10.2 Factor analysis

The principal component factor analysis, at its simplest, can be regarded as an ordination technique for reducing multivariate data into fewer dimensions (rock, 1988). Factor analysis was applied for selected elements and compounds. The analysis reveals two factor solutions (Table 4.15 & Fig. 4.61). Chemical elements, including all the heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn) with other organic compounds (TPH), are positively loaded on factor 1. This association could be related to pollution and the adsorption of heavy metals by organic matter, and may be termed "pollution factor or oil spilled factor". The second factor is a bipolar factor: TKN and TOC this factor may be related to "land pollution factor" which reflected industry and agricultural pollutions.

Fig. 4.15 illustrates the association of trace metals with TPH and TOC. There is positive correlation with trace metals and TPH correlated negatively with all trace elements except Ni = (0.09) and Co= (0.08). TOC correlated negatively with all trace elements except Pb= (0.007). This indicates that these pollutants are not related with crude oil, or natural seepage, which suggests the anthropogenic sources. 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 4.15: Factor loadings of trace elements and organic compounds of study area.

Variable	**Factor 1**	**Factor2**
TPH	-0.0101	-0.534
TKN	-0.11	0.826
TOC	-0.629	0.473
Cd	0.95	-0.07
Co	0.916	-0.229
Cr	0.956	0.08
Cu	0.9	0.358
Mn	0.982	-0.024
Ni	0.878	-0.353
Pb	0.254	0.405
V	0.685	0.525
Zn	0.939	0.22
Expl.Var	**7.787**	**2.015**
Prp.Totl	**59.9**	**15.503**

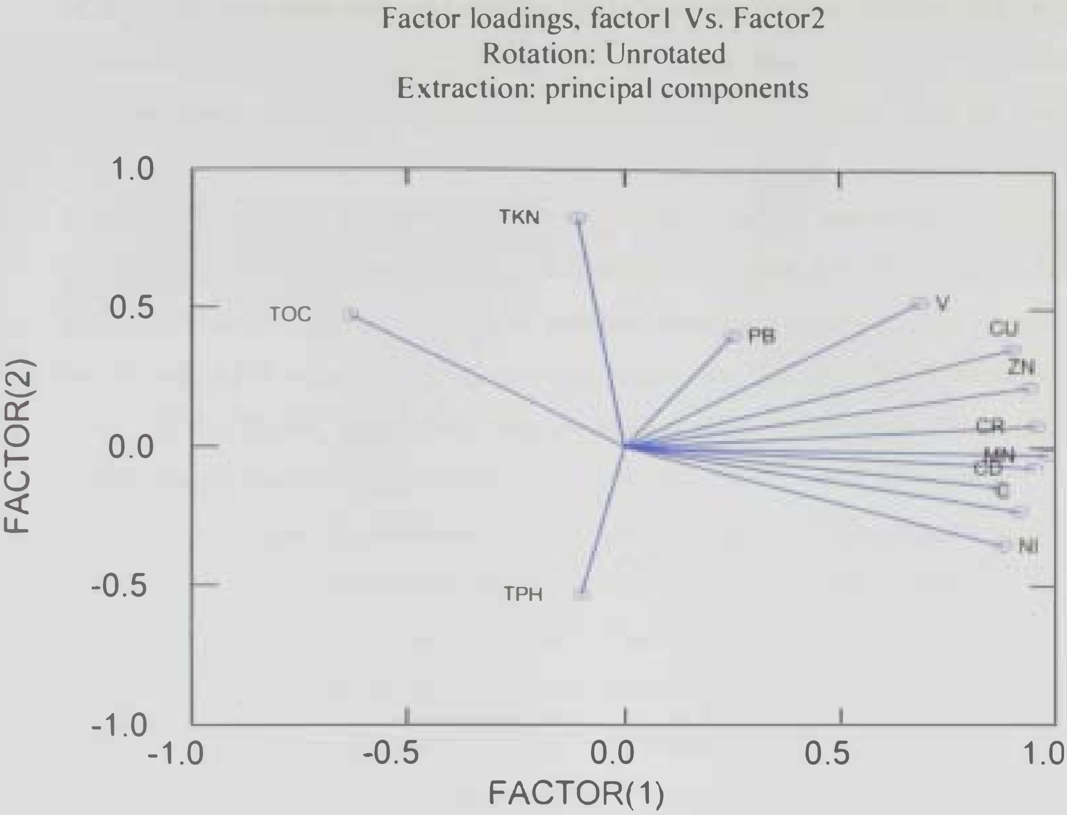


Fig. 4.61: Factor analysis of trace elements, TOC, TPH, and TKN for study area.

4.11 Effect of Grain Size in pollutants accumulation.

Tables 4.16 and 4.17 demonstrate the relation between TPH, TOC, TKN, TPAHs, PCBs, and trace elements and various grain size parameters. It is notable that the concentrations of these pollutants increase with grain size decreasing. The deviation from this trend attributed to geographical position and the distance from the source of pollution.

Figure 4.62 reflected the mean size (Φ) distribution in the eastern side of the UAE (Fujairah, Khorfakkan and Kalba). It is clearly noted that the stations from KH2 to KH12 are covered mainly by fine to medium sand and some parts by coarse sand, which only KH1 was covered by pebbles, where the highest concentration of TPH, TOC, TKN, TPAHs, and TPCBs are recorded at KH7, KH2, KH6, KH4, and KH9. The highest values of trace elements such as Mn, Ni, Co, and Cr were recorded at KH8, which covered by mediums and reflected poorly sorted. The highest value of Zn and Cu were reported at KH6, which covered by medium sand, which recorded the highest value of TKN in these stations. The highest value of Pb was recorded at KH12, which covered by medium sand and the highest concatenation of V was recorded at KH5, which covered by fine sand that recorded the highest value of TPH. The highest value of Cd were recorded at KH9 and KH11, which covered by medium to fine sand. The stations KH1, KH3, and KH10 are covered mainly by pebble to coarse sand in some parts provided the minimal levels of pollutants or unpollutant levels.

Figure 4.63 shows the sorting of eastern side of UAE at different stations. The highest value indicates more moderately sorted, which found at KH3, KH5, KH7, KH9, KH10, KH11, and KH12. Stations KH2, KH4, KH6, and KH8 have poorly sorted and have high concentrations of organic compound and trace elements. 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 4.16: Concentrations of organic compounds and various Grains – size parameters for the study area.

Stations	mean-size (M_Z)	Sorting (Φ)	TPH (mg/kg)	TOC (Wt %)	TKN (mg/kg)	TPAHs (mg/kg)	TPCBs (mg/kg)
KH1	Pebble	extremely poorly sorted	91	0.2	0	0.25	0.115
KH2	fine sand	poorly sorted	177	2.18	825	0.27	0.095
KH3	medium sand	moderately sorted	191	0.22	0	0.19	0.14
KH4	coarse sand	poorly sorted	227	0.15	0	0.19	0.145
KH5	fine sand	moderately sorted	155	0.07	0	0.09	0.08
KH6	medium sand	very poorly sorted	93	0.38	1443	0.15	0.14
KH7	coarse sand	moderately sorted	282	0.05	264	0.28	0.08
KH8	medium sand	poorly sorted	93	0.07	83.8	0.2	0.105
KH9	medium sand	moderately well sorted	235	0.08	130	0.27	0.06
KH10	fine sand	moderately sorted	168	0.31	126	0.16	0.125
KH11	fine sand	moderatley well sorted	146	0.22	130	0.24	0.105
KH12	medium sand	moderately sorted	123	0.08	103	0.07	0.06
S1	---	---	120	2.161	747	0.11	---
S2	---	---	111	2.113	782	0.18	---
S3	---	---	129	1.225	722	0.18	---

Table 4.17: Concentrations of trace elements and various grain-size parameters for the study area.

Stations	**mean-size (M_Z)**	**Sorting (Φ)**	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	V (mg/kg)	Zn (mg/kg)
KH1	**Pebble**	**extremely poorly sorted**	0.17	16.7	54.9	4.71	128	296	3.34	18.3	11.7
KH2	**fine sand**	**poorly sorted**	0.09	14.4	30.2	2.96	107	246	2.87	15.5	7.74
KH3	**medium sand**	**moderately sorted**	0.11	15.1	42.9	3.6	114	285	0.73	7.56	8.48
KH4	**coarse sand**	**poorly sorted**	0.19	25.7	31.7	2.18	178	517	0.78	6.92	12.7
KH5	**fine sand**	**moderately sorted**	0.31	28.2	108	9.61	250	502	2.1	36.3	20.3
KH6	**medium sand**	**very poorly sorted**	0.28	23.4	97	10.7	231	413	2.53	29.1	23.5
KH7	**coarse sand**	**moderately sorted**	0.27	27.9	122	10	246	482	3.66	27.4	18.1
KH8	**medium sand**	**poorly sorted**	0.34	31.6	127	9.24	289	591	1.78	24.1	20.4
KH9	**medium sand**	**moderately well sorted**	0.42	28.7	118	8.3	255	556	2.56	19.5	19.2
KH10	**fine sand**	**moderately sorted**	0.34	26.6	123	8.74	246	523	1.7	21.6	19.6
KH11	**fine sand**	**moderatley well sorted**	0.29	25.1	115	8.42	235	510	2.14	19.8	20.9
KH12	**medium sand**	**moderately sorted**	0.34	28.5	112	8.96	249	538	6.65	21.3	18.5
S-1	---	---	0.15	9.67	36.8	5.14	113	171	1.95	9.23	12.2
S-2	---	---	0.15	9.84	36.4	5.2	115	176	1.98	8.73	12.7
S-3	---	---	0.14	9.64	36.7	4.88	115	170	1.89	9.05	12

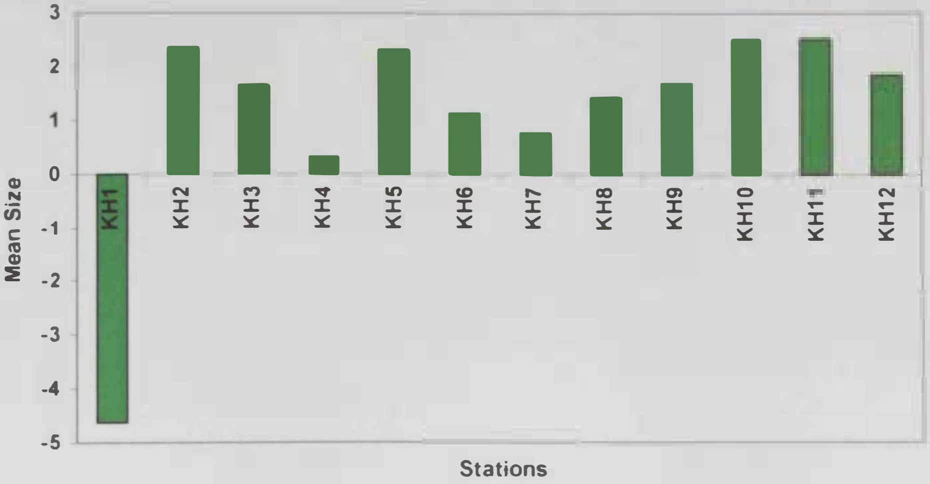


Fig. 4.62: Mean grain –size (φ) distribution in eastern side of the UAE.

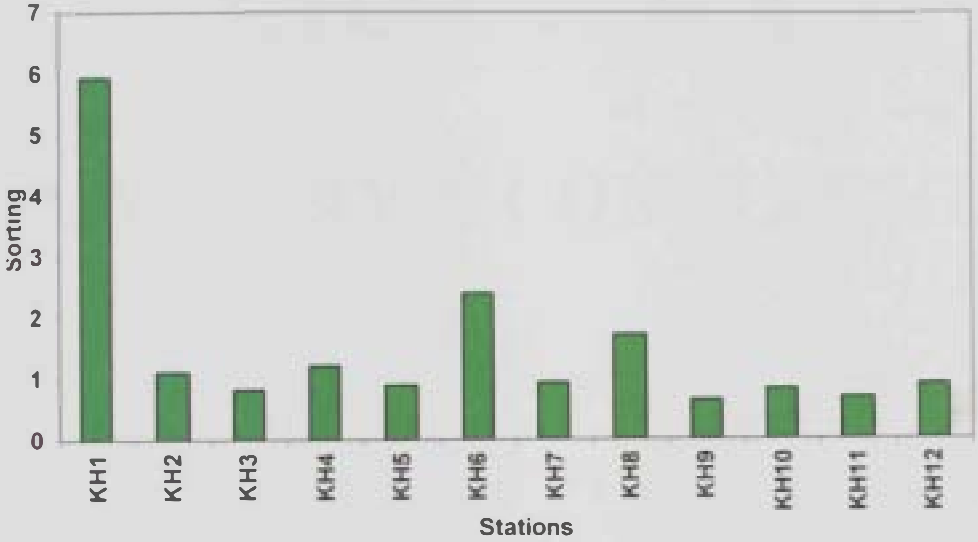


Fig. 4.63: Sorting (φ) of eastern side of the UAE.

CHAPTER 5

SUMMERY & CONCLUSION

SUMMARY AND CONCLUSION

5.1 Summary and Conclusion

The investigated area extends along eastern side of UAE offshore on the Gulf of Oman. Eastern coastal of UAE is approximately 100 km long and consists of Fujairah, Khorfakkan and Kalba. Rapid development in the UAE and the highly usage of the coastal region either for industrial activists and sewage disposal or offshore oil production, and transport, oil spills as well as from pyrolysis/combustion of fossil fuel such as vehicles or from petrogenic sources.

Hydrocarbons are commonly found in the environment as complex mixtures deriving from multiple sources. Therefore, the confident discrimination between biogenic and anthropogenic origin as well as the further recognition of inputs from petrogenic and pyrogenic sources requires the use of geochemical or molecular markers. Geochemical or molecular markers are organic compounds that maintain the signature of their origins and structural modifications which occurred during transport. The use of these compounds is also needed because various hydrocarbon classes show differences in their residence time, stability, transport mechanisms and fate, depending on their physical _ chemical properties and sources.

The present study aims to provide appropriate measurements of organic pollutants such as TOC, TKN, TPH, PAHs, and PCBs and inorganic pollutants such as Cd, Cr, Cu, Co, Pb, Mn, Ni, Zn, and V. The comprehensive perspective about the level of these pollutants is expected to be useful in management of the discharges into marine environment and solving man related problems. Also, it can be used to monitor any future improvement in sediments quality. The data produced from various analytical techniques are used to compare spill samples with sample taken from coastal and marine sediments. A variety of diagnostic ratios, especially ratios of source-specific oil constituent`s including polycyclic aromatic hydrocarbon (PAHs), n-alkanes and isoprenoid alkanes compounds for interpreting chemical data from oil spills have been successfully used for oil source identification and monitoring of weathering and biological degradation processes. In this study, first we determined the product type by recognizing distribution patterns of bulk hydrocarbon groups, then quantified biomarker and extended parent of PAH compounds and compared their distribution profiles. Finally we went the extra mile to verify our conclusions by determining a variety of diagnostic rations of sources- specific marker compounds. Furthermore, we defensibly identified and determined the input of pyrogenic PAHs or petrogenic to the spill samples.

Twelve stations were chosen to cover most fragments of the eastern side of UAE starting from KH1 to KH4 for Khorfakkan, KH5 to KH8 for Kalba and KH9 to KH12 for Fujairah, with three stations collected from marine sediments used to compare between the concentration of organic and inorganic pollutants for coastal and marine sediments. Six sample of oil collected from the spilled oil near investigated area. 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 and AAS were used to carry out the concentration of trace elements. Column chromatography was used to determine the oil samples. GC_FID used to determine the total of aliphatic hydrocarbons (n-alkane and isoprenoid). Statistic™ was used to apply statistical analysis, whereas the surfer™ 7.01 was used to provide the areal distribution of organic and inorganic pollutants.

The grain size analysis showed that about 42 % of the studied stations are covered by medium sand and 33 % covered by fine sand. There is clear trend of increasing the organic and inorganic pollutants by decreasing grain size. The TOC content varies with limited range at coastal stations except the marine samples and one station from coastal shows high concentration compared with natural background level of TOC in the bottom sediments of the Kuwait marine environment. The maximum value is about 42 times higher than the minimum values. TOC at KH2, S1, and S2 is 2.16 wt %, which is 2.6 times higher than the Kuwait background level.

The TKN content shows drastic variation from the maximum to the minimum value in coastal sediment, but marine sediments show approach value. The maximum value is about 17.2 times higher than the minimum value. Marine sediments stations were ranged from 722 to 782 mg/kg, which represent 2.6 times higher than suggested value. Also, KH2 exhibited higher TKN content, which about 9.8 times higher than the minimum value. The higher ratio of (C/N) was recorded at S1 marine sediments and this phenomenon known as deviation by increasing from Redfield ratio. The lowest ratio was reported at KH7 and this also exhibits deviation by decreasing. KH7 shows very higher TPH content, whereas KH1 shows low concentration. The maximum value is about 3.09 times higher than the minimum value. Coastal and marine sediments sample are described as moderately polluted area.

Evidently, TOC correlated significantly negative with TPH (r = -0.277) and moderately positively with TKN(r = 0.64). On the other hand, TPH correlated negative with TKN (r = -0.36). The distribution map of TOC and TPH shows trend of an increasing toward the northern part of study area. Whereas TKN shows trends of an increasing toward the southern part of study area.

The PCBs values show a wide variation from the minimum to the maximum. The maximum values were recorded at KH4 (Khorfakkan) and it is nearly 2.4 times higher than he minimum value, which was found at KH12 (Fujairah). On the other hand, the maximum values of each of individual PCBs (PCB18, PCB52, PCB101, PCB118, PCB105, PCB138, and PCB195) were recorded at KH4. Whereas the maximum value of PCB195 was found at KH4 and also the minimum value of PCB66 was found at the same station. The distribution maps of TPCBs show increasing towards the northern part of study area (Khorfakkan).

The concentration of PAH compounds vary widely among stations. Perylene compound not recorded at any stations for coastal and marine sediments, which may indicates no significant inputs of pyrolytic PAHs. KH7 station exhibits the most compounds of PAHs including Naphthalene, Acenaphthylyene, Acenaphthene, Anthracene, Flourane, Pyrene, Phenanthrene, Fluoranthene, Pyrene, Chrycene, b (k) f, and b (a) p. The maximum value of TPAHs is 4 times higher than the minimum value. The distribution maps for each of compounds show two trend of increasing one toward the southern and another toward northeast of study area. In our study used some ratio of the PAHs to indicate the sources of pollution (petrogenic, biogenic, and pyrogenic). Most ratios show petrogenic source of PAHs pollution which might come from oil spill and transportation activities. A few ratios show another type of sources which is pyrogenic pollution, which reflects industrial activities in this places and atmospheric deposition from combustion sources. Evidently, PAHs ratio indicates a combination of polluted sources in our area, so the PAH compounds not came from spilled oil near Fujairah only but also from different sources.

Aliphatic hydrocarbons analysis can be used as fingerprint spilled oil to provide the degree of degradation of the spilled and to identify the sources of pollution. The total aliphatic hydrocarbon ranging from 7.6 to 79.6 µg/g for coastal sediments, while ranging from 2.5 to 4.2 µg/g for marine sediments and from 0.3 to 5.2 µg/g for spilled oil. The dominant peaks show mainly at C_{29}, C_{31} for coastal sediments , whereas C_{30}, C_{28}, and C_{43} show for marine sediments at C_{30} and C_{32} are the most dominant peak for the oil spill samples which confirm oil spill sources. **CPI_2** at all stations are closed to the 1, which reflected petrogenic sources. The **petrogenic/ biogenic** ratios at most stations show petrogenic rather than biogenic and land-based sources. KH1, KH2, KH8, S1, S2, and S3 show long chain alkanes than the short chain alkanes, which reflected terrestrial plant sources from Fujairah and Khorfakkan harbor and industrial activities. The **Pr/Ph** ratio for stations samples indicted oil spill sources. **Alk_{terr}** are low values for almost all coastal and marine stations and this may indicates multi-sources contaminations for the study area.

Evidently, trace elements show various trends of an increasing. The highest concentrations were recorded at KH8 (Fujairah) for Cr, Mn, and Ni, whereas KH9 shows the minimum value of Cd and Co. The highest concentration of Zn was recorded at KH6, whereas the maximum value of V was recorded at KH5.

Based on the overall estimation, it can be concluded that:

1- Fine and poorly sorted sand tend to have high values of organic substance and inorganic metals. The adsorption into fine –grained sediment is probably due to the larger surface area.

2- The level of TOC is 2.6 times higher than unpolluted region in the Arabian Gulf as be recorded by same investigator.

3- TOC content can be used as indicator of hydrocarbon contamination when TPH are present in high concentration. The maximum value of TOC is 42 times higher than minimum value in our study.

4- KH7 (Kalba) station shows very higher TPH content, whereas KH1 shows low concentration. The maximum value is about 3.09 times higher than the minimum value. Coastal and marine sediments sample are described as moderately polluted area.

5- The TKN content shows drastic variation from the maximum to the minimum value in coastal sediment but marine sediments show approach value. The maximum value is about 17.2 times higher than the minimum value.

6- The presences of Zn, Cu, V, Ni and Pb with TPH suggested that the sources of pollutant are related to the crude oil.

7- There is negative correlation is which found between TPH and TKN(r= -0.36), and between TPH and TOC (r = -0.277). There is moderately positive correlation between TOC and TKN (r = 0.64).

8- S1 marine sediments exhibit the maximum value of TOC, TKN and C/N.

9- KH4 (Khorfakkan) station exhibits the maximum concentration of TPCBs, whereas KH9 show low value of TPCBs. The highest value of PCB individual was PCB195, which reflect that the source of pollution was combustion or/ and industrial activities.

10- Analyses of the PAH compositions and diagnostic ratios indicated petrogenic (petroleum pollution) PAHs at most of samples

11- KH7 station (Kalba) exhibited the most PAHs compounds including Naphthalene, Acenaphthylyene, Acenaphthene, Anthracene, Flourane, Pyrene, Phenanthrene, Fluoranthene, Pyrene, Chrycene, b(k)f , b(a)p, Cu, Cr, Mn, Ni, and V . The maximum value of TPAHs is 4 times higher than the minimum value.

12- PAHs were divided in to three groups according to the MW. Most PAHs in our study are low MW, which indicate the source of pollution was spilled oil. The ∑PAH carcinogenic ratio shows high value attained at marine sediments rather than coastal sediments.

13- Indeno(1,2,3-c,d)pyrene/(Indeno(1,2,3-c,d)pyrene+Benoz(ghi)perylene) Indeno/(indeno+BghiP) ratio recorded lower concentration than 0.33 ± 0.06 observed for automobile emission.

14- (P/N) and BaA/(BaA+ Chry) ratios indicate pyrogenic sources at all stations, whereas flu/(flu+P)>1 , which reflected petrogenic sources of oil spill.

15- Sedimentary hydrocarbons in the beach consist of anthropogenic hydrocarbon inputs were more associated with industrial discharges, shipping activities and oil spills.

16- The total aliphatic hydrocarbon ranging from 7.6 to 79.6 µg/g for coastal sediments, while ranging from 2.5 to 4.2 µg/g for marine sediments and from 0.3 to 5.2 µg/g at oil spill.

17- Diagnostic ratio of aliphatic hydrocarbon reflected at most stations petrogenic sources rather than biogenic sources, whereas some ratios in KH1, KH2, KH8 ,S1, S2, and S3 show terrestrial plant sources from Fujairah, Khorfakkan harbor and industrial activities.

18- The variation in concentration from station to another and the high relative S.D of most studied pollutants raise the suggestion of anthropogenic sources.

****

REFRENCES

ATSDR. (1990). (Agency for Toxic Substances and Disease Registry).Toxicological profile for polycyclic aromatic hydrocarbon (PAHs). Acenaphthene, Acenaphthylene, Anthracene, Benzo(a)Anthracene, Benzo(a)Pyrene, Benzo(b)Fluoranthene, Benzo(g,I,h)Perylene, Benzo(k)Fluoranthene, chrysene, Dibenzo(a,h)Anthracene, Fluoranthene. Fluorene, Indeno(1,2,3-c,d)Pyrene, phenanthrene, Pyrene. ATSDR/TP-90-20

Ahlborg, U. G. Hanberg, A, Kenne, K. risk assessment of polychlorinated biphenyls (PCBs). Nord; 1992; 26.1-86P.

Al- Abdali, F., Massoud, M.S and Al-Ghadban, A.N. (1996). Bottom Sediments of the Arabian Gulf-III. Trace metal contents as indicators of pollution and implications for the effect and fate of the Kuwait oil slick. ***Environmental Pollution***. 93:283-301.

Al- Abdul-Razzak, F.H.Y. (1984). Marine Resources of Kuwait. London: Publisher in association Kuwait University.

Al-Darwish, H. D. A. (2004). Assessment of Organic and Inorganic pollutants in the offshore sediments, Dubai, UAE. M.Sc.Thesis.UAE University P.1-163

Al-Ghadban, A., Jacob, P., and Abdali, F. (1994) Total Organic Carbon in the Sediments of the Arabian Gulf and Need for Biological Productivity Investigations, ***Mar.Pollut.Bull*** 28:356-362

Alloway, B.J. (1993). Chemical principles of environmental pollution. London: Blackee academic and professional, an important of Chapman and Hall.

Amaral, E.J. and Prauar, W.A. (1977). Depositional environment of the St. Peter sandtone deduced by textural analysis. ***Journal of Sedimentary Petrology***. 47: 32-52.

Azam khan, M.A. and Ahmed khan, Y.S. (2003). Trace metals in littoral sediments from the north east coast of the Bay of Bengal along the ship breaking area, Chittagong, Bangladesh. ***Journal of Biological Sciences***.**3 (11)**:1050-1057.

Baird, C. (1999). Environmental Chemistry, Second Edition, W. H. Freeman and Company, New York

Bloemen, M.L., Markert, B. and Lieth, H. (1995). The distribution of Cd, Cu, Pb and Zn in topsoils of Osnabruck in relation to land use. ***Sci. Total Environ***. **166**: 137-148

Cao, Z., Wang, Y., Ma, Y., Xu, Z., Shi, G., Zhuang, Y., Zhu, T. (2005). Occurrence and distribution of polycyclic aromatic hydrocarbons in reclaimed water and surface water of Tianjin, China. ***Journal of Hazardous Materials***.**A122**: 51-59.

Colombo, J.C., Barreda, A., Bilos, C., Cappelletti, N., Demichelis, S., Lombardi, P., Migoya, M.C., Skorupka, C., Suarez, G. (2005). Oil spill in the Rio de la Plata Estuary, Argentina:1. Biogeochemical assessment of waters, sediemtns, soils and biota. ***Environmental Pollution***. **134**: 277-289.

Commendatore, M.G and Esteves, J.L. (2004). Natural and Anthropogenic hydrocarbons in sediments from the Chubut River (Patagonia, Argentina).

Dahle, S., Savinov, V.M., Matishov, G.G., Evenset, A., Naes, K. (2003). Polycyclic aromatic hydrocarbons (PAHs) in bottom sedmetns of the Kara Sea shelf, Gulf of Ob and Yenisei Bay. ***The Science of the Total Environment***. **306**: 57-71.

De Leca, G., Furesi, A., Micera, G., Panzanelli, A., Costantina Piu, P., Itria pilo, M., Spano, N., Sanna, G. (2005). Nature distribution and origin of polycyclic aromatic hydrocarbons (PAHs) in the sediments of Olbia Harbor (Northern Sardinia, Italy). ***Mar.Pollut.Bull***. **50**:1223-1232.

De Mora, S., Fowler, S.W., Tolosa, I., Villeneuve, J.P., Cattini, C. (2005). Chlorinated Hydrocarbons in Marine biota and Coastal sediments from the Gulf and Gulf of Oman. ***Mar.Pollut.Bull.*** **50**: 835-849.

Dell' Anno, A., Mei, M. L., Pusceddu, A. and Danovaro, R. (2002). Assessing the trophic state and eutrophication of coastal marine systems: a new approach based on the biochemical composition of sediments organic matter. ***Mar.Pollut.Bull.*** **44**: 611-622

El-sabrouti, M. A, Dowidar, N. M and El-sammak, A.A. (1990). Distribution of organic carbon, nitrogen and phosphorus in recent sediments of the Mediterranean continental shelf of Egypt. ***Acta Adriat.*** **31(1/2)**: 23-35.

Embabbi, N.S. and Sharkawi, F.M (1989). Landform systems of the United Arab Emirates first symposium on remote sensing in the United Arab Emirates. UAE University. 19-21 February 1989 P.355-388.

EPA (Environment Protection Agency). (1993). The determination of nitrogen according to Kjeldahl using block digestion and steam distillation. AN 300.

EPA (Environment Protection Agency). (1999). Polychlorinated Biphenyls (PCBs) update: Impact on Fish Advisories. EPA- 823-F-99-019

Evans, G. (1966). The recent sedimentary facies of the Persian Gulf Region. Royal Sco. Lond.259 (1099), 291-298

Fabbri, D., Sangiorgi, F., Vassura, I. (2005). Pyrolysis --GC-MS to trace terrigenous organic matter in marine sediments: a comparison between pyrolytic and lipid markers in the Adriatic Sea. ***Analytica Chimica Acta.*** **53**: 253-261.

Fang, M.D., Lee, C.L., Yu, C.S. (2003). Distribution and source recognition of polycyclic aromatic hydrocarbons in the sediments of Hsin-Ta Harbor and adjacent coastal areas, Taiwan. ***Mar.Pollut.Bull.*** **46**: 941-953.

Faroon. O. M., Keith, L. S., smith-simon. C. De Rosa. C. T. Polychlorinated Biphenyls: Human Health Aspects. World health Organization: 2003. 1-57P.

Faust. R.A. (1994). Toxicity summary for Acenaphthylene. ***Oak Ridge Reservation Environmental Restoration Program***. 1-7

Folk. R.L. (1966). A review of grain size parameters. ***Sedimentology***. 6: 73-93.

Folk. R.L. and Ward, W.C. (1957). Brazos River bar, a study in the significance of grain- size parameters. ***Journal of Sedimentary Petrology***. 27: 3-26.

Fowler, S. W. (1988). Coastal baseline studies of pollutants in Bahrain, UAE and Oman. Proceedings of the Symposium on Regional Marine Pollution Monitoring and Research Programmes Al Aion UAE, December 8-11. ROPME/GC-4/2

Fowler. S.W., Readman. J.W., Oregioni. B., Villeneuve, J.P. and Mckay, K. (1993). Petroleum hydrocarbons and trace metals in nearshore Gulf sediments and biota before and after the 1991 war: An assessment of temporal and spatial trends. ***Mar.Pollut.Bull***. 27: 171-182.

Guinan. J. (2001). Sources and Geochemical constraints of polycyclic aromatic hydrocarbons (PAHs) in Sediments and Mussels of two northern Irish Sea-Loughs. ***Mar.Pollut.Bull.*** **42**: 1073-1081.

Hartmann, P.C., Quinn, J.G., Cairns, R.W., King, J.W. (2004). Polychlorinated biphenyls in Narragansett Bay surface sediments. ***Chemosphere***. 57: 9-20.

Hayens, D. and Johnson, J.E. (2000). Organochlorine, heavy metals and polyaromatic hydrocarbons pollutant concentrations in the Great Barrier Reef (Australia) Environment: a review. ***Mar.Pollut.Bull***. 41: 267-278

Huang, X.D., El Alawi, Y., Gurska, J., Glick, B.R., Greenberg, B.M. (2005). Amulti-process phytoremediaiton system for decontamination of persistent total petroleum hydrocarbons (TPHs) from soils. ***Microchemical Journal***. **81**: 139-147.

Kot-Wasik, A., Debska, J., Namiesnik, J. (2004). Monitoring of organic pollutants in coastal water of the Gulf of Gdansk, Southern Baltic. ***Mar.Pollut.Bull***. **49**: 264-276.

Literathy, P. (1993) Considerations for the Assessment of Environmental Consequences of the 1991 Gulf War. ***Mar.Pollut.Bull*** **27**: 349-356

Liu, W and Huang, Y. (2005). Compound specific D/H ratios and molecular distribution of higher plant leaf waxes as novel pale environmental indicators in the Chinese loess plateau. ***Organic geochemistry***. **36**: 851-860.

Ma, L.L., Chu, S.G., Wang, X. T., Cheng, H. X., Liu, X.F., Xu, X.B. (2005). Polycyclic aromatic hydrocarbons in the surface soils from outskirts of Beijing, China. ***Chemoshere*** **58**: 1355-1363.

Massoud, M.S., Al-Abdali, F., Al-Ghadban, A.N., and Al- Sarawi, M. (1996). Bottom sediments of the Arabian Gulf – II. TPH and TOC contents as indicators of oil pollution and implications for the effect and fate of the Kuwait oil slick. ***Environmental pollution***. **93**: 271-284.

Massoud, M.S., Al-Abdali, F., Al-Ghadban, A.N. (1998). The status of oil pollution in the Arabian Gulf by the End of 1993. ***Environment Internationa***l. **24(1/2)**: 11-22

Medeiros, P.M., Bicego, M.C., Castelao, R. M., Rosso, C.D., Fillmann, G., Zamboni, A.J. (2005). Natural and anthropogenic hydrocarbon inputs to sediments of Patos Lagoon Estuary, Brazil. ***Environmental International***. **31**: 77-87.

Nriagu, J.O. (1989). A global assessment of natural sources of atmospheric trace metals. ***Nature*** **38**: 47-49

O'Neill. P. (1993) Environmental Chemistry, Second Edition, Chapman & Hall, New York

Pena- Mendez, E.Ma., Astorga-Espana, Ma.S., Garcia-Montelongo, F.J. (2001). Chemical fingerprinting applied to the evaluation of marine oil pollution in the coasts of Canary Island (Spain). ***Environmental pollution***. **111**: 177-187.

ROPME. (1999). Regional Organization of Protection for the Marine Environment, Kuwait.

Rowat S.C. (1998). Integrated defense system overlaps as a disease model: with examples for multiple chemical sensitivity. Reviews in Environmental Health, 1998. *Environmental Heath Perspectives*. **106** : Supp.1

Saeed, T., Al-Ghadban. A., Al-Shemmari, H., Al-Mutairi, M. and Al-Hashash, H. (1999) Preliminary Assessment of the Impact of Draining of Iraqi Marshes on Kuwait's Northern Marine Environment. Part II. Sediment Associated Pollutants. Water Scie. and Tech.40 (7):89-98.

Sauer, T.C., Michel, J., Hayes, M.O. (1998). Hydrocarbon characterization and weathering of oiled intertidal sediments along the Saudi Arabian coast tow years after the gulf war oil spill. ***Environment International***. **24**: 43-60.

Shiriadah, M.M.A (1998). Impacts of an oil spill on the Marine environment of the United Arab Emirates along the Gulf of Oman. ***Mar.Pollut.Bull***.**36**: 876-879.

Silliman, J.E. and Schelske, C.L. (2003). Saturated hydrocarbons in the sediments of Lake Apopka, Florida. ***Organic geochemistry***. **34**: 253-260.

Sorensen, J. C. and McCreary, S. T. (1990). Coasts. Institutional arrangements for managing coastal resources and environments. Second Edition. P.3-5. National Park Service, U.S. Department of the Interior and U.S. Agency

Teresa L., Wong W., Wong Y. and Nora F., and Tam Y., (2002) Fate of Polycyclic aromatic Hydrocarbon (PAH) contamination in a mangrove swamp in Hong Kong following an oil spill, ***Mar.Pollut.Bull*** **45**: 339-347

Tolosa, I., De Mora, S. J., Fowler, S. W., Villeneuve, J. P., Bartocci, J., Cattini, C. (2005). Aliphatic and Aromatic Hydrocarbons in Marine biota and Coastal sediments from the Gulf and the Gulf of Oman. ***Mar.Pollut.Bull.*** **50**: 1619-1633

Udden, J.A. (1914). Mechanical composition of clastic sediments. ***Bull American Society***. **25**: 566-744

United Nations Environment Program (UNEP), (1999), Overview on Land- based Sources and Activities Affection the Marine Environment in the ROME Sea Area, UNEP Regional Seas Reports and Studies No. 168

United Nations Environment Program (UNEP), (2002), Regionally Based Assessment of Persistent Toxic Substances, Indian Ocean Regional Report, Switzerland

Vazquez, M.A., Allen K.W., Kattan Y.M. (1999). Long –term effects of the 1991 Gulf war on the hydrocarbon levels in clams at selected areas of the Saudi Arabian Gulf coastline. ***Mar.Pollut.Bull.*** **40**: 440-448.

Wang, Z and Fingas, M. F. (2003). Development of oil hydrocarbon fingerprintring and identification techniques. ***Mar.Pollut.Bull.*** **47**: 423-452.

Wang, Z., Fingas, M., Lambert, P., Zeng, G., Yang, C., Hollebone, B. (2004). Characterization and identification of the Detroit River mystery oil spill (2002). ***Journal of chromatography***. **1038**: 201-214.

Wislon, H.M., Gibson and P.E. O'Sullivan (1993). Analysis of current policies and policies and alternative strategies for the reduction of nutrient loads on eutophication lakes: the example of Slapton Ley, Devon, aquatic conservation: ***Marine and Freshwater Ecosystems***. **3**: 239-251.

Witt, G. (1995). Polycyclic aromatic hydrocarbons in water and sediments of the Baltic Sea. *Mar.Pollut.Bull.* 31: 237-248.

Zhu, Y., Liu, H., Cheng, H., Xi, Z., Liu, X., Xu, X. (2005). The distribution and source apportionment of Aliphatic Hydrocarbons in soils from the Outskirts of Beijing. ***Organic geochemistry***. 36: 475-483.

تم تحليل تسعه عناصر نادرة في الدراسة الحالية. وجد أن متوسط تركيز النيكل(mg/kg 398.4) و المنجنيز(191.4 mg/kg) اعلي في التركيز من العناصر الاخري. والأقل تركيزا كان الكاديوم (0.24 mg/kg). و كذلك خلصت الدراسة إلى أن مستوي التلوث بالعناصر النادرة السابقة الذكر اقل من مستوي التلوث على سواحل الغربية للدولة.

وانتهت الدراسة أيضا إلى زيادة نسبة الملوثات العضوية و غير العضوية بشكل عام في اتجاه المناطق الشمالية حيث اتجاه التيارات البحرية والقرب من المواني و النشاط الحضاري.

الملخص باللغة العربية

تهدف الدراسة الحالية إلى تحديد الملوثات العضوية و غير العضوية لرواسب الساحل الشرقي لدولة الإمارات العربية المتحدة المطل على خليج عمان (الفجيرة. خور فكان, كلباء). نتيجة للتطور السريع و الاستخدام الجائر للسواحل في الأنشطة الصناعية و إلقاء مخلفات النقل البحري أدت إلى التغير السريع في نوعية رواسب البيئة البحرية. تم جمع العينات من اثنا عشر محطة موزعة على معظم المنطقة الساحلية الشرقية و ثلاث عينات جمعت من الرواسب البحرية وأخيرا ستة عينات جمعت من بقعة للزيت تواجدت بالقرب من منطقة الدراسة.

خضعت عينات الدراسة للعديد من التحاليل والتي تشمل: التحليل الحجمي للحبيبات وتحديد الملوثات العضوية ممثلة بتعيين المحتوي الكلي للكربون العضوي والمحتوي الكلي للنيتروجين و المحتوي الكلي للهيدروكربونات البترولية والهيدروكربونات متعددة الحلقات ومركبات ثنائي الفينيل متعدد الكلور. وكذلك تم حساب الملوثات غير العضوية من خلال تعيين تركيز العناصر النادرة (الكادميوم, الكوبلت, الكروم, النحاس, المنجنيز, النيكل, الرصاص, الفناديوم, الخارصين.)

خلصت الدراسة إلى وجود اختلاف في حجم الرواسب (33%– 42%) من رمل متوسط إلى رمل ناعم مما كان له بعض الأثر في زيادة مستوي التلوث لبعض عينات الدراسة. كما أظهرت الدراسة إلى أن متوسط المحتوي الكلي للكربون العضوي هو 0.6% والذي يعتبر قيمة أعلى بالنسبة للدراسات السابقة ومتوسط المحتوي الكلي للهيدركربونات البترولية هو 156 mg/kg. وجد أيضا أن متوسط المحتوي الكلي للنيتروجين هو 357.05 mg/kg. وكذلك أثبتت الدراسة وجود علاقة قوية طردية بين زيادة المحتوي الكلي للكربون و المحتوي الكلي للنيتروجين.

وجد أيضا أن متوسط تركيزات مركبات الهيدروكربونات متعددة الحلقات هو 0.18 mg/kg والذي يعتبر أقل من الدراسات السابقة. وجد أيضا أن متوسط تركيزات مركبات ثنائي الفينيل متعدد الكلور هو 0.104 mg/kg.

جامعة الإمارات العربية المتحدة
عمادة الدراسات العليا
برنامج ماجستير علوم البيئة

تقدير التلوث البحري و الساحلي على امتداد الساحل الشرقي لدولة الإمارات العربية المتحدة

رسالة مقدمة من الطالبة:

شهيرة على جمعه على بهوان

إلى

جامعة الإمارات العربية المتحدة
استكمالا لمتطلبات الحصول على درجة الماجستير في علوم البيئة

2007

جامعة الإمارات العربية المتحدة
عمادة الدراسات العليا
برنامج ماجستير علوم البيئة

تقدير التلوث البحري و الساحلي على امتداد الساحل الشرقي لدولة الإمارات العربية المتحدة

رسالة مقدمة من الطالبة:

شهيرة على جمعه على بهوان

إلى

جامعة الإمارات العربية المتحدة
استكمالا لمتطلبات الحصول على درجة الماجستير في علوم البيئة

2007