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Bakheet Saeed Al Katheeri

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**GEOCHEMICAL STUDIES TO ASSESS
MARINE OIL POLLUTION
ZAKUM FIELD, ABU DHABI, UAE**

**THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF M.Sc. IN
ENVIRONMENTAL SCIENCE**

By

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**The Thesis of Bakheet Saeed Al Katheeri for the Degree of
Master of Science in Environment is approved**

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Abstract

The present study aims at quantifying and assessing the organic and inorganic pollutants in the offshore sediments of the Zakum Field, Abu Dhabi, UAE. Twenty-six sampling stations were selected to cover the maximum area of the field. Sediments samples were subjected to a variety of analyses including mechanical analysis, Total Organic Carbon (TOC) analysis, Total Petroleum Hydrocarbon (TPH) analysis, twenty congeners of Poly Chlorinated Biphenyls (PCBs) analysis, sixteen different Polycyclic Aromatic Hydrocarbons (PAHs) analysis and eight heavy metals analysis. For a comparison purpose six old marine seabed core samples which collected from Zakum Filed between 1966 and 1978 were analyzed for TPHs, PCBs & PAH's.

The average TOC % analyzed in the study area is 4.76 % which higher value than other regional studies. The average TPH in Zakum Field is around 22.7 ppm, which is consistent with previous studies in the area. No significant correlation observed between TPH and grain size distribution. The average concentration of PCBs in the study area is 13.5 ppb, which is slightly above the level recorded previously in the region (i.e. below 5 ppb).

The total PAH's concentration in Zakum Field area ranges between 0 and 31.5 ppb. PAHs values increases towards Northwestern area with the minimum concentration in the central part area of the field. The Average Total petroleum hydrocarbon concentration in the old seabed cores is 17.4 ppm. While the average concentration of PCBs is 39.9 ppb and the total poly Aromatic hydrocarbons is 20.9 ppb.

Eight heavy metals elements have been analyzed in this study i.e. Cr, Cu, Fe, Mn, Ni, Pb, V and Hg. The highest detected concentration is Fe with average of 23.6 ppm. The

lowest determined concentration is Ni with average of 0.035 ppm. In general, the heavy metals concentrations in the study area are low compared to previous studies in the region.

High concentration of pristane relative to phytane in most of the sediments indicates biological hydrocarbon input from a marine biological source except station no. 11 which indicates petrogenic source.

The site related operations in the Zakum field offshore area found maintaining minimum adverse effect to the marine environment.

CHAPTER 1

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Since early civilization some 4000-5000 years ago, people have been attracted to the shores of the Arabian Gulf. Before the tenth century AD, the Arabs had established a trade network extending from the Gulf eastwards as far as China (Price, 1993). The Gulf marine environment is becoming increasingly important in fulfilling the social, economic, development and strategic objectives of the region. The Arabian Gulf plays a particularly vital role in providing most of the population with desalinated water (fresh water). Fisheries are a multi million-dollar industry. The Gulf's coastal and marine environment harbors contain many significant mangroves and indigenous species such as birds and other wildlife species, which are of national and international importance. The Arabian Gulf is blessed with diverse natural resources (i.e. oil and gas) that play a pivotal role in the regional prosperity and sustainable development. Discovery of oil in the Gulf in the early 1930's and 1940's has improved significantly the economical, social, demographical, agricultural, urbanization development in the gulf countries.

The Arabian Gulf countries are well known for their large petroleum and gas reserves. Proven recoverable petroleum reserves in these countries are estimated to represent 44 % of the world recoverable reserve (UAE report, 2002). The Safaniya (Saudi Arabia) and Zakum (UAE) are considered among the largest known offshore oil fields in the world. Most oil produced from the Gulf region is exported via sea and local refining and consumption constitutes only a small proportion of the total production.

In addition to huge oil and gas production and treatment facilities, the Arabian Gulf countries have built world-class refining, petrochemical, fertilizers, and energy intensive industries such as primary aluminum, iron, steel and water desalination plants. They have, consequently had to face the mounting environmental problems associated with these industries.

Marine pollution can be defined as " the introduction by man, directly or indirectly, of substances or energy into the maritime area which results or is likely to result in hazards to human health, harm to living resources and marine ecosystems, damage to amenities or interference with other legitimate uses of the sea" (Subbarini,1989). Some potential pollutants, such as oil and litter are highly visible. However others, such as toxic chemicals and heavy metals are invisible, hidden from view. There is always a real concern that damage could be done to marine life before the source of any problem is discovered. Direct pollution can occur through deliberate disposal or through accidental loss of substances at sea whilst indirect pollution can result from land-based activities.

The Arabian Gulf is one of the busiest tanker routes in the world (Al- Lihai and Al Omaran, 1996). The major sources of pollution in the Gulf countries are related to oil and gas production operations, crude oil spills and leakage, natural gas leakage and flaring, pollutants associated with the refining operation, including refinery wastes and industrial products, by-products and wastes arising mainly from the petrochemical industry (Literathy, 1993).

The largest tanker spill in the United State history occurred in 1989 when oil tanker Exxon Valdez grounded and spilled over 11 million gallons in Alaska. During the last decade, two major catastrophic oil spills have occurred in the Gulf because of military conflicts. The Nowruz oil well blewout in 1983

releasing more than 21 million gallons of crude oil. During the Gulf war in 1991 more than 740 Kuwaiti oil wells were fired, spilling an estimated 10.8 million barrels of crude oil into the Gulf (Tawfiq and Olsen, 1993). Although the total volume of spilled oil may still be disputed, it represented the world's largest oil spill (Price, 1998). It is anticipated that oil pollution is widespread on the Arabian Gulf region and has seriously endangered the ecosystem (Douabul and Al-Shiwafi, 1998).

UAE is one of the important oil and gas producing and exporting countries that provides large supplies of energy to the world markets. The exploration of oil started in the 1930s and was followed by crude oil export in the early sixties. The first shipment of oil was from Umm Al Shaif offshore oil field on 1963. At present, UAE occupies a significant position among oil developing and exporting countries and plays an important role in securing the growth of the global economy by providing energy to the oil market. Proven recoverable oil reserves are estimated at about 100 Billion barrels of oil (10 % of the world's total) and 6 Billion cubic meters of natural gas (UAE report, 2002).

Among the major threats to the marine environment in UAE is pollution resulting from the oil and gas exploration, extracting, transportation, loading of oil tanker and downstream processing in refining and petrochemical operation.

Toxic waste is a harmful form of pollution to marine creatures. Once a form of toxic waste affects an organism, it can be quickly passed along the food chain and might eventually end up as seafood (Biomagnification), causing serious problems. Some of these pollutants are chlorinated hydrocarbons, which can

cause toxic and undesirable health effects. Other oil products pollutants can have various diverse impacts on living organisms from physical damage to carcinogenic effects.

Sediments act as pollutant sinks and provide an integrated picture of the events taking place in the water column. Studies have shown that some hydrocarbons compounds from spilled petroleum persist in the sedimentary environment for a substantial period i.e. years (Choiseul, *et al.*, 1998). Zakum Field area has been chosen as case study to assess and evaluate the marine oil pollution in UAE offshore area and consequently the Arabian Gulf area.

1.2 ZAKUM FIELD

Zakum oil field is one of the ten giant offshore oil fields in the world. It is located in the central part of the Arabian Gulf about 90 Km northwest of Abu Dhabi town (Figure 1.1). The field was discovered in July 1963 and oil production from the Zakum Central Super Complex (ZCSC) commenced in November 1967. The field consists of six reservoirs. The three lower zones being operated by Abu Dhabi Marine Operating Company (ADMA-OPCO), while Zakum Development Company (ZADCO) operates the upper three zones since 1977.

Zakum Field has three super complexes; Zakum West Super Complex (ZWSC), Zakum Central Super Complex (ZCSC) and ZADCO super complex. The prime function of the super complex is the collection and preliminary

treatment of reservoir fluids prior to delivery to Das/Zirko Islands for further processing.

1.2.1 ZWSC:

The ZWSC is a series of interlined rigid platforms standing in 40-60 feet water depth approximately. The reservoir fluids are separated into crude oil, gas, and water. Due to environmental concerns, water is no longer drained off at the separators; instead, it remains entrained in the crude oil for treatment on the Zakum process plant on Das Island. The separated gas is dehydrated in Gas Gathering (GGII) plant to sufficiently low dew point for onward transmission to Das Island via Umm Shaif Super Complex (USSC). The crude oil is transported via a new 30" main oil line approximately 93 Km long to Das Island directly. The produced condensate is spiked into crude oil or sent to ZADCO Super complex via 6" condensate line.

The oil production facilities on ZWSC include of two riser platforms, a collector separator platform (CSP), and a pipe flare system emanating from CSP and catering two flares located about 0.8 Km away from the CSP platform.

The oil production, gas and water injection wells in the offshore field are accommodated on wellhead towers (WHTs). Its own natural pressure in the reservoir initially produces oil. A secondary recovery system of water and gas injection is introduced to the reservoir to improve production potential and to overcome the depletion of pressure.

The Gas Gathering facilities consist of two platforms, GGII and Gas Injection platform (GIP). The GGII platform has a pipe flare which caters two pipe flares located about 0.8 Km from the platform. One of these flares has been used for GIP platform. GIP compressed gas to five different wellhead towers via sub sea lines.

The water injection plant utilizes raw seawater. The process involves treatment of the seawater. Water initially passes through a set of coarse to fine sand filters to remove any debris. Then it enters a deaeration tower to remove the excess oxygen finally; it is pumped with high and medium discharge pressure to the water injectors wells via several sub sea pipelines.

1.2.2 ZCSC:

It is the first super complex installed in Zakum Field on 1967. It is located 9 Km east of ZWSC, and consists of CSP, pumping platform, and water injection platform.

All oil produces from North East, East, and South East sides of the Field are routed to ZCSC, CSP then to ZWSC oil production facilities via two 24" lines. The collector separator platform is provided with three flare lines. Similarly to ZWSC there is a water injection platform contains two water modules and connected with ZWSC water injection modules by series of water injection radials configuring the water injection network throughout the field.

1.2.3 ZADCO Upper Zakum Field:

The field is divided into four areas (North, South, West & Central). Each area comprises a number of wellhead platforms connected via sub-marine

pipelines to an area gathering station called "satellite". The satellite platforms serve as first stage separation platforms. Separated oil and gas are sent to the central complex via two lines. In addition, the satellites act as a centre for water injection distribution network.

Oil from the first stage separation platform for the wells in the central area only is pumped to join the remaining flows from the satellites and Umm Al Dalkh and transported via a 42" main oil line directly to Zirku Island. The gas plant collects all the gases that were separated, recovers part to the condensate, before sending it to ADMA-OPCO, ZWSC gas treatment plant, (GGII). The recovered condensate is spiked into main oil line.

1.3 STUDY OBJECTIVES

The main objectives of this study are to:

- Assess the organic and inorganic pollutants which affect the marine environment.
- Determine the source of petroleum pollution in the marine environment.
- Assess the contamination trend(s) and determine its/ their extent.

1.4 THESIS ORGANISATION

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 methods used in this study. Chapter four reports and discusses the results of various analyses conducted in the study. The summary, conclusions and recommendation are included in the chapter five.



Figure 1.1 Location map of the Zakum field

LITERATURE REVIEW

2.1 CONSTRUCTION OF THE JOURNAL CLUB

2.1.1 Goals and Objectives

The Journal Club is a weekly discussion group held on the first Tuesday of each month from 7:00 PM to 8:30 PM in the main lounge of the hotel. The club is open to all hotel employees and is free of charge. The club is organized by the Human Resources Department. The club's primary goal is to provide a forum for the discussion of current issues in the hotel industry. The club's secondary goals are to provide a forum for the discussion of current issues in the hotel industry and to provide a forum for the discussion of current issues in the hotel industry.

CHAPTER 2

LITERATURE REVIEW

2.1 Physical properties of the Arabian Gulf

2.1.1 Depth and current movement

The Arabian Gulf is a very important navigational and industrial shallow marginal sea, located between latitudes 23.9°-30.25° N and longitude 48°-56° E and contains world's most deserts (Figure, 2.1). The Arabian Gulf is separated from the Gulf of Oman by the Strait of Hormuz, which is only 56 km wide at its narrowest point. The Arabian Gulf slopes gradually from the shallow deltaic northern part to deeper waters in the south. The maximum width of the Gulf is 338 km, and the length to its northern Coast is around 1000 km. The surface area of the Gulf approximately $2.39 \times 10^5 \text{ km}^2$, with an approximate volume of $8.63 \times 10^3 \text{ km}^3$ (Reynolds, 1993). The depth rarely exceeds 100 m along the eastern Iranian coast and is only 36 m on average (Purser and Seibold, 1973).

The main current in the Gulf is produced by a density gradient and regionally, there is a slow anticlockwise surface current covering most of the Gulf. Water of normal oceanic salinity enters through the Strait of Hormuz at the surface. The increasingly saline water becomes denser, sinks and flows down to the bottom. After sinking, the saline water exists the Strait of Hormuz below the incoming relatively low salinity water. (Reynolds, 1993)

2.1.2 Temperature and salinity

In summer, the Gulf region experiences very high temperature i.e. 45-50 °C, while in winter, water and air temperatures fall dramatically to 15 °C (Purser & Seibold, 1973).

One important feature associated with this set of conditions is increased salinity, which is commonly over 40 to 50 part per thousand across large areas (Sheppard, 1993) and even exceeds 70 part per thousand in remote lagoons and coastal embayment such as the Gulf of salwa (Purser and Seibold, 1973). However surface salinity varies between 41 parts per thousand and 43 part per thousand at Abu Dhabi offshore, UAE (Ali and Thomas, 1998).

The Northwest part of the Gulf is considered a lower salinity region because most of the river inflow into the Gulf occurs in the northern end, primarily on the Iranian side. The Gulf receives freshwater influx from the Euphrates and Tigris rivers in Iraq as well as from numerous small seasonal streams draining the Zagros mountain in Iran (Hashim,1993)

Rainfall makes a negligible contribution to the fresh-water budget of the Gulf, because the annual rainfall in the arid climate of the Gulf region is very small, of the order of 3 to 7 cm per year (Al madani and Al Sayed, 1998). The UAE has one of lowest national renewable water resource capacities, which on a per capita basis equates to 64 m³ per year, only of the order of 1% of the world average (UAE report, 2002).

2.1.3 Winds

Winds are important to marine life from the point of view of temperature effects, but they are also important in terms of the airborne particulates transported by them. This material contains absorbed hydrocarbon pollutants; metal pollutants from industry were absorbed strongly to the dust, which therefore served as a transport mechanism of pollution to the marine environment (Sheppard, 1993).

The most well known, and disreputable, weather phenomenon in the Gulf is the Shamal. The wind sets in with great sharpness and force. The Shamal wind often carries large amounts of dust and sand, which are deposited in the water of the Gulf. The Shamal usually occurs first in the northwest and then spreads southward during summer time (Reynolds, 1993).

2.1.4 Sedimentation of the Gulf

Sedimentation rates of bottom sediments in the Arabian Gulf show marked regional differences, depending on offshore morphology and type of sediment. Sediments at the bottom of the Gulf vary from autochthonous calcareous fragments mostly of biogenic origin and rock fragments derived from beach rocks and submerged reef flats to allochthonous terrigenous detritus supplied to the area mainly by dust storms and river deltas in the far northern areas and along the eastern Iranian side.

2.2 Biological environment of the Arabian Gulf

The Gulf as a whole is dominated by soft substrate ecosystems. Elevation and depth contours between Kuwait and the UAE are generally extremely gradual, leading to a sedimentary environment, encouraging growth of sea grasses and algal beds. Sea grasses represent an indirect food source and a habitat for both resident fauna and temporary visitors including commercially important fish. Sometimes overlooked is the fact they also stabilize fine sediments which otherwise would be very mobile. Thus, they reduce water turbidity and greatly reduce long shore drift of sediments, with consequent effects of shoreline stabilization (Price *et al*, 1993).

2.2.1 Mangroves

The mangroves of the Gulf are significant not just biologically as important nurseries for fish and shrimps but also historically. The strong relationship between mangrove forests and ancient cities in the area indicates that people here have long known the value of mangroves. They used the wood for fuel and building materials and the green leaves as fodder for camels and goat. Due to the unplanned coastal development, the mangroves are much less extensive in the Gulf than formerly, and only about 125-130 Km² remain. The shores of Iran contain most of the remaining mangrove, with approximately 90 Km² of mangrove vegetation, while less than 10 Km² now remain along the Gulf coast of Saudi Arabia and Bahrain, with the remainder found along the UAE coastline (Sheppard *et al.*, 1992).

2.2.2 Fisheries

The fisheries of the Gulf are of considerable economic importance to the region, and they have provided a livelihood for coastal communities since earliest history. There has been an industrial fishery sector in the Gulf since the early 1960s. The fish fauna of the Gulf is less diverse than that of the adjacent Indian Ocean but the Gulf still supports more than of 500 species (Price, *et al.*, 1993).

The pearl fisheries of the Gulf were once world famous and globally important, but declined after the arrival of cultured pearls. Sea grass beds are favored habitats for juvenile pearl oysters, whereas adults are found on rocks and other hard surfaces.

2.2.3 Birds

The Gulf supports a diverse marine bird community of great international importance. Huge numbers of sea bird breed on the Gulf offshore Islands, especially the Socotra cormorant. Other important species included oystercatchers, ringed plovers, lesser sand plover, little stint, dunlin and others (Price *et al.*, 1993).

The Gulf is particularly important for wintering waders, passage migrants and breeding seabirds. The intertidal zone is estimated to support up to 4 million waders in winter, making the area one of the five most important regions in the world for wintering waders (UNEP, 1999).

Offshore Islands provide major nesting sites. For example, In Abu Dhabi Island, the intertidal zone is one of the largest feeding areas for wading birds

in the Gulf. Over 21 species have been recorded, including plovers, greenshanks, redshanks, curlews, whimbrel, reef and grey herons, turnstones, greater flamingoes, oystercatcher, and godwits.

2.2.4 Marine mammals

Over 600 individuals of Dugongs or sea cows were observed in the Gulf of Salwah between Bahrain and Qatar peninsula (Peen, 1989). These animals also occur in significant numbers among the islands west of Abu Dhabi. The estimated population is around 7300 individuals, making the inner part of the Gulf area the most important area for this species in global importance (UNEP, 1999)

Other marine mammals of interest include whales and dolphins of which some 20 species are found in the region, representing 25 percent of all known species in the world.

2.2 Physical, Biological and chemical properties of organic pollutants

2.3.1 Polychlorinated Biphenyls (PCBS)

Polychlorinated biphenyl's (PCBs), are a class of synthetic chlorinated organic compounds. As the name indicates, it consists of a biphenyl backbone, upon which are 1 to 10 available positions for chlorine substitution (Fig.2.2), giving rise to a total of 209 different possible substitution compounds referred to as congeners. PCBs are marketed based on their average level of chlorination under various trade names such as the Aroclor, Askarel and Clophen (O' Neill, 1993).

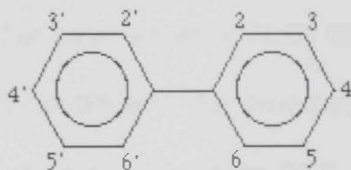


Figure 2.2: Basic Chemical Structure of PCBs after, Baird (1999)

PCBs have many attractive industrial properties; they conduct heat very well, but do not conduct electricity, and they do not burn easily. Furthermore, they are chemically stable and are not soluble in water. Therefore, PCBs gained widespread use all over the world as coolants and lubricants in transformers and other electrical equipment where these properties are essential. For several decades, PCBs were also routinely used in manufacturing wide variety of common products such as plastics, paints, pesticides, carbonless copying paper; fluorescent light ballasts (Baird, 1999).

They were widely used in a variety of industrial applications, until concern over possible adverse effects on health and the environment, resulted in the U S Congress banning the manufacture of PCBs in 1979. However PCBs containing materials still in service at the time of the ban were not required to be removed from use, and, therefore some are still in use. For example, the life expectancy of electrical transformers that contain PCBs are thirty years or more (EPA, 1999)

Despite the fact that these compounds have been banned in many developed countries and their worldwide production and use have drastically decreased in recent years, at present they are still widely distributed and have become ubiquitous contaminants of natural system. Nowadays, PCBs are the most abundant chlorinated aromatic contaminants in the ecosystem (Borrell, 1993).

It is the same properties that have allowed PCBs to accumulate and persist in the environment and thus continue to be detected long after manufacturing has ceased. Moreover, potential sources of PCB may due to past disposal practices. There are no natural sources of PCBs; therefore, all PCBs are related to commercial manufacture, use, storage, and disposal.

PCBs are highly persistent in the environment with reported half-lives in soil and sediment ranging from months to years (EPA, 1999). For instance, the half life of PCB 153 was found to be more than ten years (UNEP, 2002). These chemicals usually bioaccumulate in the food chain; because of their relative insolubility in water and high solubility in fats, moreover, PCBs are stored in body fat (EPA, 1999).

2.3.2 Health Effect

PCB's are classified as a probable human carcinogen by numerous national and international health-protective organizations, such as the USEPA, the Agency for Toxic Substances and Disease Registry (ATSDR) and the World Health Organization (WHO) (Baird, 1999)

Effects other than cancer in the liver, blood, immune system, nervous system, reproductive and other organ systems have been observed in various animal studies of PCBs. Lower birth weight was reported in some of the infants born to mothers who consumed contaminated fish (EPA, 1999).

PCBs are the only chemical family fully regulated under government act. This includes the regulation of any release of PCBs into the environment, including accidental leaks or spills. The USEPA established a Maximum Contaminant Level for drinking water of 0.005 ppm, and the continuous chronic criteria for fresh and salt water of 0.014 ppb and 0.03 ppb respectively (EPA, 1999).

2.3.3 Previous studies of PCBS in the Arabian Gulf region

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 from 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). Table 2.1 lists individual PCBs congeners analyzed in this study:

PCB 8	2,4'-diChloroBiphenyl
PCB 18	2,2',5-triCB
PCB 28	2,4,4'-triCB
PCB 52	2,2',5,5'-tetraCB
PCB 44	2,2',3,5'-tetraCB
PCB 66	2,3',4,4'-tetraCB
PCB 77	3,3',4,4'-tetraCB
PCB 101	2,2',4,5,5'-pentaCB
PCB 118	2,3',4,4',5-pentaCB
PCB 153	2,2',4,4',5,5'-hexaCB
PCB 105	2,3,3',4,4'-pentaCB
PCB 138	2,2',3,4,4',5'-hexaCB
PCB 126	3,3',4,4',5-pentaCB
PCB 187	2,2',3,4',5,5',6-heptaCB
PCB 128	2,2',3,3',4,4'-hexaCB
PCB 180	2,2',3,4,4',5,5'-heptaCB
PCB 170	2,2',3,3',4,4',5-heptaCB
PCB 195	2,2',3,3',4,4',5,6-octaCB
PCB 206	2,2',3,3',4,4',5,5',6-nonaCB
PCB 209	2,2',3,3',4,4',5,5',6,6'-decaCB

Table 2.1 PCB congeners

2.4 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 (Baird, 1999). PAHs have been contaminants 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.

Their ubiquitous environmental occurrence stems from many sources, both natural and man made. As a general rule, the PAHs are produced by combustion, which can be natural (e.g., forest fires, volcanoes) or inputs of PAHs from human activities such as oil spills from different sources i.e. offshore production platforms, oil transportation and combustion which pose serious and significant threats to all coastal habitats components such as mangroves (Teresa *et al*, 2002). 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.

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. The larger PAHs have been found to bioaccumulated in the fatty tissues of some marine organisms (Baird, 1999).

There are common parent PAHs that occur throughout the environment and may have highest toxicity, some of which are listed in table 2.2.

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

Table 2.2 Some of the commons PAH's individuals

2.4.1 Health Effect

US Department of Health and Human Services (DHHS) has determined that benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, and indeno[1,2,3-c,d]pyrene are known animal carcinogens. The International Agency for Research on Cancer (IARC) has determined the following: benz[a]anthracene and benzo[a]pyrene are probably carcinogenic to humans; benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene and indeno[1,2,3-c,d]pyrene are possibly carcinogenic to humans; and anthracene, benzo[g,h,i]perylene, benzo[e]pyrene, chrysene, fluoranthene, fluorene, phenanthrene, and pyrene are not classifiable as to their carcinogenicity to humans. EPA has determined benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-c,d]pyrene are probable human carcinogens and that acenaphthylene, anthracene, benzo[g,h,i]perylene, fluoranthene, fluorene, phenanthrene, and pyrene are not classifiable human

carcinogenicity. Acenaphthene has not classified for carcinogenic effects by DHHS, IARC, or EPA (ASTER, 1985)

2.4.2 Previous studies of PCBS in the Arabian Gulf region

Many studies have been conducted on determination of PAHs in the sediment of the Arabian Gulf. Because of the Gulf crisis especially during the Kuwait oil fires, the concentration of particulate and associated pollutants increased. Levels of PAHs were measured extensively during 1991 in Kuwait and found with the ranged from 7 to 387 ng/m³ in ambient air particulate (UNEP, 2002). The contamination screening survey conducted in 1998 revealed PAH concentrations in sediment from Kuwait of 97.7 ppb and from Saudi Arabia, 6.9 ppb (Al-Majed *et al.*, 2000). The level in sediment from Kuwait in 1991 found 30.4 ppb; in Saudi Arabia was 36.4-761 ppb; in Bahrain was 47.5-97.5 ppb; in 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 sediment from the Iranian coast was found to contain 1.63-6.48 ppb PAHs (UNEEP, 2002).

2.5 Total petroleum Hydrocarbon (TPH)

Determination of Total Petroleum Hydrocarbons (TPH) provides information on the contamination of sediment with petroleum products. TPH is an estimate of the amount of hydrocarbons present between the carbons ranges from C₈ to C₄₀. 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.

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 from heavy tanker transport activities in the Gulf and from major spills such as those that occurred during the Iran-Iraq war in 1983 and the Gulf war (Al-Ghadban *et al.*, 1994). Although the Gulf has shown a large capacity for short term self-cleaning after spills, long-term effects are still unknown (Al Ghadban, 1994). As oil degrades, these lighter weight compounds are either volatilized or degraded, leaving the heavier, larger compounds that collectively are referred to as the unresolved complex mixture (Fowler *et al.*, 1993). In area near oil spills in Kuwait and Saudi Arabia, the lighter compounds were found to be substantially reduced in sediments after about six months. However, the heavier compounds can persist for longer periods (Fowler *et al.*, 1993).

In the Arabian Gulf, sediments impacted by the Gulf War were restricted to an area within approximately 400 Km of the source of the spill in Kuwait (Fowler *et al.*, 1993). Surface sediments in this area surveyed soon after the war contained 62 to 1440 ppm of TPH. However, off the immediate coast of the UAE concentration ranged from only 0.1 to 7 ppm (Al Ghadban *et al.*, 1994; Fowler *et al.*, 1993).

The most recent two studies available on Total Petroleum Hydrocarbons concentrations in Zakum Filed area had values ranging from 2.7 to 55.5 ppm (ADMA ES, 1997) and 10 to 22 ppm (ZADCO EBS, 1999).

2.6 Total organic carbon (TOC)

Organic matter in subsurface systems is a complex mixture of natural organic substances and a variety of synthetic compounds. The transport and fate of organic contaminants is dependent on the nature and distribution of organic carbon in general. Dispersions, sorption and degradation are processes, which affect organic compound transport and fate. The estimation of their influence of these processes depends heavily on the quantitative determination of fractions of organic carbons in the sediments and aquifer (Barcelona *et al.*, 1997). 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 (Al Ghadban *et al*, 1994).

The organic matter in the sediment can be quantified by the total organic carbon (TOC), and it plays an important role in the accumulation and release of different micro pollutants. For this reason it is important to have a clear picture about the distribution of the TOC in the sediments in any given environment.

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, while 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 that the TOC of the Arabian Gulf ranged from 0.46% to 2.8 % in the bottom sediment samples of the Gulf.

In Ideal situation, higher TOC values are associated with lower sediment particle size. However, Al-Ghadban (1994) found that in the Arabian Gulf sediment, such a correlation is not evident probably owing to factors like the input of petroleum hydrocarbons and water circulation. However it is apparent that TOC concentration can be considered as an indicator of hydrocarbon pollution only when the TPH content is high (Al-Ghadban, 1994).

2.7 Heavy metals in the Arabian Gulf region

Trace elements occur in different concentrations in biological systems. They may exert beneficial or harmful effects on plant, animal, and human life depending upon the concentration. These elements are introduced into the environment through various routes, smelting processes, fuel combustion and industrialization. They find their way into aquatic systems, rivers, lakes or oceans through atmospheric fallout, dumping wastes, accidental leaks, runoff of terrestrial system and geological weathering (Al Yousuf, *et al.*, 2000).

Heavy metals became a matter of concern because of their toxicity and tendency to accumulate in food chains. They are known as non-biodegradable elements and are toxic to different organisms, plants and animals.

Several studies have been conducted on the concentration of trace metals in different location of the Arabian Gulf region. Fowler (1985) 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, V and Hg concentration in both oysters and sediments were generally low. Al Hashimi and Salman (1985) conducted a study on trace metals distribution in the sediments of the North-western Coast of the Arabian Gulf. The results of trace metals analysis revealed that the sediment from the studied area could be considered as being unpolluted. Folwer, *et.al.* (1993) studied the petroleum hydrocarbons and trace metals 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 hydrocarbons and trace metals that entered the Gulf from 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 from Saudi Arabia but elsewhere in the Gulf, they were similar to their previous levels.

Al Mahmood (1993) in his investigation in the area from Abu Ali to Tanaqib along the Saudi Arabian coast to determine the level of heavy metals in sediment in March 1992 showed that concentration of heavy metals were not heavily impacted by the huge oil spill. Similarly, Basaham and Lihaibi (1993) analyzed sediments samples collected from the western Gulf from Kuwait to Qatar for series of trace elements. Comparing the data with unpolluted sediments throughout the Gulf and worldwide, they concluded that the effect of anthropogenic enrichment upon the absolute concentration of the elements is minimal. Al Qubaisi (2001) conducted an assessment of metals pollution in sediment of the coastal area in U.A.E. She revealed that the metals concentration on the offshore sediment have a minimum metal pollution

accumulation except for those of Ni. Table 2.3 illustrates the comparative published data for heavy metals in the Arabian Gulf.

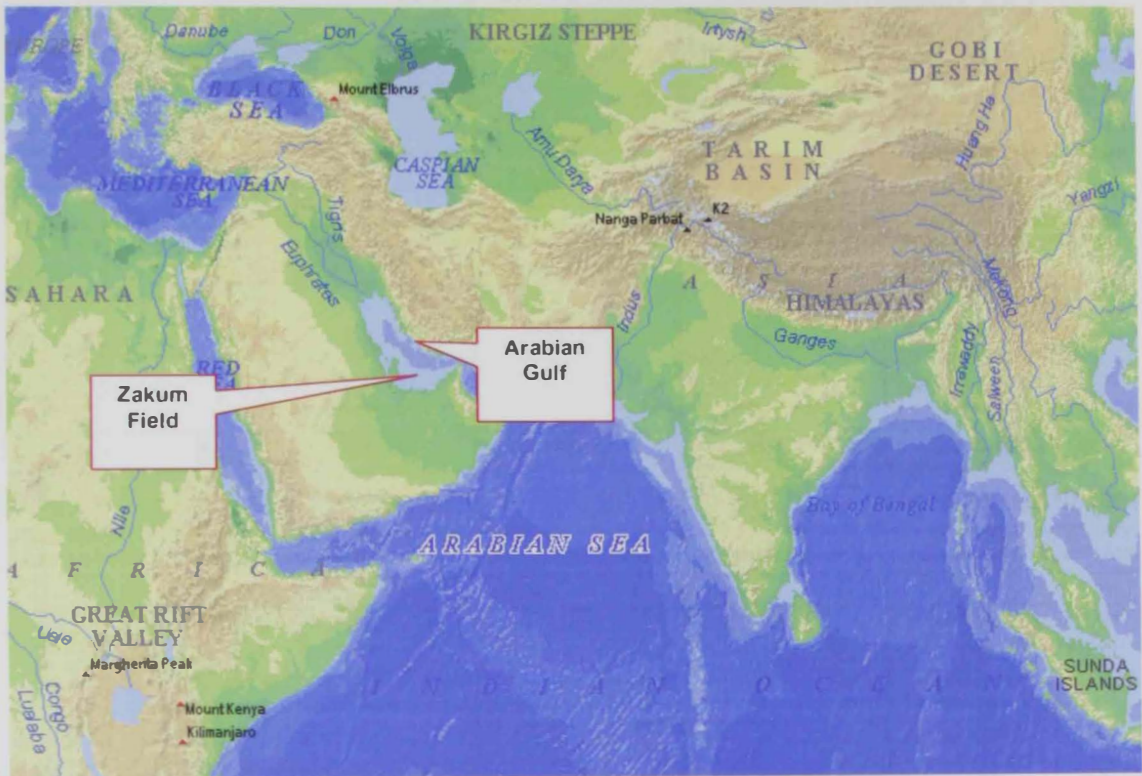


Figure 2.1 Location map of Arabian Gulf

Heavy metal	Concentration, ppm dry weight			References
	Reference 1	Reference 2	Reference 3	
Cr	43.9	43.43	16.5	1-Deshgooni,M 2-Fowler,S.W. <i>et al</i> , 1993 3- Al Arfaj, and Alam,I.,1993
Cu	37.9	2.9	5.29	1-Deshgooni,M.,2002 2- Fowler,S.W. <i>et al</i> ,1993 3- Al Arfaj,and Alam, 1993
Fe	3441	2.59	1826	1- Fowler,S.W. <i>et al</i> ,1993 2- Al Hashimi and Salman, 1985 3- Basam andAl Lihaibi, 1993
Mn	193.71	110.83	101.18	1- Basaham,A. <i>et al</i> .,1993 2- Al Qubaisi,N.,2001 3- Al Arfaj,A.and Alam,1993
Ni	29.7	14.9	25.35	1-Deshgooni,M.,2002 2- Fowler,S.W. <i>et al</i> ,1993 3- Al Arfaj and Alam,1993
Pb	3.51	22.31	55.5	1- Fowler,S.W. <i>et al</i> ,1993 2- Al Arfaj and Alam,1993 3-Deshgooni,M.,2002
V	17.6	18.25	40.1	1- Fowler,S.W. <i>et al</i> ,1993 2- Al Arfaj and Alam,1993 3- Fowler (1988)
Hg (ppb)	75	7.96		1- Fowler (1988) 2-Sadiq (1985)

Table 2.3 Comparative literature data for heavy metals in the Arabian Gulf

EXPERIMENTAL PROCEDURES

The first step in the synthesis of the polymer was the preparation of the monomer. This was done by reacting the starting materials in the presence of a catalyst. The reaction was carried out at a temperature of 100°C for 24 hours. The resulting monomer was then purified by distillation. The second step was the polymerization of the monomer. This was done by reacting the monomer with a catalyst in the presence of a solvent. The reaction was carried out at a temperature of 100°C for 24 hours. The resulting polymer was then purified by precipitation. The final step was the characterization of the polymer. This was done by measuring its molecular weight and its inherent viscosity. The molecular weight was determined by gel permeation chromatography (GPC) and the inherent viscosity was determined by measuring the viscosity of a solution of the polymer in a suitable solvent.

CHAPTER 3

The first part of this chapter describes the synthesis of the polymer. The second part describes the characterization of the polymer. The third part describes the properties of the polymer.

Sample	Molecular Weight (g/mol)	Inherent Viscosity (dl/g)
1	10000	0.1
2	20000	0.2
3	30000	0.3
4	40000	0.4
5	50000	0.5

Table 3.1: Molecular weight and inherent viscosity of the polymer.

MATERIALS AND METHODS

3.1 Sediment Sampling

Seabed sediments (the top 5-10 cm of seabed layer) were collected from twenty-six sample stations on 17th of November 2002 throughout the Zakum Field area, Abu Dhabi, UAE. The field area was divided into eight sampling sectors to ensure maximum coverage representative of the study area (Figure 3.1). All sediments samples were taken by divers at each sample station and immediately were sealed in plastic bags, refrigerated (< 4 °C) and kept frozen prior to chemical analyses. This is to prevent any volatile compounds from evaporation or chemical degradation.

For a comparison purpose six historical marine seabed core samples (i.e. the top 0.5-10 cm sediment), which collected from Zakum Filed between 1966 and 1978 (table 3.1), were analyzed for TPHs, Total PCBs & Total PAH's.

Core sample station	Date of coring
1	1978
2	1978
3	1979
4	1966
5	1968
6	1970

Table 3.1 Core sample station date of coring

All samples were labeled with a unique identifier that was used consistently during various analyses. Oil samples have been taken from Zakum field for biomarker analyses.

3.2 Grain size distribution analysis

The objectives of determining the grain size distribution of sediments in this study is to correlate the level of contaminants to grain size, and to determine the texture of the sediments i.e. percentage of fine particles in the sediment.

The grain size analysis was conducted using the standard sieving method as per ROPME (2000) procedure. Sediments were dried prior to analysis in room temperature for 24 hrs. Sieve analysis was undertaken on 100 grams of the sample. The sieving is carried out to let sediment samples pass through a series of standard test sieves having successively smaller mesh size. The samples then were shaken for 15 minutes, fractions retained on each sieve were weighed, and their percentages were recorded. Statistical parameters of the mean grain size were calculated using Folk's (1966) equations.

3.3 Determination of Total Organic Carbon content (TOC)

A sample of 5 grams is initially introduced to an inorganic carbon removal stage, where 10 % HCL acid is added to the sample. Total organic carbon analyzer instrument LECO CS 200 was used to oxidize and detect the organic carbon by combustion. Analysis is determined when carbon compounds are combusted in an oxygen-rich environment, resulting in the complete conversion of carbon-to-carbon dioxide. The carbon dioxide generated from

the oxidation process is directly related to the TOC in the sample. This instrument is used to simultaneously determine carbon and sulfur employing induction heating furnace and solid state Infrared detection system (Figure 3.2). The furnace contains combustion tube, automatic cleaner and dust collection system. LECO CS 200 includes calibration linear multi-point simultaneous for all carbon/sulfur detectors. The system is controlled by windows based software in Pentium PC tower and data transmission capability by RS232 output.



Figure 3.2 Leco CS 200 analyzer

3.4 Determination of individual 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.

Five grams of the solid sediments was mixed with equal quantity of anhydrous sodium sulphate to absorb the water moisture in the sediments then was placed in an extraction thimble. Approximately 70 ml of the

extraction solvent (1:1 Hexane: Acetone) then used to extract the sample using automatic soxhlet extraction (2050 SOXTEC, FOSSTECATOR) for two hours (Boiling 1hrs and Rinsing 1 hrs). An aliquot of the extract i.e. 1 μ L was injected to GC/ECD from GC auto sampler 2 mL vial.

GC Specification and Condition:

- Varine, Saturn 3800 GC system, equipped with Electron Capture Detector ECD and Satrun 5.52 workstation.
- GC column: CP-Sil 8, 30 m x 0.32 mm ID, df =1
- Carrier Gas: He, 1.5 mL/min
- Temperature program of the oven: 100 °C to 160 °C at 15 °C/min for 2 minutes, followed by 160 °C to 270 °C at 5 °C/min for 30 minutes.

The individual PCBs standard used (C-CCSEC, Accustandard) to plot the calibration curve concentration in ppm vs. peak size. PCBs congeners retention time and the detection limits illustrated are shown in table 3.2.

PCB	Retention time, sec
PCB 8	20.075
PCB 18	21.817
PCB 28	23.704
PCB 44	25.865
PCB 52	25.014
PCB 66	27.518
PCB 77	29.815
PCB 101	28.373
PCB 105	31.968
PCB118	30.777
PCB 126	33.518
PCB 128	34.564
PCB 138	33.052
PCB 153	31.695
PCB 170	39.132
PCB 180	36.932
PCB 187	33.896
PCB 195	43.007
PCB 206	49.361
PCB 209	53.695

Table 3.2 PCBs congeners retention time

3.5 Determination of Individual Polyaromatic Hydrocarbons by HPLC

Analysis of PAH was carried out in the Central Laboratory Unit at the United Arab Emirates University, Al Ain, UAE, as per the modified EPA-8310 procedure. Five grams of the sediment was mixed with equal quantity of anhydrous sodium sulphate to absorb the water moisture in the sediments, and placed in an extraction thimble. The sample was extracted using automatic soxhlet extraction (2050 SOXTEC, FOSSTECATOR) for two hours and fifteen minutes (Boiling 1hr, Rinsing 1 hrs and evaporation 15 minutes) with approximately 70 ml of the extraction solvent (1:1 Hexane: Acetone). The extract then transferred into a concentrator and evaporates under nitrogen to reduce solvent to about 0.5 ml using TurbonVap Evaporator, Zymark apparatus. Then 5.0 ml of Acetonitrile was added and evaporated again till 2 ml reached. An aliquot of the extract i.e. 20 μL was injected into HPLC (Fig 3.3), and the PAHs compounds were detected by ultraviolet (UV) and fluorescence detectors simultaneously.

HPLC specifications:

- HPLC equipped with auto sampler, fluorescence detector and UV detector (waters 2695 Alliance Separation Module, Waters 474 Scanning fluorescence detector coupled with Waters 486 UV detector and water Millennium 32 Chromatographic Manager workstation)
- HPLC column: Chromosphere 3 PAH column (100mm x 4.6 mm ID, 3 μm)
- Mobile phase: Deionized water and Acetonitrile

- Gradient program for liquid chromatogram pump:

Flow	Temp. °C	Time , Sec.	% H2O	% CH3CN
1.5	30	0	50	50
1.0	30	50	20	80
1.5	30	52	50	50

The 16 PAHs standard (Accustandard) and their retention time, which used in the study, are illustrated in Table 3.3

PAH	Retention time, min
Naphthalene	4.241
Acenaphthylene	5.215
Acenaphthene	6.983
Fluorene	7.407
Phenanthrene	8.866
Anthracene	10.212
Fluoranthene	12.591
Pyrene	14.053
Benzo(a)anthracene	20.747
Chrycene	21.668
Benzo(b)fluoranthene	29.008
Benzo(K)fluoranthene	31.726
Benzo(a)pyrene	34.252
Dibenzo(a,h)anthracene	41.442
Benzo(g,h,l)perylene	43.372
Indeno(1,2,3-cd)pyrene	45.575

Table 3.3 standard PAHs retention time



Figure 3.3 HPLC

3.6 Determination of Total Petroleum Hydrocarbons (TPH) by FTIR

The analysis of Total Petroleum Hydrocarbons was conducted in the Central Laboratory Unit (CLU) at the United Arab Emirates University, Al Ain, UAE, as per the EPA based CLU SOP-SP-FTIR-01 procedure. 20 grams of wet sediment sample were acidified to a low pH i.e. 2 with hydrochloric acid. Manganese Sulfate Monohydrate then added to absorb the water moisture in the sediments. The petroleum hydrocarbons were extracted from the sample using Hexane solvent. Then the residue is dissolved in fluorocarbon- 113. Infrared analysis of the solution at absorbance about 2930 cm^{-1} was performed by Nicolet Fourier Transform Infrared (FTIR) Magna-IR 560 Spectrometer (Fig. 3.4).

The determination of the concentration of TPH in the extract was made by direct comparison of the response against the calibration curve.



Figure 3.4 Nicolet Fourier Transform Infrared Manma IR 560

3.7 Determination of Heavy metals by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

The analyses of the heavy metals (Table 3.4) were carried out at the Central Laboratory Unit (CLU) at the United Arab Emirates University, Al Ain, UAE, as per the EPA-200.2 procedure. A portion of homogeneous sediment sample was accurately weighed i.e. 1 gram and digested with acid (30 ml of concentrated HCL and 10 ml of concentrated HNO₃) in a hot plate up to 120 °C (to destroy the organic matter and solubilized the recoverable elements). After cooling the sample was made up to 100 ml volume with deionized water. Then the solution was placed into Varian Vista MPX-CCD simultaneous ICP-OES with auto fit background correction (Fig. 3.5) via a nebulizer and resulting aerosol is transported to plasma torch where excitation

occurs. Element specific emission spectra are produced by radio frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and intensities of the line spectra are monitored at specific wavelengths by a charged coupled detector. The intensity of spectral line of an element is proportional to its concentration. The analyzed element detection limit (ppb) and wave lengths (nm) λ are illustrated in Table 3.4.

Element	Wave length (nm)
Cr	267.716
Cu	327.395
Fe	238.204
Mn	257.610
Ni	231.604
Pb	220.353
V	292.401

Table 3.4 The wave lengths of heavy metals



Fig 3.5 ICP Instrument

3.8 Determination of Mercury by Atomic Absorption

The analysis of Mercury in the sediments was carried out in the Central Laboratory Unit at the United Arab Emirates University, Al Ain, UAE, as per the EPA- 245.2 method.

Five grams of the sediment sample transferred to a closed glass bottle. The sample was digested with nitric acid, sulfuric acid and a dilute potassium permanganate-potassium persulfate solution for two hours at 95°C. The digestion oxidizes all forms of mercury to Hg^{+2} . Then Hg^{+2} in the sample was reduced with stannous chloride to elemental mercury, which can detect by atomic absorption. The measurement step is performed using Atomic absorption spectrophotometer GBC 906 AA with Hydride generator HG 3000 (the hydride generator HG 3000), (Figure, 3.6).



Figure 3.6 Atomic absorption spectrophotometer GBC 906 AA

3.9 Statistical analyses

Microsoft Office " EXCEL 2000TM " software and " STATISTICATM " were used to present the data as well to perform the statistical analyses i.e. Cluster analysis and correlation plots.

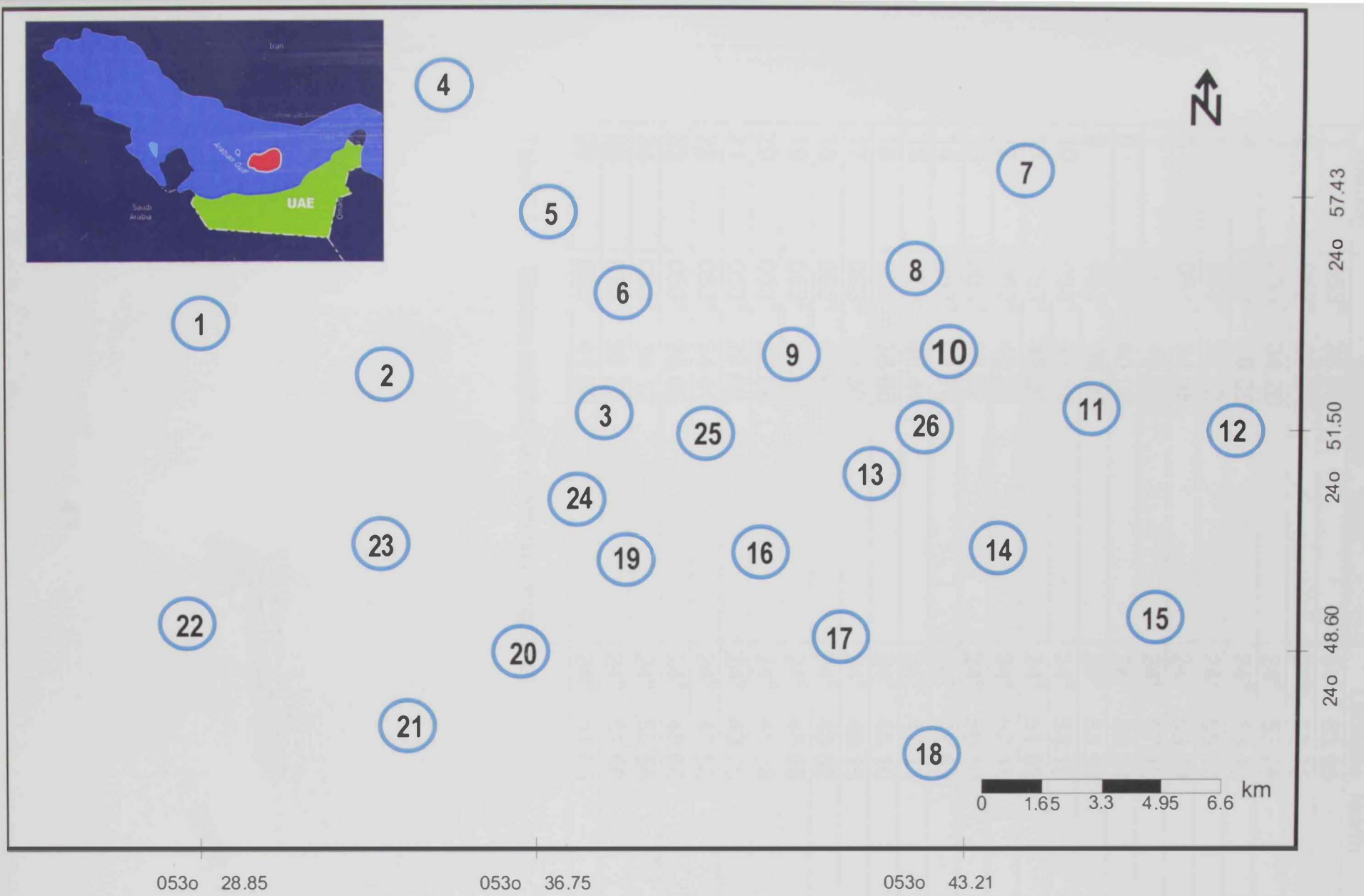


Figure 3.1 Location map of sampling station

Station	Longitude , East		Latitude, North	
1	053°	24.80	24°	53.96
2	053°	28.24	24°	52.75
3	053°	34.20	24°	52.25
4	053°	30.08	24°	58.40
5	053°	32.72	24°	55.60
6	053°	34.95	24°	53.68
7	053°	43.21	24°	57.43
8	053°	40.02	24°	55.24
9	053°	38.20	24°	53.50
10	053°	41.08	24°	52.15
11	053°	45.20	24°	51.82
12	053°	48.22	24°	52.10
13	053°	40.92	24°	50.10
14	053°	44.76	24°	48.50
15	053°	46.44	24°	47.11
16	053°	38.60	24°	48.10
17	053°	39.80	24°	46.15
18	053°	40.40	24°	43.82
19	053°	35.33	24°	48.09
20	053°	32.88	24°	45.38
21	053°	29.82	24°	43.75
22	053°	24.44	24°	47.58
23	053°	28.85	24°	48.60
24	053°	34.12	24°	50.56
25	053°	36.75	24°	51.50
26	053°	41.55	24°	51.65

Table 3.5 Stations longitude and latitude (using GPS)

Station	Longitude			Latitude		
1	053°	32.72	E	24°	55.30	N
2	053°	37.18	E	24°	52.85	N
3	053°	38.45	E	24°	47.60	N
4	053°	40.37	E	24°	52.45	N
5	053°	46.40	E	24°	51.90	N
6	053°	31.70	E	24°	51.57	N

Table 3.6 Core sample stations longitude and latitude (using GPS)

CHAPTER 4

Results and Discussion

4.1 Statistical Analysis

4.1.1 Sediment Texture

Fig. 4.1 shows the sediment texture of the study area. The sediment texture is shown in Fig. 4.1. The majority of the sediment is composed of fine sand, with 10-15% silt and 5-10% clay. The sediment texture is shown in Fig. 4.1. The majority of the sediment is composed of fine sand, with 10-15% silt and 5-10% clay. The sediment texture is shown in Fig. 4.1. The majority of the sediment is composed of fine sand, with 10-15% silt and 5-10% clay.

CHAPTER 4

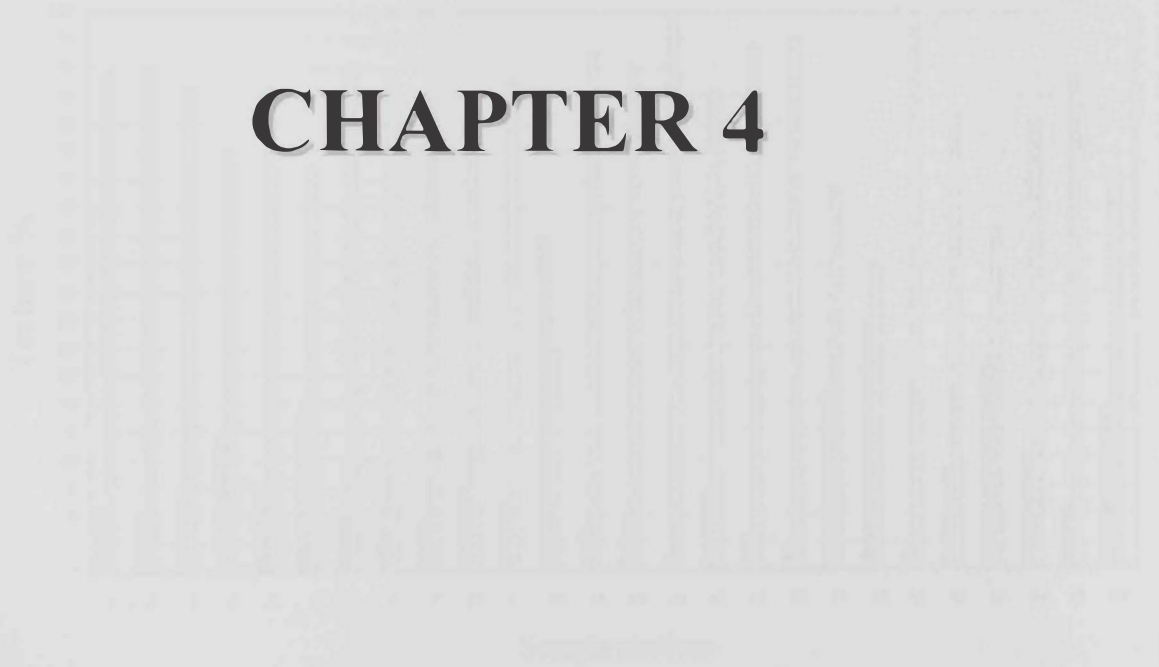


Fig. 4.1 Sediment Texture of the Study Area

Results and Discussion

4.1 Mechanical Analyses

4.1.1 Sediment Texture

The texture of Zakum Field sediments of various sample stations is illustrated in Fig. 4.1. The majority of these sediments are sandy gravel. As per (Folk, 1976) Gravel in this context defined as all sediments retained on 2.0 mm standard mesh sieve. Sand is all sediments retained on 0.0625 micron standard mesh sieve. Moreover mud is all material passing through pervious sieves.

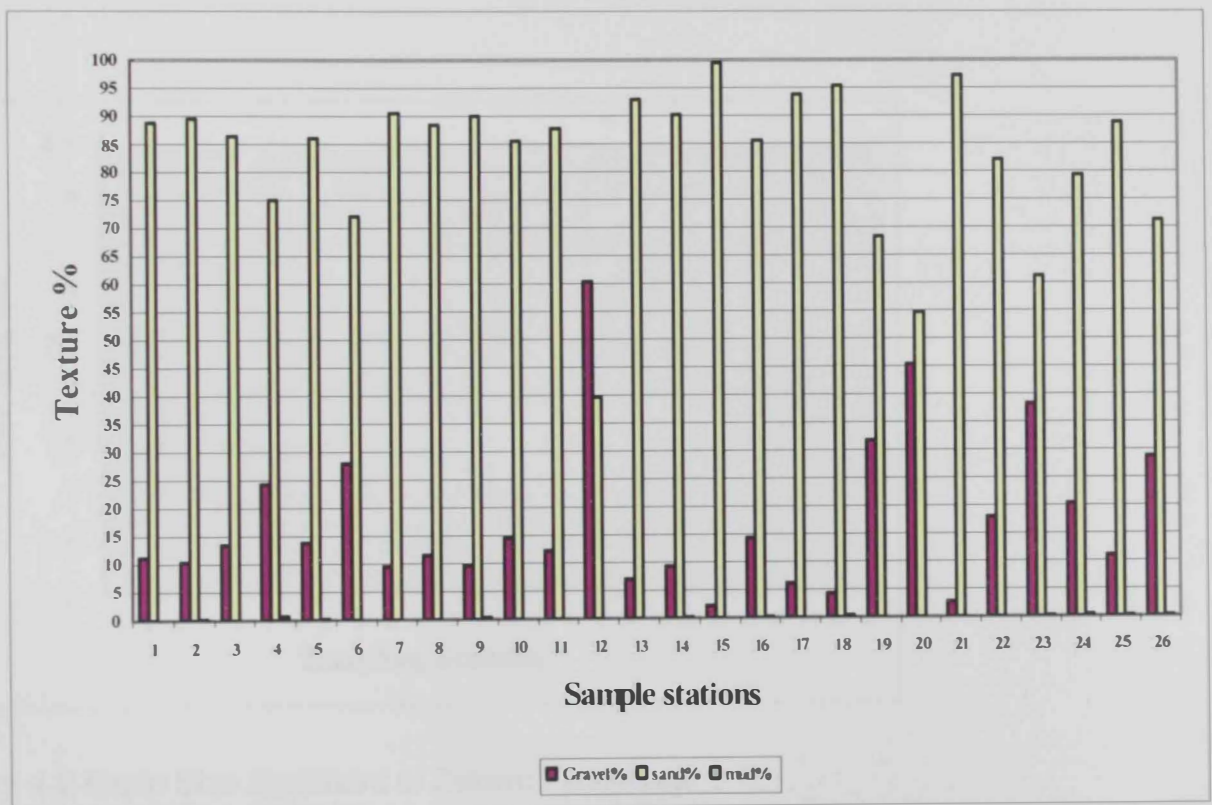


Fig. 4.1 Sediment Texture of Zakum Field Area

4.1.2 Grain size distribution

The mean grain size of Zakum Field samples is illustrated in Fig. 4.2 in mm unit, which indicated coarse to fine sand. However, in few locations there is coarse sand to granule gravel grain size distribution. The maximum grain size located in station no. 12 with grain size of 3.9 mm, which is consequently attributed to high level of gravel which exceed 60% of it's texture. The lowest grain size found on station no. 2 with grain size of 0.1 mm, the overall calculated grain size average in Zakum Field stations is 0.922 mm which is located in the coarse sand region as per Folk (1976) classification. The detailed grain size data are listed in Tables 6.1 and 6.2.

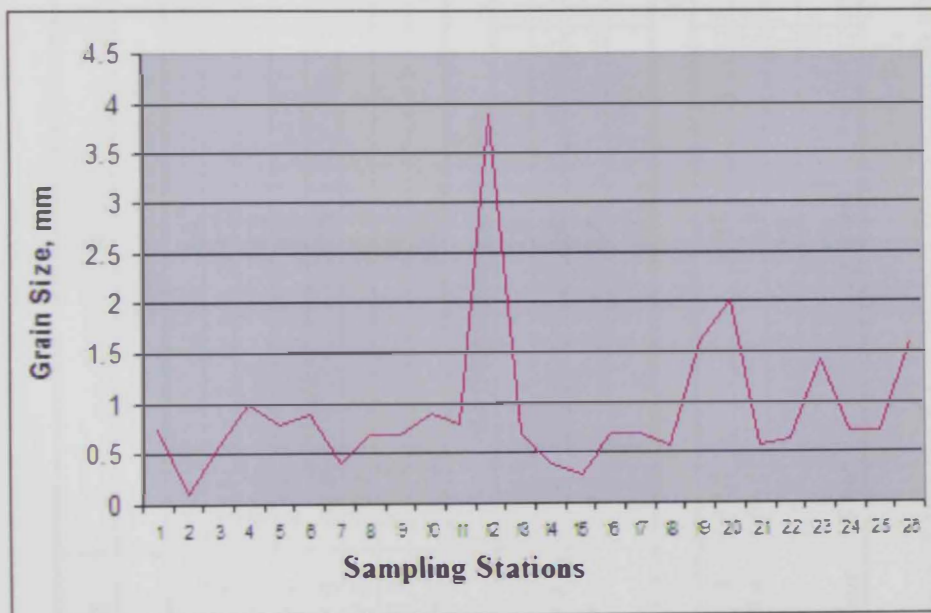


Fig. 4.2 Grain Size Sediment of Zakum Field Area

Sample no.	1	2	3	4	5	6	7	8	9	10	11	12
Phi (ϕ)	Cumulative wt. %											
-2.0	4.4	0.8	5.9	6.5	6.6	16.5	6.0	4.0	2.0	7.0	10.0	50.4
-1.0	11.2	10.4	13.5	24.2	13.8	28.0	9.5	11.5	9.7	14.5	12.3	60.4
0.0	33.5	20.0	22.3	58.3	33.2	43.5	13.0	29.3	25.3	43.0	25.0	70.4
1.0	73.8	37.6	41.2	78.0	75.8	59.0	34.0	68.0	64.0	85.0	80.0	86.4
2.0	96.2	81.6	82.3	87.3	96.4	84.0	78.0	92.5	95.7	98.8	97.5	96.8
3.0	99.7	97.6	98.2	98.8	99.2	98.0	98.0	99.3	98.7	99.8	99.5	98.2
4.0	100.0	99.8	100.0	99.3	99.8	100.0	100.0	100.0	99.7	100.0	100.0	100.0
>4	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Parameters	Statistical size parameters											
Mz	0.4	3.3	0.9	0.0	0.3	0.1	1.3	0.6	0.6	0.1	0.2	-1.9
$\bar{\phi}$	1.1	0.3	1.4	1.5	1.1	2.0	1.1	1.1	1.0	1.0	1.3	2.7
Sk ₁	-0.1	-1.3	-0.4	0.2	-0.1	-0.3	-0.2	-0.1	-0.2	-0.1	-0.3	-0.1
K _G	1.3	1.1	1.3	1.3	1.4	0.5	1.8	1.3	1.2	1.6	1.9	0.8
Percentage	Texture											
Gravel%	11.2	10.4	13.5	24.2	13.8	28.0	9.5	11.5	9.7	14.5	12.3	60.4
sand%	88.8	89.4	86.5	75.0	86.0	72.0	90.5	88.5	90.0	85.5	87.8	39.6
mud%	0.0	0.2	0.0	0.8	0.2	0.0	0.0	0.0	0.3	0.0	0.0	0.0
Texture	g.Sand	g.Sand	g. Sand	g. Sand	g. Sand	g.Sand	g.Sand	g. Sand	g. Sand	g. Sand	g. Sand	s.Gravel

Table 4.1 Grain Size Analysis of samples (from sample no.1-12)

Sample no.	13	14	15	16	17	18	19	20	21	22	23	24	25	26
Phi (Ø)														
-2.0	2.5	6.3		12.3	1.8	1.7	25.0	35.0		6.7	9.5	15.0	6.2	17.33
-1.0	7.0	9.3	0.5	14.3	6.2	4.3	31.7	45.3	2.8	18.0	38.3	20.3	11.1	28.76
0.0	25.0	14.0	2.3	32.5	22.4	14.3	53.0	57.3	20.4	30.7	71.5	26.7	27.6	51
1.0	65.0	31.8	7.3	70.5	64.0	57.7	89.7	86.3	60.4	47.3	86.3	51.7	72.6	87.07
2.0	95.0	65.5	53.3	95.3	96.0	94.3	99.0	98.7	88.0	86.0	93.5	89.3	96.6	98.5
3.0	99.5	98.8	99.0	99.3	99.6	99.0	99.7	99.7	98.4	99.3	97.8	99.0	99.4	99.6
4.0	100.0	99.5	100.0	99.8	100.0	99.7	100.0	100.0	100.0	100.0	99.5	99.7	99.9	99.9
>4	100.0	99.8	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.8	100.0	100	100
Parameters														
Mz	0.6	1.4	1.9	0.3	0.6	0.8	-0.7	-1.0	0.8	0.7	-0.5	0.5	0.47	-0.67
Ö	0.9	1.3	0.7	1.5	0.9	0.8	1.7	1.9	1.0	1.5	1.3	1.8	1.19	1.69
Sk ₁	0.0	-0.4	0.0	-0.3	-0.2	-0.1	-0.4	-0.3	0.2	-0.5	0.2	-0.5	-0.19	-0.37
K _G	1.2	1.4	1.2	1.9	1.3	1.3	0.9	0.9	1.1	1.1	1.3	1.5	1.48	1.30
Percentage	Texture													
Gravel%	7.0	9.3	2.3	14.3	6.2	4.3	31.7	45.3	2.8	18.0	38.3	20.3	11.1	28.76
sand%	93.0	90.3	99.5	85.5	93.8	95.3	68.3	54.7	97.2	82.0	61.3	79.3	88.8	71.14
mud%	0.0	0.3	0.0	0.3	0.0	0.3	0.0	0.0	0.0	0.0	0.3	0.3	0.1	0.1
Texture	g. Sand	g. Sand	sand	g. Sand	g. Sand	g. Sand	s.Gravel	s.Gravel	sand	g. Sand	s.Gravel	g. Sand	g. Sand	g. Sand

Table 42 Grain Size Analysis of samples (from sample no.12-26)

A summary of grain size characteristics of the study area samples is illustrated in Table 4.3, which shows that 59% of the samples are formed of coarse sand with 73% of which are poorly sorted.

Parameters	Description	Percentage of samples
Mz	Granule	7 %
	Very Coarse Sand	14%
	Coarse Sand	59 %
	Medium sand	17%
	Very fine Sand	3%
O'	Very well sorted	3%
	Moderately well sorted	7%
	Moderately sorted	17%
	Poorly sorted	73%
Sk1	fine -sekwed	10%
	Near symmetrical	17%
	Coarse skewed	38%
	Strongly coarse skewed	35%
KG	Very platykurtic	3%
	mesokurtic	10%
	Leptokurtic	70%
	Very leptokurtic	14%
	Platykurtic	3%

Table 4.3 Summary of size characteristics of Zakum samples

4.2 Total Organic Carbon

The concentration and distribution map of TOC % in Zakum Field area are illustrated in Fig. 4.3 and 4.4 respectively throughout the 26 sampling stations.

The maximum and minimum values were recorded in station no. 7 and 15

with 0.14 % and 14.96 % respectively. The average TOC % was 4.76 %, which is a higher value than previous studies in the region (Al Ghadban, 1994). The concentration in far field stations (i.e. no. 18 & 22) is also having relatively high value with 4.10 % & 4.82 % respectively. Figure 4.4 shows a general trend towards the north to the northeast area of relatively high TOC % as compared to the southeast area of the field, which has the lowest TOC % concentration.

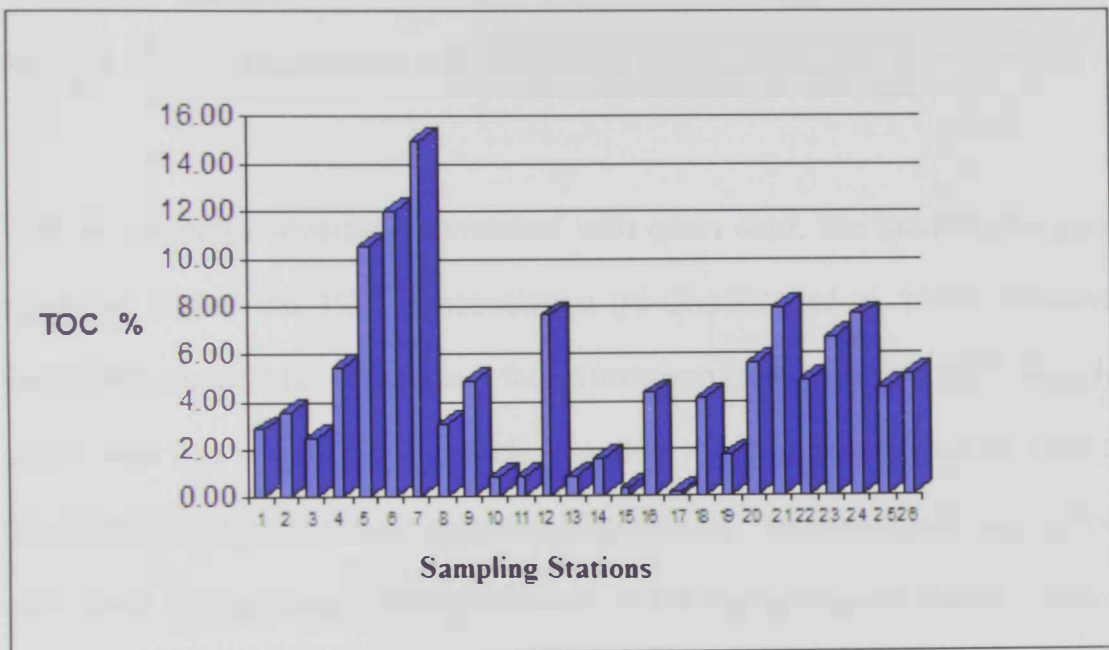


Fig. 4.3 Variation in TOC % Concentration

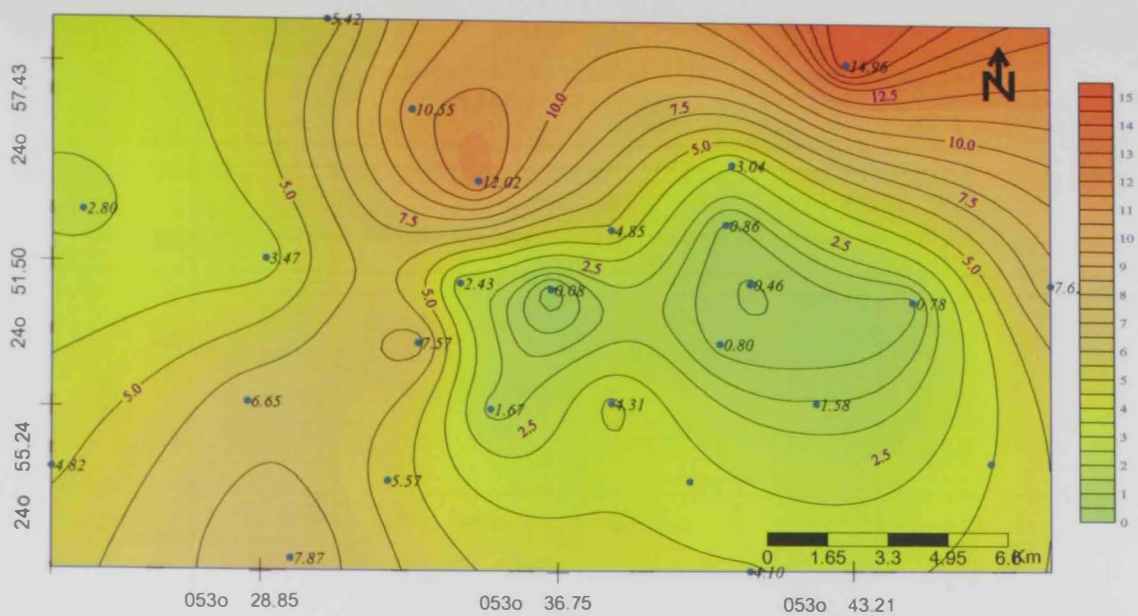


Fig. 4.4 Distribution map of TOC % in Zakum Field

TOC is generally inversely correlated with grain size; the smaller the grain sizes the higher the TOC concentration (Al-Ghadban *et al*, 1994). However insignificant correlation coefficient found between grain size and TOC % in the study area (i.e. $r = 0.15699$), which may due to the multi-sources of TOC or the presence of undissolved dolomite (Figure 4.5). This result is in agreement with other studies conducted previously in the region mainly due to various source inputs of organic matters such as petroleum hydrocarbon in the Gulf (Al Gahdaben *et al.*, 1994).

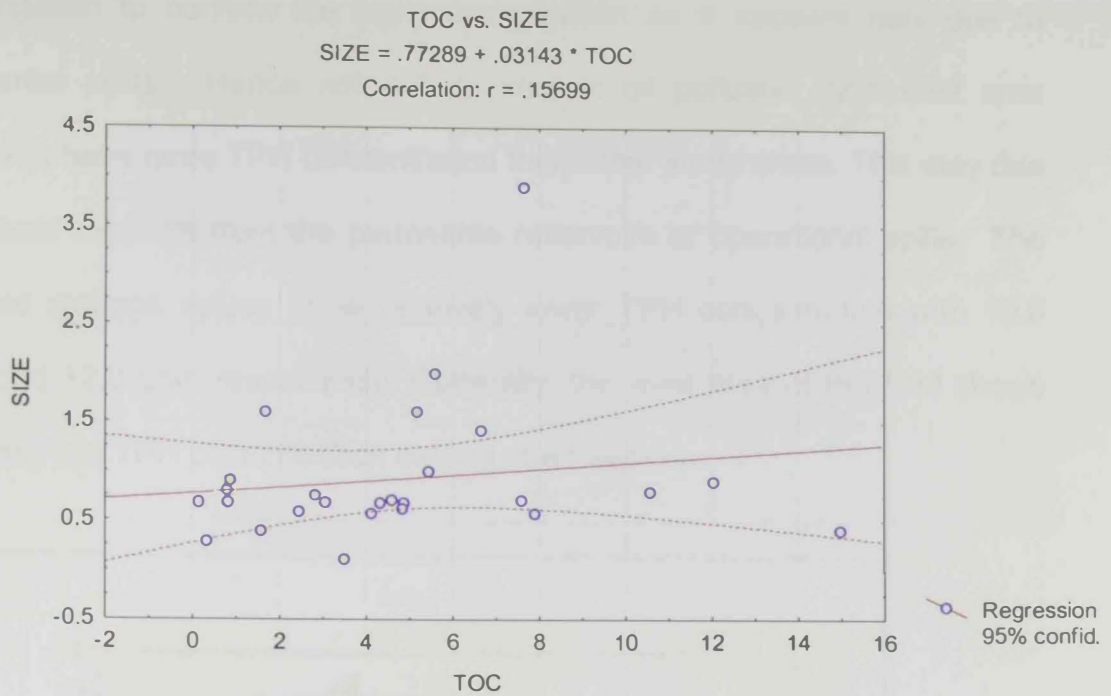


Figure 4.5 Scatter plots of TOC vs. grain size

4.3 Total Petroleum Hydrocarbons (TPH)

The total petroleum hydrocarbons concentration and distribution map variation in study area are shown in figures 4.6 and 4.7 respectively. The maximum and minimum TPH concentrations values were recorded in station no. 1 and 11 with 6.14 ppm and 62.7 ppm respectively. The average TPH is 22.7 ppm, which is consistent with previous studies in the area (i.e. ADMA EMA-1997 & ZADCO EMP, 1999).

The inverse relationship between TOC and TPH in the study area may due to the multi-sources of TOC and the limited sources of TPH to petroleum hydrocarbons.

The TPH variation in Zakum Field area is within low limits except for one isolated station (i.e. station no.11 with 62.7 ppm), which required more

investigation to confirm the high concentration as it appears may due to accidental spills , Hence not due to chronic oil pollution. Northeast area seems to have more TPH concentration than other study areas. This may due to natural seepage from the permeable reservoirs or operational spills. The far field stations values show relatively lower TPH concentration with 15.8 ppm and 12.8 ppm respectively. Generally, the west area of the field shows relatively low TPH concentration among other sectors.

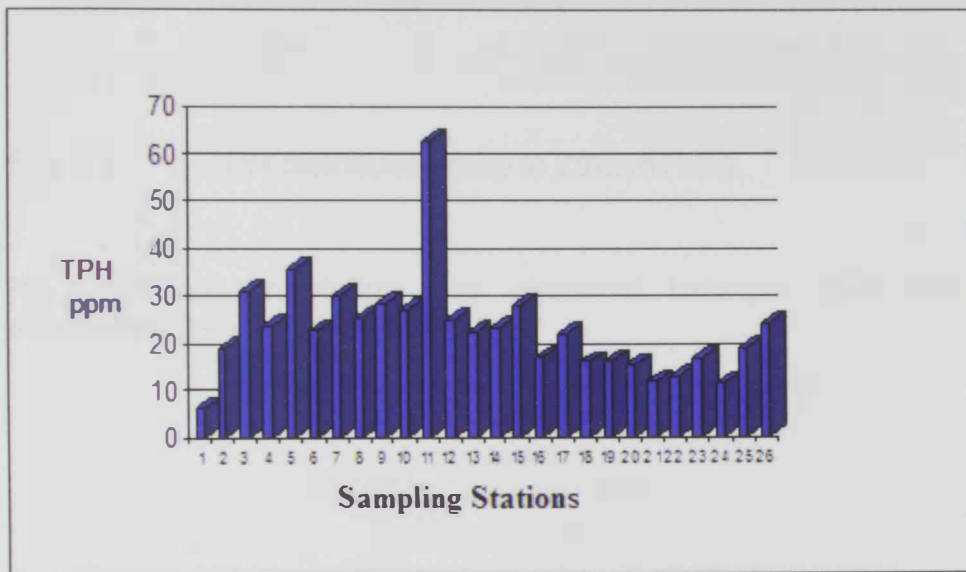


Fig. 4.6 TPH variation in Zakum Field

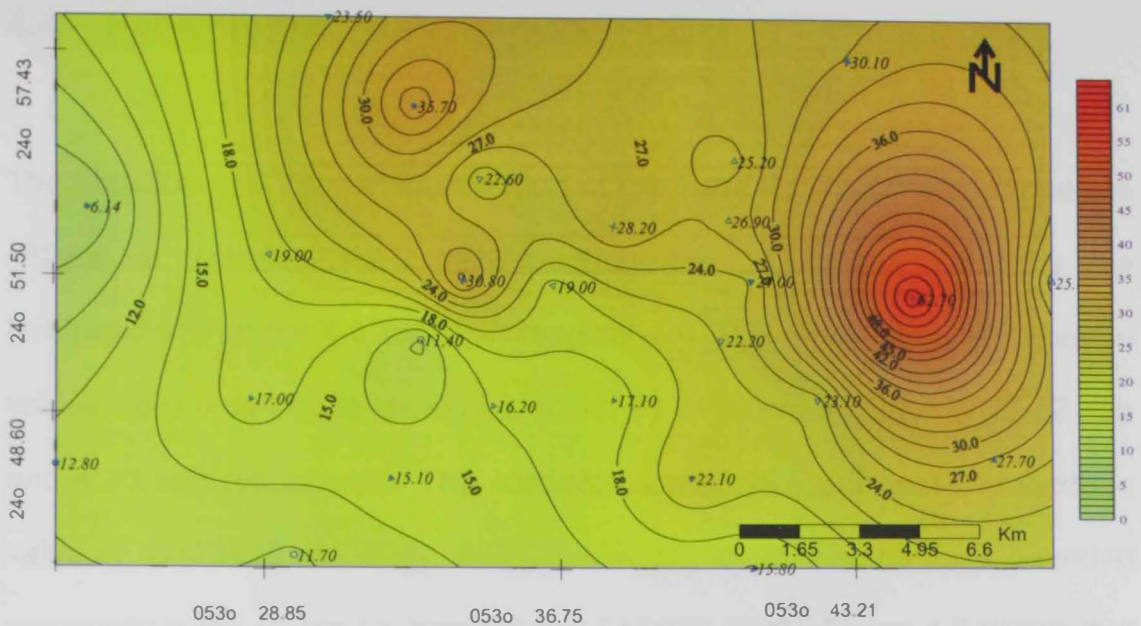


Fig. 4.7 TPH distribution map in Zakum Field

No significant correlation was observed between TPH and grain size distribution ($r = -0.0312$) (figure 4.8)

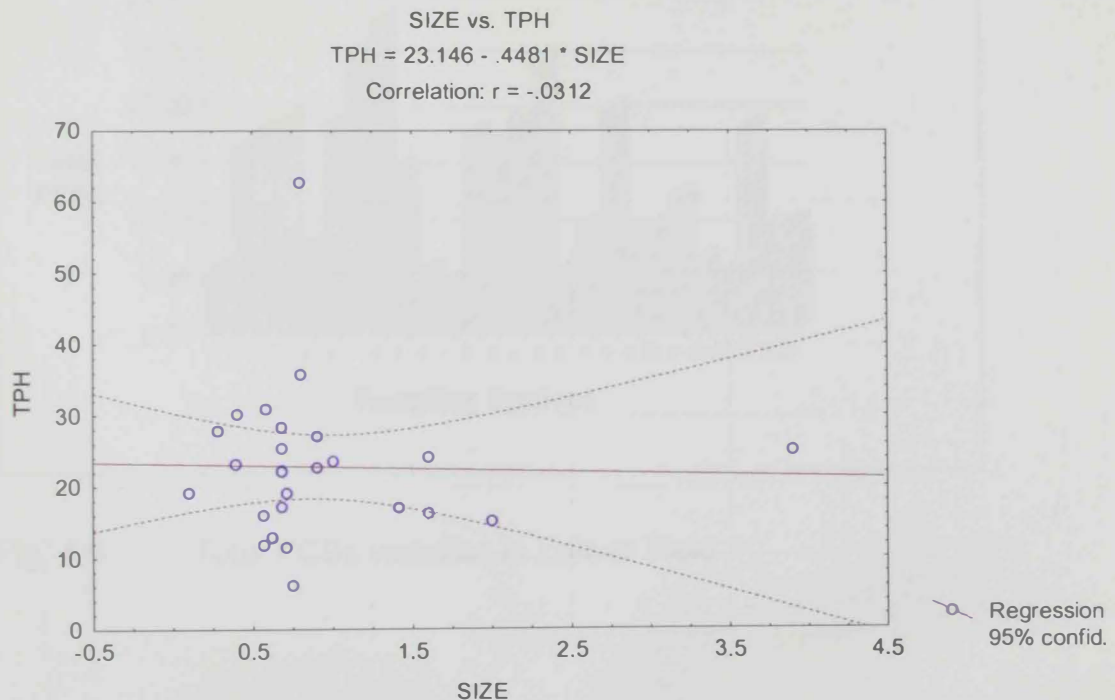


Fig. 4.8 TPH vs. Grain size distribution scatter map in Zakum Field area

4.4 Polychlorinated Biphenyl's (PCBs)

The variation and the distribution map of the Total Polychlorinated Biphenyls (PCBs) in Zakum Field area throughout the 26 sampling stations are illustrated in Figures 4.9 and 4.10 respectively. The maximum and minimum values were recorded in station no. 8 and 11 with concentration of 27.52 ppb and 4.30 ppb respectively. The concentration of 13.5 ppb was the average value of total PCBs in study area. This is slightly above the level recorded previously in the region i.e. below 5 ppb (UNEP,1999). Figure 4.8 shows that the highest concentrations are located in the northeastern and southeastern side of the field.

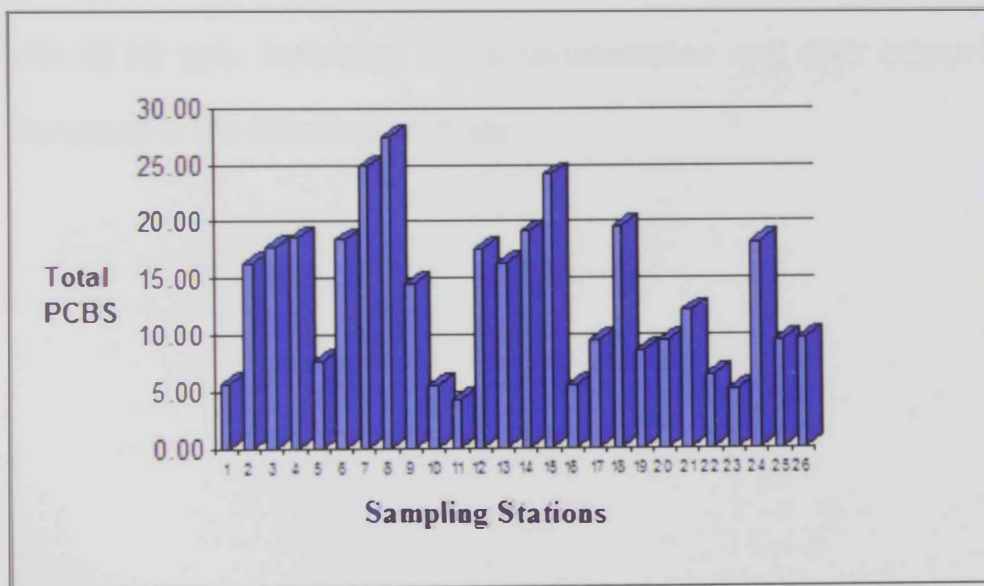


Fig. 4.9 Total PCBs variation in Zakum Field

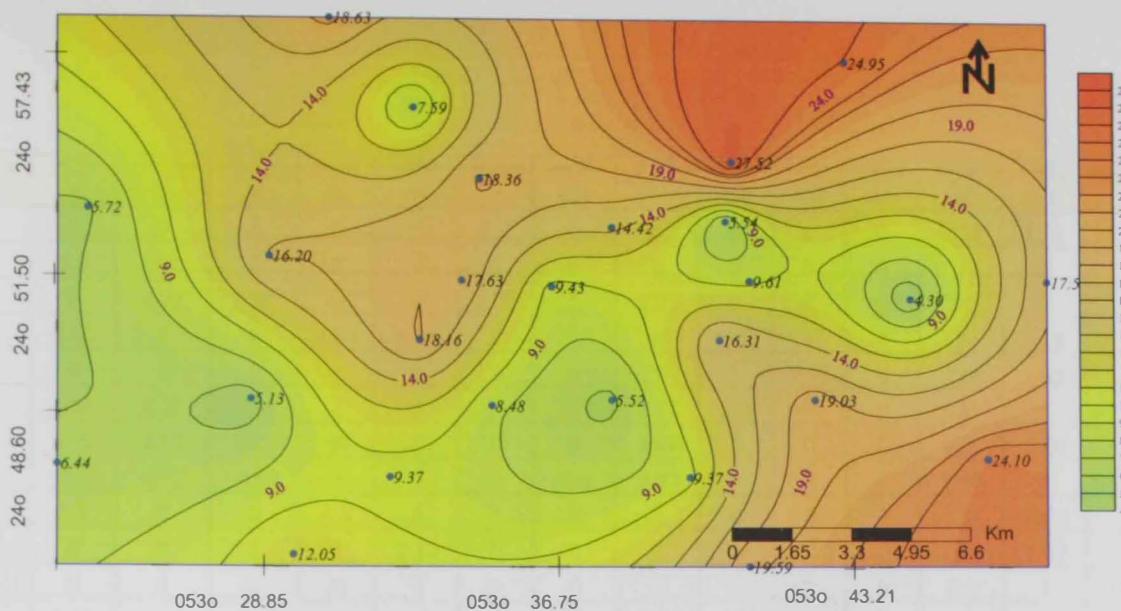


Fig. 4.10 Total PCBs distribution map in Zakum Field

Table 4.4 shows the concentration of individual PCBs in the study area in ppb unit. PCB-180 concentration is the highest among the other individual PCBs with 62.02 ppb. Individual PCBs concentration and their interpretation are discussed in the following sections.

Station no.	PCB 8	PCB 18	PCB 28	PCB 52	PCB 44	PCB 66	PCB 101	PCB 77	PCB 118	PCB 153	PCB 105	PCB 180	PCB 170	PCB 195	Total PCB
1	0	0	0	0	0	2.2	0	0	0	0	0	2.34	1.18	0	5.72
2	5.5	5.22	0	0	3.74	0	0	0	0	0	0	1.74	0	0	16.20
3	0	6.32	3.61	0	0	2.09	0	3.71	0	0	0	1.9	0	0	17.63
4	5.53	0	0	2.65	6.24	0	0	0	1.22	0	0	2	0.99	0	18.63
5	0	0	0	0	0	1.67	0	0	0	2.13	0	2.76	1.03	0	7.59
6	4.58	5.32	2.8	0	0	0	0	2.11	1.24	0	0	2.31	0	0	18.36
7	5.19	8.13	4.31	0	0	0	0	3.44	0	0	0	2.8	1.08	0	24.95
8	13.3	4.12	4.18	0	0	0	2.4	2.03	0	0	0	1.49	0	0	27.52
9	3.8	0	0	8.3	0	0	0	0	0	0	0	1.37	0.95	0	14.42
10	0	0	0	0	2.33	0	0	0	0	0	0	2.29	0.92	0	5.54
11	0	0	0	0	0	0	0	0	0	0	0	3.3	1	0	4.30
12	3.03	3.36	0	0	7.21	0	0	0	0	0	0	3.1	0.88	0	17.58
13	0	0	4.69	0	3.14	0	1.91	3.62	0	0	0	2	0.95	0	16.31
14	4.83	0	2.37	0	0	0	6.88	3.44	0	0	0	1.51	0	0	19.03
15	0	0	8.09	3.93	7.15	0	0	4	0	0	0	0	0.93	0	24.10
16	0	4.43	0	0	0	0	0	0	0	0	0	1.09	0	0	5.52
17	0	0	3.44	0	0	0	0	3.54	0	0	0	1.35	1.04	0	9.37
18	0	0	7.88	0	4.19	0	0	4.56	0	0	0	1.82	1.14	0	19.59
19	0	0	0	0	0	0	0	3.8	0	0	0	3.41	1.27	0	8.48
20	0	0	0	0	0	0	0	4.46	0	0	0	3.78	1.13	0	9.37
21	0	0	0	5.72	1.9	0	0	0	0	0	0	2.55	0	1.88	12.05
22	0	0	0	0	2.5	0	0	0	0	0	0	2.88	1.06	0	6.44
23	0	0	0	0	0	0	0	0	0	0	0	3.92	1.21	0	5.13
24	4.84	3.16	0	0	0	0	5.68	0	0	0	0	3.58	0	0.9	18.16
25	2.47	0	0	0	1.81	0	0	0	0	0	1.71	3.44	0	0	9.43
26	6.32	0	0	0	0	0	0	0	0	0	0	3.29	0	0	9.61

Table 4.4 PCBs concentration in the study area

4.4. 1 PCB 8

The variation and distribution map of PCB 8 in Zakum Field area at 26 different stations are shown in figures 4.11 and 4.12 respectively. The maximum value was recorded in station no. 26 with concentration of 6.32 ppb. The majority of PCB-8 was detected in the northeast side of the field. PCB 8 was not detected in the south side area of the field.

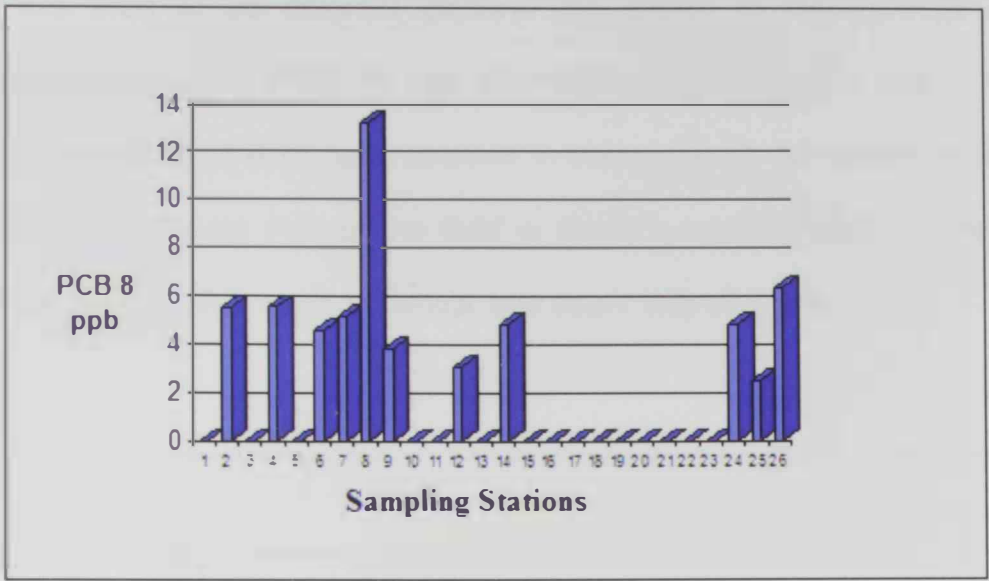


Fig. 4.11 PCB 8 variation in Zakum Field

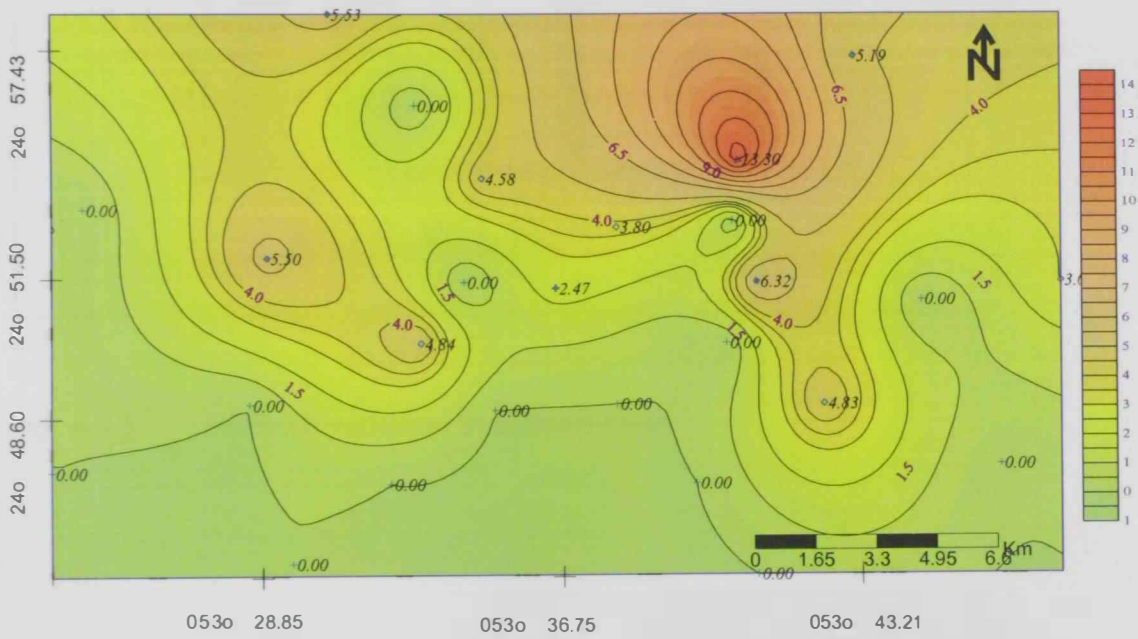


Fig. 4.12 PCB 8 distribution map in Zakum Field

4.4.2 PCB 18

The variation and distribution map of Polychlorinated Biphenyl 18 in Zakum Field area at 26 different stations are shown in figures 4.13 and 4.13 respectively. The PCB 18 was detected in eight stations with a maximum concentration of 8.13 ppb recorded in station no. 7. As shown in figure 4.13 the far northeast side of the field is characterized by high concentration of PCB 18 with high spots in central and south side of the field.

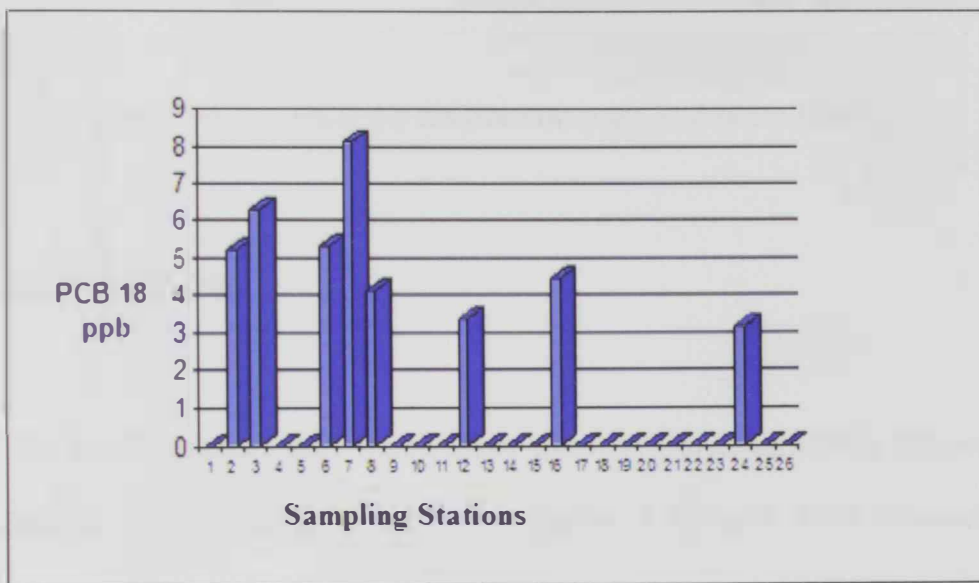


Fig. 4.13 PCB 18 variation in Zakum Field

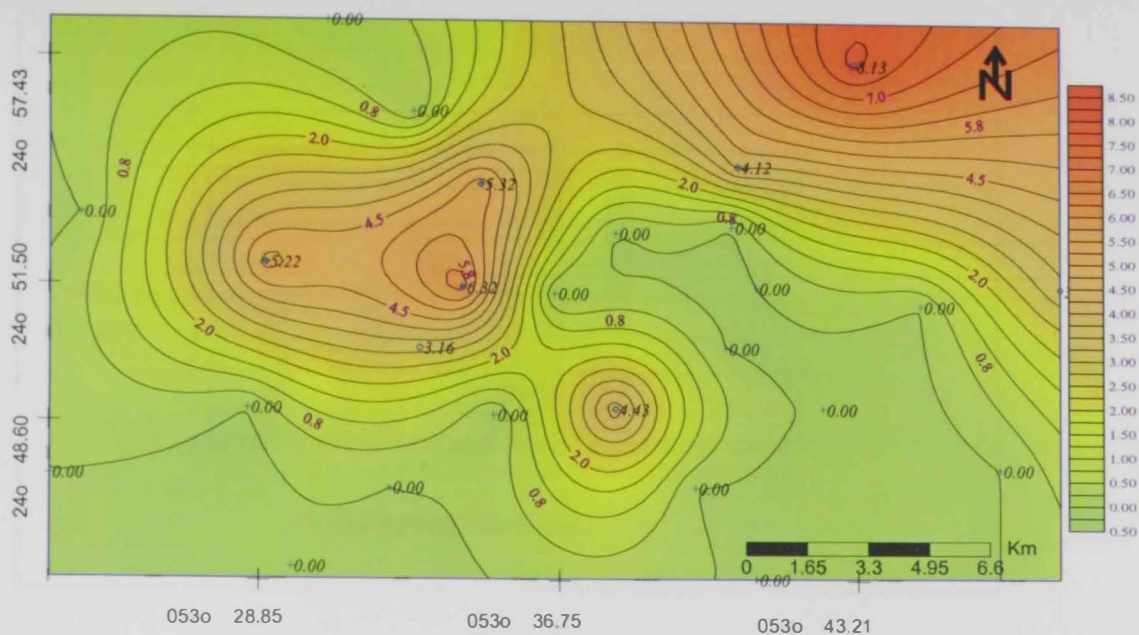


Fig. 4.14 PCB 18 distribution map in Zakum Field

4.4.3 PCB 28

The concentration and distribution map of Polychlorinated Biphenyls 28 in Zakum Field area are shown in figures 4.15 and 4.16 respectively. The maximum concentration was recorded in station no. 15 with a concentration of 8.09 ppb. It is observed that the Northeast side area has the highest concentration among other areas of the field.

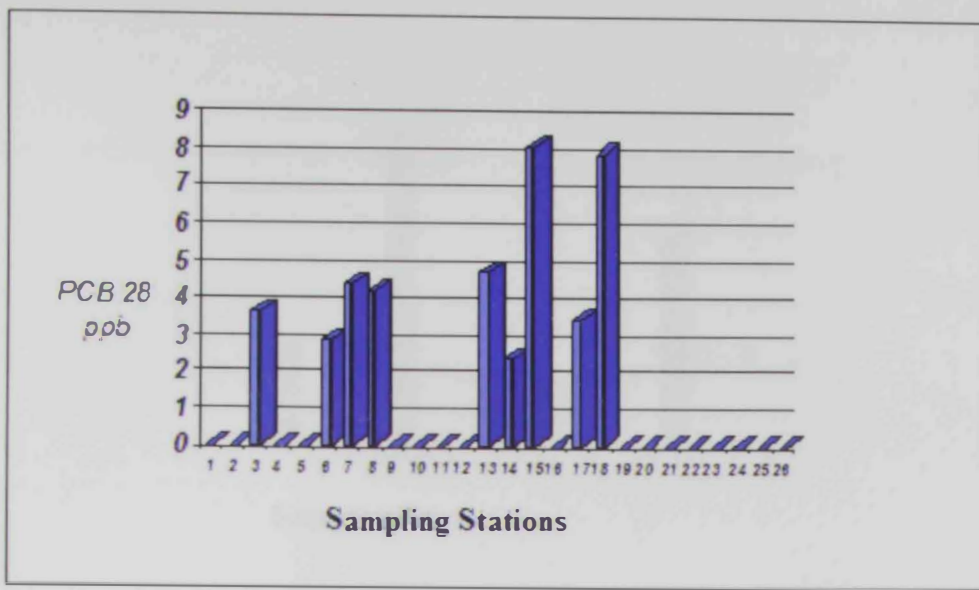


Fig. 4.15 PCB 28 variation in Zakum Field

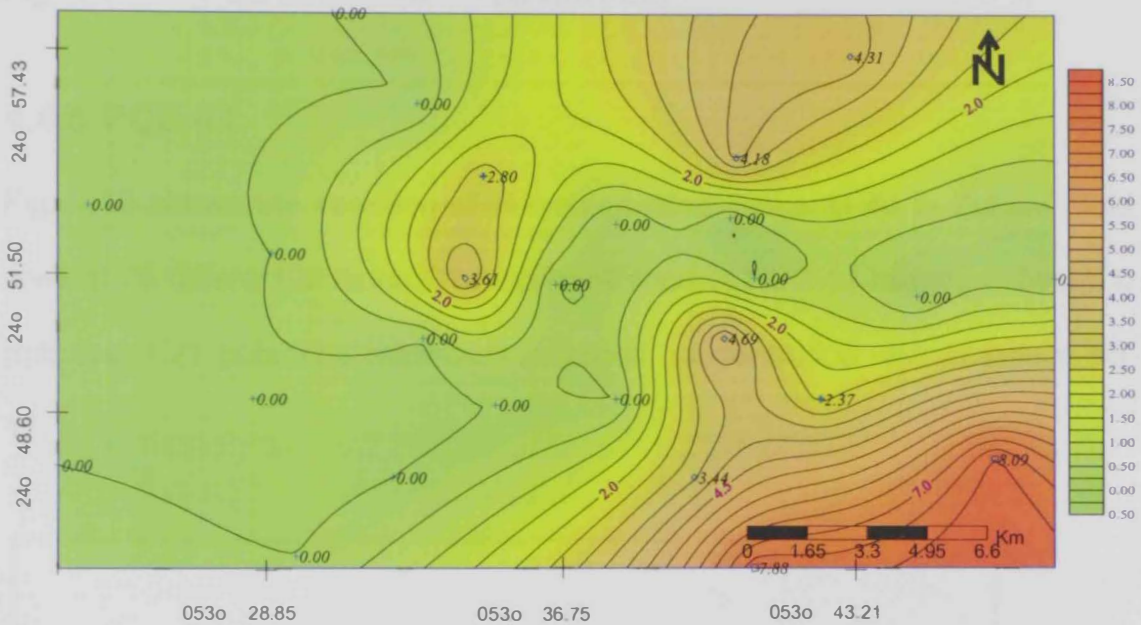


Fig. 4.16 PCB 28 distribution map in Zakum Field

4.4.4 PCB 52

Fig. 4.17 shows the variation of Polychlorinated Biphenyls 52 in Zakum Field area at 26 different stations. The PCB 52 detected in four stations with a maximum concentration of 8.3 ppb, which recorded in station no. 9.

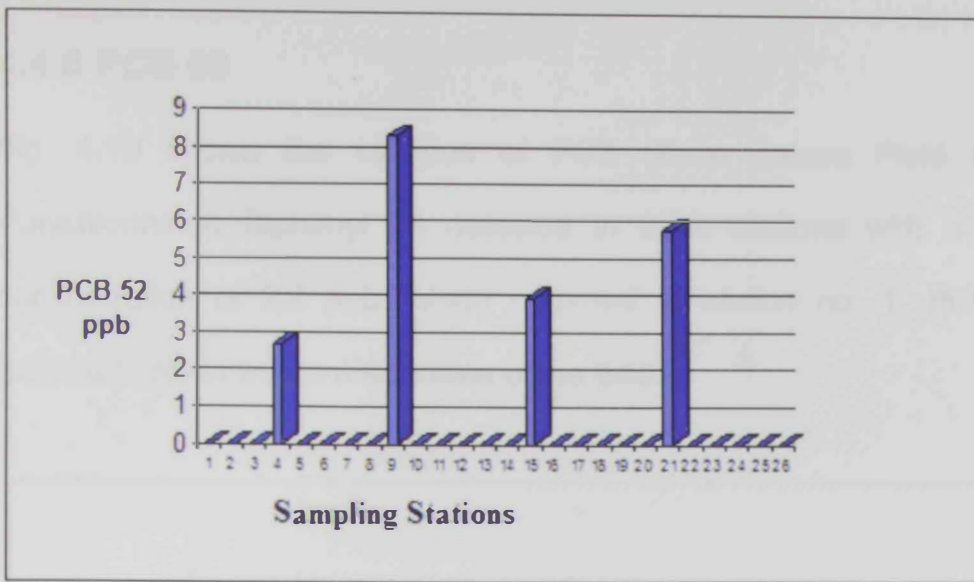


Fig. 4.17 PCB 52 variation in Zakum Field

4.4.5 PCB 44

Fig. 4.18 shows the variation of Polychlorinated Biphenyl 44 in Zakum Field area at 26 different stations. The concentration of PCB 44 ranges between 0 ppb and 7.21 ppb. The maximum recorded concentration was in station no. 12.

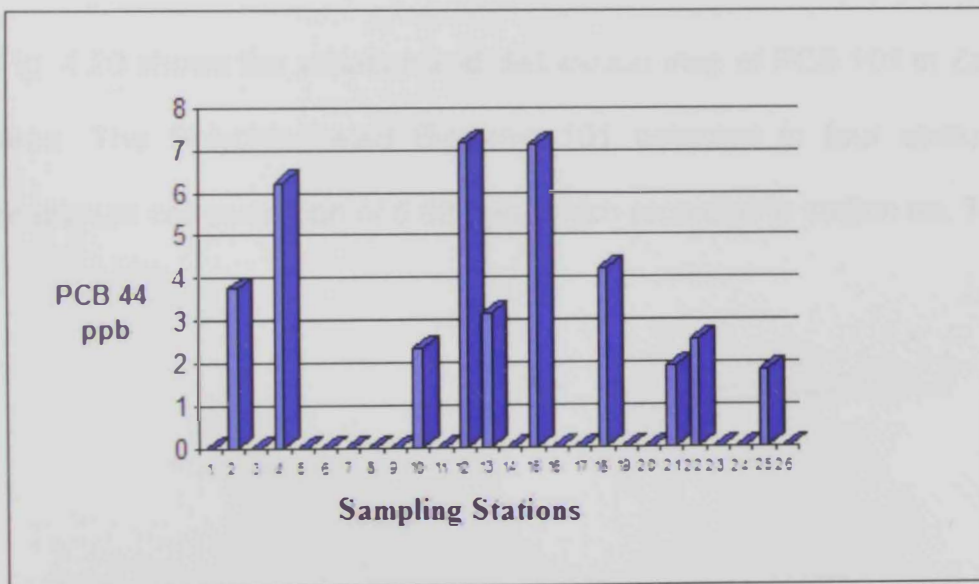


Fig. 4.18 PCB 44 variation in Zakum Field

4.4.6 PCB 66

Fig. 4.19 shows the variation of PCB 66 in Zakum Field area. The Polychlorinated Biphenyl 66 detected in three stations with a maximum concentration of 2.2 ppb, which recorded in station no. 1. PCB 66 was detected only in western side area of the field.

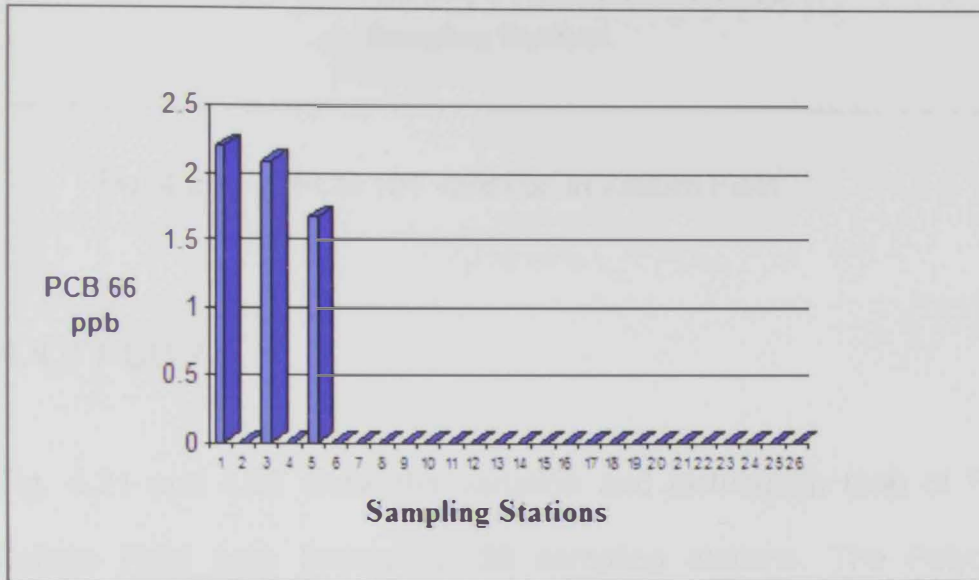


Fig. 4.19 PCB 66 variation in Zakum Field

4.4.7 PCB 101

Fig. 4.20 shows the variation and distribution map of PCB 101 in Zakum Field area. The Polychlorinated Biphenyl 101 detected in four stations with a maximum concentration of 6.88 ppb, which recorded in station no. 14.

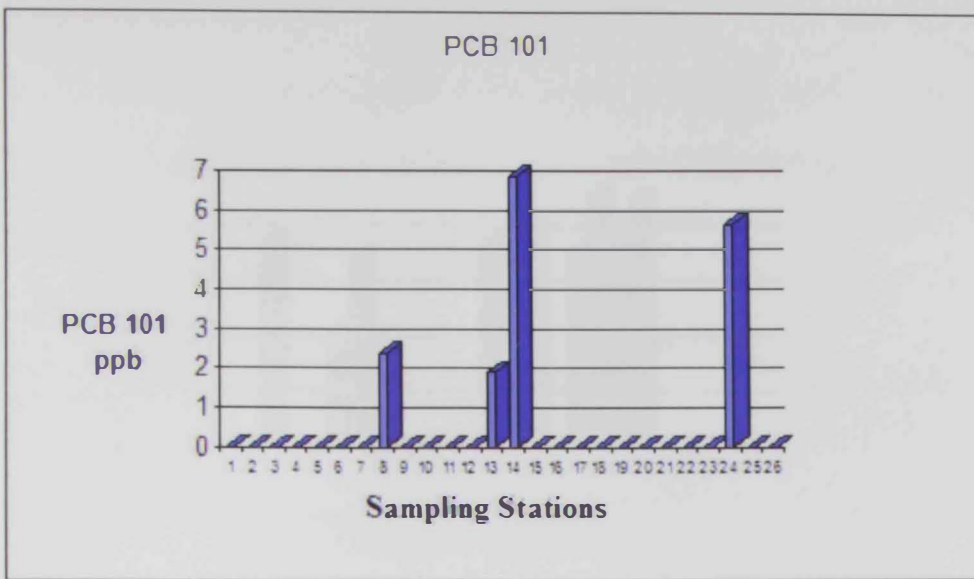


Fig. 4.20 PCB 101 variation in Zakum Field

4.4.8 PCB 77

Fig. 4.21 and 4.22 show the variation and distribution map of PCB 77 in Zakum Field area throughout 26 sampling stations. The Polychlorinated Biphenyl 77 ranges between 0 and 4.56 ppb. The maximum recorded concentration was in station no. 18. As shown in the distribution map, the highly concentrated area is located in the southern part of the field.

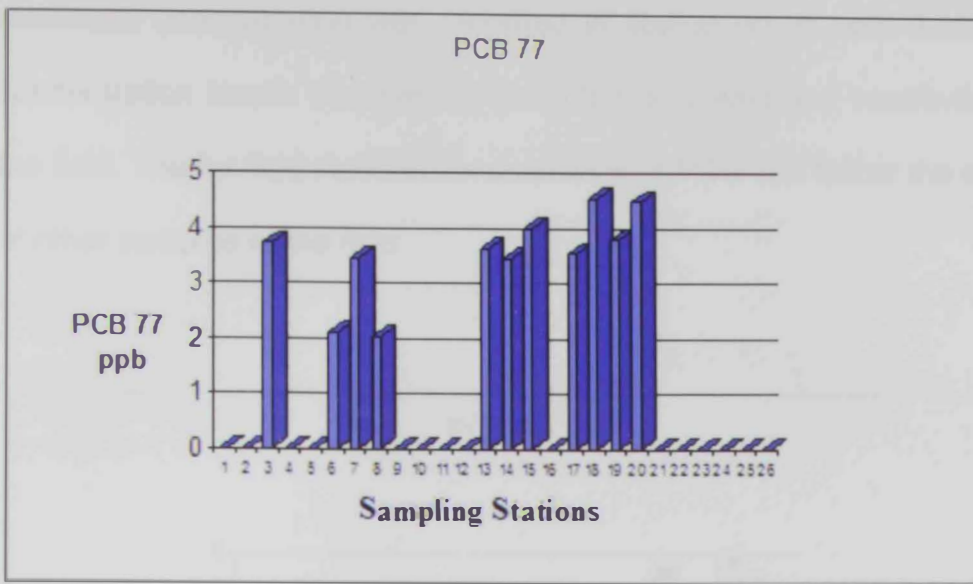


Fig. 4.21 PCB 77 variation in Zakum Field

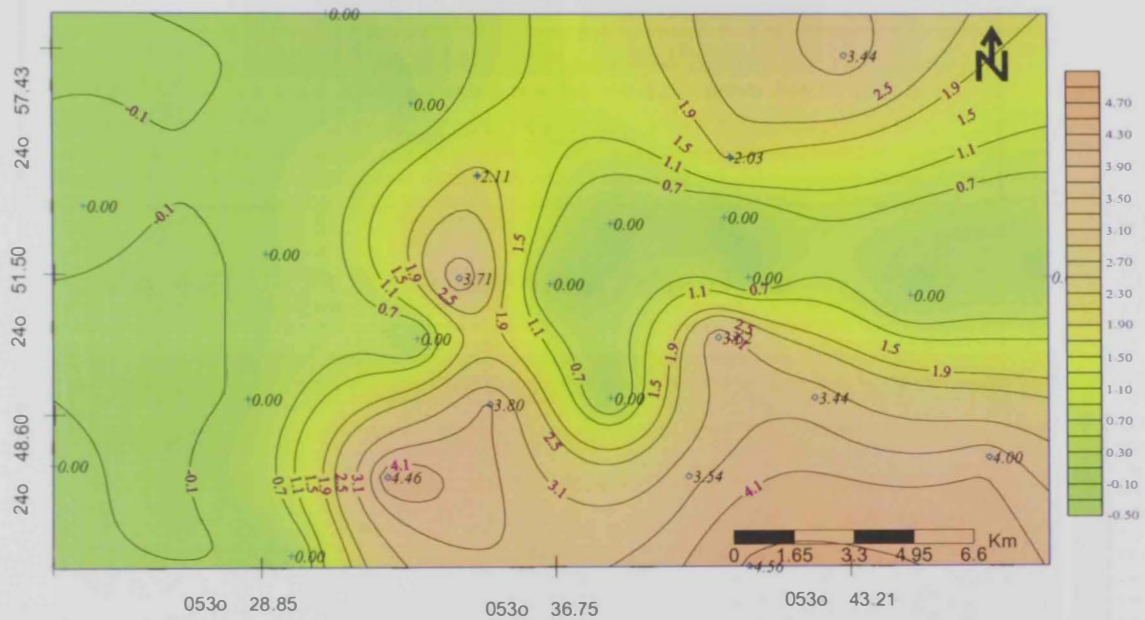


Fig. 4.22 PCB 77 distribution map in Zakum Field

4.4.9 PCB 180

The variation and distribution map of PCB 180 in the study area throughout the 26 sampling stations are shown in figures 4.23 and 4.24. PCB 180 has detected almost in all the sampling stations except one (station no. 15). The

maximum concentration was recorded in station no 24 with 3.92 ppb. The concentration trends observed towards the northeast and southwest sides of the field. The far field stations concentration of PCB 180 follow the same trend of other samples of the field.

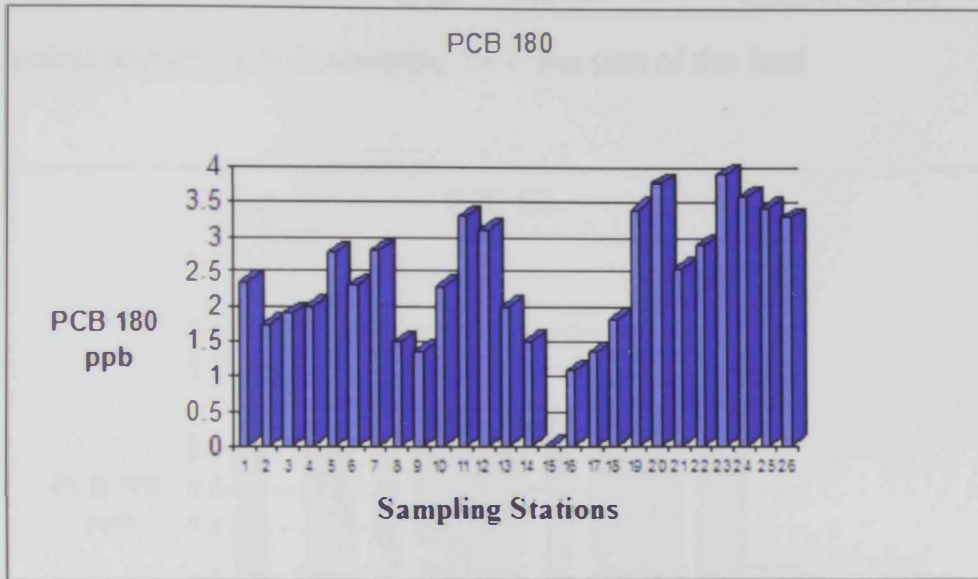


Fig. 4.23 PCB 180 variation in Zakum Field

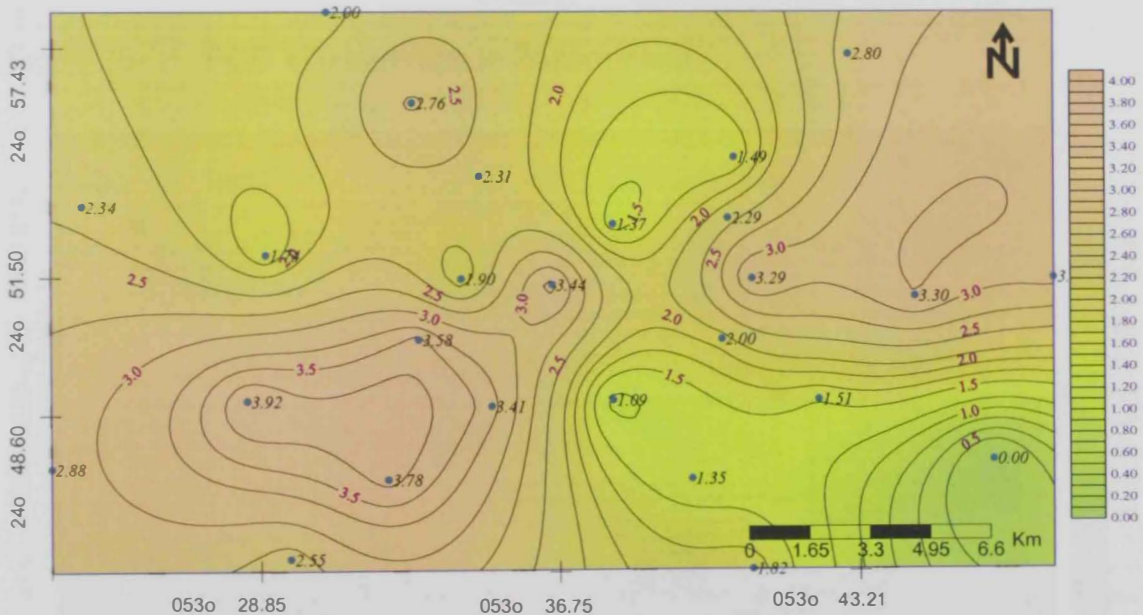


Fig. 4.24 PCB 180 distribution map in Zakum Field

4.4.10 PCB 170

Figures 4.25 and 4.26 show the variation and distribution map of PCB 170 in Zakum Field area. The Polychlorinated Biphenyl 170 concentration ranges between 0 and 1.27 ppb. The maximum concentration was recorded in station no. 19. As shown in Fig. 4.26, the PCB 170 trend increases from the central part of the field towards the outer part of the field.

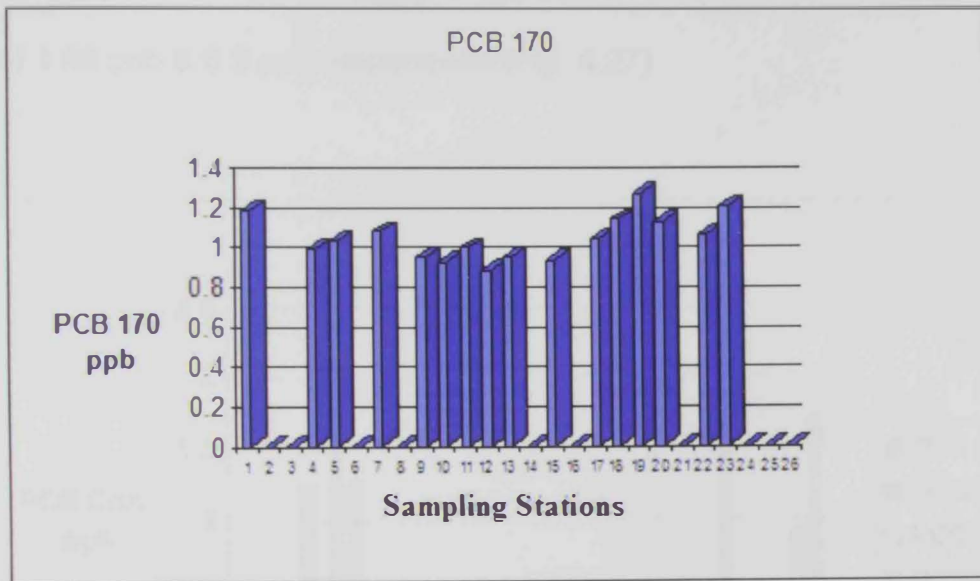


Fig. 4.25 PCB 170 variation in Zakum Field

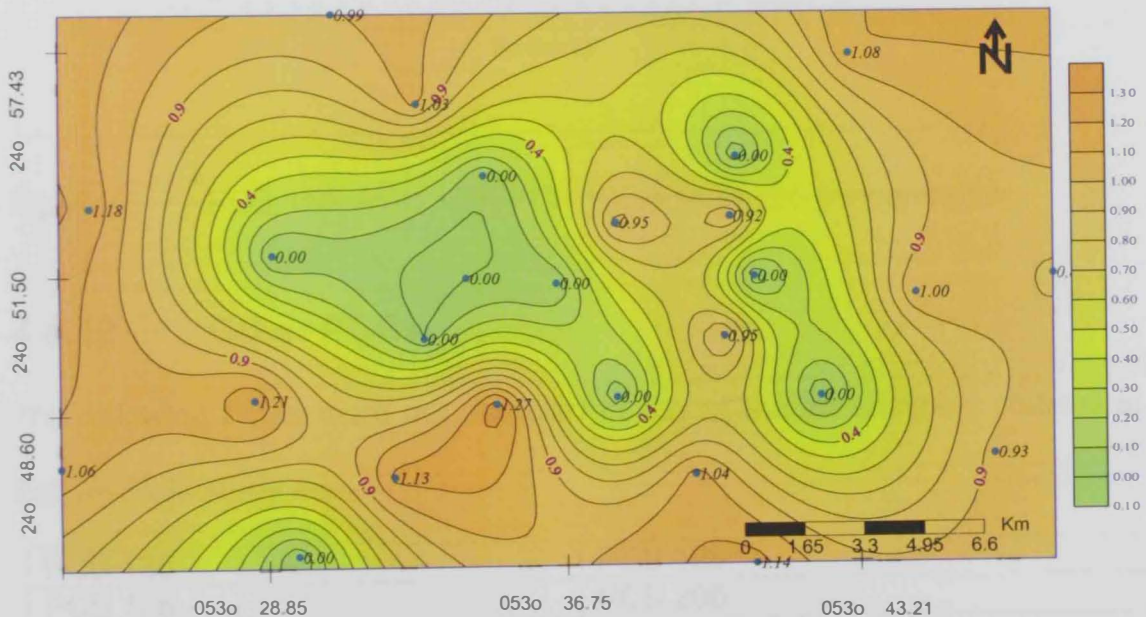


Fig. 4.26 PCB 170 distribution map in Zakum Field

4.4.11 PCB 105, PCB 118, PCB 153 & PCB 195

The PCB 105 detected in only one station with 1.71 ppb, which recorded in station no. 25. PCB 118 detected in two stations i.e. no. 4 & 6 with concentrations of 1.22 ppb and 1.24 ppb respectively. PCB 153 detected in only one station with concentration of 2.13 ppb, which recorded in station no. 5. The PCB 195 was detected in two station i.e. no. 21 & 24 with concentration of 1.88 ppb & 0.9 ppb respectively (Fig. 4.27)

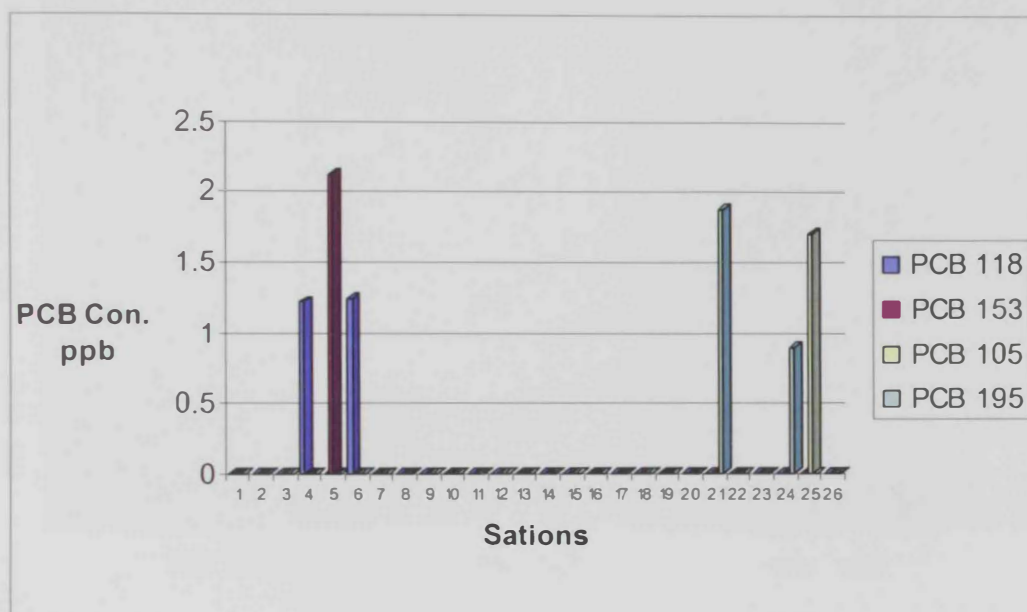


Fig. 4.27 PCB 118, PCB 153, PCB 105 & PCB 195 concentration

4.4.12 Other PCBs

The following PCBs were not detected in any of the 26 sampling stations in Zakum Field study area:

PCB 138	PCB 128
PCB 126	PCB 206
PCB 187	PCB 209

4.5 Poly Aromatic Hydrocarbons:

The concentration and distribution map of total Poly Aromatic Hydrocarbons, (PAHs) in Zakum Field area are illustrated in figures 4.28 and 4.29. The total PAHs ranges between zero (in case of not detected) and 31.5 ppb. The maximum value was recorded in station no. 21. Total PAHs concentration trend increases towards Northwest area of the field, consequently the minimum concentration found in the central part area of the field.

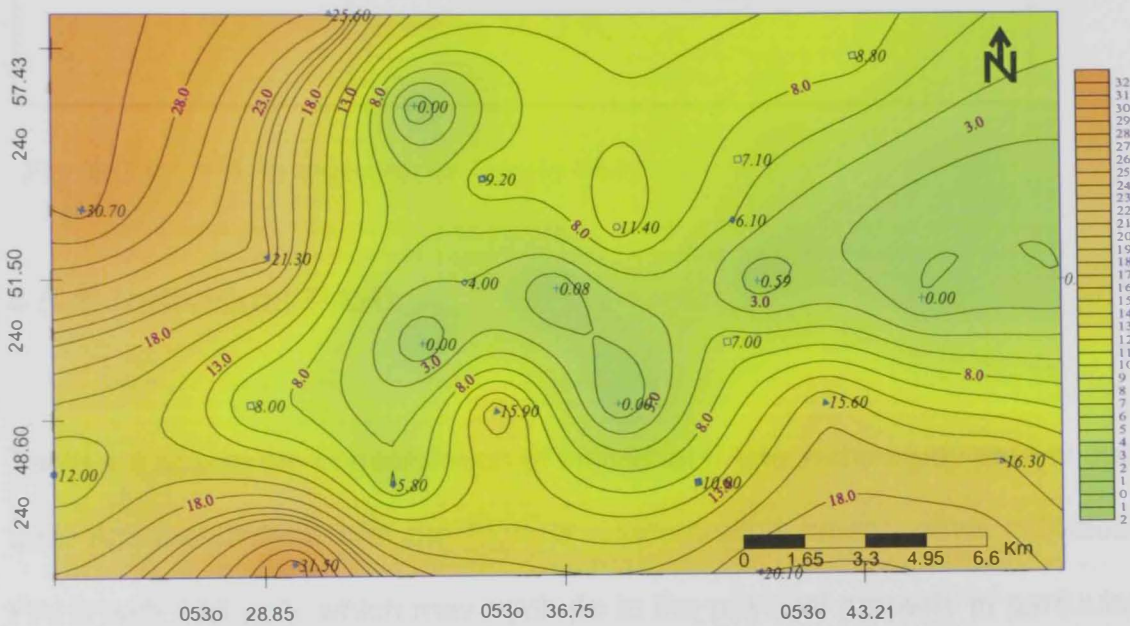


Fig. 4.28 PAHs distribution map in Zakum Field

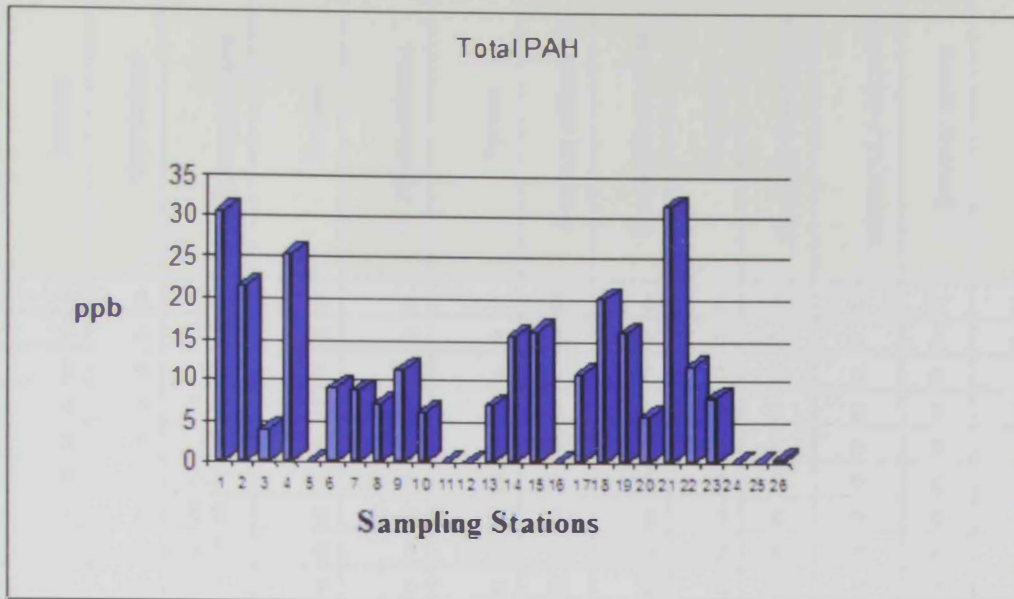


Fig. 4.29 PAHs variation in Zakum Field

4.5.1 Individual PAHs

Table 4.5 shows the concentration of individual PAHs in the study area in ppb unit. Acenaphthylene has the highest concentration among other individual PAHs with 154 ppb, which may attribute to the physical property in particular adsorption to the study area sediments. Concentration results and interpretation details are discussed in the following sections.

Stations	Naphthalene	Acenaphthylene	flourene	Pheneanthrene	Pyrene	Benzo(a) anthracene	Benzo(K)flouranthene	Chrysene	Benzo(B) flouranthene	Indeno(1,2,3-cd) pyrene	Benzo(a) pyrene	Total PAH, ppb
1	0	12.7	5	0	0	0	0	0	0	0	0	30.7
2	5	8.3	0	0	8	0	0	0	0	0	0	21.3
3	0	0	0	0	0	0	0	0	4	0	0	4
4	0	5.6	0	9	11	0	0	0	0	0	0	25.6
5	0	0	0	0	0	0	0	0	0	0	0	0
6	0	5.2	0	0	0	0	0	0	0	0	0	9.2
7	0	8.8	0	0	0	0	0	0	0	0	0	8.8
8	0	7.1	0	0	0	0	0	0	0	0	0	7.1
9	5.3	6.1	0	0	0	0	0	0	0	0	0	11.4
10	0	6.1	0	0	0	0	0	0	0	0	0	6.1
11	0	0	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0	0	0
13	0	7	0	0	0	0	0	0	0	0	0	7
14	0	15.6	0	0	0	0	0	0	0	0	0	15.6
15	0	16.3	0	0	0	0	0	0	0	0	0	16.3
16	0	0	0	0	0	0	0	0	0	0	0	0
17	0	5.9	0	0	5	0	0	0	0	0	0	10.9
18	0	16.1	0	0	4	0	0	0	0	0	0	20.1
19	0	15.9	0	0	0	0	0	0	0	0	0	15.9
20	0	5.8	0	0	0	0	0	0	0	0	0	5.8
21	0	5.1	16.1	0	0	0	0	0	0	0	0	31.5
22	0	6	0	0	6	0	0	0	0	0	0	12
23	0	0	0	0	8	0	0	0	0	0	0	8
24	0	0	0	0	0	0	0	0	0	0	0	0
25	0.1	0	0	0.02	0	0	0	0	0	0	0	0.08
26	0	0	0	0.06	0.11	0.03	0.04	0.1	0.1	0.03	0.07	0.59

Table 4.5 PAH's concentration

4.5.2 Naphthalene:

Figure 4.30 shows the variation of Naphthalene in Zakum Field area through out the sampling stations. Naphthalene was detected in three stations with highest concentration of 5.3 ppb in station no. 9.

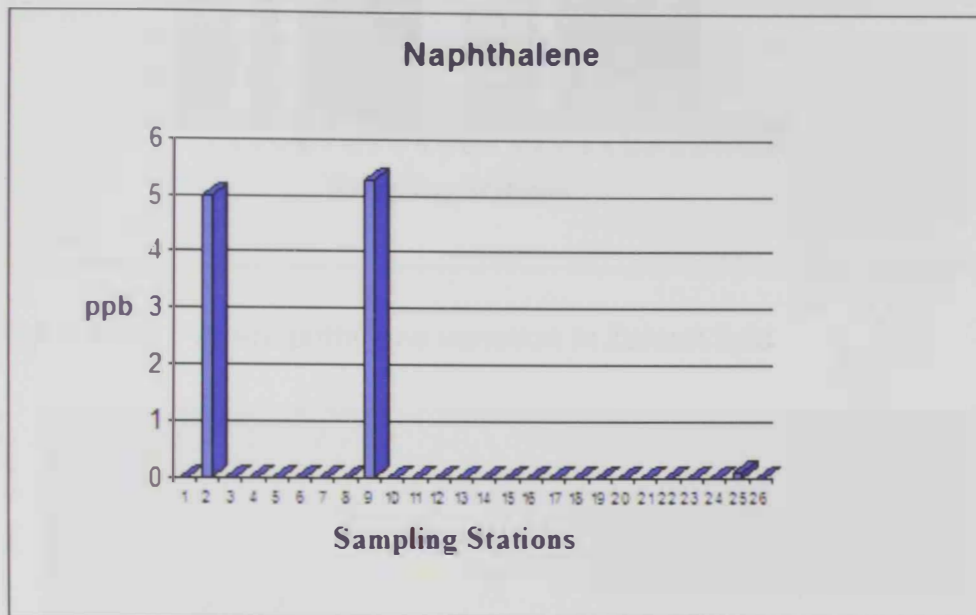


Fig. 4.30 Naphthalene concentration in Zakum Field

4.5.3 Acenaphthylene

The concentration and distribution map of Acenaphthylene in Zakum Field area throughout 26 different stations are shown in figures 4.31 and 4.32. The concentration ranges between 0 ppb and 16.3 ppb. The maximum concentration recorded was in station no. 16. Various high concentration spots of Acenaphthylene in the study area has been observed as shown in figure 4.32 i.e. in south, southeast and far west sides. However, the central part of the field shows low Acenaphthylene concentration.

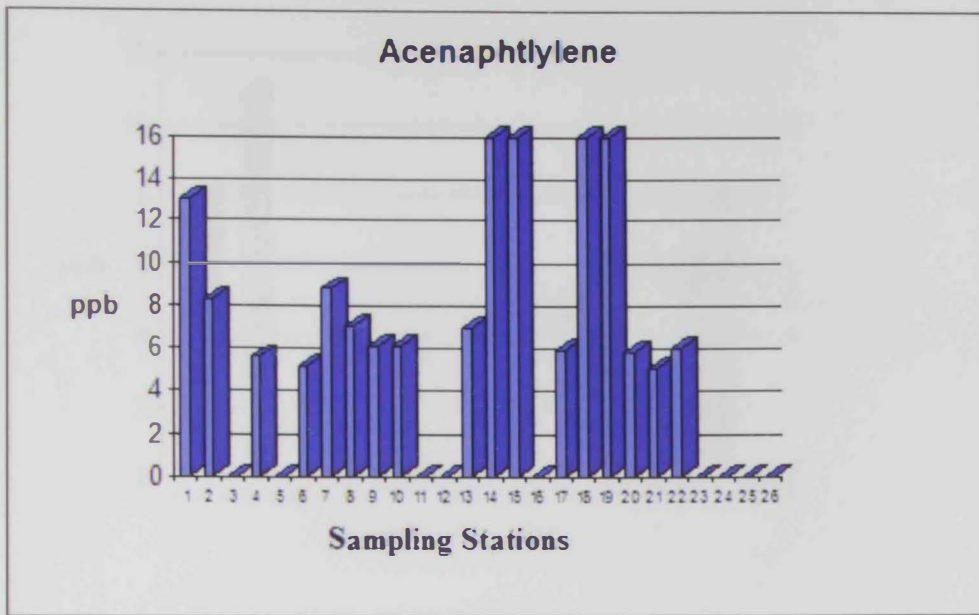


Fig. 4.31 Acenaphtylene variation in Zakum field

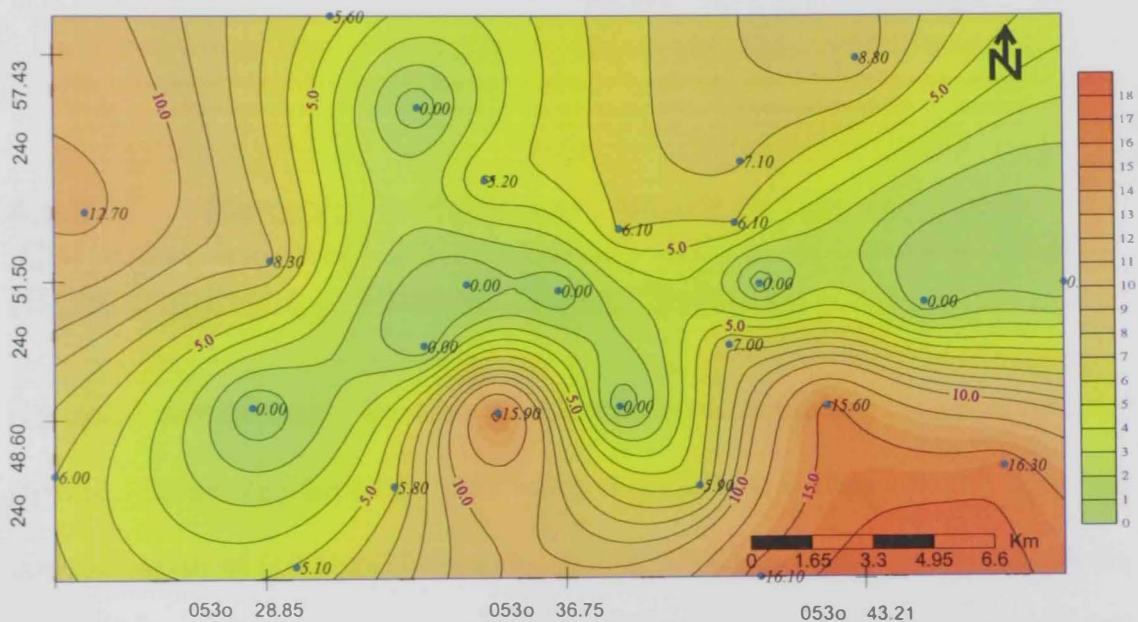


Fig. 4.32 Acenaphtylene distribution map in Zakum field

4.5.4 Pyrene

The concentration of the Pyrene in Zakum Field area throughout the 26 sampling stations is shown figure 4.33. The concentration ranges between 0 ppb and 11 ppb. The maximum concentration recorded was in station no. 4.

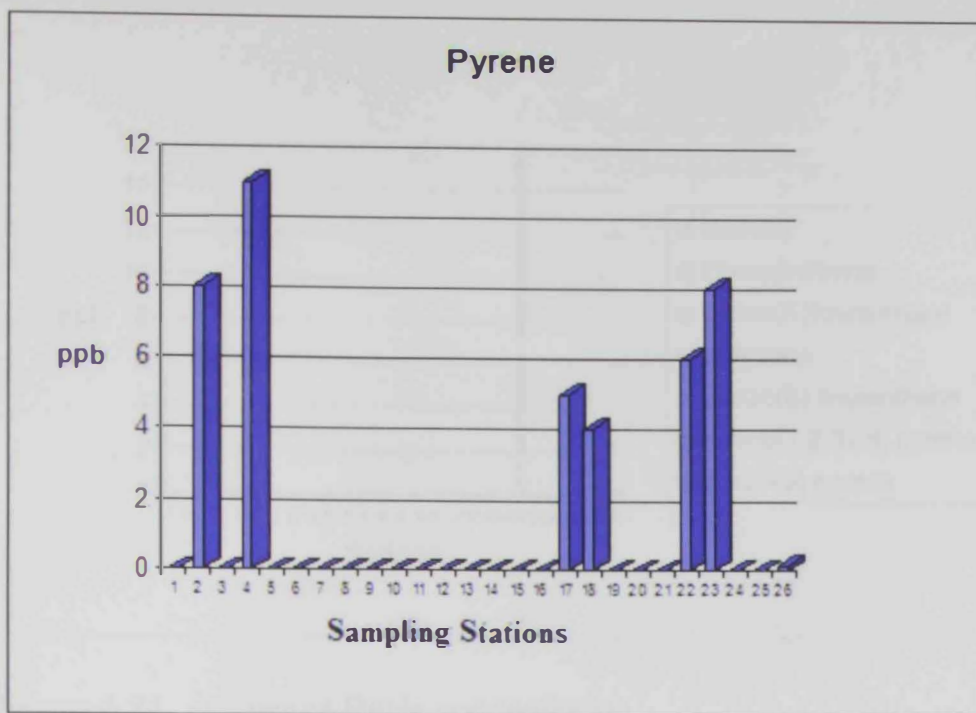


Fig. 4.33 Pyrene variation in Zakum Field

4.5.5 Benzo(a) anthracene , Benzo (K) flouranthene ,Chrycene, Indeno(1,2,3-cd) pyrene ,Benzo (a) pyrene , Benzo (B) flouranthene , Phenanthrene, Fluorene:

Benzo(a) anthracene , Benzo (K) flouranthene, Chrysene ,Indeno(1,2,3-cd) pyrene, Benzo (a) pyrene, and were detected in station no. 26 only with concentration of 0.03 ppb,0.04 ppb, 0.01ppb,0.03 ppb,0.07 ppb respectively. Benzo (B) flouranthene is detected in two stations (i.e. no. 3 & 26) with concentration of 4.00 ppb and 0.1 ppb. Phenanthrene is detected at three stations with highest concentration of 9.0 ppb in station no. 4. Fluorene is detected in two stations (i.e. no. 1 & 21) with concentration of 5.0 ppb and 16.1 ppb respectively (Figure 4.34).

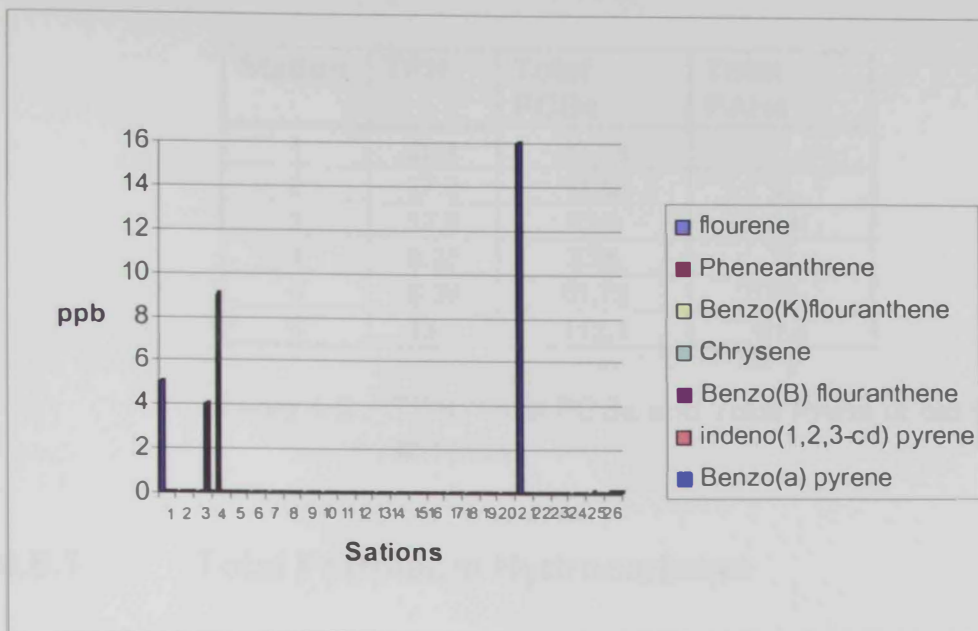


Figure 4.34 Individual PAHs concentration

4.5.6 PAH not detected in the study

The following PAHs were not detected in any of the 26 sampling stations in Zakum Field study area:

Acenaphthene	Dibenzo(a,h)anthracene	Fluoranthene
Anthracene	Benzo(g,h,i)perylene	

4.6 Previous seabed core samples analyses results

TPH, PCBs and PAHs analyses were carried out for six old seabed core samples, which collected during 1970's, for comparison purpose. Table 4.5 shows the concentration of TPH, Total PCBs and Total PAHs. The following sections discuss the results interpretation.

Station	TPH	Total PCBs	Total PAHs
1	28.4	37.13	0
2	27.8	13.55	0
3	17.8	11.3	5.1
4	8.93	3.55	0
5	8.09	61.72	59
6	13.5	112.1	61.4

Table 4.5 TPH, Total PCBs and Total PAHs of old seabed samples

4.6.1 Total Petroleum Hydrocarbons

Total petroleum hydrocarbons concentration in the old seabed cores from Zakum Field area ranges between 28.4 to 8.09 ppm in station no. 1 and 5 respectively (figure 4.35).

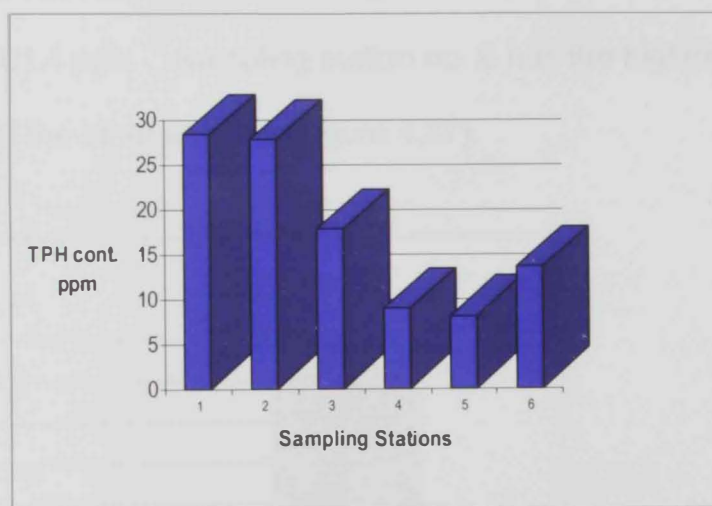


Figure 4.35 TPH concentrations of old Zakum Field seabed core samples

4.6.2 Total Poly chlorinated Biphenyl

Total polychlorinated biphenyl concentration in Zakum old seabed cores ranges between 3.5 and 112.1 ppb in stations no. 4 and 6 respectively (figure 4.36).

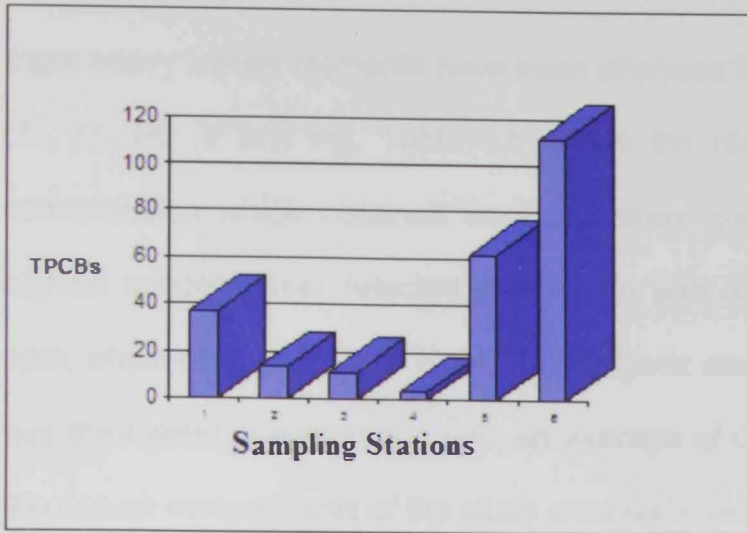


Figure 4.36 Total PCBs concentration of old Zakum Field seabed core samples

4.6.3 Total Poly Aromatic Hydrocarbons

Total poly aromatic hydrocarbons ranges in Zakum Field old core samples between 0 to 61.4 ppb. Sampling station no. 6 has the highest concentration of PAH among the other samples (figure 4.37).

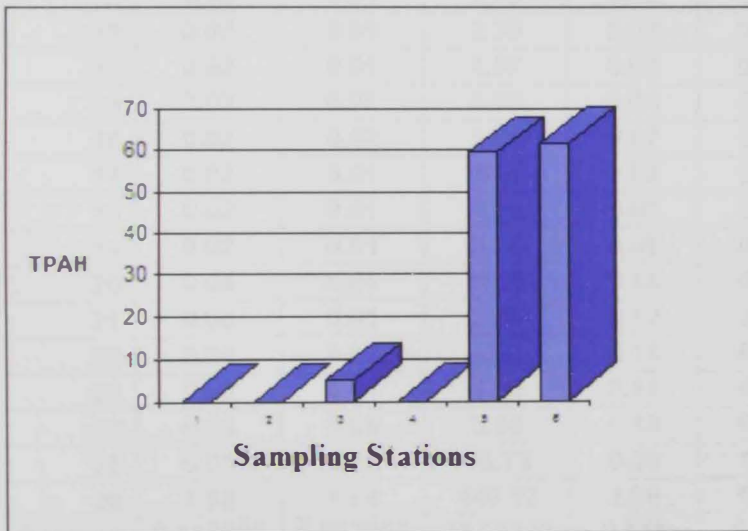


Figure 4.37 Total PAHs concentration of Zakum Filed old seabed core samples

4.7 Heavy Metals

Eight heavy metals elements have been analysed in this study i.e. Cr, Cu, Fe, Mn, Ni, Pb, V and Hg. Table 4.6 shows the results of the heavy metals concentration which obtained from the study area sampling stations. The highest concentration detected was for Fe with an average amount of 23.6 ppm, which may attribute to highly Fe lithogenic source. On the other hand, Ni has the lowest concentration with an average of 0.035 ppm, which confirms the non-oil contaminants of the study area sediments.

Station	Cr	Cu	Fe	Mn	Ni	Pb	V	Hg
1	0.04	0.01	4.16	0.08	0.01	0.01	0.04	0
2	0.04	0.01	5.01	0.14	0.02	0.01	0.03	0
3	0.14	0.02	3.18	0.09	0.02	0.02	0.02	0
4	0.06	0.02	8.80	0.22	0.04	0.01	0.04	0.022
5	0.07	0.01	15.18	0.14	0.02	0.01	0.09	0.015
6	0.04	0.01	3.42	0.12	0.01	0.01	0.03	0
7	0.02	0.02	2.81	0.08	0.01	0.01	0.02	0
8	0.05	0.01	5.89	0.11	0.01	0.01	0.05	0
9	0.09	0.01	16.42	0.23	0.02	0.01	0.12	0.013
10	0.03	0.01	3.24	0.11	0.01	0.01	0.04	0
11	0.03	0.04	2.43	0.07	0.01	0.01	0.02	0
12	0.02	0.01	2.55	0.08	0.01	0.01	0.03	0.012
13	0.02	0.01	2.78	0.07	0.01	0.01	0.02	0
14	0.02	0.01	1.57	0.05	0.01	0.01	0.02	0.020
15	0.03	0.02	1.59	0.04	0.01	0.01	0.02	0.009
16	0.02	0.02	3.61	0.07	0.01	0.01	0.02	0.009
17	0.02	0.01	1.51	0.03	0.01	0.01	0.02	0.013
18	0.02	0.01	1.52	0.03	0.01	0.00	0.02	0.016
19	0.02	0.01	2.75	0.09	0.01	0.01	0.03	0
20	0.04	0.01	6.56	0.14	0.02	0.01	0.05	0.012
21	0.05	0.01	7.45	0.12	0.02	0.01	0.05	0.369
22	0.04	0.01	4.06	0.11	0.02	0.01	0.02	0.26
23	0.03	0.01	5.22	0.11	0.02	0.01	0.02	0.66
24	0.03	0.06	3.56	0.12	0.04	0.01	0.03	0.38529
25	0.05	0.06	48.73	0.28	0.03	0.04	0.04	0.029507
26	1.85	1.84	449.92	2.08	0.50	1.30	0.26	0.052383
Average	0.110385	0.087308	23.61231	0.185	0.035	0.060769	0.044231	0.072968

Table 4.6 Heavy metals concentration in Zakum Field area (ppm)

4.7.1 Cr:

The distribution of Cr concentration in Zakum Field area throughout the 26 sampling stations is shown in figures 4.38. The maximum and minimum values were recorded in stations no. 26 and many stations with concentration of 1.85 and 0.02 ppm, respectively with Average value of Cr is 0.11 ppm. The Cr concentration is low compared to similar previous studies values in the region.

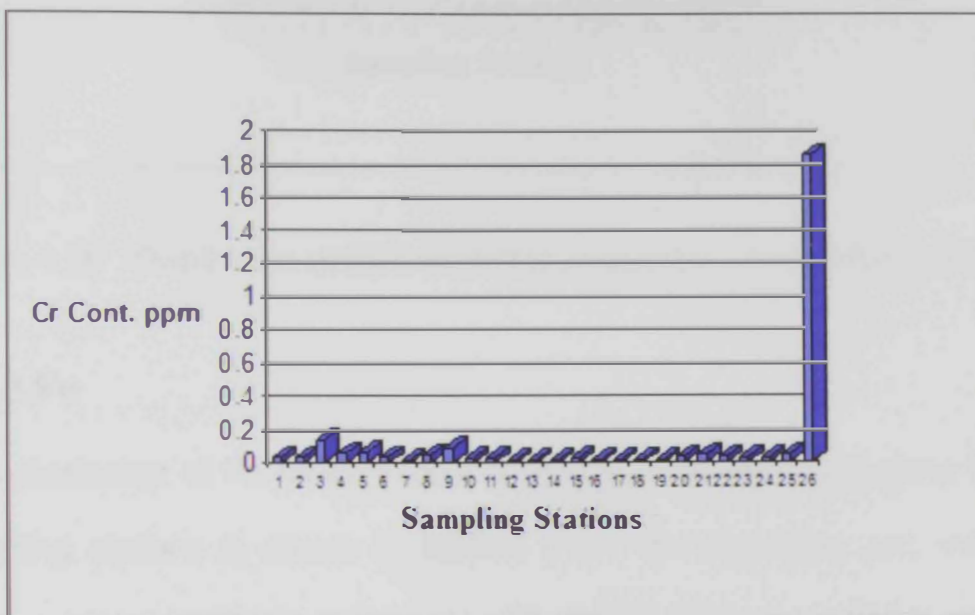


Figure 4.38 Distribution of Cr concentration (ppm) in Zakum Field area

4.7.2 Cu

The distribution of Cu concentration in Zakum Field area throughout the 26 sampling stations is shown in figures 4.39. The maximum and minimum values were recorded in stations no. 26 and 12 with concentration of 1.84 and 0.01 ppm, respectively and a average value of 0.09 ppm. The Cu concentration in the study area is low compared to previous studies in the region (Table 2.3).

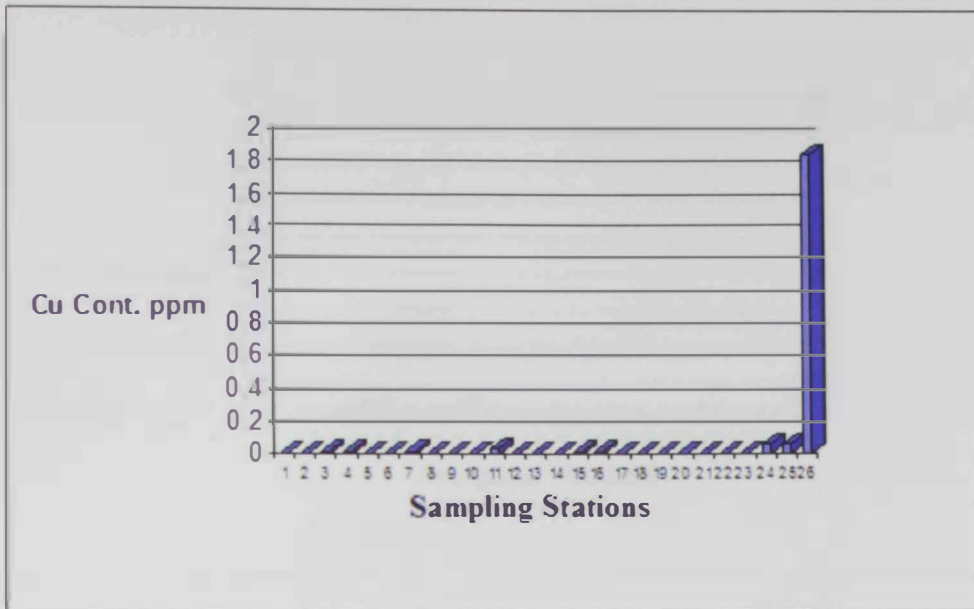


Figure 4.39 Distribution of Cu concentration (ppm) in Zakum field area

4.7.3 Fe

The distribution of Fe concentration in Zakum Field area throughout the 26 sampling stations is shown in figures 4.40. The maximum and minimum values were recorded in stations no. 26 and 17 with concentration of 449.9 and 1.51 ppm, respectively with average value of 23.61 ppm. The Fe concentration in this study is low compared to previous studies in the region (Table 2.3).

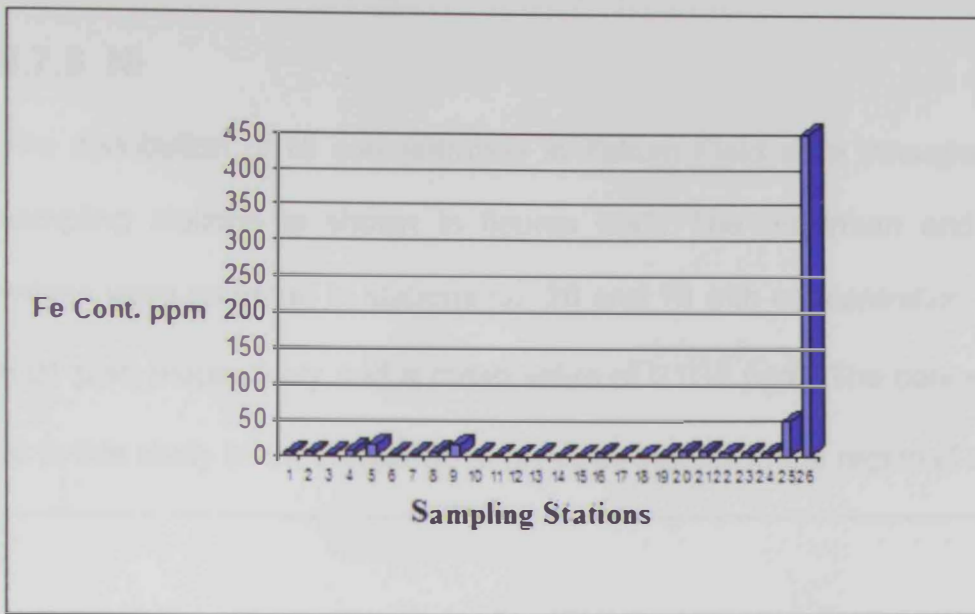


Figure 4.40 Distribution of Fe concentration (ppm) in Zakum Field area

4.7.4 Mn :

The distribution of Mn concentration in Zakum Field area is shown in figures 4.41. The maximum and minimum values were recorded in stations no. 26 and 17&18 respectively with concentration of 2.08 and 0.03 ppm respectively. Mn average value is 0.185 ppm. The concentration of Mn in this study is low compared to previous studies in the region.

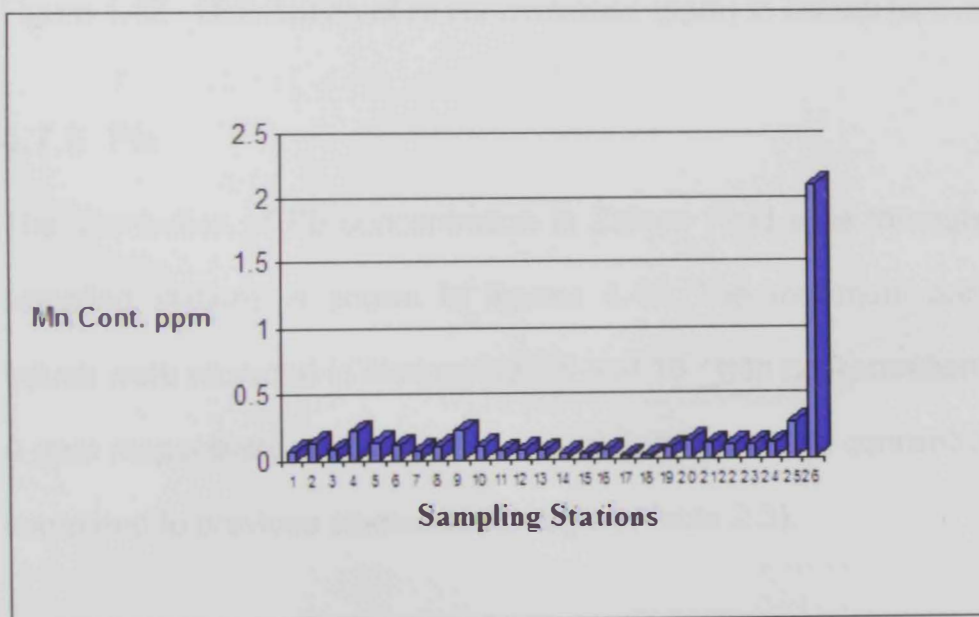


Figure 4.41 Distribution of Mn concentration (ppm) in Zakum Field area

4.7.5 Ni

The distribution of Ni concentration in Zakum Field area throughout the 26 sampling stations is shown in figures 4.42. The maximum and minimum values were recorded in stations no. 26 and 19 with concentration of 0.5 and 0.01 ppm respectively and a mean value of 0.035 ppm. The concentration of Ni in this study is low compared to previous studies in the region (Table 2.3).

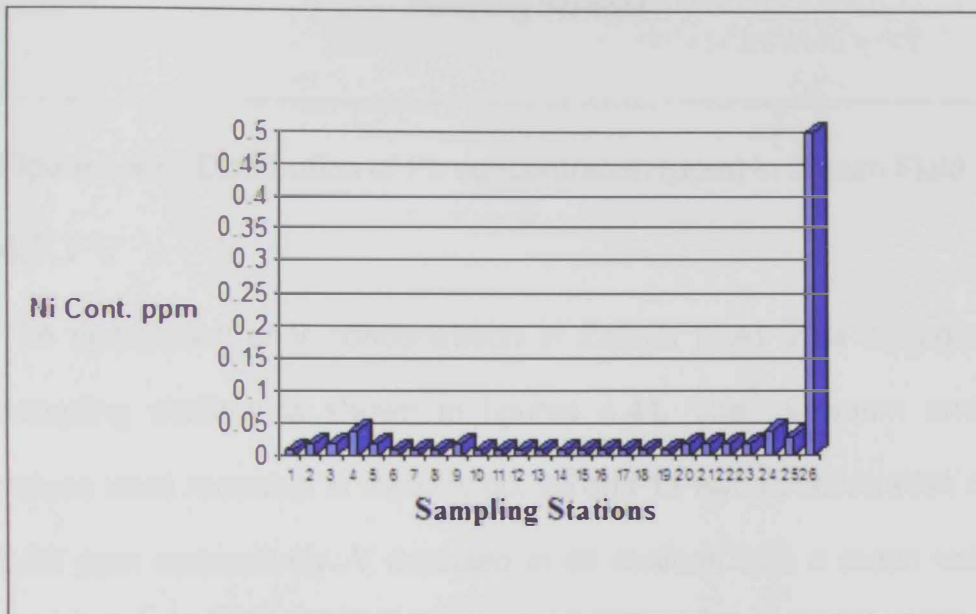


Figure 4.42 Distribution of Ni concentration (ppm) in Zakum field area

4.7.6 Pb

The distribution of Pb concentration in Zakum Field area throughout the 26 sampling stations is shown in figures 4.43. The maximum and minimum values were recorded in stations no. 26 and 18 with concentration of 1.3 and 0 ppm respectively and a mean value of 0.06 ppm. The concentration is low compared to previous studies in the region (Table 2.3).

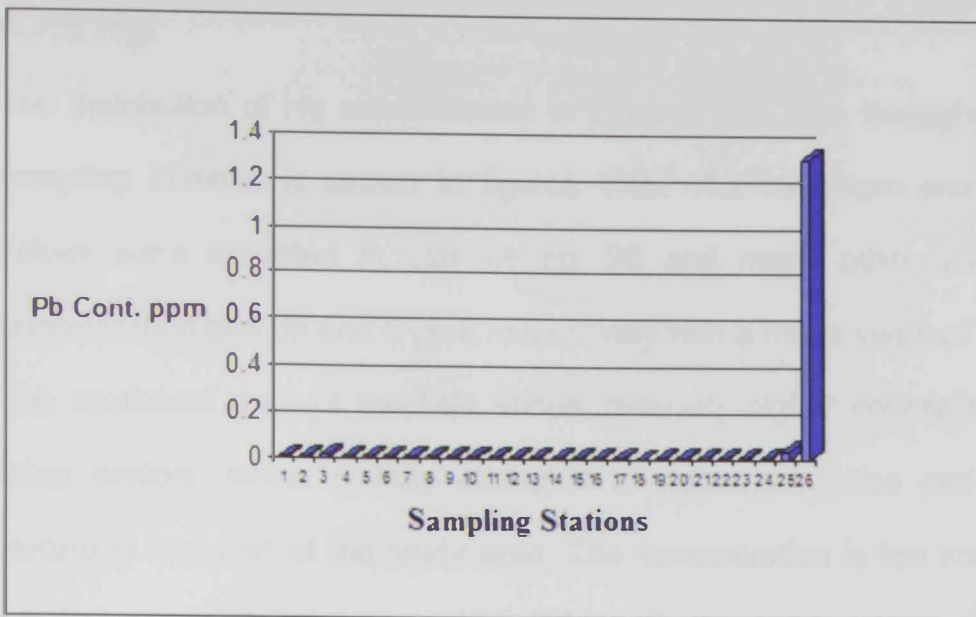


Figure 4.43 Distribution of Pb concentration (ppm) in Zakum Field area

4.7.7 V

The distribution of V concentration in Zakum Field area throughout the 26 sampling stations is shown in figures 4.44. The maximum and minimum values were recorded in stations no. 26 and 11 with concentration of 0.26 and 0.02 ppm respectively. V detected in all stations with a mean value of 0.04 ppm. The concentration is low compared to previous studies in the region.

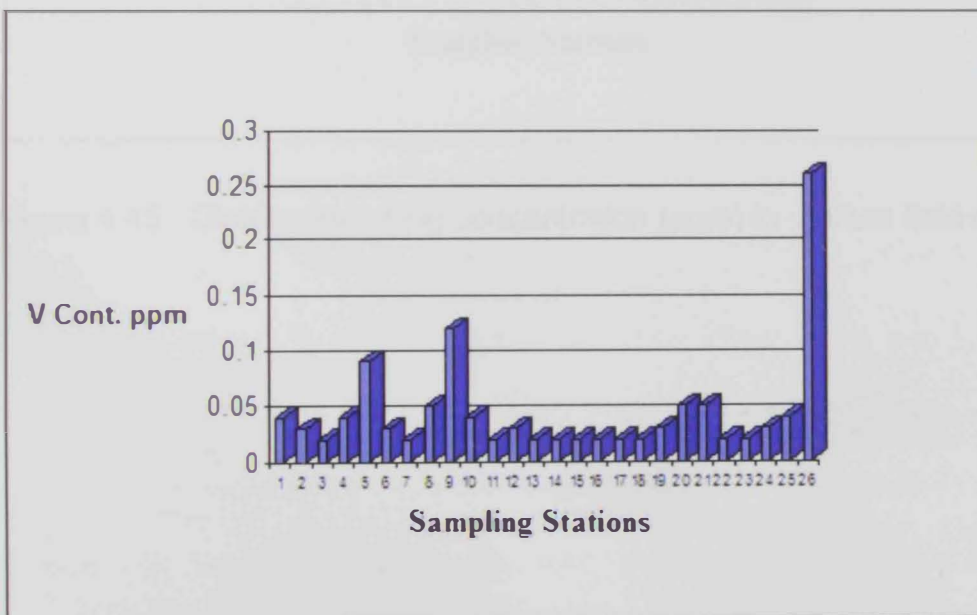


Figure 4.44 Distribution of V concentration (ppm) in Zakum Field area

4.7.8 Hg:

The distribution of Hg concentration in Zakum Field area throughout the 26 sampling stations is shown in figures 4.45. The maximum and minimum values were recorded in stations no. 26 and many other stations with concentration of 0.66 and 0 ppm respectively with a mean value of 0.07 ppm. The southeast area of the field shows relatively higher concentration than other sectors, which is may attributed to water circulation and sediment texture in that part of the study area. The concentration is low compared to previous studies in the region (Table 2.3).

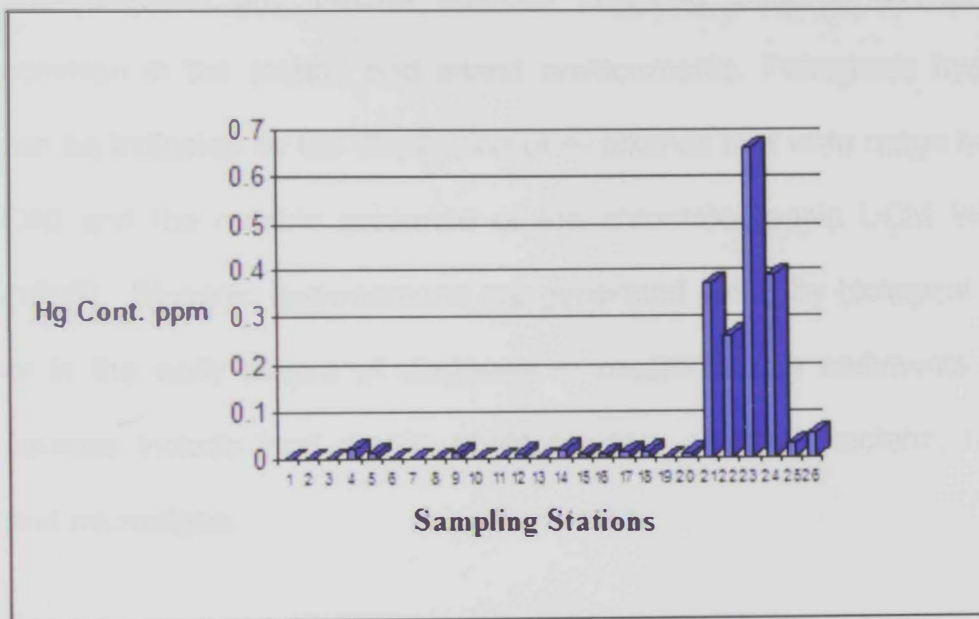


Figure 4.45 Distribution of Hg concentration (ppm) in Zakum field area

4.8 Distinguishing biogenic hydrocarbons from petrogenic hydrocarbons

Characterization and differentiation of hydrocarbons from different sources is an essential part of any oil pollution assessment study. After oil spills, oil hydrocarbons often mix with other background hydrocarbon sources in the impacted area. One of the potential sources of hydrocarbons contributing to the background is a biogenic hydrocarbon. Hydrocarbons from both anthropogenic and natural sources including biogenic source are very common in the marine and inland environments. Petrogenic hydrocarbons can be indicated by the distribution of n- alkanes in a wide range from C15 to C40 and the notable presence of the chromatographic UCM Wang et al. (1995). Biogenic hydrocarbons are generated either by biological processes or in the early stages of diagenesis in recent marine sediments. Biological sources include land plants, phytoplankton, animals, bacteria, macroalgae and microalgae.

The distinct characteristics of biogenic hydrocarbons including much higher abundance of odd n-alkanes in the wide range of n- C21 to n- C33 and resulting in unusually high carbon preference index (CPI) values, which is defined as the sum of the odd carbon numbered Alkanes to the sum of the even carbon numbered Alkanes (oils characteristically have CPI values around 1.0). High CPI and high pristane / phytane values. Also notable is the absence of the "unresolved complex mixture (UCM)" hump in the chromatograms.

In this study pristane / phytane ratio ranges from 0.38 to 1.59. CPI values ranges from 0.45 to 1.16 (Table 4.6 and figures 4.46-4.50). High concentrations of pristane relative to phytane in most of the offshore sediments indicate biological hydrocarbon input from a marine biological source (i.e. phytoplankton / bacterial) origin.

Samples	25	18	15	11	9	4	3
pr/ph	1.59	1.02	0.95	1.02	0.88	0.95	0.46
CPI	0.94	0.49	0.79	1.11	0.95	0.82	1.16

Table 4.6 Parameters from Zakum Field sediments

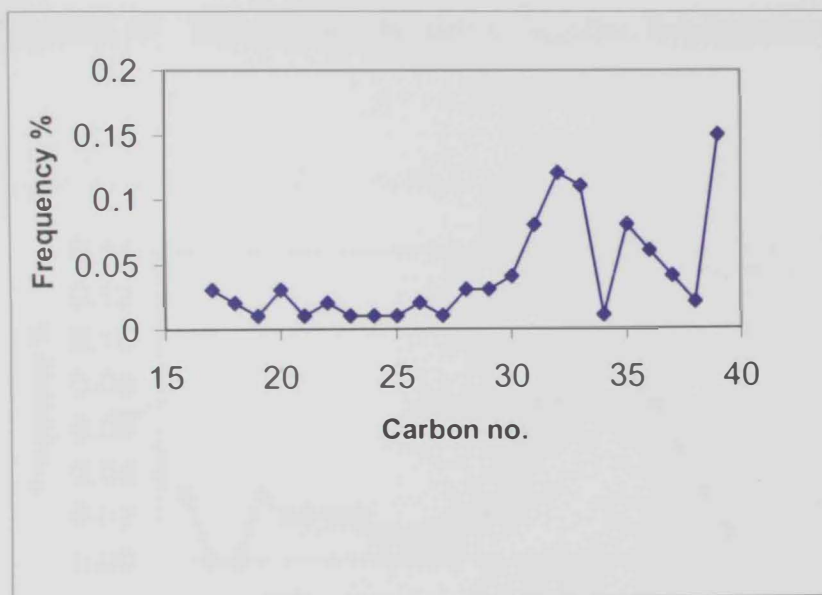


Figure 4.46 Sample no. 3 carbon number distributions vs. frequency

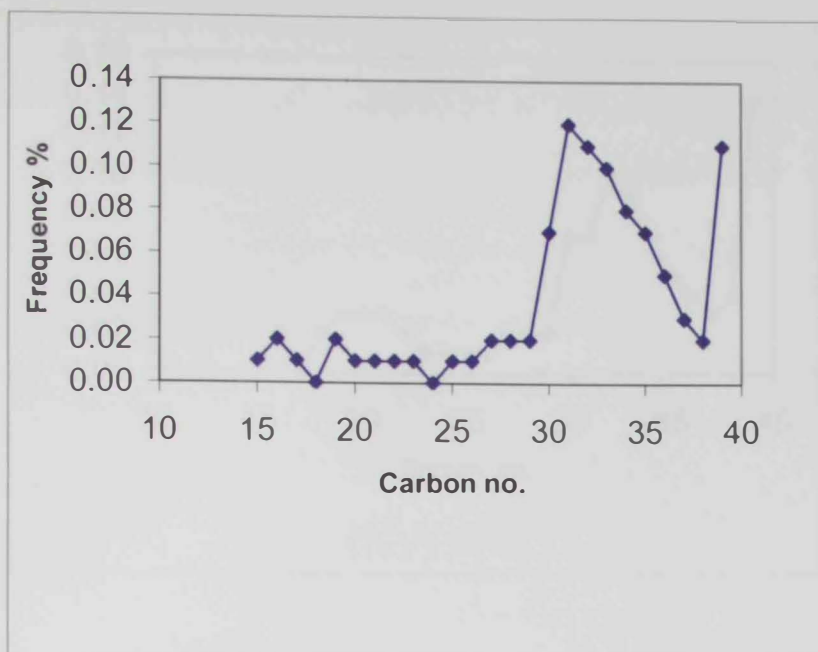


Figure 4.47 Sample no. 25 carbon number distributions vs. frequency

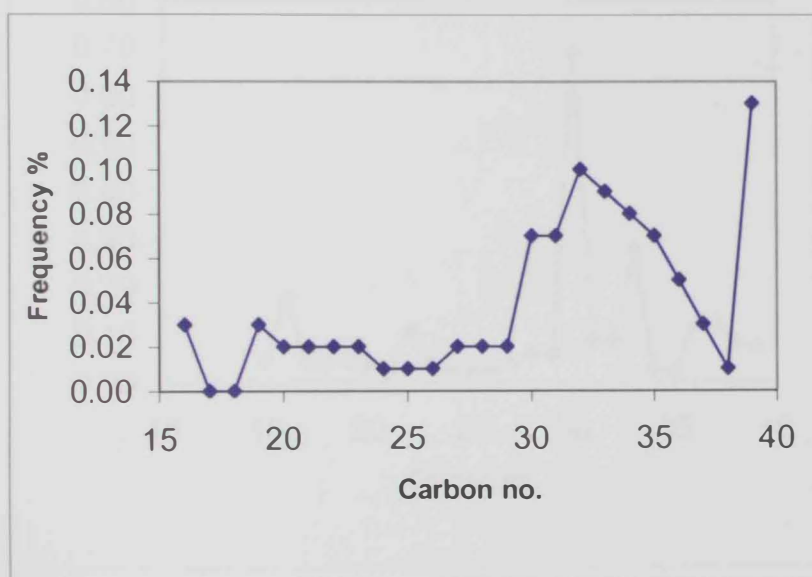


Figure 4.48 Sample no. 4 carbon number distributions vs. frequency

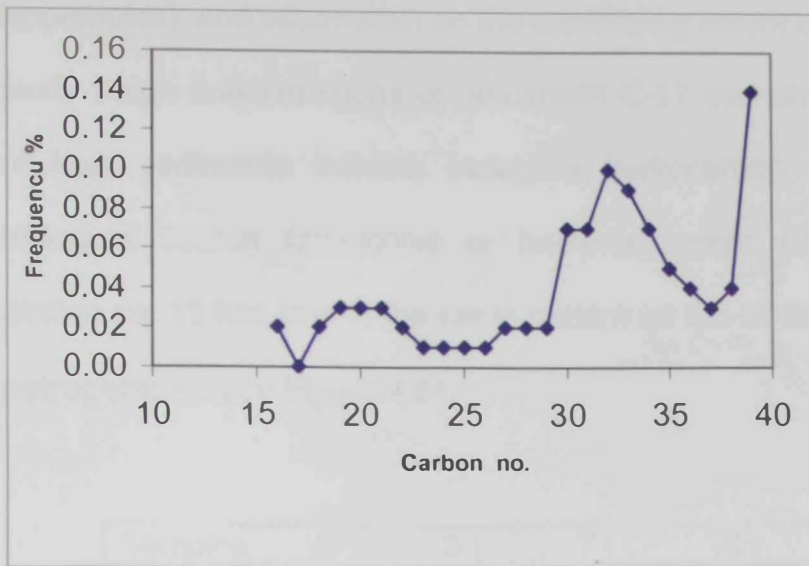


Figure 4.49 Sample no. 15 carbon number distributions vs. frequency

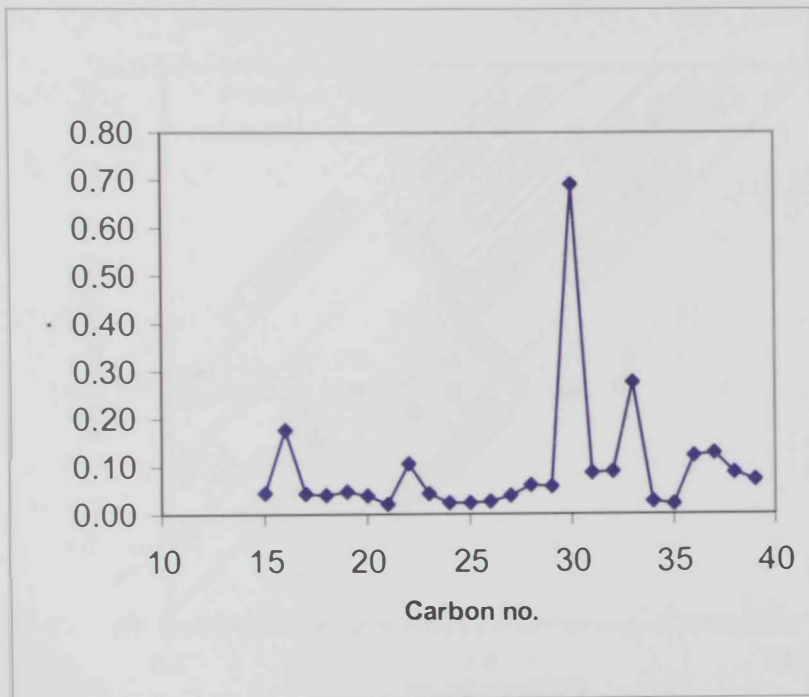


Figure 4.50 Sample no.18 carbon number distribution vs. frequency

GC – FID chromatograms also provide a distribution pattern of petroleum hydrocarbons (e.g., carbon range and profile of UCM), fingerprints of the major oil components (e.g., individual resolved n-alkanes and major

isoprenoids), and information on the weathering extent of the spilled oil. In this study, high concentrations of pristane/n-C-17 and phytane/n-C-18 in most offshore sediments indicate biological hydrocarbon input from a marine biological source (planktonic or bacterial) origin (Shannungham, 1985). Station no. 11 has lays in the same pattern as the oil sample, which indicates petrogenic source Figure 4.51.

Samples	3	7	18	11	20
pr/nc17	0.96	0.91	0.93	0.75	0.92
ph/nc18	2.93	1.99	0.83	0.61	0.4

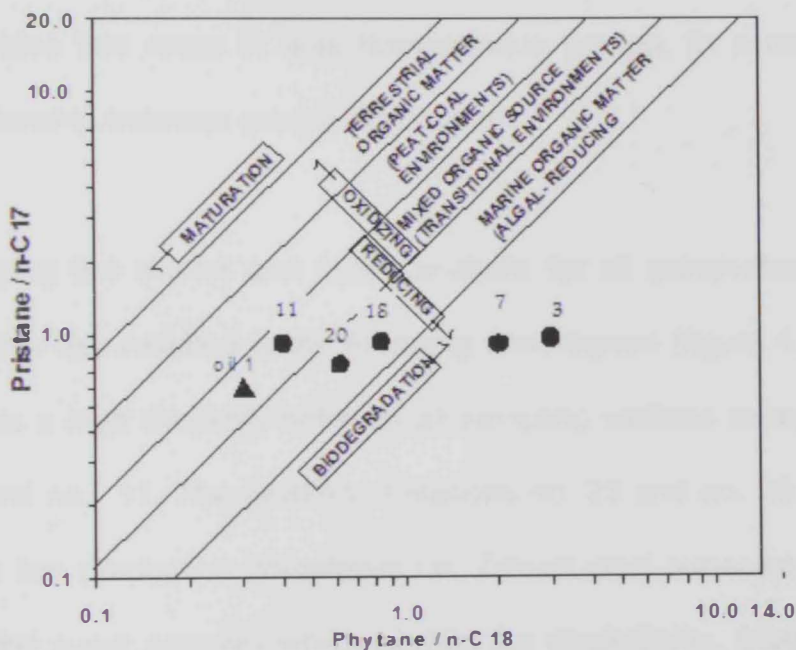


Figure 4.51 Ph/nc18 vs. Pr/nc17 of Zakum oil sample and sediments extract

4.9 Statistical Analyses

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 closest or farthest individuals (Rock, 1988). The input matrix, 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).

To study the similarities between stations, multivariate statistical analysis in the form of cluster analysis which had been used. Classification is placing of variables into more or less homogenous groups, in a manner so that the relationship between groups is revealed.

Applying the cluster and factor analysis for all parameters on all sampling stations has resulted in the following dendrogram (figure 4.50), which mainly shows a high similarity between all sampling stations except stations no. 25, 26 and no. 11. The location of stations no. 25 and no. 26 is underneath the main two production complexes i.e. Zakum west super complex and Zakum Central super complex which explain the dissimilarity. Station no. 11 has the highest TPH concentration with other high pollutants concentrations, which support the dissimilarity from other stations throughout the field.

The chemical associations of the various metals and pollutants can also be assessed using multivariate statistical analysis. The cluster analysis i.e. single linkage, Euclidean distance was performed on the data matrix comprising 13

variables and 26 observations (sampling stations). The obtained dendrogram (Figure 4.53) shows five clusters, six heavy metals i.e. V, Ni, Pb, Mn, Cu, and Cr with grain size distribution as one cluster. Which is clustered with TOC then to TPAH and TPCB then clustered to TPH at higher linkage distance. Fe is the least cluster associated element in this study.

First cluster elements are supported by high correlation between them (Table 4.7). The concentration of heavy metals in this study is not resulting from oil pollution source as they have insignificant correlation factor.

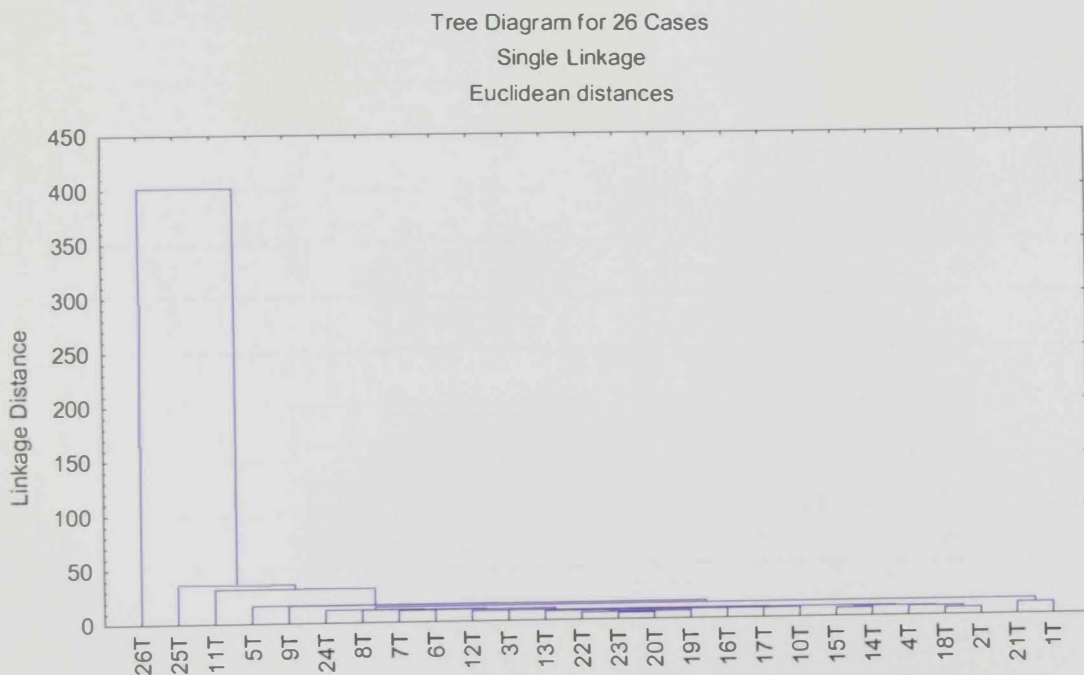


Figure 4.52 Cluster analysis Dendrogram for all sampling stations

Tree Diagram for 13 Variables
 Single Linkage
 Euclidean distances

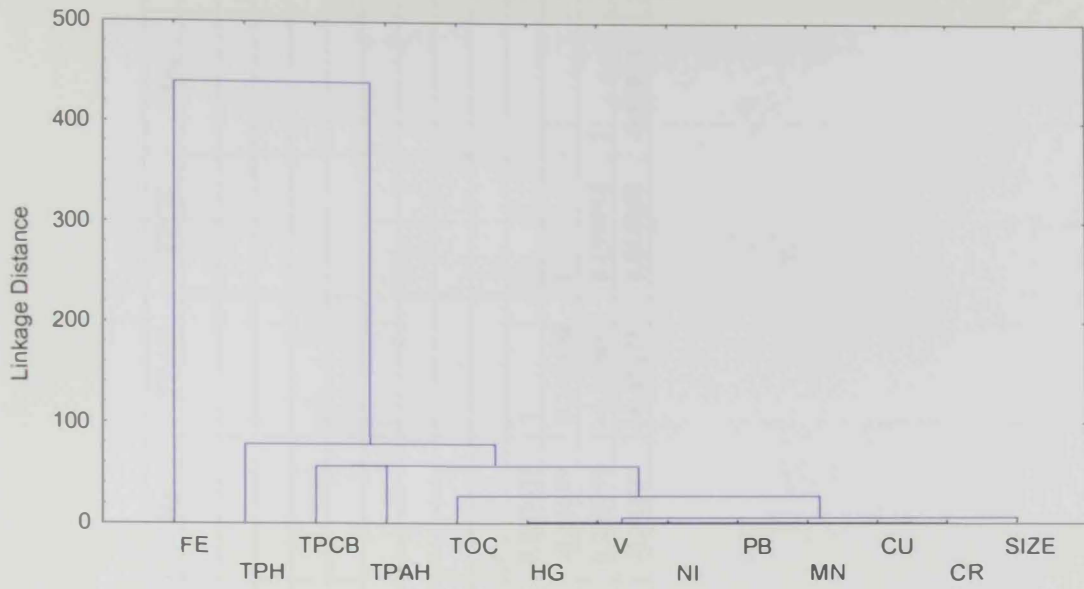


Figure 4.53 Cluster analysis Dendrogram for all sampling stations

	<i>Size</i>	<i>Cr</i>	<i>Cu</i>	<i>Fe</i>	<i>Mn</i>	<i>Ni</i>	<i>Pb</i>	<i>V</i>	<i>Hg</i>	<i>TPAH</i>	<i>TPCB</i>	<i>TOC</i>	<i>TPH</i>
<i>Size</i>	1												
<i>Cr</i>	0.173509	1											
<i>Cu</i>	0.180665	0.996471	1										
<i>Fe</i>	0.178981	0.993644	0.995622	1									
<i>Mn</i>	0.18621	0.99068	0.989765	0.995703	1								
<i>Ni</i>	0.179776	0.995397	0.996892	0.994343	0.993913	1							
<i>Pb</i>	0.185136	0.997511	0.999481	0.996221	0.990411	0.996147	1						
<i>V</i>	0.177122	0.897426	0.880273	0.898705	0.915566	0.889758	0.88359	1					
<i>Hg</i>	0.025993	-0.03135	-0.02049	-0.02911	-0.01682	0.01125	-0.02738	-0.0725	1				
<i>TPAH</i>	-0.31442	-0.21071	-0.22476	-0.22917	-0.21483	-0.20791	-0.21667	-0.1832	0.057426	1			
<i>TPCB</i>	-0.15221	-0.11155	-0.11765	-0.13429	-0.13115	-0.11682	-0.12043	-0.14018	-0.22639	0.140138	1		
<i>TOC</i>	0.156986	0.024244	0.022617	0.033507	0.058908	0.041777	0.020174	0.118867	0.230978	-0.11806	0.199952	1	
<i>TPH</i>	-0.03118	0.037369	0.03066	0.02084	0.014288	0.004494	0.024853	0.058079	-0.34207	-0.43175	0.014259	-0.07873	1

Table 4.7 Correlation matrix of different pollutants in Zakum Field area

Summary and Conclusions

4.1. Molecular Analysis

The average molecular weight of the poly(amide-imide) copolymer was determined by gel permeation chromatography (GPC) using polystyrene as a standard. The number-average molecular weight (M_n) was found to be 12,500 g/mol, and the weight-average molecular weight (M_w) was 25,000 g/mol. The polydispersity index (PDI) was 2.0, indicating a broad molecular weight distribution. The GPC analysis also revealed that 95% of the samples were in the range of 10,000 to 30,000 g/mol.

4.2. TGA and Kinetic Analysis

The average TGA residue at 500 °C was 45.5%, which is slightly higher than that reported for the poly(amide-imide) copolymer. The TGA curve shows the onset of weight loss at 200 °C, which is attributed to the degradation of the poly(amide-imide) copolymer. The kinetic analysis of the TGA data revealed that the degradation follows a first-order reaction mechanism. The activation energy for the degradation was found to be 120 kJ/mol, which is relatively low compared to other poly(amide-imide) copolymers. The results of the TGA analysis are summarized in Table 5.1.

CHAPTER 5

5.1. Total Polymerization Process (TPP)

The total polymerization process (TPP) was investigated by studying the reaction of the poly(amide-imide) copolymer with various diisocyanates. The reaction was carried out at 120 °C for 24 hours. The average molecular weight of the TPP was found to be 25,000 g/mol, which is higher than that of the poly(amide-imide) copolymer. The TGA analysis of the TPP revealed that the degradation follows a first-order reaction mechanism. The activation energy for the degradation was found to be 150 kJ/mol, which is higher than that of the poly(amide-imide) copolymer. The results of the TPP analysis are summarized in Table 5.2.

Summary and Conclusions:

5.1 Mechanical Analyses

The sediment texture of Zakum Field sediments of various sample stations revealed sandy gravels from most sediment. In a few locations there is some coarse sand to granule gravel grain size distribution. The grain size characteristics of sampling stations revealed that 59% of samples are coarse sand with 73% poorly sorted.

5.2 Total Organic Carbon

The average TOC % in the study area is 4.76 %, which is higher value than other studies for the region (0.46%-2.8%). The trend towards the north and northeast sides shows most of TOC % compared to the southeast area of the field. It is observed that the site related operation in the super complexes is not significant to increase the TOC % in its vicinity, which results from site practices in marine pollution prevention and control.

5.3 Total Petroleum Hydrocarbons (TPH)

The maximum and minimum TPH concentration values were recorded in station no. 1 and 11 with 6.14 ppm and 62.7 ppm respectively. The average TPH in Zakum Field study area is 22.7 ppm, which is consistent with other studies in the area i.e. 22 ppm (ZADCO, 1999). The TPH variation in Zakum field area is within low limits except for one isolated station (i.e. station no.11

with 62.7 ppm). The Northeast area has higher TPH concentration rather than other areas of the field, which required further investigation. The far field stations values show relatively lower TPH concentration with 15.8 ppm and 12.8 ppm. Generally the west area of the field shows relatively low TPH concentration than other sectors of the field.

No significant correlation was observed between TPH with grain size distribution ($r = -0.0312$). This confirms the findings of other studies in the area (Al Lihaibi & Al Omran, 1996). Therefore, the observed distribution of petroleum hydrocarbons associated with sediments is not governed by sedimentary characteristics; instead, it may be controlled by the prevailing current in the area and localized sources of inputs.

5.4 Polychlorinated Biphenyl's (PCBs)

The maximum and minimum values of Total PCBs were recorded in stations no. 8 and 11 with concentration of 27.52 ppb and 4.30 ppb respectively. The average concentration of PCBs in the study Area is 13.5 ppb. It is slightly above the level recorded previously in the region (i.e. below 5 ppb). The highest concentrations are located in the northeastern and southeastern side of the field. There is no single source of high PCBs concentration around the main offshore installation i.e. super complexes. The far field stations (no. 18, 22) have relatively high concentration of PCBs, which indicates the source of the PCBs is mainly due to water current outside the field.

PCB-180 concentration is the highest among the other individual PCBs with 62.02 ppb. The maximum value of PCB-180 was recorded in station no. 26 with concentration of 6.32 ppb. The majority of PCB-8 was detected in the northeast side of the field. PCB 8 was not detected in the south side of the field.

PCB 18 was detected in eight stations with a maximum concentration of 8.13 ppb recorded in station no. 7. The far northeast side of the field dominates the highest concentration of PCB 18 with high spots in central and south side of the field. The maximum concentration of Polychlorinated Biphenyls 28 in the Zakum Field area is recorded in station no. 15 with a concentration of 8.09 ppb. The Northeast side has the highest concentration among other areas of the field.

Polychlorinated Biphenyls 52 in Zakum Field area detected in four stations with a maximum concentration of 8.3 ppb, which recorded in station no. 9. The concentration of PCB 44 ranges between 0 ppb and 7.21 ppb which is recorded in station no. 12. The Polychlorinated Biphenyl 66 was detected in three stations with a maximum concentration of 2.2 ppb, which recorded in station no. 1. PCB 66 detected only in the Western side area of the field.

The Polychlorinated Biphenyl 101 was detected in four stations with a maximum concentration of 6.88 ppb, which recorded in station no. 14. The Polychlorinated Biphenyl 77 concentration ranges between 0 and 4.56 ppb. The maximum was recorded in station no. 18. The highly concentrated area with PCB 101 is located in the southern part of the field.

PCB 180 was detected in almost in all the sampling stations except one station i.e. station no.15. The maximum concentration was recorded in station no. 24 with 3.92 ppb. The concentration trends observed towards the northeast and southwest sides of the field. The Polychlorinated Biphenyl 170 concentration ranges between 0 and 1.27 ppb. The maximum concentration is recorded in station no. 19. PCB 170 trend increased from the central part of the field towards the outer part of the field. PCB 105 was detected in only one station with concentration of 1.71 ppb, which recorded in station no. 25. PCB 118 was detected in two stations i.e. no. 4 & 6 with concentrations of 1.22 ppb and 1.24 ppb respectively. PCB 153 was detected in only one station with concentration of 2.13 ppb, which recorded in station no. 5. PCB 195 was detected in two stations i.e. no. 21& 24 with concentration of 1.88 ppb & 0.9 ppb respectively. PCB-138, PCB-126, PCB- 187, PCB-128, PCB-206, PCB-209 were not detected in any of the 26 sampling stations in Zakum Field area.

There is no single source of high PCBs concentration around both super complexes (station no. 25 and no. 26). The reference stations (no. 18, 22) have relatively high concentration of PCBs, which indicates the source of the PCBs is not related to site operation which may due to water current outside the field.

5.5 Poly Aromatic Hydrocarbons

The total PAHs in Zakum Field area ranges between zero (in case of not detected) and 31.5 ppb. The maximum value was recorded in station no. 21. Total PAHs trend increases towards Northwest area and with the minimum

concentration in the central part area of the field. Acenaphthylene has the highest concentration among other individual PAHs.

Naphthalene was detected in three stations with the highest concentration of 5.3 ppb in station no. 9. Acenaphthylene concentration ranges between 0 ppb and 16.3 ppb. The maximum concentration recorded was in station no. 16. Various high concentration spots of Acenaphthylene in the study area are in south, southeast and far west sides. However, the central part of the field shows low acenaphthylene concentration. The concentration of Pyrene in Zakum Field area ranges between 0 ppb and 11 ppb, which recorded in station no. 4.

Benzo(a) anthracene , Benzo (K) flouranthene, Chrysene ,Indeno(1,2,3-cd) pyrene, Benzo (a) pyrene, were detected only in station no. 26 with concentration of 0.03 ppb,0.04 ppb, 0.01ppb, 0.03 ppb, 0.07 ppb respectively. Benzo (B) flouranthene is detected in two stations (i.e.no. 3 & 26) with concentration of 4.00 ppb and 0.1 ppb. Phenanthrene was detected at three stations with highest concentration of 9.0 ppb in station no. 4. Fluorene was detected in two stations i.e. no. 1 & 21 with concentration of 5.0 ppb and 16.1 ppb respectively. Acenaphthene, Dibenzo(a,h)anthracene, Fluoranthene, Anthracene ,Benzo(g,h,i)perylene were not detected in any of sampling station in the study area. In general, the Poly Aromatic Hydrocarbon concentration in study area is low compared to previous studies in the region.

5.6 Previous seabed core samples analyses results

TPH, PCBs and PAHs analyses carried out for six old seabed core samples, which were collected during 1970's, for comparison purpose. Total petroleum

hydrocarbons concentration in the old seabed cores from Zakum Field area ranges between 3.55 to 61.72 ppm in station no. 4 and 5 respectively. Total polychlorinated biphenyl concentration ranges between 3.5 and 112.1 ppb in station no. 4 and 6 respectively. Total poly aromatic hydrocarbons concentration ranges between 0 to 61.4 ppb. Core sample station no. 6 has the highest concentration of PAH among the other samples.

5.7 Heavy Metals

Eight heavy metals elements have been analyzed in this study i.e. Cr, Cu, Fe, Mn, Ni, Pb, V and Hg. The Fe was the highest concentration deduced in this study with an average concentration of 23.6 ppm. While the lowest concentration detected was Ni with average amount of 0.035 ppm.

The maximum and minimum values of Cu concentration were recorded in stations no. 26 and 12 with concentration of 1.84 and 0.01 ppm respectively and a mean value of 0.09 ppm. The maximum and minimum values of Fe were recorded in stations no. 26 and 17 with concentration of 449.9 and 1.51 ppm respectively and a mean value of 23.61 ppm. Station no. 26 required more investigation to assess the high Fe contents. The maximum and minimum values of Mn were recorded in stations no. 26 and 17&18 with concentration of 2.08 and 0.03 ppm respectively and a mean value of 0.185 ppm.

The maximum and minimum values of Ni were recorded in stations no. 26 and 19 with concentration of 0.5 and 0.01 ppm respectively and a mean value of 0.035 ppm. The maximum and minimum values of Pb were recorded in

stations no. 26 and 18 with concentration of 1.3 and 0 ppm respectively and a mean value of 0.06 ppm. The maximum and minimum values of V were recorded in station no. 26 and 11 with concentration of 0.26 and 0.02 ppm respectively. V is detected in all stations with a mean value of 0.04 ppm. The maximum and minimum values of Hg were recorded in station no. 26 and many other stations with concentration of 0.66 and 0 ppm respectively with mean value of 0.07 ppm. In general, the heavy metals concentration in study area is low compared to other previous studies in the region.

5.8 Distinguishing biogenic hydrocarbons from petrogenic hydrocarbons

In this study a pristane / phytane ratio ranges from 0.38 to 1.59. CPI values ranges from 0.45 to 1.16. High concentration of pristane relative to phytane in most off shore sediments indicate biological hydrocarbon input from a marine biological source (i.e. phytoplankton / bacterial) origin. High concentrations of pristane/N C-17 and phytane/N C-18 in most offshore sediments indicate biological hydrocarbon input from a marine biological source (planktonic or bacterial) origin. Station no. 11 has shows the same pattern as the oil sample which indicates petrogenic source.

5.9 Statistical Analyses:

Applying the cluster factor analysis for all parameters on all sampling stations shows high similarity between all sampling stations except station no. 25, 26

and no. 11. The location of stations no. 25 and no. 26 is underneath the main two offshore production installation complexes i.e. Zakum west super complex and Zakum Central super complex which confirms the dissimilarity. Station no. 11 has the highest TPH concentration with other high pollutant concentrations, which support the dissimilarity from other stations throughout the field as well.

The chemical associations of the various metals and pollutants also been assessed using multivariate statistical analysis. Single linkage, Euclidean distance was performed on the data matrix comprising 13 variables and 26 observations (sampling stations). The obtained dendrogram shows five clusters, six heavy metals i.e. V, Ni, Pb, Mn, Cu, and Cr with grain size distribution as one cluster. Cluster one elements are clustered with TOC %, which is clustered to TPAH, and TPCB and they clustered to TPH at higher linkage distance. Fe is the least cluster associated element in this study. The concentration of heavy metals in this study seems to be not resulting from oil pollution source as they have insignificant correlation factor with TPH.

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الملخص باللغة العربية

تهدف الدراسة الحالية الى قياس وتقدير الملوثات العضوية والغير عضوية في الرواسب البحرية لحقل زاكم ، أبو ظبي ، الإمارات العربية المتحدة . تم اختيار ستة وعشرون محطة لجمع العينات لتغطي أقصى أرجاء الحقل .

خضعت العينات للعديد من التحاليل و التي تشمل : تحليل حجمي للحبيبات ، و تحديد الملوثات العضوية ممتدة بتعيين المحتوى الكلي للكربون العضوي و المحتوى الكلي للهيدروكربونات البترولية و الهيدروكربونات متعددة الحلقات ومركبات ثنائي الفينيل متعدد الكلورة . كذلك تم حساب الملوثات غير العضوية من خلال تعيين تركيز المعادن الثقيلة . وللمقارنة تم تحليل ست عينات قديمة من حقل زاكم والتي جمعت ما بين 1960 و 1978 .

خلصت الدراسة الى ان متوسط المحتوى الكلي للكربون العضوي هو %4.76 والذي يعتبر قيمة أعلى بالنسبة للدراسات السابقة ومتوسط المحتوى الكلي للهيدروكربونات البترولية في حقل زاكم هو 22.7 جزء في المليون والذي يتوافق مع الدراسات السابقة للمنطقة . وكذلك لا يوجد ارتباط ذو دلالة ما بين المحتوى الكلي للهيدروكربونات البترولية و توزيع حجم الحبيبات للعينات .

وجد ايضا أن متوسط تركيزات مركبات ثنائي الفينيل متعدد الكلورة في منطقة الدراسة هو 13.5 جزء في البليون والذي يعتبر أعلى بمقدار بسيط مع المستوى المقاس في المنطقة سابقا (أقل من 5 جزء في البليون) . ومجموع التركيزات الكلي للهيدروكربونات متعددة الحلقات في منطقة حقل زاكم كانت ما بين 0 و 31.5 جزء في البليون ، والقيمة تزداد باتجاه الشمال الغربي لمنطقة الدراسة مع أقل تركيز في المنطقة الوسطى للحقل . ومتوسط تركيز المحتوى الكلي للهيدروكربونات البترولية في العينات القديمة هو 17.4 جزء في المليون . بينما متوسط تركيزات مركبات ثنائي الفينيل متعدد الكلورة هو 39.9 جزء في البليون و متوسط التركيزات الكلي للهيدروكربونات متعددة الحلقات هو 20.9 جزء في البليون .

تم تحليل ثمانية عناصر ثقيلة في الدراسة الحالية وهي الكروم ، الكالسيوم ، الحديد ، المنجنيز ، النيكل ، الرصاص ، الفانديوم ، والزنك . وجد أن تركيز الحديد في الدراسة الحالية هو 23.6 جزء في البليون والذي يعتبر الأعلى في التركيز بين العناصر الأخرى و الأقل تركيزا كان النيكل مع معدل تركيز 0.035 جزء في المليون . بصفه عامه كانت تركيزات العناصر الثقيلة في منطقة الدراسة بكميات قليلة مقارنة بالدراسات السابقة في المنطقة مما يؤكد ندرة مصادر التلوث النقطي بالمنطقة .

تركيز البريستان (Pristane) الأعلى نسبيا مقارنة بالفيتان (Phytane) في معظم عينات الدراسة وكذلك زيادة تركيزات الألكانات احادية الرقم يشير ان الى تجمع الهيدروكربونات من مصدر بيولوجي بحري ماعدا المحطة رقم 11 والتي وجد أن تجمع الهيدروكربونات بها يعتبر بيرولي المنشأ .

خلصت الدراسات ايضا الى أن عمليات المنشآت البترولية في حقل زاكم تحافظ على أقل المعدلات اضرارا بالبيئة البحرية .



دراسات جيوكيميائية لتقييم التلوث البترولي , حقل زاك
أبوظبي , الامارات العربية المتحدة

أطروحة مقدمه لا استكمال متطلبات الحصول على درجة الماجستير
في علوم البيئة

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عمادة الدراسات العليا
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