OIL POLLUTION ON THE LIBYAN COAST

By

Walid Walda

Centre For Environmental Sciences
University of Southampton

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ABSTRACT

Oil pollution in Libyan coastal waters was investigated using chemical and ecological approaches. Chemical assessment of petroleum hydrocarbons (HCs) showed that levels of oil pollution were linked to localised sources such as coastal refineries and seaports. Concentrations of HCs were up to 33 ppm in seawater and up to 660 ppm in sediments near to coastal oil refineries. Possible measures to reduce inputs from such sources were investigated by determining long-term changes in HCs in sediments in Southampton Water following improvements to cooling water management at the Fawley refinery. These changes resulted in a reduction of sediment HCs of *ca.* 50% between 1978 and 2001. Similar improvements could be made in Libya to reduce HCs pollution from refineries but the timescale for such reductions cannot currently be predicted accurately.

Determination of the deposition of oil on sandy beaches showed that tar balls were deposited mainly between 2 m and 16 m from the water's edge. The average concentration of tar balls on the most polluted beach was 24 gm^{-2}. Deposition of oil on rocky shores resulted in considerable smothering of the substrate and accounted for up to 38 % of surface area on rocky shores close to Tripoli, probably as the result of small oil spillages during routine seaport activities and the disposal of municipal and industrial sewage.

The impact of oil pollution on rocky shore communities was determined by comparing the abundance of major species on rocky shores at sites in heavily polluted and less polluted regions. Rocky shores in polluted areas were characterised by very low species abundance, with *Patella* sp., for example, being present at less than 20 individuals m^{-2} on rocky shores near to Tripoli. Species abundance on rocky shores was negatively related to the proportion of substrate smothered by tar deposits.

The implications of the findings of this study for the protection of the Libyan coast against the impacts of oil pollution are discussed and priorities for mitigation are suggested.

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CHAPTER ONE: INTRODUCTION

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1.1 General Overview

The importance of studying oil pollution in Libya arises from three main reasons. Firstly, there is very little known about oil pollution in Libya internationally and even in the country itself. Secondly, as a major oil producer and exporter, Libya is more vulnerable to oil pollution than other countries in the region. Thirdly, it has one of the longest coastlines in the Mediterranean, Libya is therefore very important within the Mediterranean context (Ali *et al,* 1998), in which about 27% of oil exporting ports in this sea are located (Elazzabi, 1992).

The threat of oil pollution can be evaluated in the context of the western coastal region of Libya (Tripolitania). This region is the most populated in the country on which many seaports, oil-processing industries, and pollution sources are located (Ali *et al,* 1998). This research studied the problem of oil pollution in this coastal region, which is about 500 km long, as an example of the entire Libyan coast.

The objectives of this research are to investigate the problem of oil pollution on the Libyan coast from different aspects. Firstly, studying the sources and the inputs of oil pollution. Second, evaluation of the levels of petroleum hydrocarbons in seawater and sediments and studying their geographical distribution patterns in the study area. Third, studying the deposition of oil on coastal habitats and identifying the affected areas. Fourth, assessing the impact of oil pollution on rocky shore communities as an example of the impact on the coastal habitats.

1.2 Oil pollution in the marine environment

The importance of the study of oil in the marine environment arises from two opposing aspects of man's activities. One is the pollution arising from activities undertaken to meet man's needs, and the second aspect is the desire to preserve living marine resources and biodiversity for current use and as a legacy for future generations.

Oil pollution on a substantial scale commenced with the introduction of oil as a source of fuel for shipping. Oil pollution increased as the demands of industry required the carriage of cargo across waterways (National Research Council, 1985). As the world economy has become more dependent upon international trade, the rates of shipping goods between countries have grown. This increase has led to two major sources of oil pollution: the operational discharge and the accidental spillage of crude oil and oil products (Clark, 2001).

1.2.1 Sources and inputs of oil to marine environments

Oil enters the marine environment via a number of different pathways. These include natural and anthropogenic sources (National Research Council, 1985), each of which contribute to the total input on a global basis (Table 1.1).

Tanker accidents

Some oil tanker accidents are very large and huge quantities of crude oil and oil products spill out to the seawater causing great damage to the marine environment (Atia, 1993; Clark, 2001). Tanker accidents, usually, are due to human mistakes, and usually happen near to shores, in narrow straits, and near entrances to ports where the density of shipping is high (Elazzabi, 1992).

Natural sources

Although the definition "natural source" may suggest that this should not be considered as source of pollution, the natural occurrence of oil in the marine environment can cause environmental problems through additions to other inputs such as tanker accidents and industrial sewage (Domovic, 1992).

Table 1.1 Estimated world inputs of petroleum hydrocarbons to the sea (Clark, 2001).

Source	Source type	Estimated input (million tonne year^{-1})	Total (million tonne year^{-1})
Transportation	**Tanker operations**	**0.163**	
	Tanker accidents	**0.162**	
	Bilge water and fuel oils	**0.524**	
	Dry docking	**0.009**	**4.630**
	Non-tanker accidents	**0.020**	
	Scrapping of ships	**0.002**	
	Atmospheric emissions	**3.750**	
Fixed installations	**Coastal refineries**	**0.10**	
	Offshore production	**0.05**	
	Marine terminals	**0.03**	**0.180**
Other sources	**Municipal waste**	**0.70**	
	Industrial waste	**0.20**	
	Urban run-off	**0.12**	
	River run-off	**0.04**	
	Atmospheric fall-out	**0.30**	
	Ocean dumping	**0.02**	**1.380**
Natural inputs	**0.250**		
Total	**6.440**		

Urban runoff

Oil products and lubrication greases are spilt on roads and garage forecourts in different incidents and by different causes e.g. in the motor and transport industries. This is washed down drains by rain and it eventually reaches the sea, adding more petroleum hydrocarbons in seawater. Used engine oil might find its way into drains during oil changes by motorists and even, sometimes, in garages. This also ultimately ends up in the sea.

Municipal and industrial waste

In coastal regions, municipal and industrial wastes are often discharged into the sea (Goldberg, 1972). These wastes, depending on the type of industrial activity, usually contain oils and greases even when treated prior to discharge, and is thought to be a considerable source of petroleum hydrocarbons to the sea.

Oil marine terminals

Accidents during routine oil loading operations and pipeline leakage occur frequently in oil marine terminals (Magazzu & Angot, 1981). Accidental spills also occur during discharge of oil or oil products to these terminals. Human error, pipeline leakage, and failure of mechanical devices are the major causes of oil spills into the sea from marine terminals (Tluba, 1991).

Marine workshops and dry docking

Dry-docking is essential to all ships for repairs, cleaning the hull, and for periodic general servicing. All oil is removed from fuel tanks and cargo compartments. Some amount of the removed oil may reach the marine environment during maintenance operations and engine oil changes (Tluba, 1991).

Ballast and bilge water

Ships carry ballast water usually in special tanks for this purpose, to maintain stability on the high seas following unloading, or in bad weather. Oil residues in these tanks are pumped into the sea with the ballast water when discharged. Furthermore, bilge water contains oil from the ship's engine. This may be discharged illegally into the sea especially at ports that do not provide reception facilities (Tluba, 1991). However, there are measures that have been introduced recently to reduce the amount of oil entering the sea as a result of these operations. Contact between ballast water and oil may be avoided by, for example, by use of separate compartments for oil and ballast water (Clark, 2001).

Oil refineries

Oil refineries discharge wastewater containing petroleum hydrocarbons into the marine environment (Knap, 1978). Some refineries use a steam-cracking process in which water comes in contact with oil (Clark, 2001). The effluent in this type of refineries, therefore, contains high levels of petroleum hydrocarbons (Dicks & Iball, 1981; Knap, 1988; Savari, 1988). In some modern refineries, this has been taken in account in their design and oil does not come in contact with water which reduces the amount of hydrocarbon in the effluent. Nevertheless, refineries require a large volume of water and the total discharge of oil in seawater, therefore, is not negligible (Dicks & Iball, 1981; Knap, 1988).

Offshore oil production

The production water, drilling mud, blowouts, and the incidental discharge of oil are the major inputs to seawater during offshore oil production (Grant & Briggs, 2002). The production water is the water that comes with the oil when extracted from below the seabed. This water is often discharged into the sea after extracting the oil, but could have an oil content as much as 40 ppm (Clark, 2001). Drilling mud also may contain oil and is usually dumped on the seabed beneath the production platforms (Grant & Briggs, 2002).

1.3 Oil spills: Behaviour and Response

Most of the oil that spills into the seawater is in the form of crude oil. The spills are either due to natural leakage from underground sources, or due to human action in connection with exploration, production, or transportation. The behaviour of spilled oil depends on the origin of the crude oil, as well as the water and air temperature, and wind and wave conditions (Oebius, 1999). Oil spreads rapidly over a large area (Quinn *et al*, 1994). The spreading of oil causes the lighter fractions of the oil to disappear rapidly by evaporation, leaving only the heavier parts in the water. Finally, wave action mixes water into the oil, forming a heavy and sticky water-in-oil emulsion (Clark, 2001; Sharma *et al*, 2002).

The behaviour of the spilled oil determines how action should be taken to deal successfully with an oil spill. A minimal response time, an efficient and fast concentration of the widely spread oil, use of skimmers and pumps which can skim and suck high viscosity emulsions, and an appropriate temporary storage capability are all required (Shelton, 1971; Tennyson, 1990; Duke *et al,* 2000).

The most common treatment technique is by mechanical clean-up involving containment with large floating barriers, and removal with specialised ships that either vacuum the oil off the sea or soak it up with absorbent material (Tennyson, 1990). Chemical treatment technique using dispersants, solvent and detergent chemicals that break up continuous spills into droplets, is also sometimes used to prevent oil from fouling sensitive coastal habitats (Duke *et al,* 2000). Although dispersants can prevent deposition of oil on shorelines if used correctly, they do not remove the oil and can make an acutely toxic concentration of oil available to marine life directly under the slick (Duke *et al,* 2000; Shelton, 1971; Tennyson, 1990).

1.4 Effects and fate of oil in the marine environment

Oil pollution from tankers, drilling operations, natural seeps, and other sources cause a concentrated input of oil into the marine environment. These often occur over a very short period of time (Riley, 1985). Such inputs may have serious effects on animal and plant life and on land cherished for its recreational value (Ramamurthy, 1991; Riley, 1985; Suchanek, 1993). The seriousness of an oil release depends on several factors, including quantity and type of released oil, final destination of the oil, and environmental factors such as current direction and wave action (Riley, 1985).

Oil is a very complex mixture made up of hundreds of compounds, mostly hydrocarbons. Lighter fractions of the oil, though more toxic than crude oil, are more likely to evaporate before they can reach sensitive shoreline habitats (Sharma *et al*, 2002). Heavier oil that does not evaporate, although it is not as toxic as refined oil, can wash onto rocky and sandy shores and can cause serious harm to shellfish, plant life, and other organisms (Riley, 1985). In the early stages of an oil spill, sea birds and mammals may be killed by contact with the freshly spilled oil (Day *et al*, 1997; Jenssen, 1996; Walton *et al*, 1997). Effects on fish are documented in many studies and oil spills can have adverse effects on adult fish, floating fish eggs, and larvae (Gallego *et al*, 1995; Heintz *et al*, 2000). The least volatile fraction of oil forms tarry lumps that float, sink, or cover habitats of shallow water organisms, or foul sand beaches and rocky shores.

Effects on resources of economic value

In case of oil spills on the coast, oil coats the shoreline, killing plants and animals as well as preventing mammals and birds from utilising the area (Day *et al*, 1997; Jenssen, 1996; Riley, 1985; Walton *et al*, 1997). Resources of economic value are damaged, first of all, because of the loss of non-renewable oil and therefore money. Secondly, there is damage caused to fisheries from lost fish and suspension of fishing.

The most obvious impact on resources of economic value is, perhaps, the reduction of fish stocks (Hughes, 1999) through habitat alteration, tissue contamination, and death. Oil spills can cause damage to fish eggs and larvae as well as adults (Gallego *et al*, 1995; Heintz *et al*, 2000).

Apart from the direct effect on fisheries through reduction of stocks by death, tainting can have serious economic effects. Petroleum hydrocarbons in tainted fish and seafood are detectable at very low levels of contamination imparting an unpleasant flavour making seafood, including fish, unmarketable as the oily taste is repulsive (Clark, 2001).

Damage to recreational resources can occur through fouling of sandy beaches and the rocky shores by heavy weight fractions of hydrocarbons. This damage can have noticeable economic impact, especially in countries that depend on tourism as an important source of income (Roehl & Ditton, 1993).

Effects on the marine ecosystem

Effects of oil pollution on coastal ecosystems are of major concern for three main reasons. First, the available habitat is generally much more limited in extent in coastal than in offshore ecosystems; some coastal areas also provide unique habitat and ecosystems due to geographical and environmental circumstances. Secondly, living resources are generally more concentrated in coastal habitats. Thirdly, some species that live away from coasts may be dependent on the coastal ecosystems for part of their lives.

Obviously, a large oil spill would have enormous effects on the marine ecosystem and associated resources. Oil, first of all, coats a large area preventing sunlight and oxygen from filtering into the water that may adverse effects on plants and animals (Pezeshki *et al*, 2000). Oil may also directly cover the marine flora and fauna, causing mortality through suffocation (Pezeshki *et al*, 2000).

Fixed vegetation such as mangroves on coasts may be affected badly by oil pollution (Ellison, 1999). They are very important to the whole coastal ecosystem because they are a source of organic production that is transferred to the sea, and they provide shelter for early life stages of marine organisms (Abuodha & Kairo 2001). The coastal ecosystem as a whole could be affected as a result of these effects.

Biological effects on marine organisms

Biological effects of petroleum hydrocarbons on marine organisms depend on the persistence of hydrocarbons and the ability of the organism to accumulate and metabolise various hydrocarbons (Capuzzo, 1981).

Oil could have adverse biological effects on marine organisms through external direct contact. Depending on the nature and the age of the oil, a considerable variety of animals and the more sensitive red and green algae can be killed by external contact (Clark, 2001). Surface contact with oil may cause irritation and inflammation of eyes and sensitive mucous membranes especially in mammals and birds, as well as skin damage (Boesch and Rabalais, 1987). Oil adheres to the feathers of seabirds and the fur of mammals and reduces their insulating and waterproofing properties (Stephenson, 1997). The risk of deaths from exposure is therefore increased.

Inhalation of petroleum vapours such gasoline in an oil spill by mammals can be or it can develop inflammation, haemorrhage and congestion of the lungs (Boesch & Rabalais, 1987). Additionally, oil clogs the nostrils and mouth of mammals and birds, and causes irritation to the eyes (Tseng, 1999). Adverse effects can be caused through ingestion of oil by, for example, turtles and seabirds (Tseng, 1999). These include ulceration and bleeding in the gastrointestinal tract, and toxins may be absorbed through the skin and the pancreas (Briggs *et al*, (1997).

1.5 Bio-accumulation in marine organisms

Although bioaccumulation of persistent pollutants has been observed in marine organisms, evidence to suggest bioaccumulation of petroleum hydrocarbons has not been widely reported (Clark, 2001). However, accumulation of pollutants such as petroleum hydrocarbons can occur at different rates from seawater, suspended particles, and sediments and through the food chain (Fig. 1.1). The rate at which accumulation occurs in an organism depends on the availability of the pollutant, the ability of the organism to excrete the pollutant or alternatively store it, and on a whole range of biochemical and environmental factors (Baussant *et al*, 2001). Several studies have shown that marine organisms such as shellfish may accumulate petroleum hydrocarbons to different levels and at different rates. Some shellfish, which filter large volumes of water while feeding, can take up and concentrate hydrocarbons from water either from solution or adsorbed to suspended particles (Bryan, 1979; Riley, 1985).

The relationship between the levels of external concentration of organic pollutants such as petroleum hydrocarbons and the concentration in the organism tissues is complex (Baussant *et al*, 2001). Different species may bio-concentrate different pollutants depending on factors such as life style and metabolic capability to degrade the potential harmful substances (Baussant *et al*, 2001).

The concentrations of petroleum hydrocarbons in marine organism tissues are likely to be proportional to the availability of hydrocarbons in the environment depending on the ability to excrete or store the pollutant at different levels of input (Baussant *et al*, 2001; Bryan, 1979).

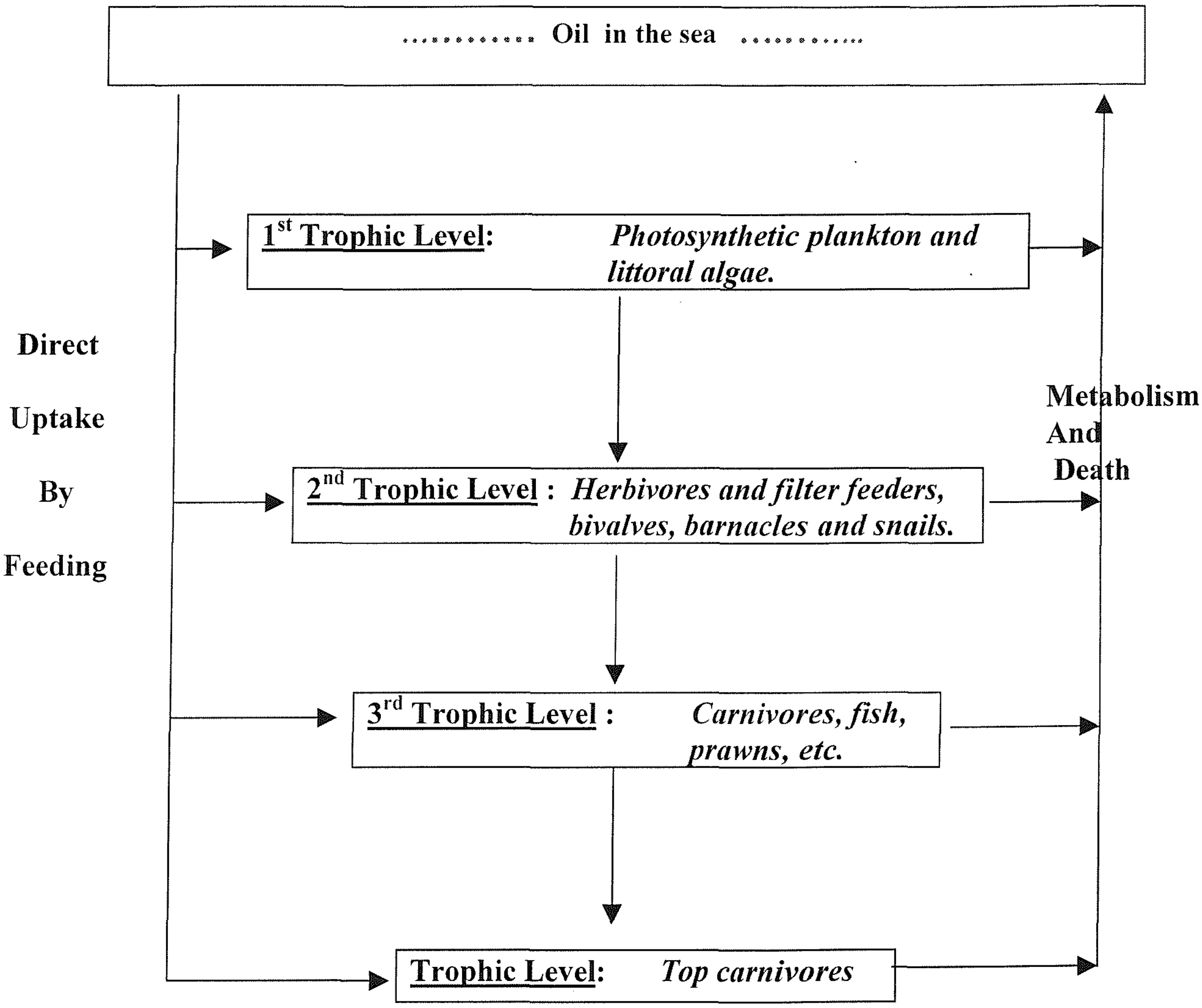


Figure 1.1 Possible oil concentration mechanism in the ecosystem (Goldberg, 1972).

1.6 Toxicity of petroleum hydrocarbons

Crude oil and oil products contain a wide range of compounds that can be toxic to marine plants and animals (Grant & Briggs, 2002). Aromatic hydrocarbons, particularly, are known to be more toxic than aliphatic hydrocarbons, and the medium molecular weight fractions are more toxic than high-molecular ones (Clark, 2001). Toxicity of crude oil depends largely upon volatile aromatic hydrocarbons (Barron *et al*, 1999) which form only a small proportion of most crude oils and are rapidly lost due to weathering (Sharma *et al*, 2002). Therefore, toxic effects of crude oil in the open sea tend to be insignificant due to the huge diluting power of the sea, and because of oil weathering (Shelton, 1971).

1.7 Biological Degradation

There are numerous micro-organisms in the marine environments that oxidise various hydrocarbons (Ron & Rosenberg, 2002). The most varieties occur in places that have been subject to chronic oil pollution either from natural seeps or by human activity, and they include bacteria, fungi, and yeast species (Clemente *et al*, 2001; Oh *et al*, 2001). Each species metabolises only a narrow range of hydrocarbons by producing enzymes that catalyse their oxidation (Zobell, 1972).

Many factors may affect the rate of biological degradation of oil in the sea. Essentially, the kind and the number of micro-organisms available, the chemical composition of the oil, and environmental parameters are the main factors affecting this process. Environmental parameters such as oxygen availability, seawater temperature, salinity requirements, and concentration of organic matter in seawater, are important parameters determining the biological degradation process (Zobell, 1972). The effects of mixing of oil slicks by waves include rupturing the slick into bands and streaks and spreading over a larger area, evaporation enhancement by breaking waves, dispersion of oil droplets into the water column, and formation of water-in-oil emulsion (Santas & Santas, 2000; Sharma *et al*, 2002). A recent study presented evidence that shows that wave action accelerates hydrocarbon biodegradation in the intertidal zone by improved oxygenation and increased physical contact between bacteria and oil (Santas & Santas, 2000). Wave action may also affect biodegradation indirectly through accelerated volatilisation of small organic compounds that are highly toxic to oil-degradation bacteria (Galt *et al*., 1991).

1.8 Oil pollution in the Mediterranean Sea and the North African coast

The Mediterranean Sea is a semi-enclosed sea and whose surrounding lands developed major centres of human civilisation as early as 4000 BC (Meadows, 1992). The geographical location and the related functions of the Mediterranean as a semi-enclosed sea, as well as its early history and the development of recent industrialised centres, make it very unique in many aspects. Eighteen countries surround the Mediterranean Sea with a very wide range of industrial centres that have, undoubtedly, some sort of environmental impact on this sea. Some countries have a short coastline such as Albania and Palestine, others have a long one such as Turkey and Libya (Table 1.2). The coastlines of the Mediterranean Sea suffer from the effects of all the major global industries developed by man.

Oil pollution, as a result of oil exploration; exploitation; and transportation, is considered as a major environmental problem in the Mediterranean. The sea itself is the most polluted in the world, mainly due to heavy oil traffic, amounting to about 350 million tons annually, carried by about 1500 tankers (World Bank, 1996).

1.8.1 Sources and inputs

Petroleum hydrocarbons released into the Mediterranean Sea come from different sources. The major sources are oil production, oil brought into the basin by pipelines, oil transport within or through the sea, land-based sources, and tanker accidents.

Oil production

Libya, Algeria, Tunisia, Egypt, Spain, Italy and Greece are the countries that produce oil in the Mediterranean. Some of these countries such as Libya have offshore fields. The quantity of oil produced within the area is only partly used or processed within the area itself; a major part of it is for export. Oil production operations, especially in offshore fields, involve many processes that may cause major pollution.

Oil brought into the basin by pipelines

The Mediterranean is one of the major world regions for the transit of oil. Very large quantities of crude oil are transported by sea through pipelines connecting internal and distant oil fields to the coasts. Pipelines bring crude oil from the production areas such as the Sahara to places where it is refined and exported. Several terminals in the eastern Mediterranean and the North African coast are assigned for this purpose. In addition, there are a number of large pipelines, some of which are cross- border, such as Iraq to Tripoli (Lebanon) and Syria, Saudi Arabia to Sidon-Lebanon. The most recent pipeline will link the Libyan coast with Italy, which will be the longest to cross the Mediterranean Sea.

Oil transport through the Mediterranean Sea

More than 20% of the world oil transport takes place in the Mediterranean, which covers only 0.8% of the world's oceans by area (U.S. National Academy of Science, 1975). This makes it more vulnerable to pollution, especially by oil. A satellite monitoring system was suggested to monitor oil transport in this sea (Calabresi, 1996). Oil traffic monitoring is very important to identify illegal dishrags from ships and to reduce collision incidents in the Mediterranean that may cause serious oil spills (Calabresi, 1996, Daidola *et al*, 1997).

Land-based sources

These sources are mainly oil refineries and oil-related onshore activities such as exporting terminals and petrochemical industries. These sources make a considerable contribution to the overall input especially in Libyan waters (Magazzu & Angot, 1981; UNEP, 1978). The United Nations Environment Program (UNEP) reports show that the most polluted area from these sources in the Mediterranean is the Libyan waters and the region between Tunisia and Scilly (UNEP, 1978; UNEP, 1996).

Table 1.2 Coastal areas, population, and oil production for Mediterranean countries (UNEP, 1996).

Country	**Length of coastline (kilometres)**	**Population (thousands)**		**Average annual Volume of goods loaded and unloaded 1988-90 (thousand metric tons)**			**Offshore oil and gas resources**					
							Annual Production				Proven Reserves	
				Petroleum		Dry cargo	Oil (thousand metric tons)		Gas (million cubic metres)		Oil (million metric tons)	Gas (billion cubic metres)
		Total	Mediterranean	Crude	Products		1982	1992	1982	1992	1992	1992
Albania	418	3 256	1 325	X	71	1 673	0	0	0	0	67	0
Algeria	1 200	23 039	10 105	29 110	24 409	15 266	0	0	0	0	0	0
Bosnia –Herzegovina	20	4 470	300	X	X	X	0	0	0	0	0	0
Croatia	5 790	4 900	1 520	X	X	X	0	0	0	0	0	0
Cyprus	782	503	503	545[b]	502	4 586	0	0	0	0	0	0
Egypt	950	58 978	24 004	146 855	4 204	25 351	28 386	0	755	0	367	142
France	1 703	56 556	5 839	68 135	40 443	110 786	0	0	0	0	0	0
Greece	15 000	10 264	9 209	15 407	4 590	26 680	0	299	0	0	4	11
Palestine	160	5 472	3 041	6 463[b]	1 412	15 593	0	0	0	0	0	0
Italy	7 953	57 104	32 621	88 893	46 074	100 510	498	3 685	10 523	3 618	8	227
Lebanon	225	3 000	2 700	23[b]	205[b]	1 058	0	0	0	0	0	0
Libya	***1 770***	***4 900***	***3 920***	***48 241[a]***	***4 545***	***7 242***	***0***	***6 972***	***0***	***0***	***109***	***3***
Malta	180	362	362	X	564	1 546	0	0	0	0	0	0
Monaco	4	30	30	X	X	X	0	0	0	0	0	0
Morocco	512	26 074	3 670	4 910	140	28 990	0	0	0	0	0	0
Slovenia	32	2 020	250	X	X	X	0	0	0	0	0	0
Spain	2 580	39 434	15 926	47 932	22 958	89 71	1 413	697	0	920	1	7
Syria	183	14 186	1 362	16 233	3 287	6 070	0	0	0	0	0	0
Tunisia	1 300	8 785	6 164	4 330[a]	937	13 762	1 520	1 245	0	0	34	0
Turkey	5 191	56 473	11 336	87 729	57 969	64 083	0	0	0	0	0	0

a. Goods loaded; **b**. Goods unloaded; **0** = zero or less than half the unit of measure; **X** = not available.

Accidents

Although the quantity of oil spilled in the sea is huge, accidents contribute only 5 – 10 % to the total input (Domovic, 1992). The significance of this source is because it releases large quantities of oil into a limited sea surface in a relatively short period of time. Accidents are usually caused be grounding, fires, explosions, collisions, and ramming during terminal operations (Daidola *et al*, 1997). The records of the Regional Oil Combat Centre in Malta (ROCC) show, for example, that between August and December 1988 the total number of accidents in the Mediterranean was 106, and 56% of these resulted in spillage of oil (Domovic, 1992).

1.8.2 pollution by pelagic and deposited tar in the Mediterranean Sea and its coastlines

Oil deposition in the form of tar balls is a major environmental hazard on many beaches of the Mediterranean (Aybulatov *et al,* 1981). Many coastlines in the Mediterranean are severely polluted with tar balls (El- Ghirani, 1981). They degrade very slowly and may persist as long as 20 years (Vandermeulen & Singh, 1994).

Pelagic tar balls are a common problem in most areas of the Mediterranean coastline (Aybulatov *et al,* 1981; Golik *et al,* 1988). Systematic investigations of tar distribution in the Mediterranean started as early as 1969 (Horn, 1970). The areas between Cyprus and Turkey and in the Gulf of Sirte off Libya are the most polluted by pelagic tar in the Mediterranean (Golik *et al*, 1988).

1.8.3 Oil pollution: the North African coast

The North African coast has been heavily exploited because of its abundant natural resources (Meadows, 1992). As a consequence, the need for coastal zone management (CZM) is emerging as an issue of regional importance to control the increasing environmental pollution, (Snoussi & Aoul, 2000). The south coast of the Mediterranean, about 5500km long (table 1.2), has very high incidences and concentrations of oil pollution within the Mediterranean region (Meadows, 1992). The average concentration of tars in the surface water is about 38 mg/m^2, which is very high compared with the average for all oceans is which is 0.8 mg/m^2 (World Bank, 1996). The North African countries are parties to the Barcelona Convention (1976) on combating oil spills and other international conventions for protecting the Mediterranean Sea against pollution (table 1.3).

Table 1. 3 Conventions and Protocols for the Protection of the Mediterranean Sea against Pollution. Source: UNEP (1996).

	Convention for the Protection of the Mediterranean Sea against Pollution	**Protocol for the Prevention of Pollution of the Mediterranean Sea by Dumping from Ships and Aircraft**	**Protocol concerning Co-operation in Combating Pollution of the Mediterranean Sea by Oil and Other Harmful Substances in Cases of Emergency**	**Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources**	**Protocol Concerning Mediterranean Specially Protected Areas**	**Protocol for the Protection of the Mediterranean against Pollution Resulting from Exploration and Exploitation of the Continental Shelf and the Sea-bed and**
Place/Date Adoption	Barcelona: 16. 2.1976	Barcelona: 16. 2.1976	Barcelona: 16. 2.1976	Athens: 17. 5.1980	Geneva: 3. 4.1982	Madrid : 14.10.1994
Entry into force	12.02.1978	12. 2.1978	12. 2.1978	17. 6.1983	23. 3.1986	
Albania	30.05.1990(AC)	30. 5.1990(AC)	30. 5.1990(AC)	30. 5.1990(AC)	30. 5.1990(AC)	
Algeria	16.02.1981(AC)	16. 3.1981(AC)	16. 3.1981(AC)	2. 5.1983(AC)	16. 5.1985(AC)	
Bosnia	22.10.1994(AC)	22.10.1994(AC)	22.10.1994(AC)	22.10.1994(AC)	22.10.1994(AC)	
Croatia	12.10.1993(AC)	12.10.1993(AC)	12.10.1993(AC)	12.10.1993(AC)	12.10.1993(AC)	14.10.1994 (S)
Cyprus	19.11.1979 (R)	19.11.1979 (R)	19.11.1979 (R)	28. 6.1988(AC)	28. 6.1988(AC)	14.10.1994 (S)
EC	16. 3.1978(AP)	16. 3.1978(AP)	12. 8.1981(AP)	7.10.1983(AP)	30. 6.1984(AP)	
Egypt	24. 8.1978(AP)	24. 8.1978(AP)	24. 8.1978(AP)	18. 5.1983(AC)	8. 7.1983 (R)	
France	11. 3.1978(AP)	11. 3.1978(AP)	11. 3.1978(AP)	13. 7.1982(AP)	2. 9.1986(AP)	
Greece	3. 1.1979 (R)	3. 1.1979 (R)	3. 1.1979 (R)	26. 1.1987 (R)	26. 1.1987 (R)	14.10.1994 (S)
Palestine	3. 3.1978 (R)	1. 3.1984 (R)	3. 3.1978 (R)	21. 2.1991 (R)	28.10.1987 (R)	14.10.1994 (S)
Italy	3. 2.1979 (R)	3. 2.1979 (R)	3. 2.1979 (R)	4. 7.1985 (R)	4. 7.1985 (R)	14.10.1994 (S)
Lebanon	8.11.1977(AC)	8.11.1977(AC)	8.11.1977(AC)	1994 (AC)	1994 (AC)	
Libya	***31. 1.1979 (R)***	***31. 1.1979 (R)***	***31. 1.1979 (R)***	***6. 6.1989(AP)***	***6. 6.1989(AP)***	
Malta	30.12.1977 (R)	30.12.1977 (R)	30.12.1977 (R)	2. 3.1989 (R)	11. 1.1988 (R)	14.10.1994 (S)
Monaco	20. 9.1977 (R)	20. 9.1977 (R)	20. 9.1977 (R)	12. 1.1983 (R)	29. 5.1989 (R)	14.10.1994 (S)
Morocco	15. 1.1980 (R)	15. 1.1980 (R)	15. 1.1980 (R)	9. 2.1987 (R)	22. 6.1990 (R)	
Slovenia	15.3.1994 (AC)	15.3.1994 (AC)	15.3.1994 (AC)	15.3.1994 (AC)	15.3.1994 (AC)	10.10.1995 (S)
Spain	17.12.1976 (R)	17.12.1976 (R)	17.12.1976 (R)	6. 6.1984 (R)	22.12.1987 (R)	14.10.1994 (S)
Syria	26.12.1978(AC)	26.12.1978(AC)	26.12.1978(AC)	1.12.1993 (AC)	11.9.1992 (AC)	29.9.1995 (S)
Tunisia	30. 7.1977 (R)	30. 7.1977 (R)	30. 7.1977 (R)	29.10.1981 (R)	26. 5.1983 (R)	14.10.1994 (S)
Turkey	6. 4.1981 (R)	6. 4.1981 (R)	6. 4.1981 (R)	21. 2.1983(AC)	6.11.1986(AC)	

S = Signature R = Ratification AC = Accession AP = Approval

1.9 Oil pollution in the Libyan coast

The first oil well was opened in 1959. Since the production of the first barrel of oil, the country has started a new era of high growth rates in population, industry, and energy demand and consumption. The fast uncontrolled growth in all industrial sectors has resulted in an increasing generation of environmental pollution.

Although Libya is not highly populated, about 80 % of the people are concentrated in a narrow strip along the coast where the main industrial, commercial and other activities are located (National Academy of Scientific Research, 1991). Libya has one of the longest coastlines in the Mediterranean (Table 1.2) with different topographical formations. Nevertheless the Libyan coastline is the least known by naturalists (UNEP, 1990).

1.9.1 Sources and inputs to the coastal environment

According to Magazzu & Angot (1981) and El-Ghirani (1981), pollution by oil in the Libyan waters is mainly a result of tank washing operations and ballast water released at sea by tankers. According to the 1954 convention on the prevention of oil pollution at sea, appropriate reception facilities have to be provided in ports and terminals for the unloading of the oily residues contained in the ballast water. Most of tankers make use of the possibility offered by the 1962 amendment to the convention of 1954 which allows the discharge of oil residues at sea but distance of over 100 miles from land. Two international discharge zones are specified for this purpose in the Mediterranean. One is located between Italy and Libya, and the other is Southwest of Cyprus (El-Ghirani, 1981). Tankers often discharge their oily residues and ballast water in the area located north of the Gulf of Syrte and west of Cyrenacia (eastern Libya) (Magazzu & Angot, 1981; El-Ghirani, 1981).

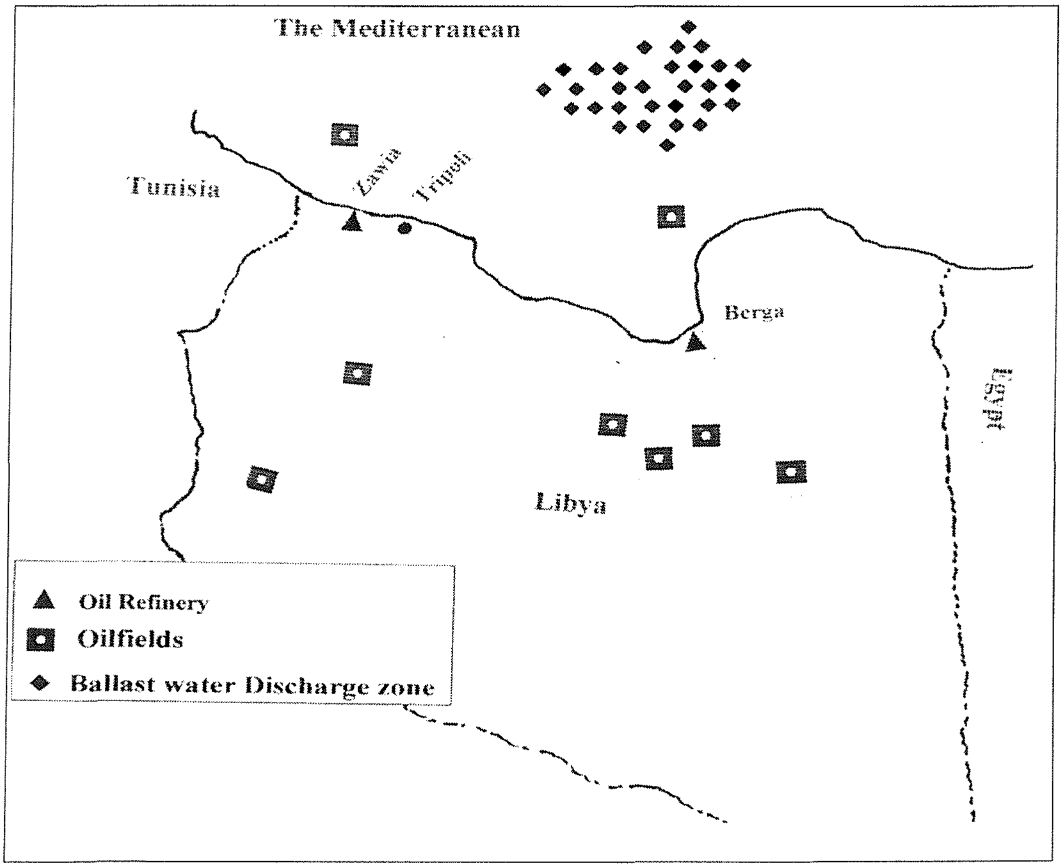


Figure 1.2 Location of the international ballast water discharge zone, oilfields and oil refineries in Libya.

After some time, the released ballast water moves according to the prevailing circulation and wind pattern to affect the North African coast (mostly the Libyan coast) if it has not degraded before reaching it (Fig. 1.2) (Aybulatov *et al*, 1981; Magazzu & Angot, 1981; Golik *et al*, 1988). As there are no reception facilities for ballast water in any of the Libyan ports (Tluba, 1991), and because there is no surveillance of any kind in the area, tankers operators have more excuses to discharge their polluted water and oiled residues near Libyan waters (Magazzu & Angot, 1981).

Another significant source is the incidental spills and pipeline leakage during transfers from and to oil refineries (Elazzabi, 1992). Oil fields are connected to Mediterranean terminals by an extensive network of pipelines. Libya has three domestic oil refineries. The Zawia refinery is located in the north-western region, and the Berga and Ras Lanuf export refineries are located on the Gulf of Sirte (Fig. 1.2). Almost all the produced oil is processed within the country by petrochemical complexes and oil refineries such as Zawia and Brega. Typically, the quantities of crude oil produced in Libya range from 0.16 to 0.35 million m^3 per day (Table 1.4).

Table 1.4 Typical quantities of crude oil produced in Libya.

(National Academy of Scientific Research, 1991).

YEAR	OIL PRODUCED (million m^3/day)
1973	0.350
1974	0.238
1975	0.235
1976	0.308
1977	0.328
1978	0.315
1979	0.332
1980	0.288
1981	0.192
1982	0.200
1983	No data
1984	0.168

Other sources that contribute to inshore and offshore releases of oil include illegal discharges of exhausted oils and lubricants from ships and boats that belong to different Libyan authorities and from privately owned boats (Tluba, 1991). Discharges of oil and oiled wastes from shipyards in harbours, and discharges from oil spill incidents, particularly during loading or unloading of crude oil or oil products in ports, are also common (Tluba, 1991). Table 1.5 shows examples of the scale of release of this type in seaports.

Table 1.5 Examples of oil spills recorded in seaports, Libya. (Socialist ports Co.)

DATE	QUANTITY (L)	TYPE OF OIL	RESPONSE TYPE	SEA PORT
20.08.1986	148000	Light oil	Mechanical	Misurata
08.03.1989	800	Light oil	chemicals	Misurata
17.01.1990	250	Diesel oil	chemicals	Misurata
6.09.1997	400	Light Oil	chemicals	Misurata
10.06.1997	130	No information	chemicals Mechanical	Derna

Municipal sewage, which is discharged into seawater in most cities without proper treatment and the industrial sewage are significant sources of oil pollution. The uncontrolled discharge of industrial and domestic wastewater is a widespread problem through the coastal zone input (Elazzabi, 1992). It is estimated that the emissions of organic water pollutants in 1980 in Libya were 3,532 kg/day and 0.21 kg/day/worker (World Bank, 1998). This figure is relatively high compared with other countries that have a larger population. In Italy, for example, the figure was 0.13 kg/day/worker for the same year (World Bank, 1998). It is estimated that 130,000 m^3 of domestic wastewater is generated every day in Tripoli alone (Baghni, 1998). Most of this wastewater goes to directly the sea untreated or partly treated. In summer 1991 estimates indicated that 70,000 m^3 of wastewater goes every day to the sea in front of Tripoli city directly, without any sort of treatment (Baghni, 1998). This wastewater contains oils and greases of petroleum origin and undoubtedly contributes to the oil pollution problem.

Levels of oil pollution in the Libyan seawater have increased over time as a result of increased oil exploitation activities (Petroleum Research Centre, 1987). Measurements undertaken in the 1970s in parts of the Mediterranean Sea indicated that the area off Libya had a mean petroleum hydrocarbon concentration of 24.9 ppm (Zsolnay, 1979).

The first survey to assess the levels of oil pollution in the Libyan waters was undertaken in 1977 (Elazzabi, 1992). According to Magazzu & Angot (1981) petroleum hydrocarbon concentration in Libyan seawater reached 27.63 ppm in 1981. Higher concentrations of petroleum hydrocarbons were found near seaports, oil refineries, and in the vicinity of coastal cities (Elazzabi, 1992; Petroleum Research Centre, 1984). A recent study showed that the highest concentrations were found in the vicinity of cities and industrial activities, and was linked particularly to municipal sewage discharges (Ali *et al*, 1998).

1.9.2 The legislative and managerial context

Regulations for the protection of the environment in Libya started as early as 1971. Although the existing regulations are dedicated to this purpose, the environmental legislation process in Libya is still in its early stage. The development of environmental regulations is taking place slowly as public awareness grows and more environmental impacts emerge (Det Norske Veritas, 2001). A general review of the existing environmental regulations would indicate the breadth of the environmental issues covered by the relevant acts. Table 1.6 lists the chronological development of the environmental legislation.

A competent environmental authority was established in 1984 according to the environment protection act (7) of 1982. The environmental authority defines strategies and co-ordinates the relevant monitoring functions of national institutions. A number of national research centres provide technical assistance to the environmental authority (Det Norske Veritas, 2001).

Arrangements for the establishment of a national contingency plan for oil spill combat had started in 1995. The basic principles of the plan were established but unfortunately, the plan has not been completed yet as a final approved plan for different reasons, including administrative ones.

Table 1.6 Development of environmental legislation in Libya.

Date of issue	**Type of legislation**	**Legislation description**
1971	Decision	Approval of participation in the international convention of marine pollution of 1954 and amended in 1962.
1973	Act	Prevention of oil pollution in the sea
1973	Act	Public health and the environment.
1982	Act No.3	Regulation of water exploitation.
1982	Act No.5	Protection of green areas.
1982	Act No.7	Environmental protection.

1.9.3 International co-operation

Although the Libyan government has enacted a number of national regulations regarding marine pollution, it believes that regional co-operation is the only effective way to deal with the problem. Therefore, Libya has become a party to a number of international conventions (Table 1.3).

Many of Libya's national environmental concerns are part of a larger regional and/or global problem. Therefore, Libya became a member of many international organisations, treaties, and international bodies. Like most of the developing countries, Libya is still facing difficulties in the implementation of the international conventions regarding marine pollution. These difficulties include inadequacy of administration, lack of facilities and lack of skilled personnel (Atia, 1993).

1.10 Research approaches and thesis structure

The research methodology consisted of two main approaches in order to fulfil the research objectives. The ecological approach consisted of ecological surveys that were designed to assess the impact of oil deposition on coastal habitats. This approach was mainly based on quantifying of the deposition of oil on rocky shores and sandy beaches; and comparing the abundance of selected species in different sites in order to assess the impact and identify the affected areas.

The analytical procedure was designed to evaluate the levels of petroleum hydrocarbons in the seawater and sediments within the study area. This approach was employed to evaluate the existing status of this increasing background pollution. This was vital to understand the geographical distribution patterns of oil pollution and, consequently, assessing the impact and identifying the affected areas. This analytical approach was an essential prerequisite to the ecological approach, in spite of the fact that they are inter-linked.

Chapter Two: *Distribution of hydrocarbons on the Libyan coast.* The aim of this research programme was to study the distribution patterns of oil pollution in the study area. The levels of petroleum hydrocarbons in seawater and sediments were evaluated using an analytical procedure. The levels of this background pollution were studied and linked with probable sources.

Chapter Three: *Oil pollution reducing measures: an example of Southampton Water and its applicability to the Libyan western region.* The purpose of this chapter was to study changes in oil pollution levels in Southampton Water by comparing past and recent levels, to investigate measures taken for reducing oil pollution in Southampton Water, and to assess the applicability of such measures to the Libyan case.

Chapter Four: *Deposition of tar on the Libyan Coast:* this chapter studied the deposition of tar on sandy beaches and rocky shores. The existing levels of tar deposition were estimated, their distribution patterns examined, and changes in amount of tar on selected sandy beaches were measured over a one month period.

Chapter Five: *Impact of oil pollution on the rocky shores:* This chapter examined the impact of chronic oil pollution on the Libyan rocky shores. The study is based on the comparison of the abundance of species found on the rocky shores in different sites in order to assess the impact and identify the affected areas. Comparison was made between heavily polluted and less polluted sites. The geographical and spatial aspects of the environmental impact were also examined.

Chapter Six: *General Discussion:* The main findings of the thesis are summarised and discussed. Recommendations for the protection of the Libyan coast against oil pollution are presented, and considerations for future research are suggested.

CHAPTER TWO: DISTRIBUTION OF HYDROCARBONS ON THE LIBYAN COAST

Chapter Two: Distribution of Hydrocarbons on the Libyan coast

2.1 Introduction

Libya is one of the major oil producers and exporters in the Middle East and North Africa and Europe's biggest North African oil supplier (Schmitz, 2001). In addition to the extremely high-quality low-sulphur crude oil (Lavecchia & Zugaro, 2000), supplies from Libya to European destinations have the advantage of being cost-effective (Schmitz, 2001).

Oil exploration began in 1955 with the first oil fields discovered in 1959. Currently, Libya has more than 12 oil fields with reserves accounting for more than 84% of the Mediterranean region's oil and gas reserves (Schmitz, 2001).

The major component of Libya's expansion plans is the development of offshore oil production. The discovery and development of the El-Bouri offshore oil field, the largest producing oil field in the Mediterranean Sea (SMI Group, 2000) added another source of oil pollution in the Libyan waters. A project is underway to supply Italy by natural gas and oil from this field and other inland oil fields (DNV, 2001) via pipelines under the Mediterranean Sea, which adds more risk of oil spills occurring in the sea.

Oil pollution along the Libyan coast is therefore significant as a result of oil exploration, exploitation and transportation. Oil spills from tankers, leakage from offshore production, ballast water and tank washing operations, discharges from small shipyards in harbours, and discharges and pipelines leakage from oil refineries are major sources of coastal pollution (Magazzu & Angot, 1981). In addition, oiled wastes, lubricants and greases are released in different forms from different industrial centres.

It is important to evaluate the existing levels of oil pollution and its distribution patterns in order to use this information to provide an indication of possible sources, and identify response priorities. In some areas, oil pollution monitoring is an established operational procedure, but elsewhere such as in Libya a first step can be made by undertaking one-off surveys to indicate the overall status of the area. The aims of this chapter are to evaluate the levels of oil pollution in the study area by measuring the levels of petroleum hydrocarbons in the seawater and the sediments, and to study the geographical and spatial distribution patterns of this background pollution.

2.2 Geographical area of study

The coastal zone of Tripolitania from the west of Tripoli to the east of Misurata (formerly called Tripolitania) has a long coast on the Mediterranean. About 500 km of rocky shores and sandy beaches accommodate a significant part of the country's industrial and commercial activities (Ali *et al,* 1998). The activities in this area include crude oil refining, iron and steel manufacturing, petrochemical industry and, recently, natural gas treatment (DNV, 2001).

Four main commercial seaports are located in this coastal zone, one of which is Tripoli, the biggest and the busiest in the country. This coastal zone is relatively close to the offshore petroleum and natural gas production at the Bouri oil field, which is about 30km from the coast (SMI Group, 2000). It is also linked to Italy by the new oil and gas pipeline which will provide Italy with large amounts of oil and gas (DNV, 2001). Moreover, about 50% of the Libyan population are concentrated in a narrow coastal strip within this area. Therefore this area is probably the most vulnerable to oil pollution on the Libyan coast.

The availability of information on hydrography is a key to understanding marine pollution problems. The vertical structure and the circulation pattern of water masses, along with other factors, control the distribution of pollutants (Magazzu & Angot, 1981). Unfortunately, there are no oceanographic data available about the Libyan waters in Tripolitania's coast; oceanographic conditions of this region have been poorly studied (Magazzu & Angot, 1981). Only one study has been carried out during 1973- 1974 (Sogreah, 1977) which provides a description of the oceanographic regime on a seasonal basis.

The oceanographic patterns of the Libyan waters (Figs. 2.1 & 2.2) are characterised by the presence of three water masses: Atlantic water, intermediate water and surface water (Fig. 2.2). These patterns have been described by Sogreah (1977) and Magazzu & Angot (1981).

In this context, two main regimes can be identified: the summer regime and the winter regime. In winter, water originating from the Atlantic is found at the surface. This current exists along the coast with temperature ranges from 14°C to 16°C. The cold Atlantic current separates into two branches that merge off Tripoli; one current becomes warmer as it moves east (Fig. 2.2). It becomes warmer through mixing with water masses by the time it reaches Misurata (Magazzu & Angot, 1981).

In summer, the temperature of surface water increases, with a surface value of around 26° C (Magazzu & Angot, 1981). This water originally came from the Atlantic but its properties have changed due to the summertime climate conditions while typical Atlantic water can be found underneath (Fig. 2.1, 2.2).

A warm water current reaches the Tripolitanian coast off Zwara, coming from the northern area between the islands of Linosa and Malta. The coastline diverts part of this current towards Tripoli and Misurata.

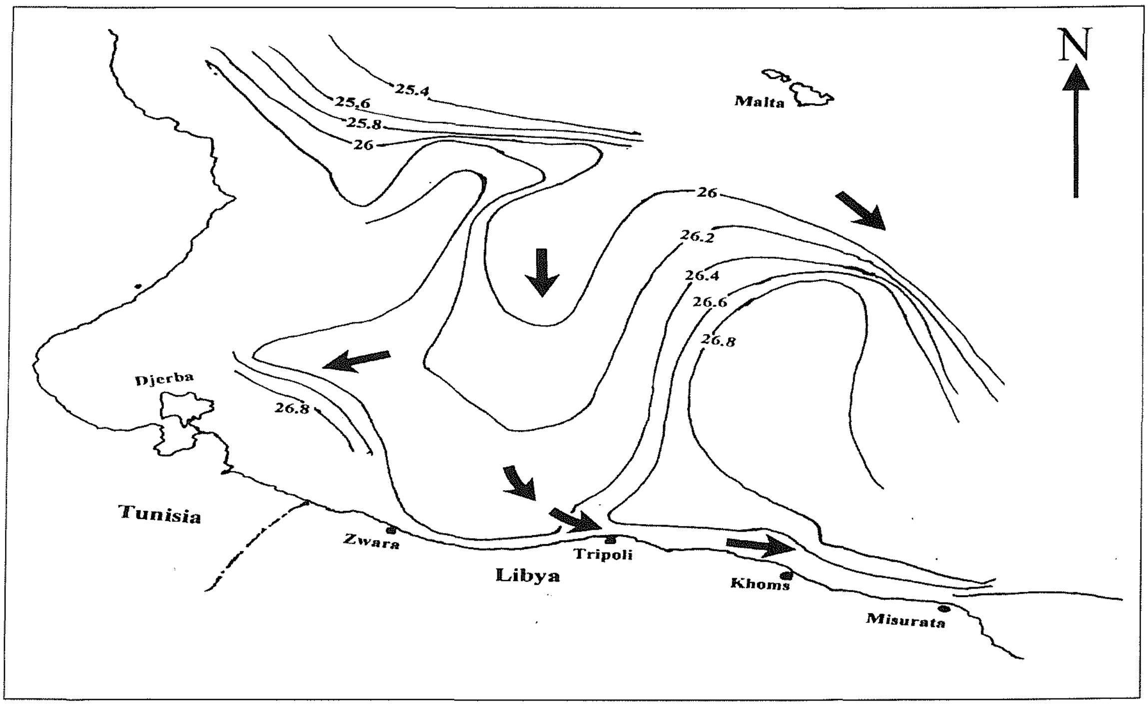


Figure 2.1 Isotherms (°C) and currents of surface water during summer (Not to scale). (Magazzu & Angot, 1981).

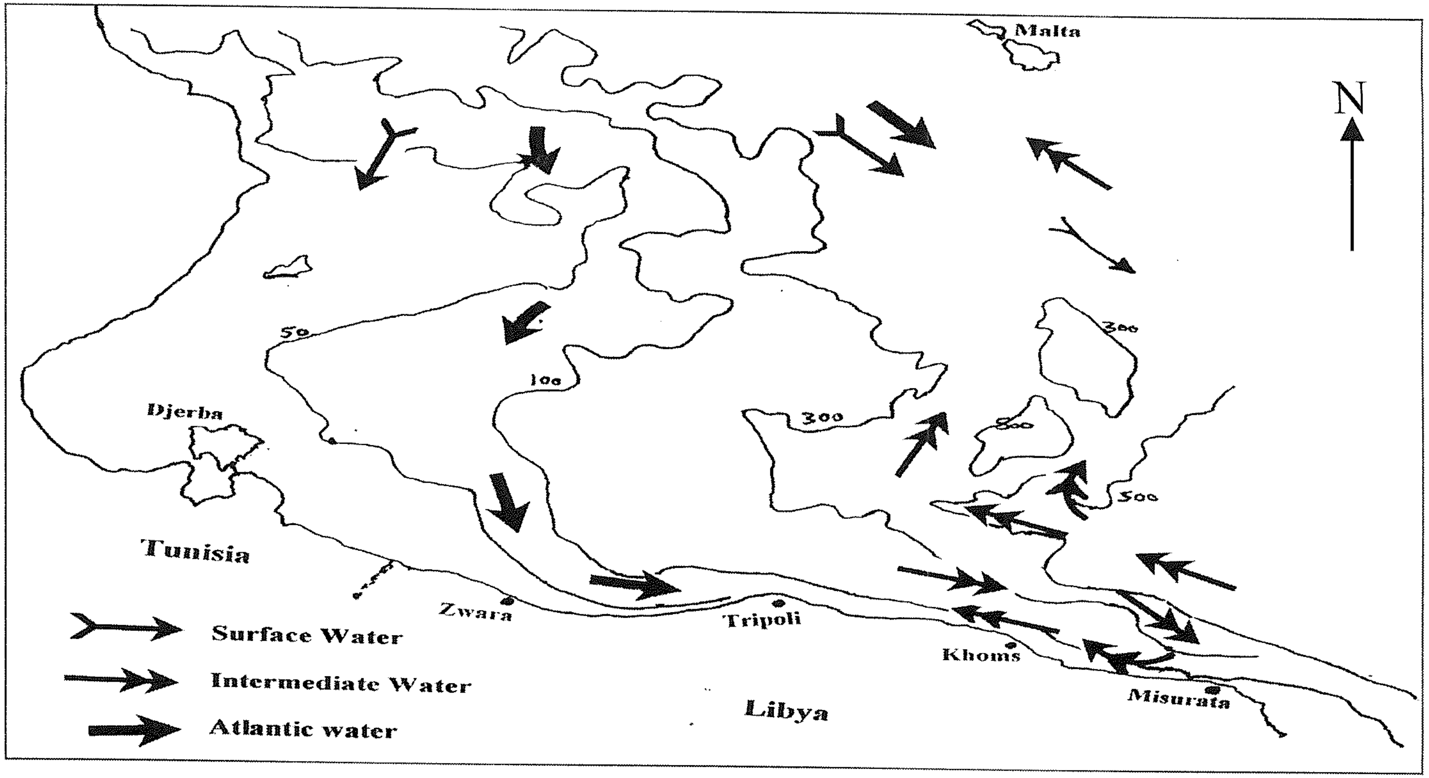


Figure 2.2 Pattern of summer currents along the Libyan coast. Not to scale; contours show depth in m. (Magazzu & Angot, 1981).

2.3 Sampling sites

Sampling sites were chosen to represent both polluted areas and less polluted or unpolluted areas for comparitive purposes (Fig. 2.4).

Sampling was carried out in the vicinity of expected pollution sources such as oil refineries, and municipal sewage discharges. Samples were also taken from the neighbouring areas east and west of each city. Distances between the neighbouring areas and the cities were measured from the end of population settlements. These landmarks were considered as city boundaries.

In all cases, sampling sites were no further than 40 km from each other. This sampling scheme is typical for dealing with an environment such as the case of Libyan coast where no basic data exist to make a reasonable choice of sampling locations (Magazzu & Angot 1981). Two sites were selected as control sites: 40km east of Misurata (control site 1) and Zliten (control site 2). These sites are relatively far from possible sources of pollution (Fig. 2.3 & 2.4).

Region	Site	Nearest possible source of pollution (within 5km)
Misurata	40km east	None
	Iron & Steel Complex	Industrial Sewage
	Seaport	Seaport
	City (Jannat)	Municipal Sewage
	30km west (Dafnia)	None
Zliten	3km east	None
	3km west	Municipal Sewage
Khoms	3km east	Municipal Sewage
	Seaport	Seaport
	3km west	Municipal Sewage
Tajora	3km east	Municipal Sewage
	3km west	Municipal Sewage
Tripoli	3km east	Municipal Sewage
	Seaport	Seaport
	3km east	Municipal Sewage
	10km west (Janzour)	Industrial Sewage
Zawia	3km east	Municipal Sewage
	Oil Refinery	Oil Refinery
	3km west	Municipal Sewage
Zwara	3km east	Municipal Sewage
	3km west	Municipal Sewage
	Abo-Kammash	Industrial Sewage

Figure 2.3 Sampling sites.

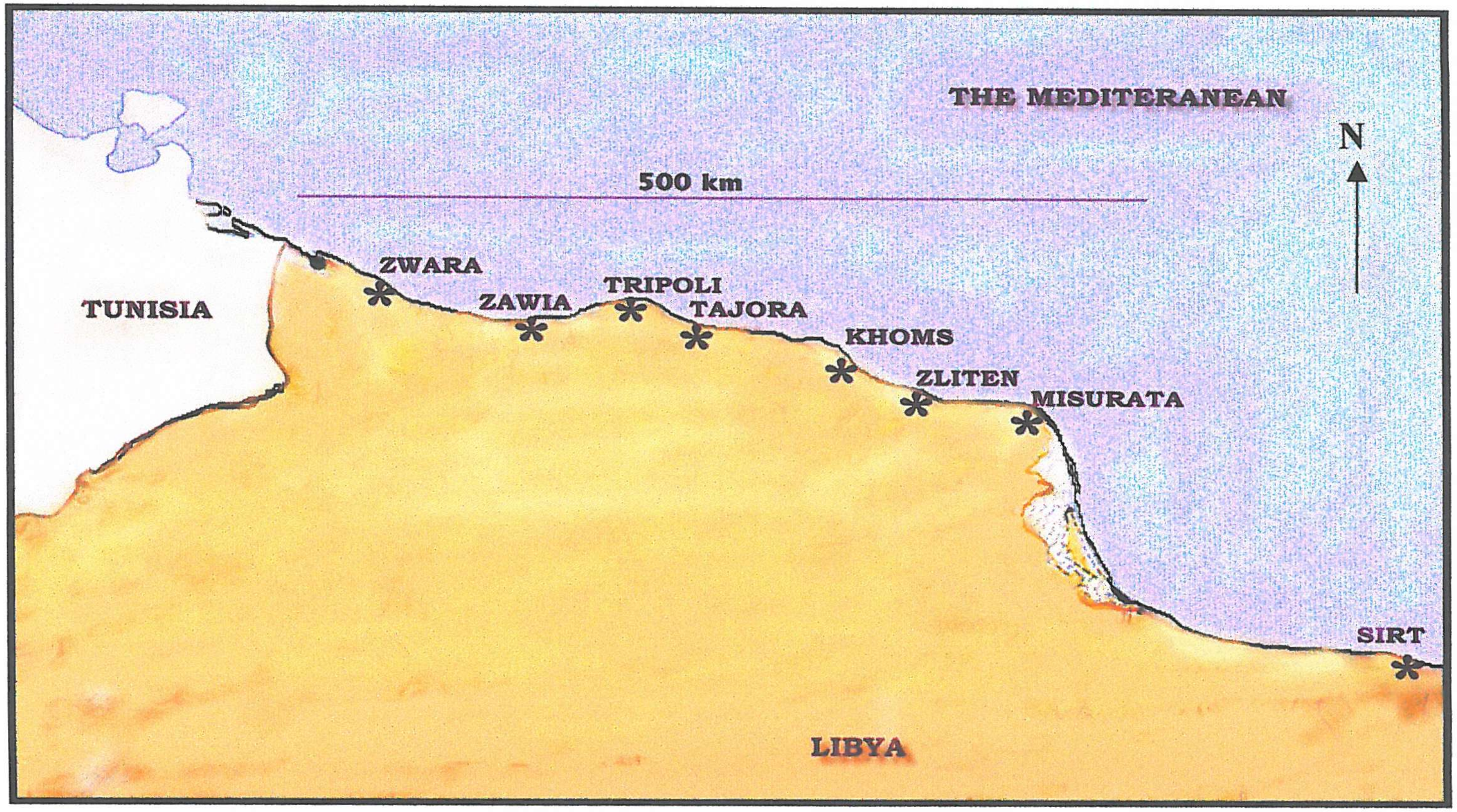


Figure 2.4 Location of sampling sites and study area.

2.4 Measurement of oil pollution

Concentrations of hydrocarbons were measured both in seawater and sediments from selected sites using the gravimetric determination technique. This technique was selected for three reasons. Firstly, this technique was used in a similar study for a part of the study area (Ali *et al,* 1998), so results can be comparable. Secondly, it is simple and relatively quick analytical procedure considering the limited time and the analytical facilities available during the fieldwork trip. Thirdly, it provides a quantitative measure of the total extractable hydrocarbon content of the water and sediment samples; and is approved method by the American Society for Testing and Materials for this kind of study (ASTM, 1996).

2.4.1 Seawater

Sampling: Samples were collected in 1.5 litre glass bottles from 22 different sites from the surface water along the study area. The bottles were washed and dried, and were rinsed with chloroform immediately before collection of samples.

A duplicate sample was taken from each site and the average was calculated for each site after the analysis. Samples were collected from 3m offshore. A 40ml aliquot of solvent (chloroform) was added immediately to the sample after collection.

Analytical procedure: An aliquot of 250ml of seawater was extracted with chloroform in a separator funnel. Chloroform (60ml) was added to the sample and shaken vigorously for 3-5 minutes and transferred to a separator funnel and shaken. The extract was separated easily because of a difference in the specific gravity between water and chloroform. The extract was then transferred to a boiling flask of a known weight, the solvent evaporated in a hot water bath and recovered. The remaining residues were dried in a desiccator for one hour, removed, and weighed immediately on an electronic balance. Every care was taken to ensure accuracy during transferring and weighing the extract. Sample bottles were rinsed twice with the solvent and added to the sample in the separator funnel. The exterior of the flasks was wiped with a lint-free cloth and a small amount of acetone to remove any adhering water, and metal tongs were used to handle the glassware. Calculations were made as follows:

$$\textbf{HC conc. (mg/L)} = \left[{}^{(B-A)}/{}_{C}\right] \times 1000$$

Where:

A= Original weight of boiling flask (mg).

B= Weight of boiling flask after removal of the solvent (mg).

C= Volume of sample (ml).

2.4.2 Sediments

Sampling: Samples were collected from 22 different sites along the study area. Sediments were sampled by hand or by a means of a grab from 3m offshore. A duplicate sample was taken from each site and the average was calculated for each site.

Analytical procedure: Hydrocarbons in 50g of wet sediments were extracted with 200ml chloroform in a soxhlet apparatus for six hours. The extract then was separated transferred to a boiling flask of a known weight. The solvent was then evaporated on a hot water bath and rotary evaporator. The remaining residues were dried in a desiccator for one hour at 105°C, removed, and weighed immediately on an electronic balance. Every care was taken to ensure accuracy during transferring and weighing the extract. The exteriors of flasks were wiped with a lint-free cloth and a small amount of acetone to remove any adhering water, and metal tongs were used to handle the glassware to avoid deposition of body oils.

Calculations were made as follows:

$$\textbf{HC conc. (mg/L)} = \left[{}^{(B-A)}/_{C}\right] \times 1000$$

Where:

A= Original weight of boiling flask (mg).

B= Weight of boiling flask after removal of the solvent (mg).

C= Weight of sample (mg).

2.5 Results

Hydrocarbon levels in the sediments have been compared with data from the survey of Ali *et al* (1998). Although the survey of Ali *et al* (1998) did not include all of the sampling sites that have been covered by this study, the results of both studies are comparable as they followed the same analytical technique. The study of Ali *et al* (1998) covered Tajora, Zawia, Zwara, and Abou-Kammash. There was a considerable rise in hydrocarbon levels in the sediments at all sites since 1998 expect Tajora where the average concentration in 1998 was 126 ppm and decreased slightly to 112 ppm in 1999 (Fig. 2.5).

The highest level of hydrocarbons in the sediments at these sites was recorded in Abou-Kammash in 1998 with an average concentration of 167 ppm. The average hydrocarbon concentration in this site in 1999 was 465 ppm (Fig. 2.5).

The lowest hydrocarbon concentrations in the sediments among these sites in 1998 were recorded in Zawia and Zwara with averages of 110 ppm and 63 ppm respectively. The hydrocarbon concentration increased considerably in 1999 at these two sites to 657.5 ppm and 252.5ppm respectively (Fig. 2.5).

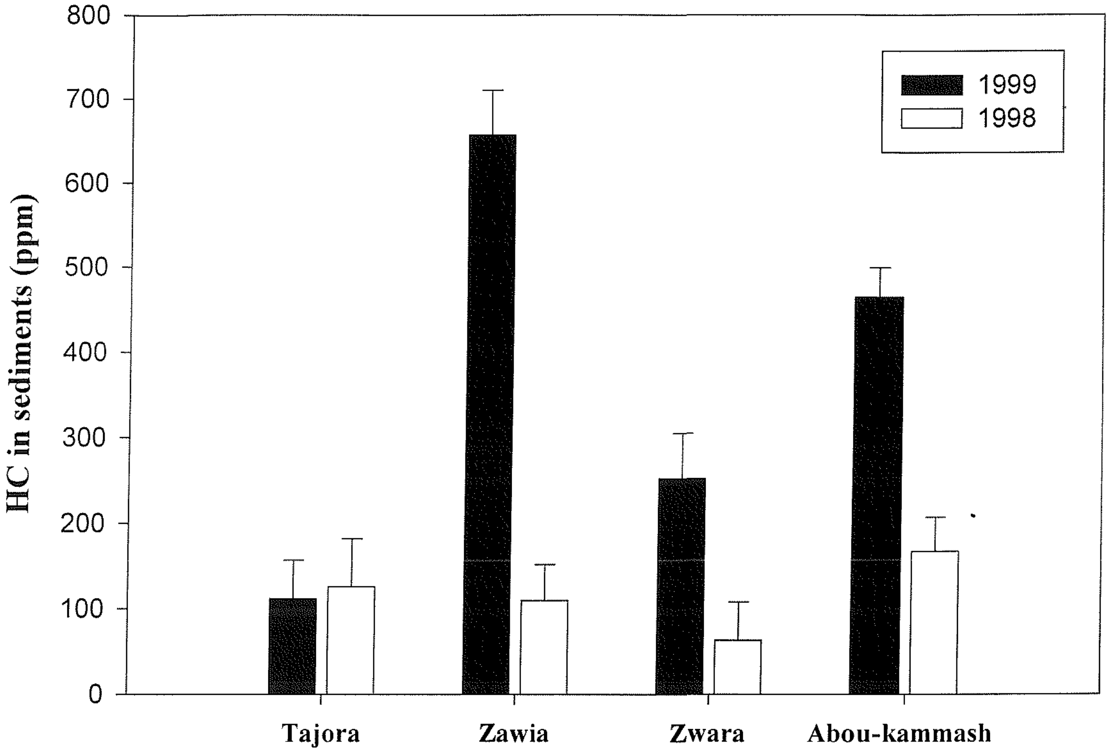


Figure 2.5 HC in the sediments at the sampling sites in 1998 and 1999. Vertical bars show standard difference.
Source of 1998 data: (Ali *et al*, 1998).

In all of the sampling sites, the concentrations of hydrocarbons were much higher in the sediments than in the water samples (Fig. 2.6). The lowest level of hydrocarbons were found in samples from the control sites 1 and 2 (i.e. 40km east of Misurata and Zliten) with averages of 34 ppm and 134 ppm in the sediments; and 2 ppm and 5 ppm in the seawater (Fig. 2.6).

The highest concentrations of hydrocarbons in the sediments were recorded in Khoms and Zawia, with averages of 931 ppm in Khoms and 657.5 ppm in Zawia (Fig. 2.6). In the seawater the highest concentrations of hydrocarbons were recorded in Zawia and Tripoli with averages of 32.75 ppm and 14.5 ppm respectively.

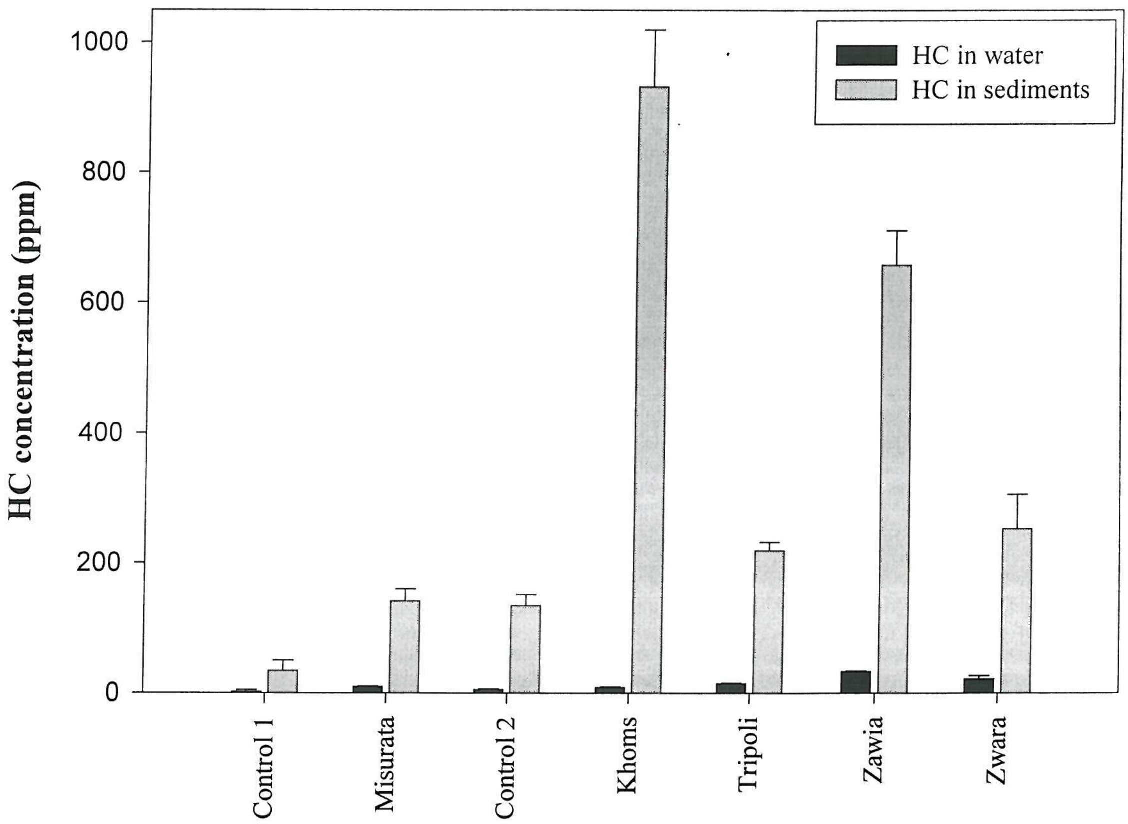


Figure 2.6 HC in seawater and the sediments.
Vertical bars show standard difference.

The results showed a gradual increase of hydrocarbons in seawater towards the western sites (Fig. 2.7). This pattern excludes the sites that are in the immediate vicinity of localised pollution sources such as the municipal sewage outlets and the seaports. The average concentration of hydrocarbons in the seawater increased from 2 ppm in control site 1, which is at the eastern end of the study area, to 21.75 ppm in 3km west of Zawia. The average hydrocarbon concentration in the seawater was 5 ppm in control site 2, 8 ppm in Khoms, 9 ppm in Tajora and 14 ppm in Tripoli.

The average hydrocarbon concentration in the sediments increased toward the western sites of the study area but the pattern was not as clear as in the seawater samples (Fig. 2.7). The average concentration of hydrocarbons in the sediments increased gradually from 34 ppm in control site 1 to 330 ppm in 3km west of Zawia with exception of Khoms. In Khoms the concentration of hydrocarbons in the sediments was the highest among other sites with an average of 931.5 ppm (Fig. 2.7).

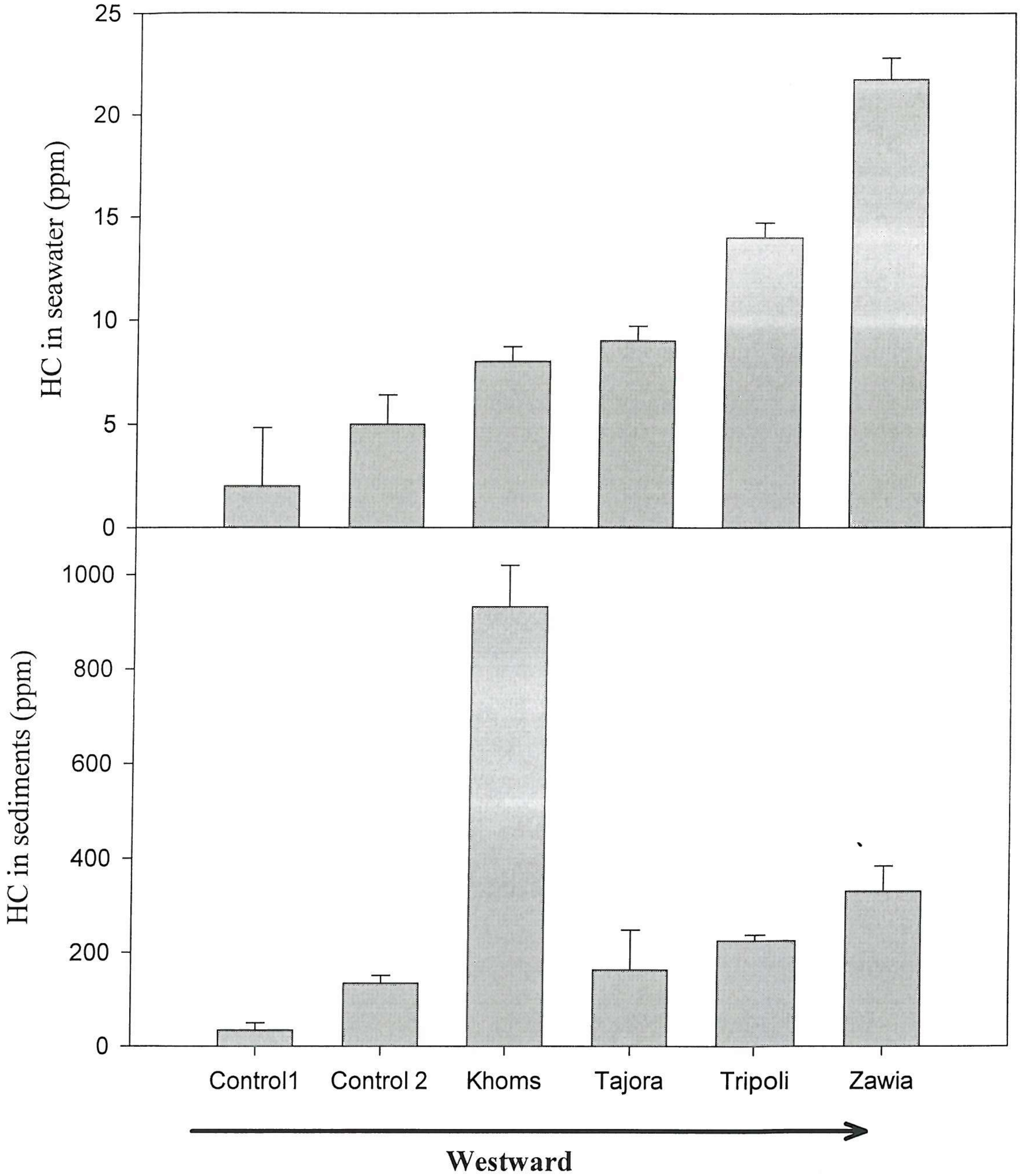


Figure 2.7 Distribution pattern of HC on the study area (Excluding sites that are in the immediate vicinity of pollution sources). Vertical bars show standard difference.

Levels of hydrocarbons were much higher in seaports compared with the neighbouring areas (Fig. 2.8). In Misurata, the average concentration of hydrocarbons in the sediments was 429 ppm in the seaport, 219 ppm 3km east of the seaport, and 141 ppm 3km west of the seaport. In Khoms seaport, the average was 1454.5 ppm while in the neighbouring areas the averages were 931.50 ppm and 1037 ppm 3km east and west respectively.

In Tripoli's seaport, the average was 553.5 ppm while in the neighbouring areas the averages were 224.5 ppm and 219 ppm 3km east and west respectively.

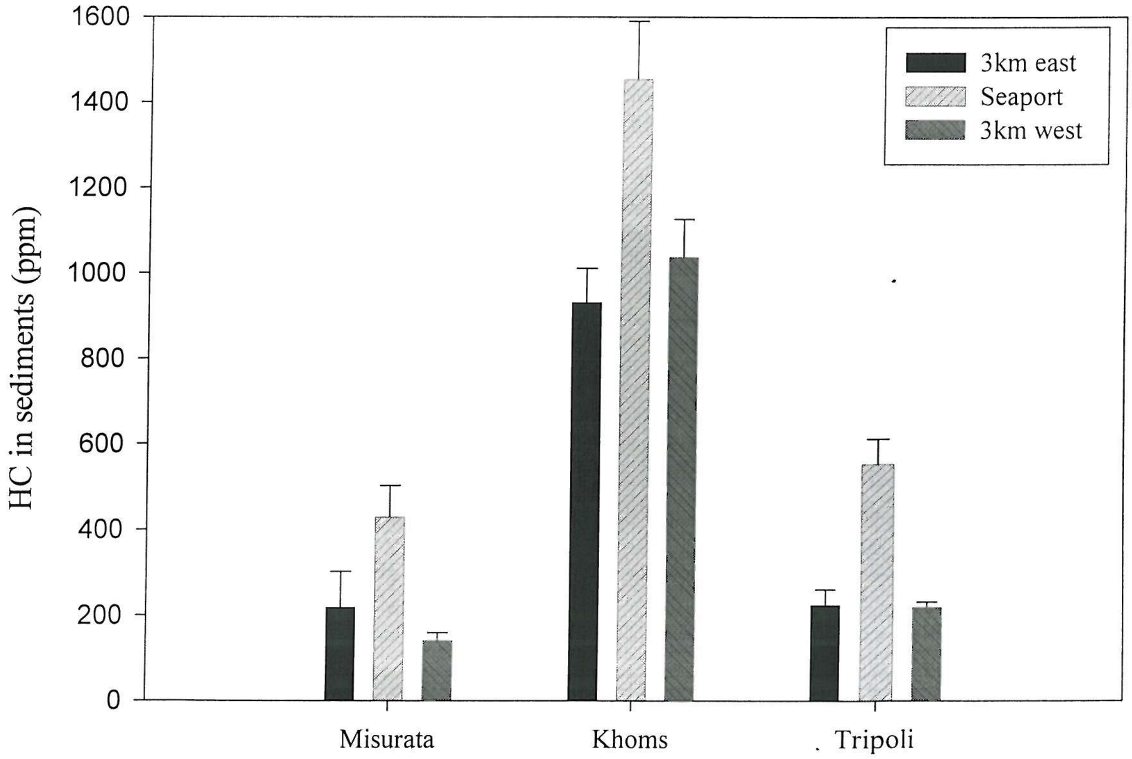


Figure 2.8 HC in sediments (seaports versus the neighbouring areas). Vertical bars show standard difference.

Levels of hydrocarbons were much higher in the seawater and the sediments adjacent to most of the cities compared with the neighbouring areas (excluding the seaports) (Fig. 2.9). In Tripoli, for example, the average concentration of hydrocarbons in seawater was 14 ppm in front of the city, 9 ppm east of the city, and 7 ppm west of the city (Fig. 2.9).

The highest concentration of hydrocarbons in the sediments compared with the neighbouring areas was recorded in Khoms. The average in Khoms was 1037.5 ppm, while to the east of the city the average was 107.5 ppm, and to the west of the city the average was 119 ppm. Other cities had higher concentration of hydrocarbons in the sediments compared with the neighbouring areas but not as high as in Khoms. In Tripoli, for example, the average concentration in the sediments was 224.5 in front of the city, 162.5 ppm east of the city, and 127.5 ppm west of the city (Fig. 2.9).

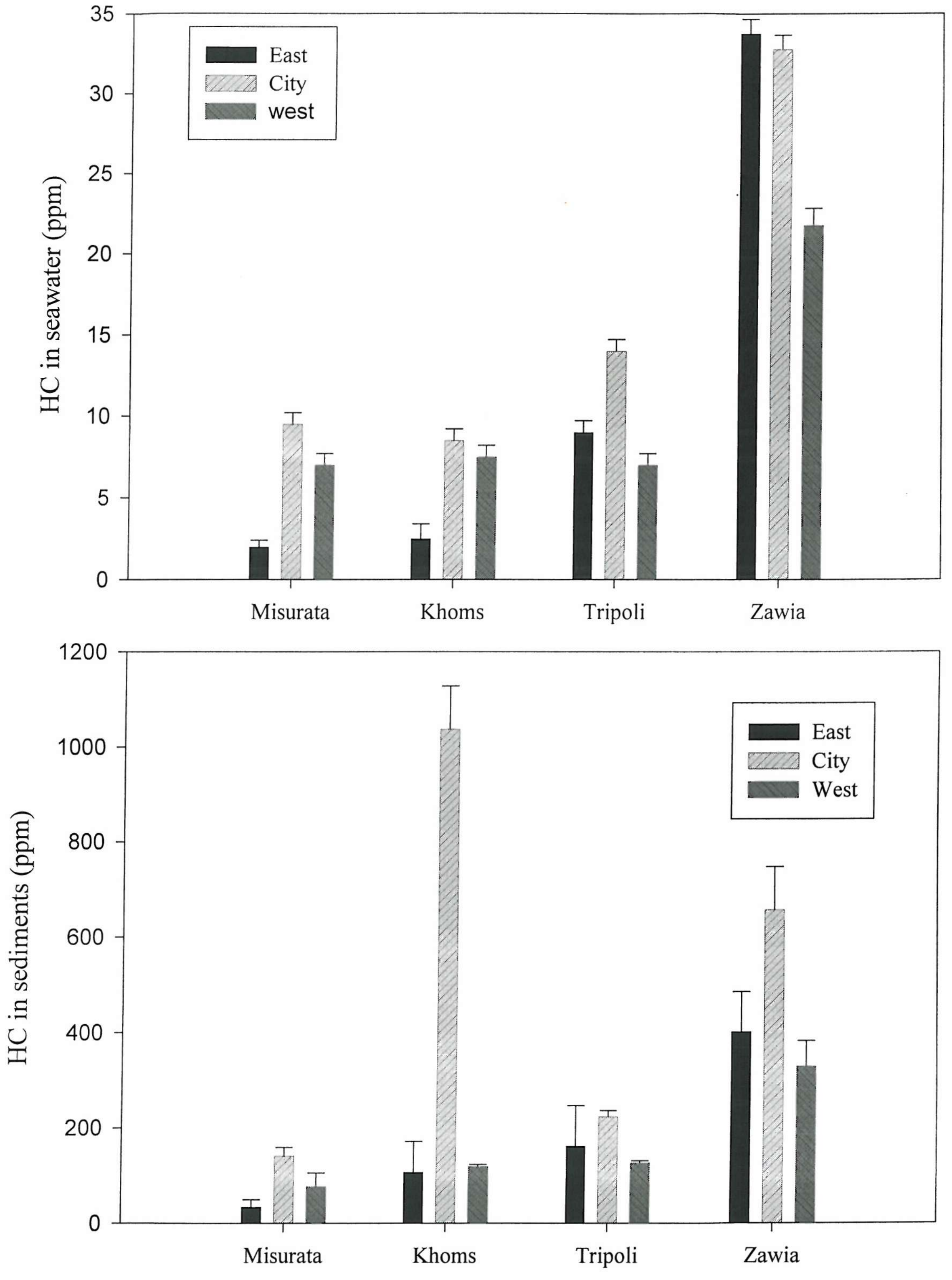


Figure 2.9 HC in the seawater and the sediments in the vicinity of the cities versus the neighbouring areas. Distance between cities and the neighbouring areas range from 3km to 40km east and west of the cities).
Vertical bars show standard difference.

2.6 Discussion

There was a considerable rise in hydrocarbon levels in the sediments of the study area since 1998 (Fig. 2.5). This change indicates the possible accumulation of hydrocarbons in the sediments. Accumulation of petroleum hydrocarbons on the near-shores sediments occurs in higher rates than in offshore sediments (Lipiatou *et al*, 1997).

In all of the sampling sites the concentrations of hydrocarbons were much higher in sediments than in the water samples (Fig. 2.6). This suggests that the dispersion process is probably much slower than the deposition rate, which make hydrocarbons accumulate on the sediments in large quantities. The strong affinity of hydrocarbons, particularly the polycyclic aromatic hydrocarbons, for sediments and other particulate matter makes them accumulate to much higher concentrations on the seafloor than in the overlying waters (Kennish, 1998).

Many factors the such as the wave action and wind speed may affect the dispersion process of petroleum hydrocarbons in the marine environment (Santas & Santas, 2000; Thorpe, 2000). In coastal or continental shelf waters such as this part of the Libyan coast, where winds are usually moderate, the wind speed can be a major influencing factor in this process (Thorpe, 2000).

The lowest levels of hydrocarbons in sediments were found in samples from the control sites 1 and 2: 40km east of Misurata and Zliten. The highest levels of hydrocarbons in the sediments where found in samples at Khoms (Fig. 2.6). Although there are less pollution inputs from inland sources in the vicinity of Khoms compared with other sites such as Tripoli and Zawia, but most of the municipal sewage in this town is discharged directly into the sea without proper treatment. Samples taken from this site could contain high levels of hydrocarbons that originated from this source of pollution. Another feasible explanation is that the samples could have been taken a short time after a minor oil spill incident in the seaport or in the neighbouring area. Unfortunately such incidents are rarely reported in Libya and are difficult to trace.

It was noted that the concentrations of hydrocarbons increase towards the west (Fig. 2.7). Factors such as the presence of more inland pollution sources (i.e. oil refinery and industrial activities), offshore oil production in the western area, and the pattern of sea currents are likely to account for this finding (Fig. 2.2).

There is a gradual increase in hydrocarbon concentration towards the western sites (Fig. 2.7). This pattern excludes the sites that are in the immediate vicinity of localised pollution sources such as the municipal sewage outlets and the seaports. Such sites are under the direct influence of pollution inputs and therefore may not probably represent the general distribution pattern of hydrocarbons in the study area.

It was found that there is a clear pattern of hydrocarbon increase in the seawater towards the west while it is not very clear in the sediments (Fig. 2.7). This probably can be explained by the behaviour of oil in the sea and the direction of water currents adjacent to the coastline of the study area (Fig. 2.2). Part of the hydrocarbons that enter the sea is deposited on the seabed and mix with sea sediments for some time, other parts remain suspended in the water column (Shelton, 1971). Parts which are suspended in the water column can be carried in any direction according to the prevailing current, and may be transported over hundreds of kilometres (Noji *et al*, 2002; Witt, 2002).

It is thought that the most important factor in this particular process is the pattern of the currents in the surface waters adjacent to the coastline. Thus, the sea currents in this part of the Libyan coast carry the hydrocarbons that are suspended in the water column from the eastern sites towards the western sites such as Khoms, Tripoli and Zawai.

Levels of hydrocarbons were much higher in seaports compared with the neighbouring areas particularly in the sediments (Fig. 2.8). Oil product loading operations, activities in maritime workshops, and other daily work practices are the main inputs of oil pollution in the Libyan ports (Tluba, 1991). Seaports, as semi enclosed basins, retain pollution due to less interaction with the open sea. Hydrocarbons degrade faster in the open sea (Zobell, 1972) because of mixing and oxygenation through the movement of sea currents and the wave action (Santas & Santas, 2000).

Apart from seaports, levels of hydrocarbons were much higher both in seawater and sediments in most of the cities compared with the neighbouring areas (Fig. 2.9). Pollution sources such as municipal sewage discharges and industrial activities are concentrated in cities. Inputs from these sources are probably the main cause of this finding.

The highest levels of hydrocarbons in seawater (except for seaports) were found in the vicinity of Zawia (Fig. 2.9). It is thought the presence of an oil refinery in this city is responsible for this finding. Unexpectedly, the highest level in sediments (expect for seaports) was found in Khoms (Fig. 2.9). Khoms is a relatively small city with a smaller population and fewer pollution sources in comparison with cities like Tripoli or

Zawia. This site contained the highest concentration of hydrocarbons in the sediments but not in the seawater, which may suggest that this is a result of a single pollution incident occurred sometime before sampling.

Frequent input from stationary sources such as an oil refinery or sewage discharges would ensure the presence of high levels of hydrocarbons in the water column as well as in the sediments. On the contrary, a single incident would release hydrocarbons in the sea which part of it will, eventually, degraded by various processes or carried away the prevailing sea current (Noji *et al*, 2002; Witt, 2002). Other parts will deposit in the seabed and mix with the sediments, thereby remaining for a longer time (Noji *et al*, 2002; Shelton, 1971; Zobell, 1972).

It was noted that the levels of hydrocarbons in both seawater and sediments at Zawia (Fig. 2.9) were the highest among all sites, except for seaports. The high levels of hydrocarbons in the seawater and in the sediments of Zawia may be attributable to frequent inputs from the oil refinery.

CHAPTER THREE: OIL POLLUTION REDUCING MEASURES: AN EXAMPLE OF SOUTHAMPTON WATER AND ITS APPLICABILITY TO THE LIBYAN WESTERN REGION

Chapter Three: Oil Pollution Reducing Measures: An Example of Southampton water and its applicability to the Libyan western Region

3.1 Introduction

Southampton Water has a long association with the oil industry from the 1920s when a small scale oil refinery was constructed on the estuary's bank (Knap, 1978). Oil refining in Southampton was expanded by the construction of a new refinery in 1951 and the expansion continued over the years until the late 1970s, when the total refining capacity reached just under 20 million tonnes per year, making it one of the largest refineries in the world (Lockwood, 1986). Oil refining, along with other industries such as the power station and the chemical industries on the western shore of the estuary (Fig.3.1), are considered the main sources of oil pollution in Southampton Water (Williams, 1996).

A programme was initiated in the 1970s to reduce the oil input in the effluent water discharged into Southampton Water (Dicks, 1977; Dicks & Iball, 1981; Dicks & Hartley, 1982). A programme like this is very much needed in Libya where oil pollution, especially in the western region, is a growing and ongoing problem, as discussed in the previous chapter. Oil refineries such as the Zawia refinery, have significant contribution to the oil pollution problem in Libya. Oil pollution can have significant adverse effects on the environment unless suitable measures are taken to reduce the amount of oil entering the environment. The measures taken to reduce oil pollution in Southampton Water can be used as an example that may be applied to the Libyan case.

The purpose of this chapter is to study improvements in oil pollution levels in Southampton Water by comparing past and recent levels, and to investigate measures taken for reducing oil pollution in Southampton Water and the applicability of such measures to the Libyan situation.

3.2 Measures taken to reduce oil pollution in Southampton water

An ongoing programme was initiated during the 1970s at the Fawley refinery to reduce the oil input in the effluent water discharged into Southampton Water (Dicks, 1977; Dicks & Iball, 1981; Dicks & Hartley, 1982). The ongoing programme included the incorporation of several managerial and technical improvements (Field Studies Council, 1994). These measures have been proven to be effective and have reduced the oil content in the refinery effluent (Esso & ExxonMobil, 2000). In 2000, the oil content in the refinery effluent has been reduced to 35% compared with 1995 (Esso & ExxonMobil, 2000).

The measures taken to reduce oil pollution from the refinery (Field Studies Council, 1994) included:

- Reduction of the flow of the effluent water from the refinery and improvement of quality.
- Commissioning of an effluent water filtration plant capable of reducing the oil content in the effluent by about 97%. The filtration plant passes the effluent through beds of anthracite and sand to remove oil and solids prior to the discharge.
- Treating all oil process water from the refinery units.
- Implementing efficient operating measures that have improved the effluent quality. Such measures included training personnel on how to avoid leaks and spills that may occur during various operation activities, and modifications in the production processes that reduce the amount or toxicity of wastes that are generated.

3.3 Sampling Procedure

Surface sediments were taken by means of a metal grab deployed by a clean rope. The grab was allowed to free-fall to the seabed at stern of the boat. The grab then was brought inboard each time and its contents transferred to clean aluminium trays using a metal trowel. The trays were washed by acetone prior to sampling to avoid contamination. The trays were sealed with aluminium lids and stored in the freezer below -15 °C immediately. The sampling process was performed to follow recognised sampling procedures (Law *et. al*, 1988).

Twenty four samples were taken from locations in Southampton Water (Fig. 3.1). Replicate samples were taken from each site. Positions of sampling sites were taken by means of an onboard Magellan GPS unit. Depths were measured by means of an onboard echo sounder (Table 3.1). The sampling sites were chosen, for comparison purposes, to be the same sites used by Knap (1978). Four samples were taken from the nearby site (Beaulieu River) as a control site (Fig. 3.1) for comparison purposes. This site is assumed to be not very polluted as it is relatively far from the industrial and shipping sources of pollution (Knap, 1978) The depth at this site was measured using the grab rope. Samples were taken around high tide.

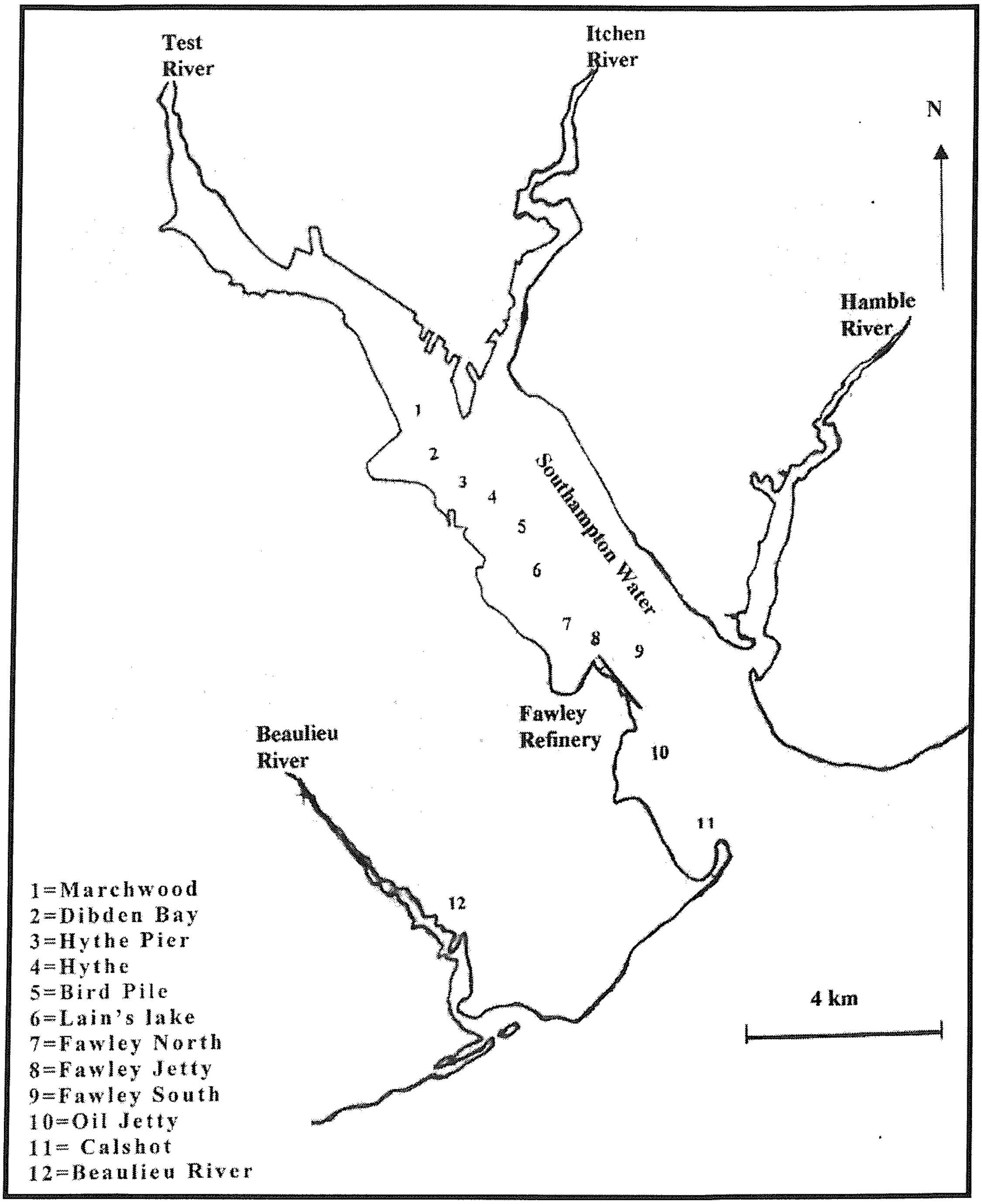


Figure 3.1 Location of the sampling sites and the Esso oil refinery.

Table 3.1 Sampling record for grab samples taken from Southampton water.

Sample No.	Replicates	Latitude	Longitude	Depth(m)	Site Name
1	A & B	50°53.48' N	001°23.64' W	2.40	Marchwood
2	A & B	50°53.12' N	001°24.35' W	3.00	Dibden Bay
3	A & B	50°52.72' N	001°23.98' W	3.00	Hythe Pier
4	A & B	50°52.27' N	001°23.47' W	3.50	Hythe
5	A & B	50°52.02' N	001°23.04' W	3.50	Bird Pile
6	A & B	50°51.66' N	001°23.44' W	3.00	Lain's lake
7	A & B	50°51.43' N	001°21.91' W	3.50	Fawley North
8	A & B	50°51.07' N	001°21.16' W	3.00	Fawley Jetty
9	A & B	50°50.90' N	001°20.69' W	3.00	Fawley South
.10	A & B	50°50.72' N	001°20.27' W	5.00	Oil Jetty
11	A & B	50°50.54' N	001°20.38' W	4.00	Calshot
12	A,B, C&D	-	-	3.00	Beaulieu River

3.4 Analytical Methodology

It is important in a study of this nature to avoid contamination at all stages of the analysis. Therefore all glassware was soaked in a detergent solution for 12 hours, washed with hot water several times, then with distilled water, dried at 50°C, stored until required, and rinsed with pentane immediately prior to use.

Sediments were extracted wet to avoid loss of volatile hydrocarbon material during oven drying or freeze-drying. Since the estuarine samples differ in their water content (Knap, 1978), the expression of the results for sediment samples are usually expressed against dry weight (Law *et. al*, 1988).

The dry weight percentage was determined by using a 65g of separate sub-samples that were weighed, dried at 105°C in an oven for 16 hours, allowed to cool, and weighed again. A mean dry weight percentage was calculated from 6 sub-samples (Table 3.2).

Sub-samples of 25g of well-mixed sediments were placed in a 250ml round-bottomed flask with 3 g of potassium hydroxide, 100 ml of methanol and few anti-bumping granules. Two sub-samples were taken from each separate sediment sample. The samples were then digested for 2 hours using a heating mantle.

The digests were then filtered through Whatman's filter papers that were cleaned with pentane prior to filtration. The filtrates were passed through a separation funnel and extracted with 50 ml of pentane twice. After shaking the first 50 ml pentane extract and allowing it to separate, the bottom layer from the first extraction was collected in a clean flask. The second aliquot of the pentane extract was treated the same way and the two extracts were combined in a clean conical flask. The combined extract was then transferred to a 100ml volumetric flask and made up to 100 ml with pentane prior to Ultra Violet Fluorescence (UVF) analysis.

Standard concentration solutions were prepared using Arabian light crude oil in pentane with one blank solution. The standard solutions were scanned using a Perkin-Elmer LS-5 luminescence spectrofluorimeter. All measurements were made within the linear range of the spectrofluorimeter and a linear calibration plot was obtained (Fig 3.3). Fluorescence intensity is directly proportional (linear) to concentration (Guilbault, 1990). There are, however, factors that may affect this linear relationship such as the chemical composition of the sample and the adjustments of the instrument (Guilbault, 1990). The instrument was set on the following parameters: excitation = 280 nm, emission = 374 nm, delta wavelength = 25, low scan limit = 230, high scan limit = 650, and a scan speed = 240 nm/min.

The sample extracts were scanned using the spectrofluorimeter and the obtained measurements were compared with that of the standard solutions. Samples that exhibit greater fluorescence than the standards were diluted to bring them within the linear range of the calibration plot and the results were calculated taking into account the dilution factors and the dry weight percentage.

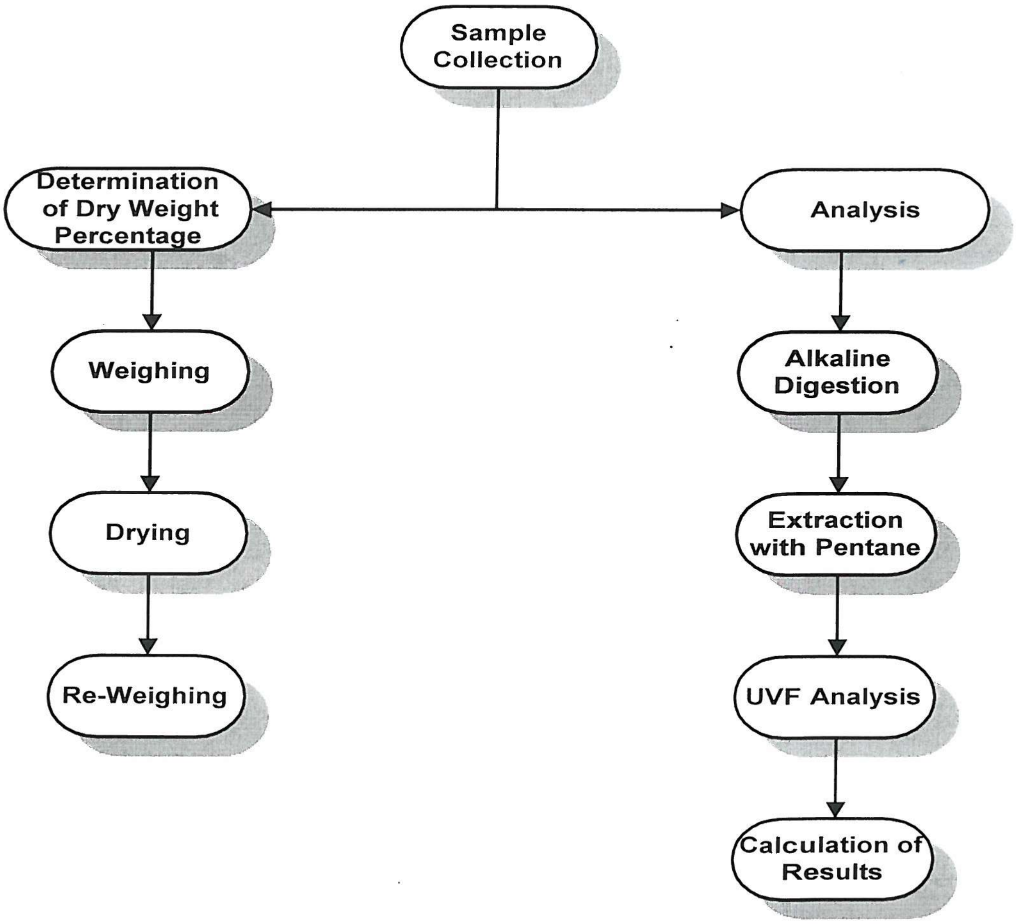


Figure 3.2 Analytical procedure flow chart.

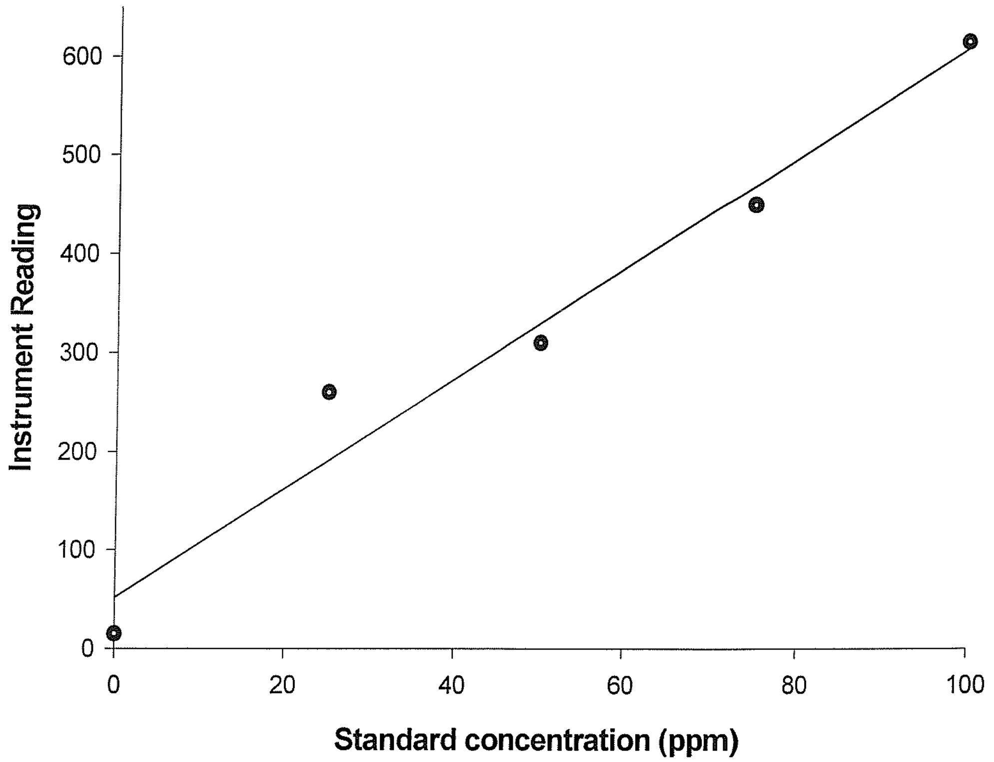


Figure 3.3 Spectrofluorimeter calibration plot (linear regression line, $r^2 = 0.965$) using Arabian light crude oil.

3.5 Results

Dry weights of sub-samples were first determined as described in the analytical methodology. The average dry weight percentage (Table 3.2) was calculated as follows:

D = 100 - [(A – B) 100/A]

Where:

A= Weight of wet sub-sample (g).

B= Weight of dry sub-sample (g).

D= Dry weight percentage.

Table 3.2 Dry weight percentage of sediment samples from Southampton Water

Sub-sample No.	Weight of wet sub-sample (g)	Weight of dry sub-sample (g)	% Dry weight
1	65	36.9	56.7
2	65	40.1	61.6
3	65	38.5	59.2
4	65	38.6	59.3
5	65	38.1	58.6
6	65	39.5	60.7
Average dry weight percentage			59.35 ± 0.695

The concentration of total hydrocarbons was calculated for each sample replicate as Arabian light crude oil equivalent using the linear relation between the instrument reading and the standard concentration (Fig. 3.3) with a regression coefficient $r^2 = 0.965$ according to the following formula:

$$\mathbf{HC = [(\alpha \times R) - \beta]\ D \times F}$$

Where:

HC = Hydrocarbon Concentration ($\mu g\ g^{-1}$) dry weight as crude oil equivalent.

R= Instrument Reading

α = Constant coefficient = 0.180

β = Constant coefficient = 9.353

D= Constant coefficient of weight, dry weight percentage, and volume conversions = 6.739

F= Dilution factor (varies for each sample according to the concentration of hydrocarbons and the need for dilution to keep the linearity of the calibration plot).

Results show a distinct high concentration of hydrocarbons associated with the refinery area (720-1490 $\mu g\ g^{-1}$ dry weight) and much lower concentrations in other parts of the estuary (Table 3.4). Samples from the Beaulieu River, a relatively unpolluted site, showed the lowest values among the results with a mean value of 145 $\mu g\ g^{-1}$ dry weight.

Results were tested statistically using one way analysis of variance (ANOVA - Tukey Test). It was found that there is statistically significant difference between the values of hydrocarbon concentration in the sites that are close to the refinery area compared with the sites that are far from the refinery area (Table 3.3). It also, was found that there is statistically significant difference between the values of hydrocarbon concentration in all of the sampling sites compared with the control site (Table 3.3).

The results have been compared statistically with results of a similar study in 1978 (Knap, 1978) using the "paired t-test". It was found that there is a statistically significant difference between the results of Knap (1978) and the results of this study. It was found that the levels of hydrocarbon in the estuary sediments have decreased significantly in all of the study sites since 1978 (Table 3.4). Only samples from Beaulieu River (the control site) have shown a slight increase in the levels of hydrocarbons.

Table 3.3 A comparison between the values of hydrocarbon concentration at the sampling sites (Based on ANOVA -Tukey Test).

(✔) = Statistically significant difference.

(✕) = No statistically significant difference.

	Marchwood	Dibden Bay	Hythe Pier	Hythe	Bird Pile	Lain's lake	Fawley North	Fawley Jetty	Fawley South	Oil Jetty	Calshot	Beaulieu River
Marchwood	✕	✕	✕	✕	✔	✔	✔	✔	✔	✔	✕	✔
Dibden Bay	✕	✕	✕	✕	✔	✔	✔	✔	✔	✔	✕	✔
Hythe Pier	✕	✕	✕	✔	✔	✔	✔	✔	✔	✔	✕	✔
Hythe	✕	✕	✔	✕	✔	✔	✔	✔	✔	✔	✔	✔
Bird Pile	✔	✔	✔	✔	✕	✔	✔	✕	✔	✕	✔	✔
Lain's lake	✔	✔	✔	✔	✔	✕	✕	✔	✔	✔	✔	✔
Fawley North	✔	✔	✔	✔	✔	✕	✕	✔	✔	✔	✔	✔
Fawley Jetty	✔	✔	✔	✔	✕	✔	✔	✕	✔	✕	✔	✔
Fawley South	✔	✔	✔	✔	✔	✔	✔	✔	✕	✔	✔	✔
Oil Jetty	✔	✔	✔	✔	✕	✔	✔	✕	✔	✕	✔	✔
Calshot	✕	✕	✕	✔	✔	✔	✔	✔	✔	✔	✕	✔
Beaulieu River	✔	✔	✔	✔	✔	✔	✔	✔	✔	✔	✔	✕

According to Knap (1978) high concentration of hydrocarbons were found in sites close to the refinery area such as Fawley and Lain's lake. It was found that the spatial distribution patterns of hydrocarbons in the estuary are similar to those that described by Knap (1978) (Table 3.4). The decrease of hydrocarbon levels in the sediment ranges from 31.6% in Fawley North to 68.1% in Hythe Pier. On the other hand, the increase in Beaulieu River reached 9% (Table 3.4).

Table 3.4 Percentage of change in the levels of hydrocarbons in sediment samples from Southampton Water since 1978. (Positive change indicates increase from 1978 to 2001. No 1978 data for Calshot site.)

Site Name	HC in 1978 as μg g^{-1} dry weight (Knap, 1978)	HC in 2001 as μg g^{-1} dry weight	% change
Marchwood	506.00	285.00 ±8.49	- 43.7
Dibden Bay	540.00	273.00 ±4.24	-49.5
Hythe Pier	760.00	243.00 ±28.28	-68.1
Hythe	750.00	350.00 ±12.73	-53.4
Bird Pile	1377.00	673.00 ±7.07	-51.2
Lain's lake	2416.00	1490.00 ±12.73	-38.4
Fawley North	2063.00	1412.00 ±24.04	-31.6
Fawley Jetty	1506.00	720.00 ±2.83	-52.2
Fawley South	2671.00	1220.00 ±36.77	-54.4
Oil Jetty	1287.00	640.00 ±41.01	-50.3
Beaulieu River	132.00	145.00 ±4.24	+9

3.6 Discussion

Concentrations of hydrocarbon in the sediments were much higher in sites nearer to the refinery and the concentrations become lower gradually away from this source of pollution. There are distinct high levels of oil pollution associated with the refinery area (Table 3.3; 3.4), which indicates the impact of the polluted effluent from the refinery that have been discussed by several studies (e.g. Savari, 1988; Knap, 1988; Dicks & Iball, 1981).

All sites have shown a marked decrease in oil pollution levels since 1978. The lowest percentage of decrease since 1978 (Table 3.4) was in Fawley where the refinery effluent, presumably, would have the highest impact as it is the nearest site to the refinery outfalls. The percentage decrease was higher in sites that are far from the refinery area. This probably suggests that the refinery effluent still have an impact on the area close to the refinery but to a lesser degree compared to 1978.

The increase in the Beaulieu River is low but may indicate the possibility of further increases in the future. Although the Beaulieu River is a relatively unpolluted site because it is relatively far from large sources of oil pollution such the refinery, it may still receive small inputs of hydrocarbons from other sources such as the extensive use of boats in the river.

The strong affinity of hydrocarbons for sediments and other particulate matter makes them accumulate to much higher concentrations on the sediments than in overlying waters (Kennish, 1998). Some studies suggest that the analysis of hydrocarbons in the sediments can serve as an index of hydrocarbon input rates to the marine environments (Guzzella &De Paolis, 1994).

The concentration of hydrocarbons present in the sediments should give an idea of the impact of the refinery on Southampton estuary as a whole (Knap, 1978). Thus, the large decrease in hydrocarbon levels in the sediments since 1978 should reflect directly the effectiveness of the measures taken to reduce oil pollution in the estuary. The rate of change cannot, however, be inferred without a more finely resolved series of measurements over an extended period.

Based on the case of Southampton Water, results of any changes in Zawai refinery to reduce the inputs of oil into the sea may take several years before any improvements can be noticed.

By comparing the refinery in Fawley and the refinery of Zawia (Table 3.5) it is thought that the measures taken to reduce oil pollution in the estuary of Southampton can be used in Libya to reduce the hydrocarbon input from the Zawia refinery. Factors such as the geographical location and the refinery capacity of Zawia could make the measures even more effective if applied in Libya. Unlike the refinery in Fawley, Zawia refinery is located on an open sea where its effluent is discharged. The impact of oil pollution and the sedimentation process in the open sea is much less than in closed or semi-closed systems like Southampton Water (Sharma *et al*, 2002; Shelton, 1971; Zobell, 1972).

A filtration plant such as the one used in Fawley refinery which can reduce the oil content in the effluent to 97% (Field Studies Council, 1994), can reduce inputs of oil into the sea if applied to the refinery of Zawia. Thus, the technical and operational improvements made in Fawley refinery to reduce oil pollution in Southampton Water can be effective if applied to Zawia refinery and probably would reduce the chronic inputs of oil from the refinery.

Table 3.5 comparing the Zawia refinery and Esso Fawley refinery. (bpd = barrel per day).

Refinery	Zawia	Esso - Fawley
Location	Open sea (The Mediterranean)	Estuary (Southampton Water)
Refining Capacity	120 bpd	317 bpd
Seawater use	Cooling system	Cooling system
Quantity of seawater used for cooling	90,000 tonne/day	250,000 tonne/day
Highest Hydrocarbon Concentration in sea sediments within 3km radius	1499 ppm	695 ppm
Filtration plant	None	Filtration of effluent water through beds of anthracite and sand.

CHAPTER FOUR: DEPOSITION OF TAR ON THE LIBYAN COAST

Chapter Four: Deposition of tar on the Libyan Coast

4.1 Introduction

Tar deposition on the beaches is likely to have considerable effects on many coastal communities. There is evidence that the deposition of oil on coastal areas affects turtle eggs as well as other species (Bishop *et al.*, 1998). Mollusc communities, for example, can be directly affected by deposition of tar (Nagelkerken & Debrot, 1995). The Libyan coast is probably the most affected by the deposition of tar in the entire Mediterranean. It is estimated that the Libyan coastline receives about 2,000 tons of tar every year (El-Ghirani, 1981), which could cause significant damage to the communities and species on its sandy beaches and rocky shores.

The Libyan beaches are the most important nesting places for endangered species of marine turtles in the Mediterranean (Patel, 1995) which include the loggerhead turtle (***Caretta caretta***), the green turtle (***Chelonia mydas***), and the leatherback turtle (***Dermochelys coriacea***) (Laurent *et al.*, 1998). The Libyan coast includes the second largest Mediterranean sea grass meadows, which provide important nesting and feeding areas for marine turtles and other Mediterranean species (Patel, 1995).

The importance of studying the distribution of tar on the Libyan coast arises from three main reasons. Firstly, beaches are an important and common habitat along the Libyan coast (El-Ghirani, 1981) on which pollution could have a great impact. Secondly, the pattern of tar distribution can be a good indicator of the extent of exposure of the coast to oil pollution (El-Ghirani, 1981). Thirdly, the study can provide information on the extent of environmental impact.

The purpose of this chapter is to estimate the existing levels of tar deposition on the sandy beaches and the rocky shores, to study their geographical and spatial distribution patterns, and to measure the increment of tar on the sandy beaches over time.

4.2 Methodology

The western coast of Libya is a combination of rock and sand plateaux (DNV, 2001; Laurent *et al.*, 1998). In order to assess the impact of oil pollution on this part of the Libyan coast, it is important to study the deposition of tar on the sandy beaches as well as on the rocky shore.

These coastal habitats have different physical and biological characteristics and therefore vary in their vulnerability to oil pollution (Hayes *et al.*, 1992; Owens and Robilliard, 1981).

Therefore different techniques were used for the estimation of tar deposition on sandy beaches and on rocky shores.

4.2.1 Sandy Beaches

The method used by El-Ghirani (1981), which is the only published work about the distribution of tar on the Libyan coast, was used as a guidance in order to obtain comparable results, but with some adaptations. The method used in this study is a combination of the techniques used by El-Ghirani (1981) and that described by Demetropoulos (1986).

In order to study the pattern of distribution and to obtain comparable results, study sites were selected according to defined criteria. To avoid artificial change of the distribution of tar balls, beaches were selected where little or no public activity occurs. It was decided to study beaches with a width as close as possible to 25m perpendicular to the water edge. It was observed during the fieldwork that this distance is the upper-most point that waves could reach on the beaches of the study area. In beaches where there are many irregular configurations, it was decided to collect samples where there was the smallest possible change in the structure of the beach such as in the middle of a bay or away from any protecting rocks.

Four straight lines or transects, 25m each, were marked perpendicular to the water's edge in each sampling site (Demetropoulos, 1986). Lines were five metres apart. Tar balls were picked up and weighed for every square metre along each line using a $1m^2$ wooden quadrat. The quadrat was rolled over the marked line to the top of the beach making square number one as the closest to the water edge and the following ones being numbered consecutively.

In each square metre, all tar balls were picked up by hand and weighed using an electronic balance. Tar balls were collected at the surface of the sand and to a depth of 5cm. No attempt was made to collect tar balls buried deeper than 5cm.

Tar balls were weighed individually and the average weight of tar balls was calculated for each sampling site. The diameter of each tar ball was measured using an ordinary vernier calibar and the average size of tar balls was calculated for each sampling site.

Accumulation of tar: All tar balls were removed from the sampling sites during the survey, and the increment of tar deposition was measured in exactly the same locations after one-month using the same technique. Sampling areas were the same as used to study hydrocarbon concentration in seawater and sediment (Fig. 2.3).

4.2.2 Rocky shores

Despite an extensive search in the relevant literature, no standard technique on the estimation of tar deposition on rocky shores was found. Therefore a technique was developed to estimate the percentage cover of tar deposited on the Libyan rocky shores. However, Nagelkerken & Debrot (1995) described a similar technique for the estimation of tar cover on rubble shores.

A wooden quadrat ($1m^2$) was used to estimate the percentage cover of deposited tar. The quadrat was divided into 100 small squares by plastic strings making each square 10 cm^2. The division of the quadrat to small squares gives more accuracy when estimating the percentage of tar covering the rocky shores. Each small square represents 1 % of the quadrat area. Thus, the quadrat would give a direct and more accurate estimate of the percentage cover of tar.

Four transects were selected randomly in each sampling site. In each transect a perpendicular line from the water's edge was marked on the bedrock platform. Each sampling transect was 4m long. This is the average length of bedrock platform in the study area. The quadrat was rolled over along the marked line and the percentage of tar covering the rocks was estimated for each square metre.

As the purpose of this study was to look at the spatial distribution and to estimate tar cover on the rocky shore, this technique was found more appropriate for this kind of survey. Unlike the random quadrat-throwing technique that is used in ecological surveys, the practice used in this survey would give information on the spatial distribution of tar from the water's edge to the end of the bedrock platform. The sampling areas were the same as those used to study the hydrocarbon concentration in seawater and sediments (Fig. 2.3).

4.3 Results

Sandy beaches: Tar abundance on sand beaches was higher in the vicinity of Zawia, Misurata and Tripoli. Tripoli had the highest tar abundance among all sites. Tar abundance ranged from an average of 2.23 gm^{-2} in Tajora to 24.45 gm^{-2} in Tripoli. Although the abundance of tar was higher in some sites and relatively low in others, no clear pattern of geographical distribution of tar balls was apparent (Fig.4.1A).

The spatial distribution of tar balls on sand beaches varied at each site. Tar balls were not found at the immediate proximity of the water line. The distribution of tar balls ranged from 1m to 16m from the water's edge. Tripoli had the highest distribution range, 3 m to 16 m. The nearest tar balls to the water were found in Zawia at one metre from the water's edge (Fig.4.1B). The average weight and size of tar balls differed from site to another and were thought to have a direct effect on the spatial distribution of tar balls. Therefore the average weight and diameter of tar balls was compared against the distribution range in each site (Fig.4.1C,D).

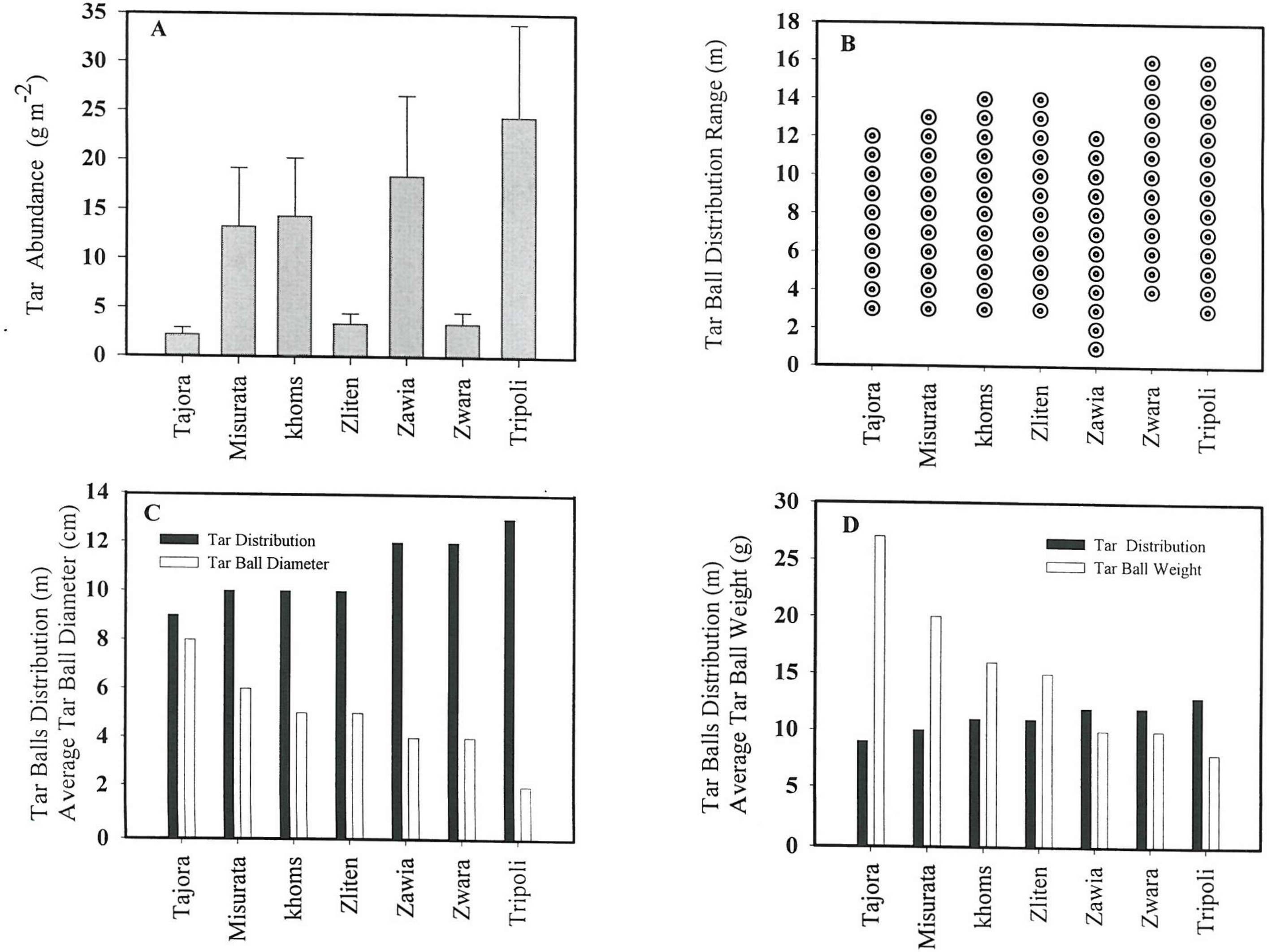


Figure 4.1 Tar abundance and distribution patterns on sandy beaches. (Sub-graphs: A= tar abundance at the sampling sites. B= tar balls distribution at the sampling sites. C= tar balls distribution (maximum distance from water's edge) versus tar ball size. D= tar balls distribution (maximum distance from water's edge) versus tar ball weight.

Tar ball increments on sandy beaches:

New tar balls were deposited at some of the sampling sites after one month. The increment of tar on sand beaches in a one-month period was low in all sites. The highest increment value was in Khoms. The incremental increase of tar on sand beaches ranged from zero increment in Zliten and Tajora to 20g in Khoms (Fig. 4.2). Tar balls during the one-month increment period were not found at the immediate proximity of the water line, from 2m to 3m from the water's edge (Fig. 4.2).

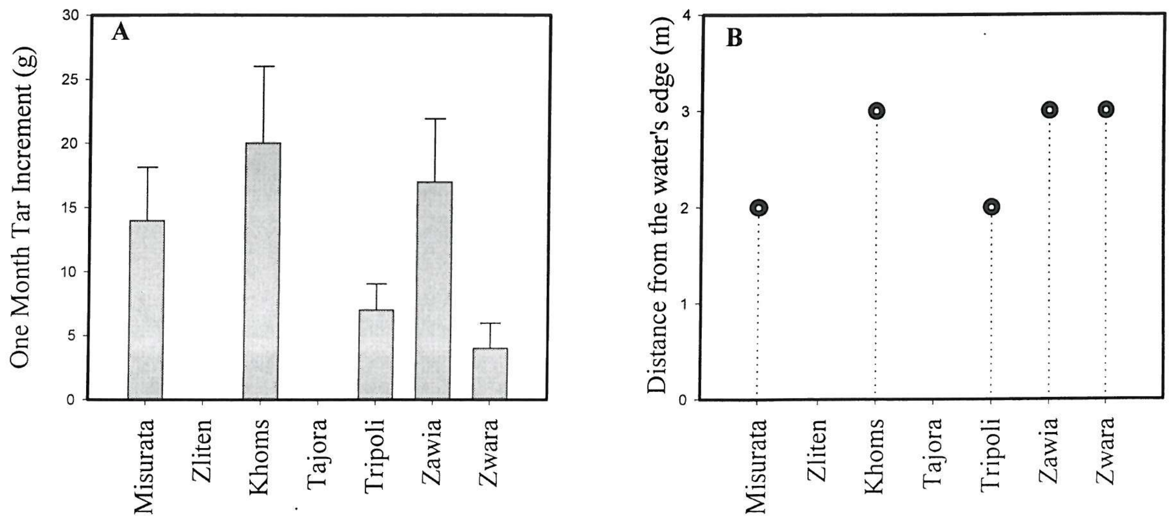


Figure 4.2 Tar increment and distribution on sandy beaches (in one-month period / July-August 1999). (Sub-graphs: A= the increment of tar balls at the sampling sites, vertical bars show standard error. B= Distribution of tar balls, the symbol "⊙" represents tar balls.

Rocky shores: The percentage cover values of tar on rocky shores in 1m^2 ranged from 13.5% to 37.9%. The highest value was on the rocky shores of Tripoli while the lowest value was in Tajora (Fig. 4.3). Zliten, Tajora, and Zwara had much lower values compared to other sites.

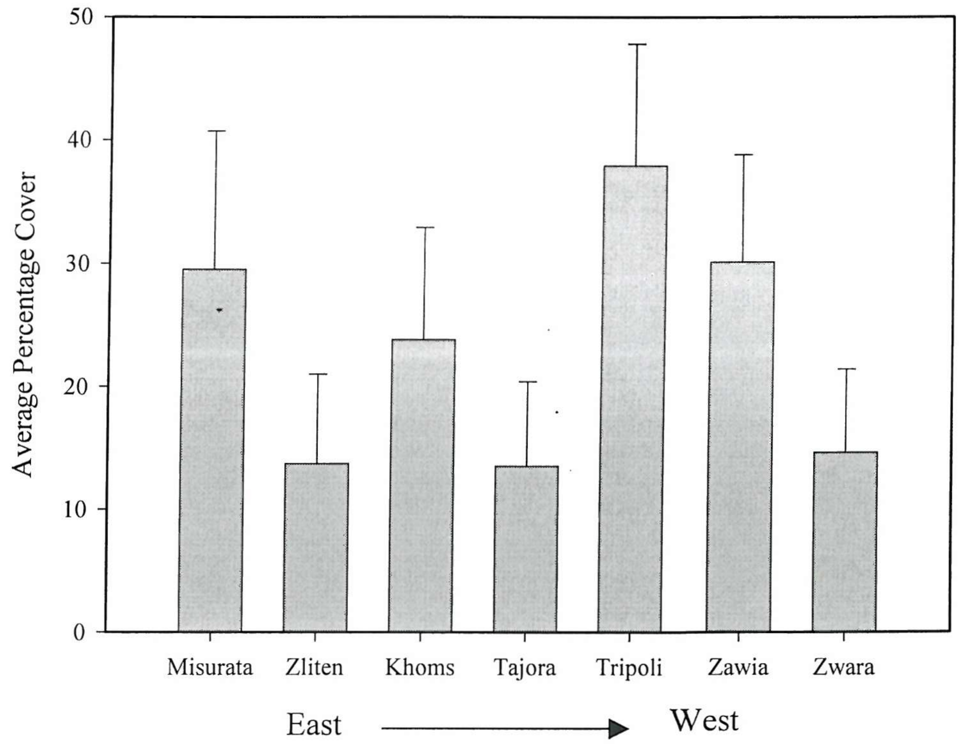


Figure 4.3 Tar abundance on rocky shores. (Vertical bars show standard error)

Higher tar percentage cover values were recorded for rocks near the water's edge in all sites. The values became lower as the distance from the water's edge increased (Fig 4.4). This pattern is clearer in Tajora and Zliten where the average percentage cover values are lower compared with other sites.

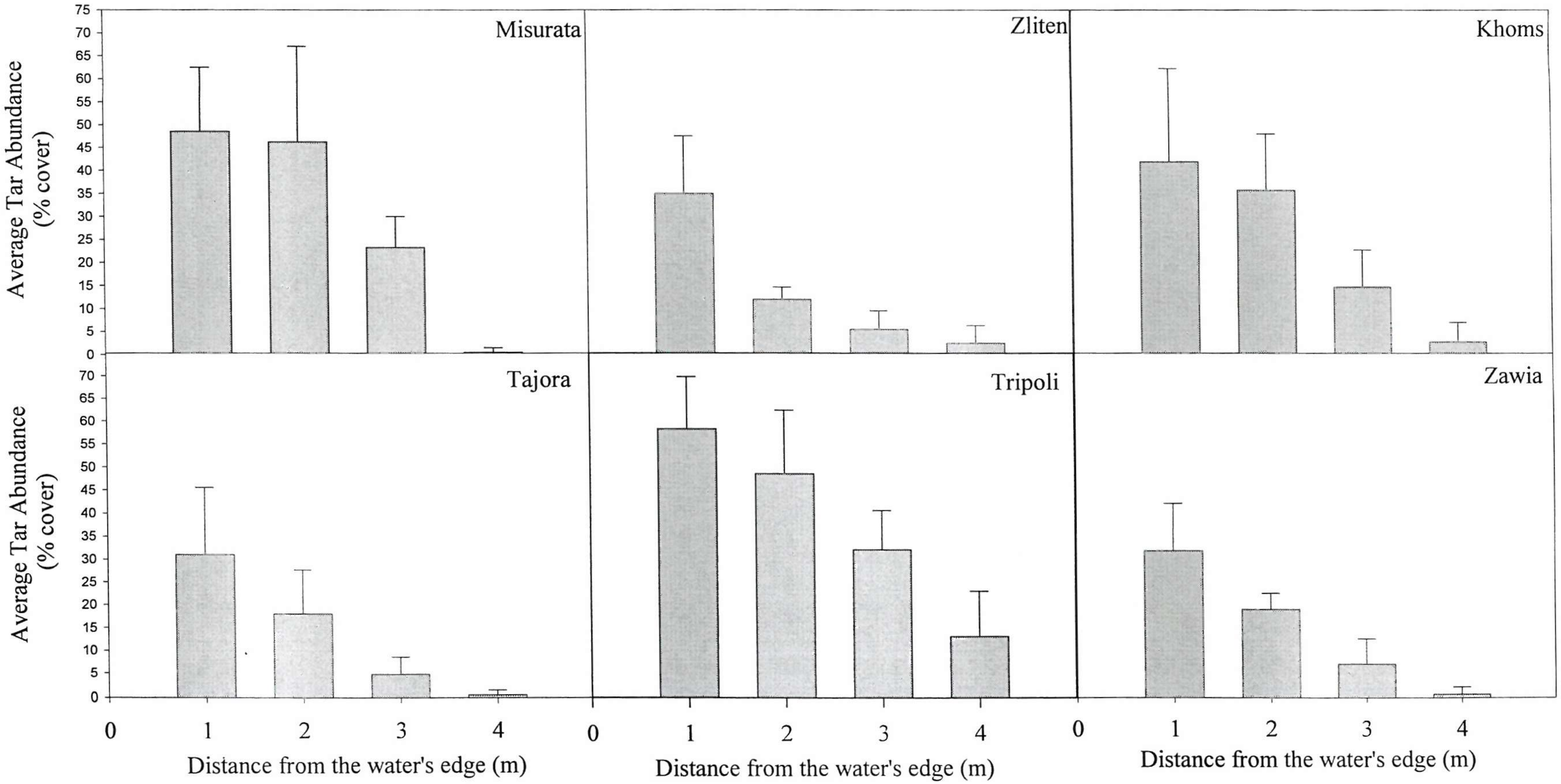


Figure 4.4 Tar distribution patterns on rocky shores at the sampling sites. Abundance of tar on rocky shores plotted versus the distance from the water's edge. Vertical bars show standard error.

4.4 Discussion

Tar abundance on sand beaches was higher in the vicinity of Zawia and the cities of Khoms, Misurata and Tripoli (Fig.4.1). The presence of an oil refinery in Zawia and big seaports in Misurata, Khoms, and Tripoli probably explain this finding. The high values of tar abundance on sand beaches near to these site indicates the direct effect of oil processing and transportation activities on the deposition of oil residues on the beaches (Aybulatov *et al,* 1981).

Abundance of tar on sand beaches was higher in the vicinity of Zawia oil refinery and cities with seaports (Fig.4.1). This probably indicates that the effect of the localised pollution sources on the deposition of tar on beaches. Other factors such as the sea currents and the geographical characteristics of the area may affect this process (Golik *et al,* 1988). However, patterns of geographical distribution of tar on the Libyan coast can be linked to various factors including the location of oil loading terminals and seaports, the presence of the international deballasting zone, and the proximity of city's sewage (El-Ghirani, 1981).

The topography of the location such as the presence of a line of rocks standing in inshore waters or the presence of small islands can affect the distribution and deposition of tar on the coast.

Rocky peninsulas in certain positions, especially when horizontal to the sea currents, may act as natural barriers that prevent tar balls from reaching beaches. On the contrary, a peninsula or a bay in another position could form a location where tar balls get trapped (Nielsen, 1999). Field observations support this hypothesis.

On all sand beaches, tar balls were not found at the immediate proximity of the water-line and the spatial distribution varies accordingly for each site (Fig. 4.1). Many factors may effect the spatial distribution of tar on beaches (Al-madfa *et al*, 1999; Irvine *et al*, 1999; & Guidetti *et al*, 2000). At all the sampling sites, weight and size of tar balls were the most feasible factor affecting the spatial distribution. In sites where the average tar ball diameter was the smallest, the distribution range of tar balls was the highest and vice versa. The same applies to the tar ball weight (Fig. 4.1).

The increment of tar on sand beaches after a one-month period was low in all sites but the values were higher in those near the source of pollution such as the Zawia oil refinery and cities with seaports such as Misurata, Khoms and Tripoli. On the contrary, other sites such as Zliten, which are relatively far from pollution source, have no new tar added over the period of observation. This indicates the influence of localised pollution sources on the deposition of tar on the beaches (Fig. 4.2).

Tar balls were not found at the immediate proximity of the water-line after the observation period (Fig 4.2). This pattern is the same as when these sites were previously surveyed. This suggests that wave action keeps the tar balls two or three metres away from the water edge even in summer season when the sea is usually calm.

The arrival of tar can be effected by many factors such as the movement and direction of sea currents and the occurrence of oil spill incidents (Al-madfa *et al*, 1999; Aybulatov *et al,* 1981; Golik *et al,* 1988; & Guidetti *et al*, 2000; Irvine *et al*, 1999). Thus, although the increment was low during the one-month period, it can be much higher at other times.

Considerable areas of the bedrock platforms were covered by tar. The tar was deposited in form of patches or pellets (Plate 4.1). The abundance of tar on rocky shores was the most in Tripoli, Zawia, Khoms and Misurata compared with other sites (Fig. 4.3). These four sites accommodate many activities such as oil refining, and marine transportation. Moreover, these cities have a higher population compared with the other sites. All these factors can be linked to the high amounts of tar deposited on the rocky shores of these sites.

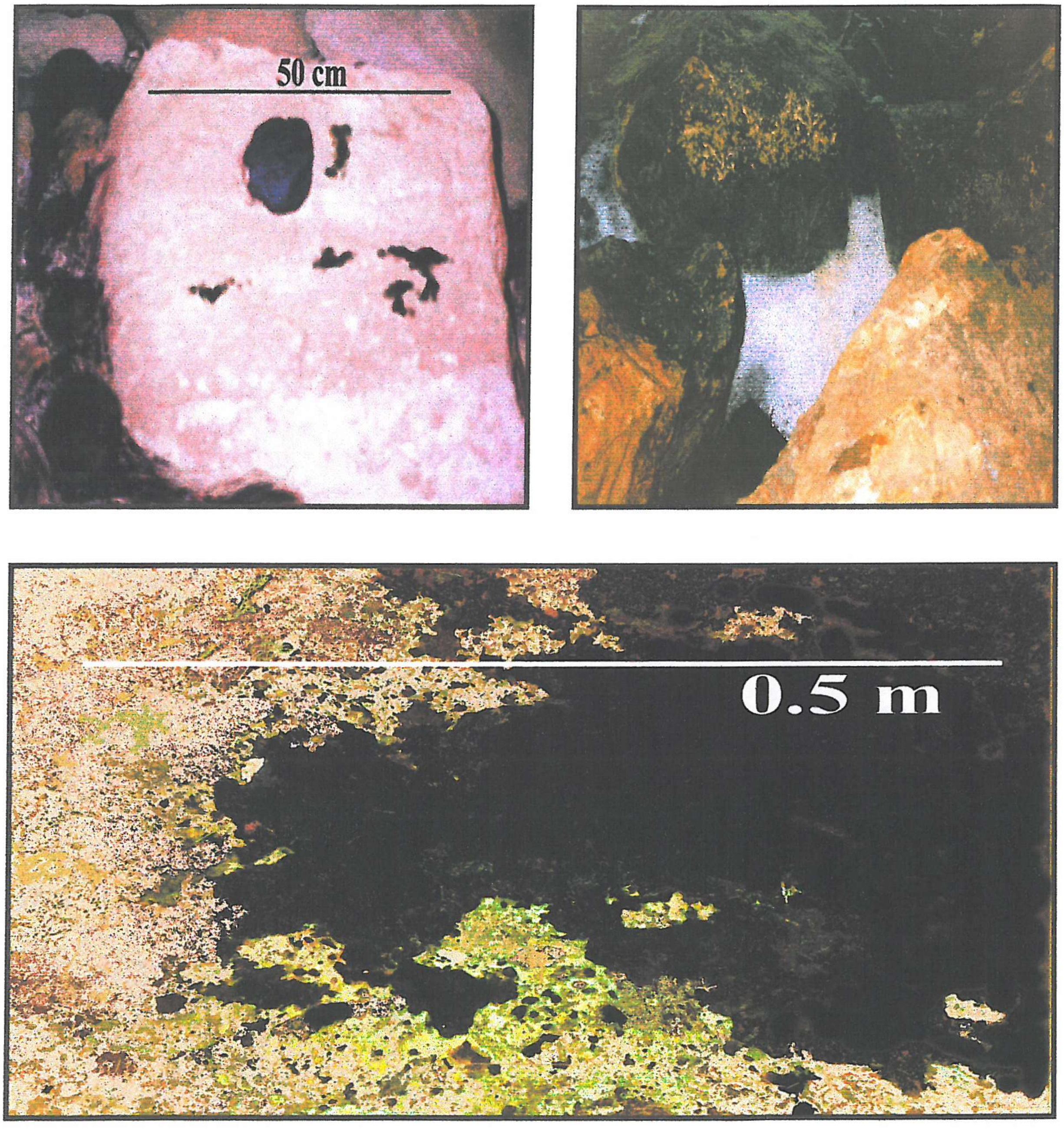


Plate 4.1 Tar deposited on rocky shores in different forms and different distribution patterns.

There is a clear pattern of spatial distribution of tar on the rocky shore at all sites. This pattern is recognised by the gradual decrease of tar abundance as the distance from the water edge increases (Fig. 4.4). Unlike sandy beaches, rocky shores have more of tar on the immediate proximity of the water's edge (Fig. 4.4). This probably can be explained by the fact that wave action has a limited effect of the distribution of tar on the rocky shores in comparison with the sandy beaches. The wave action loses its effect on tar balls when they hit the first rocks in the immediate proximity of the water edge. The tar balls then get trapped on the uneven surface of the bedrock platform and accumulate over time. This would cause more accumulation of tar on the rocks near the water's edge compared with the rest of the bedrock platform away from the water. This hypothesis is strongly supported by the findings of the survey and field observations.

CHAPTER FIVE: IMPACT OF OIL POLLUTION ON ROCKY SHORES

Chapter Five: Impact of oil pollution on rocky shores

5.1 Introduction

Rocky shores are a prominent feature of the world's coastlines and play an important role within coastal ecosystem (Clark, 2001; Hawkins & Jones, 1992). Many studies suggest that discharges containing hydrocarbons have a considerable effect on rocky shore communities (Forde, 2002; Raffaelli & Hawkins, 1999; Newey & Seed, 1995; Suchanek, 1993; Terlizzi *et al*, 2002). The effects of manmade or natural disturbances on a particular site can be predicated once the major components of these assemblages and their interactions have been studied (Hartnoll & Hawkins, 1985; Peterson *et al*, 2001).

This chapter studies the impact of chronic oil pollution on the Libyan rocky shores through an ecological approach. The study is based on the comparison of the abundance of species found on the rocky shores at different sites. The comparison is between heavily polluted and less polluted sites. The geographical and spatial aspects of the environmental impact are also discussed.

5.2 Characteristics of the study area

Although many studies have reviewed the fauna and the flora of Mediterranean coastlines (Gamulin-Brida, 1967; Peres, 1967; Campbell, 1982; Steuber & Loser, 2000), very limited information can be found on the ecology of the Libyan coastal region (Enbyah *et al*, 1986). The works of Huni and Aravindan (1984), Buisa *et al* (1985) and Enbyah *et al.* (1986) appear to be the only published studies on the ecology of the Libyan rocky shores.

As on most of the Mediterranean coastlines, the Libyan shores have very low tidal range. According to the Mediterranean Pilot (1963) tides in the Mediterranean region are of semidiurnal nature with a range of 15 cm. However, during the spring season the mean sea level may vary as much as 0.5 m mainly as result of meteorological changes and wave action (Enbyah *et al*, 1986).

Rocky shores range in their exposure to wave action from exposed to sheltered shores (Davies & Moss, 2002) which effects the distribution of the communities that live on these habitats (Hawkins & Southward, 1992; Lewis, 1964; Raffaelli & Hawkins, 1999; Stephenson & Stephenson, 1972). Based on the European Nature Information System (EUNIS) Habitat classification code, all of the rocky shores in the study area can be described as moderately exposed (Davies & Moss, 2002) with gradually sloping bedrock platforms and irregular surfaces (**McLeod, 1996**) (Table 5.1, Fig. 5.1A-D).

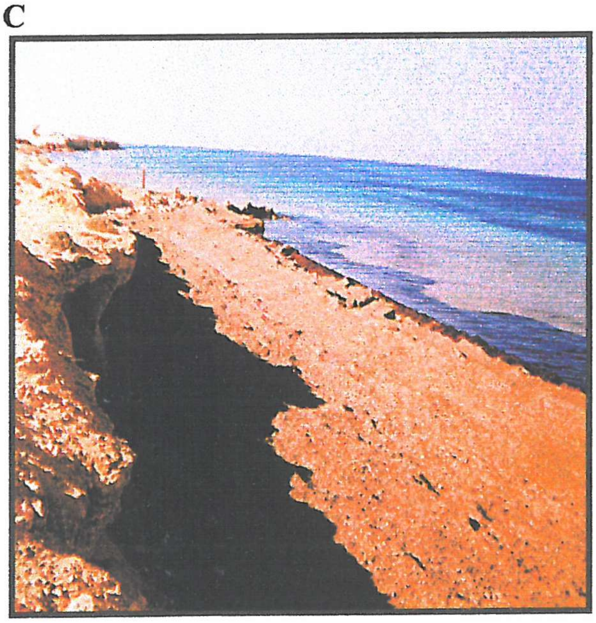
Table 5.1 Description of rocky shores at the sampling sites.

Factor	Description	Definition
Exposure	Moderately Exposed	Moderately exposed coasts is defined as open coasts facing away from prevailing winds and without a long fetch but where strong winds can be frequent (Davies & Moss, 2002).
Topography	Uneven gradually sloping bedrock	Bedrock is defined as any stable hard substratum, not separated into boulders or smaller sediment units **(McLeod, 1996).**
Temp. range around the year (°C)	10 - 42	An average of 4 years (Meteorological Authority, Tripoli, 1994- 1998).

A

B

C



D

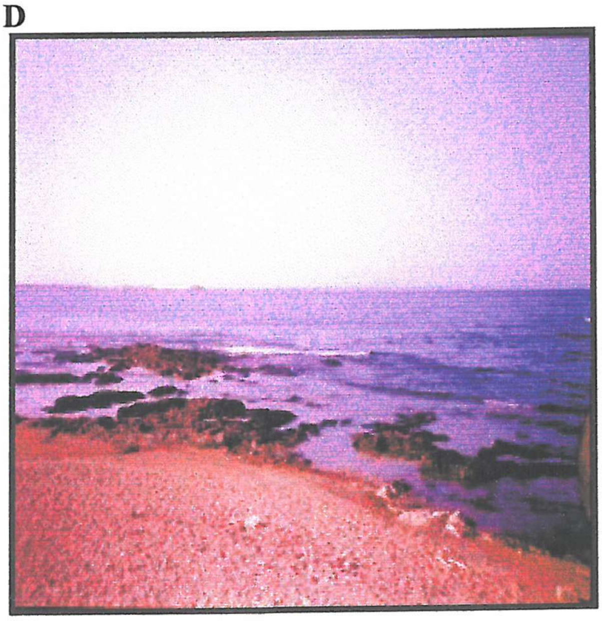


Plate 5.1 Examples of rocky shores in the study area. All sites are moderately exposed, gradually sloping, and have a combination of rock and sand plateaux .

5.3 Methodology

5.3.1 Sampling sites

Six sampling sites were selected to represent heavily polluted and less polluted areas, with two control sites in 30 km east of Misurata (control site 1) and Zliten (control site 2). The control sites were far from pollution sources and considered clean or less polluted. The polluted sites were in Misurata, Khoms, Tripoli and Zawai. These were the same sampling sites that used to study hydrocarbon distribution in seawater and sediments, and the deposition of tar on the coast (Table 2.3).

Spatial distribution of rocky shore communities can be affected by environmental factors such as the exposure of shore to wave action (Hawkins & Hartnoll, 1983; Lewis, 1964; Stephenson & Stephenson, 1972). Moreover, factors such as the slope of the shore and nature of substrata can influence the distribution patterns of these communities, especially in the absence of appreciable tidal amplitude, as in the Libyan coastlines (Enbyah *et al*, 1986). Therefore, sampling sites were chosen to have the same degree of exposure and a similar topography (Table 5.1) to reduce variability that can be caused by these factors.

5.3.2 Sampling method

A square metre quadrat was used to estimate the percentage cover of algae and the numbers of individuals of species existing on the study sites. The quadrat was divided into 100 small squares by plastic strings, making each square 1 % of the quadrat area. The quadrat was thrown randomly on the bedrock platform and the species within the quadrat were counted as individuals and percentage cover was estimated for the algal species.

The sampling was focused on transects extending about 4-6m horizontally from the water's edge. Two transects were selected randomly in each site. Five samples were taken on each transect. The average length of bedrock platform in the sampling sites was 4-6m. This part of the shore is the most affected by oil deposition therefore no attempt was made to survey the bedrock platforms further than 6m from the water's edge.

Five commonly found species on the study area were selected for the survey that included barnacles, periwinkles, limpets and algae (Table 5.2). The selected species were ***Melarhaphe neritoides, Osilinus turbinatus, Chthamalus spp., Patella spp.,*** and macroalgae. Algal species commonly found in the study area included ***Padina pavonia***, ***Enteromorpha intestinalis, Ulva spp., Corallina officcinalis*** and ***Cystoseira spp.*** (Enbyah *et al*, 1986).

The species were counted as individuals within the quadrat including the barnacles (***Chthamalus spp.***). The density of ***Chthamalus spp.*** was very low in the entire sampling sites therefore it was decided to express the abundance of this species as a number of individuals. The algal species were not individually identified but percentage cover of the existing algae was estimated.

These species vary in their sensitivity to oil pollution. Red and green algae as well as limpets, particularly ***Patella spp.,*** are known as highly sensitive to oil pollution (Hill, 2000; Clark, 2001, Glegg *et al*, 1999; & Hawkins & Southward, 1992). Other species such as ***Chthamalus spp.*** have lower degree of sensitivity to oil pollution and hydrocarbon contamination (Riley, 2002).

The seasonal and spatial variations of these species were discussed by Enbyah *et al* (1986). Seasonal variations can affect the results of a study of this nature. The survey took place on July-August 2001 when these species are expected to have maximum densities. According to Enbyah *et al* (1986) the maximum densities of ***Patella spp.*** and algae were observed during May to September. Thus, the effect of seasonal variations was reduced.

Table 5.2 Species commonly found on rocky shores of the study area. (Buisa *et al,* 1985; Campbell, 1982; Enbyah *et al*, 1986; Huni & Aravindan, 1984).

Scientific Name	Common Name	Description
Melarhaphe neritoides	Small Periwinkle	Periwinkle
Osilinus turbinatus	Toothed Winkle	Sea Snail
Chthamalus spp.	Star Barnacle	Barnacle
Patella spp.	Mediterranean Limpet	Limpet
Vermetus triqueter	Worm Shell	Worm Shell
Padina pavonia	Lamouroux Frond	Brown Algae
Enteromorpha intestinalis	Link Frond	Green Algae
Ulva spp.	Sea Lettuce	Green Algae
Corallina officcinalis	Linnaeus Frond	Red Algae
Cystoseira spp.		Brown Algae

5.4 Results

Among the sessile and sedentary species ***Chthamalus spp.*** was the most dominant at all sites while ***Patella spp.*** had the lowest abundance values compared with other species. ***Chthamalus spp.*** ranged from 76 individual m^{-2} in Khoms to 23 individuals m^{-2} in Tripoli while ***Patella spp.*** ranged from 38 individuals m^{-2} in the control site 1 (30 km east of Misurata) to 14 individual m^{-2} in Tripoli (Fig. 5.1).

Melarhaphe neritoides and ***Osilinus turbinatus*** had a similar average number of individuals in all sites. This is clear in control site 1 where the averages were 62 and 64 individuals m^{-2} consecutively, in control site 2 where the averages were 62 and 65 individuals m^{-2} respectively, and in Khoms the averages were 54 and 55 individuals m^{-2} respectively. The highest number of individuals of ***Osilinus turbinatus*** was found in Zliten (control site 2) with an average of 65 individuals m^{-2} while the lowest number of individuals of this species was found in Tripoli with an average of 25 individuals m^{-2} (Fig. 5.1).

Much lower numbers of individuals and percentage cover of algae were found in Misurata, Khoms, Tripoli and Zawia compared with control site 1 and 2. Tripoli had the lowest average number of animals and the lowest average percentage cover of algae among all sites (Fig. 5.1).

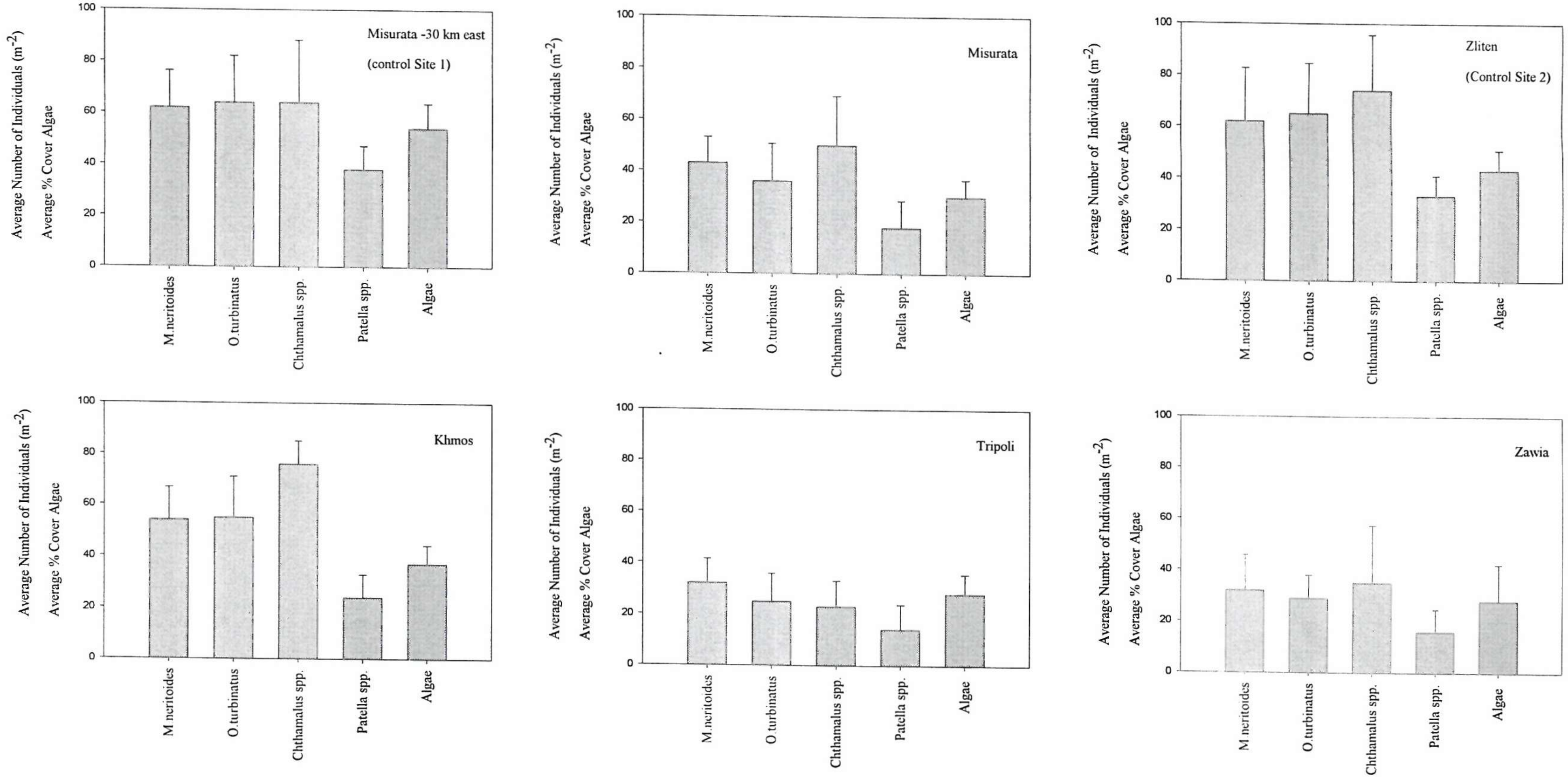


Figure 5.1 Abundance of major species at the sampling sites.
Vertical bars show abundance of ***M. neritoides*, *O. turbinatus*, *Chthamalus spp.***, and ***Patella spp***. as numbers of individuals m^{-2}.
Vertical bars for Algae show abundance of algal species as a % cover.
Error bars show standard error. Averages were calculated for 10 samples in each site.

The number of individuals of ***Patella spp.*** was the lowest in Tripoli with an average of 14 individuals m^{-2} followed by Zawia and Misurata. In Zawia the average number of individuals of ***Patella spp.*** was 16 individuals m^{-2} while in Misurata the mean was 18 individuals m^{-2}. The highest number of individuals of this species was recorded 30 km east of Misurata (control site 1) and in Zliten (control site 2) respectively. The average in control site 1 was 38 individuals m^{-2}, and in control site 2 the average was 74 individuals m^{-2} (Fig. 5.2).

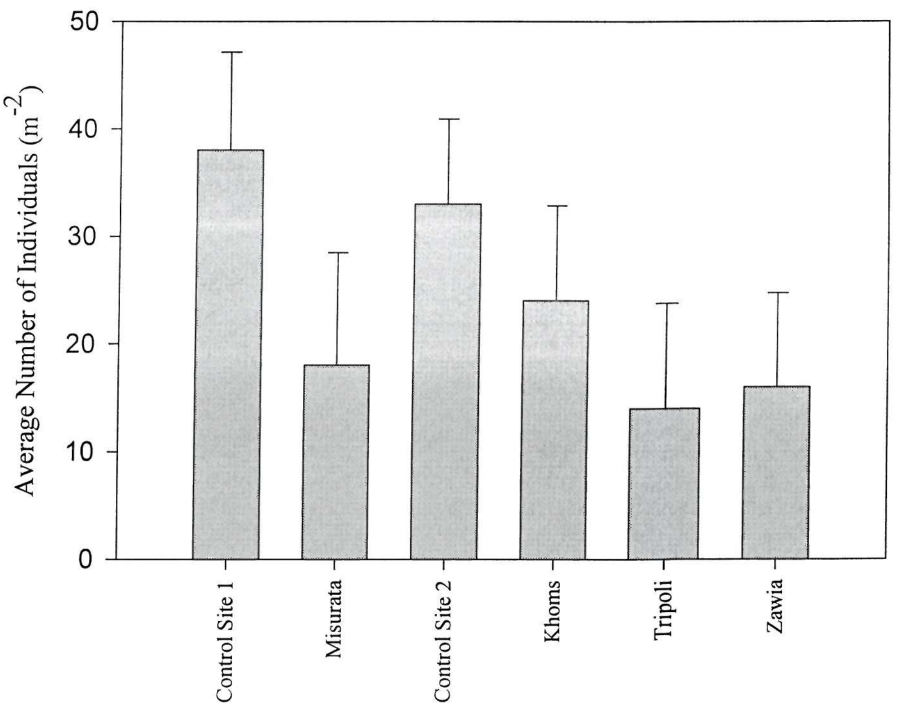


Figure 5.2 Abundance of *Patella spp.* in the sampling sites. Vertical bars show standard error. Averages were calculated for 10 samples.

The abundance values of ***Patella spp.*** were tested statistically using one way analysis of variance (ANOVA - Tukey Test). It was found that there is a statistically significant difference between the mean abundance values of ***Patella spp.*** in both control sites compared with the polluted sites with the exception of Khoms compared with control site 2 (Table 5.3).

Table 5.3 A comparison between the abundance values of *Patella spp.* at the sampling sites based on Tukey Test.

(✔) = Statistically significant difference ($P < 0.05$).
(×) = No statistically significant difference($P > 0.05$).

	Control 1	**Control 2**	**Misurata**	**Khoms**	**Tripoli**	**Zawia**
Control 1	-	×	✔	✔	✔	✔
Control 2	×	-	✔	×	✔	✔

The percentage cover of algae was the lowest in Tripoli and Zawia with an average of 28% in both sites. The highest percentage cover of algae was found in control site 1 (30 km east of Misurata) with an average of 54% (Fig 5.3). In Khoms and Misurata the average percentage cover of algae was 37% and 30% (Fig 5.3).

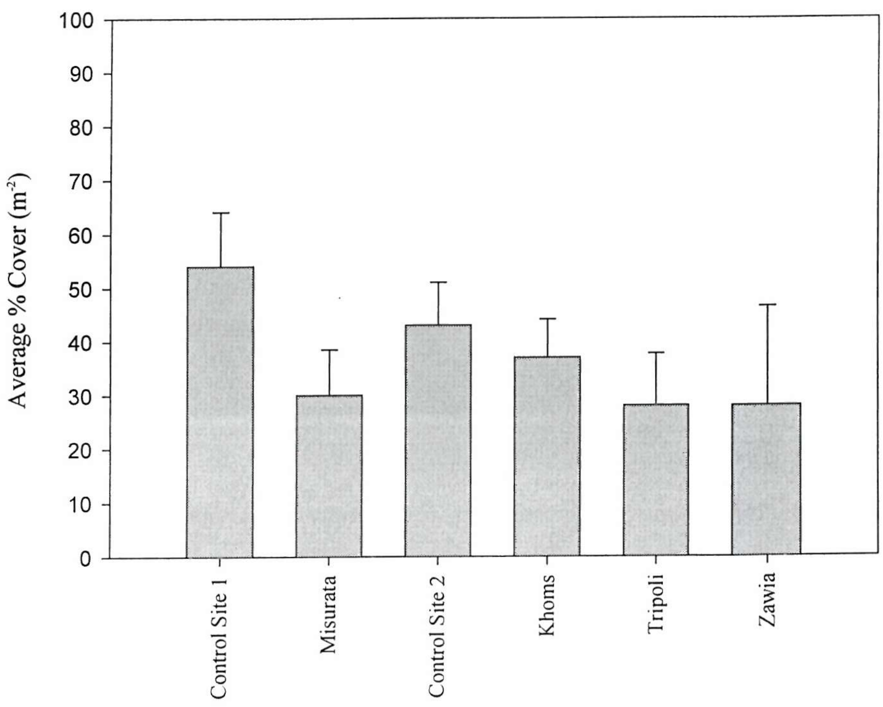


Figure 5.3 Densities of algae cover in the sampling sites. Vertical bars show standard error. Averages were calculated for 10 samples.

The abundance values of algae were tested statistically using one way analysis of variance (ANOVA - Tukey Test). It was found that there is a statistically significant difference between the mean abundance values of algal species in both control sites compared with the polluted sites with the exception of Khoms compared with control site 2 (Table 5. 4). This pattern was the same as the abundance patterns of ***Patella spp.***

Table 5.4 A comparison between the density values of algae at the sampling sites based on Tukey Test.

(✔) = Statistically significant difference ($P < 0.05$).
(✕) = No statistically significant difference ($P > 0.05$).

	Control 1	Control 2	Misurata	Khoms	Tripoli	Zawia
Control 1	-	✕	✔	✔	✔	✔
Control 2	✕	-	✔	✕	✔	✔

Similarities between abundance of all species in the sampling sites were calculated using the Bray-Curtis coefficient. On the Bray-Curtis similarity scale the analysis have shown that the control sites 1 and 2 are the most similar with a similarity value of 96% (Fig. 5.4). Tripoli, Zawia and Misurata are the least similar as a group compared with the control sites 1 and 2 as a group with a similarity value of 83 % (Fig. 5.4).

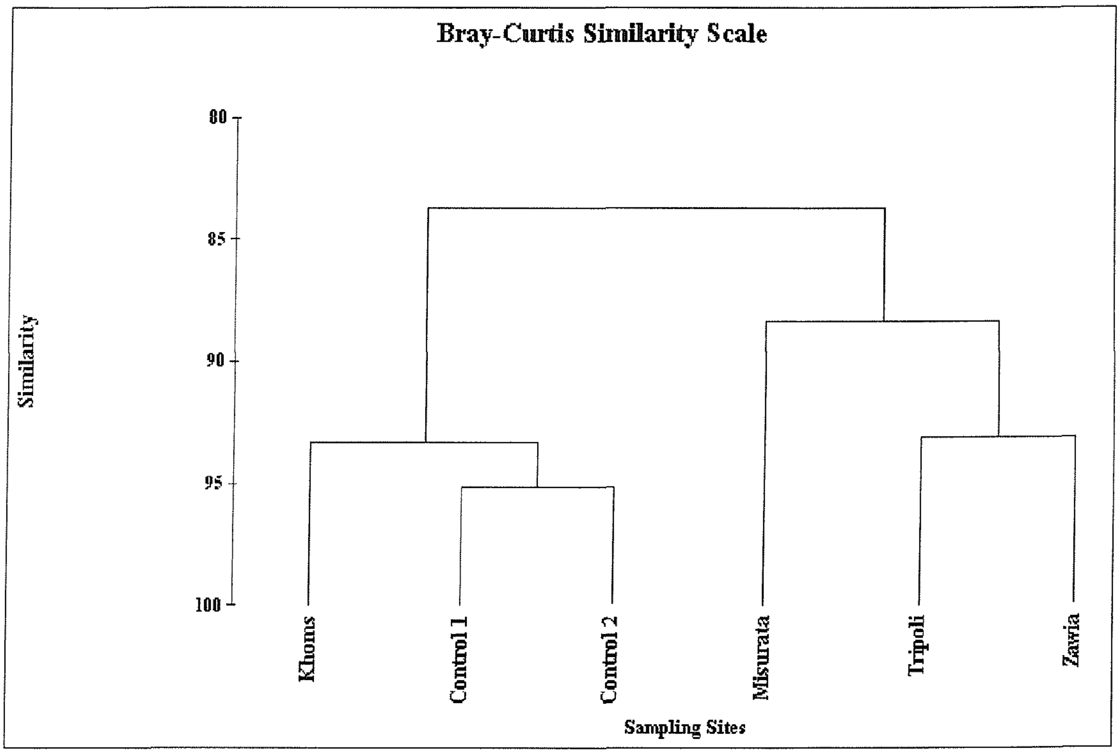


Figure 5.4 Analysis of similarities between the species abundance in the sampling sites using the Bray-Curtis similarity scale.

The analysis of similarities between the sampling sites using the non-metric multi-dimentional scaling (MDS) has shown a clear pattern between the control sites and the polluted sites (Fig. 5.5). In comparison with the control sites Tripoli was the least similar followed by Zawia, Misurata and Khoms respectively (Fig. 5.5).

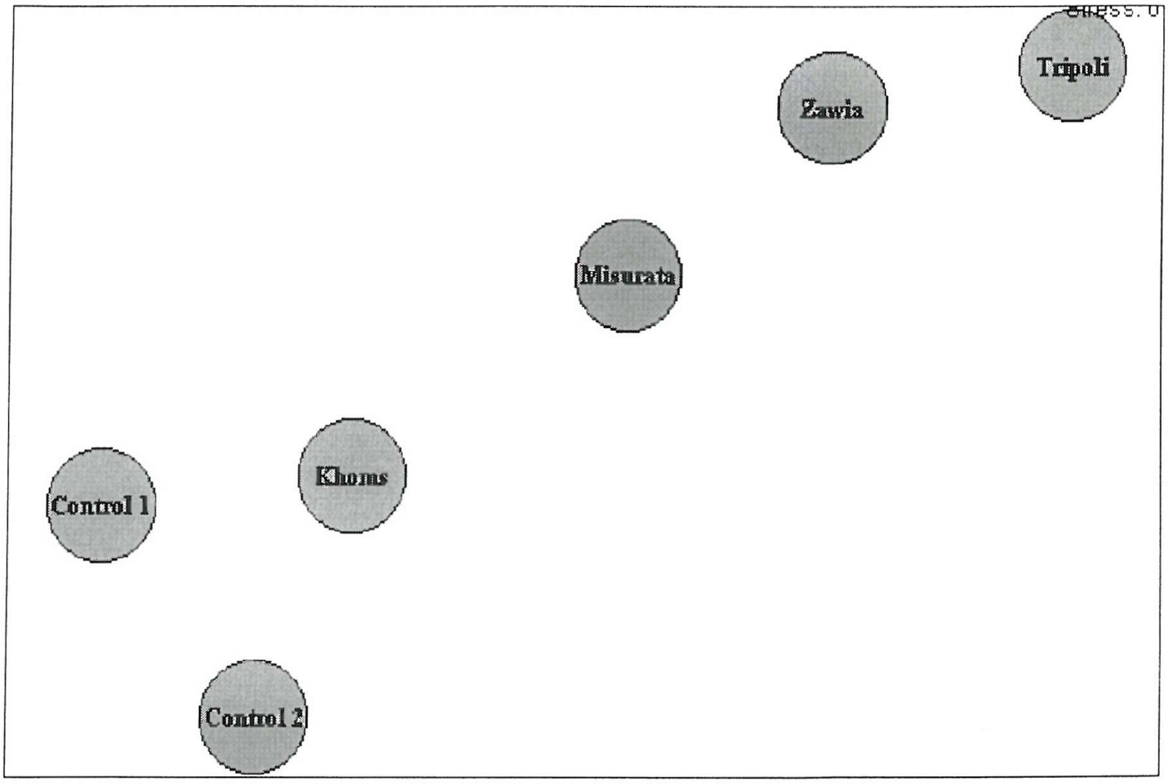


Figure 5.5 Analysis of similarities between the species abundance in the sampling sites using the non-metric multi-dimentional scaling (MDS).

5.5 Discussion

Rocky shores exhibit a range of vulnerabilities to oil pollution as they vary in exposure to wave action (Davies & Moss, 2002; Lewis, 1964; Raffaelli & Hawkins, 1999; Stephenson & Stephenson, 1972,). Some rocky shores are cleaned quickly by natural forces, others can trap oil and take years to recover (Clark, 2001; Hawkins *et al*, 1999). Most rocky shores in the study area (i.e. Tripolitania) can be described as moderately exposed and gradually sloping platforms with uneven surfaces (Davies & Moss, 2002; **McLeod, 1996)** (Table 5.1). The exposure to wave action and the topography of these shores make tar balls adhere to the substrate and accumulate over time. Thus the Libyan rocky shores act as a trap for deposited oil in the form of tar balls. Abundance of tar on these shores is very high in some areas. Tar coverage reaches more than 35% of the substratum in some sites (Figs. 4.3 & 5.3). Therefore the area available for sessile and sedentary species is very limited.

Oil deposition on rocky shores can have various types of effects on shore communities. These effects can be physical actions such as smothering and loss of habitat or bio-physiological action via toxicity of oil (Clark, 2001; Forde, 2002; Newey & Seed, 1995; Suchanek, 1993; Terlizzi *et al*, 2002). Much of the oil that reaches the coastline in the form of tar balls has been in the sea for some time and lost much of its toxic constituents, i.e. aromatic and volatile constituents, by weathering (Shelton, 1971). Therefore, the toxic effects of oil deposited on rocky shores are limited and may not harm some species (Clark, 2001; Newey & Seed, 1995).

Deposition of tar on rocky shores may cause a loss of habitat of some species that would lead to a decrease in community richness. The richness of shore communities can also be affected by manmade disturbances other than oil pollution such as the discharge of industrial and municipal sewage (Hartnoll & Hawkins, 1985). Areas such as Khoms, Misurata and Tripoli have more pollution inputs from seaports, industries and municipal sewage that can affect richness of shore communities.

The results of this study suggest that the shore communities are affected the most by oil pollution more than any other type of pollution. This hypothesis is supported by the findings that were discussed in the previous chapter regarding deposition of tar on rocky shores where the tar coverage on the substrata was more than 35% in some sites (Figs. 4.3 & 5.6).

The loss of such a considerable area of the substrata by the shore community can affect their abundance. The results of this survey showed that lower values of species abundance found in sites that have higher values of tar coverage and vice versa (Figs. 4.3, 5.1, 5.6).

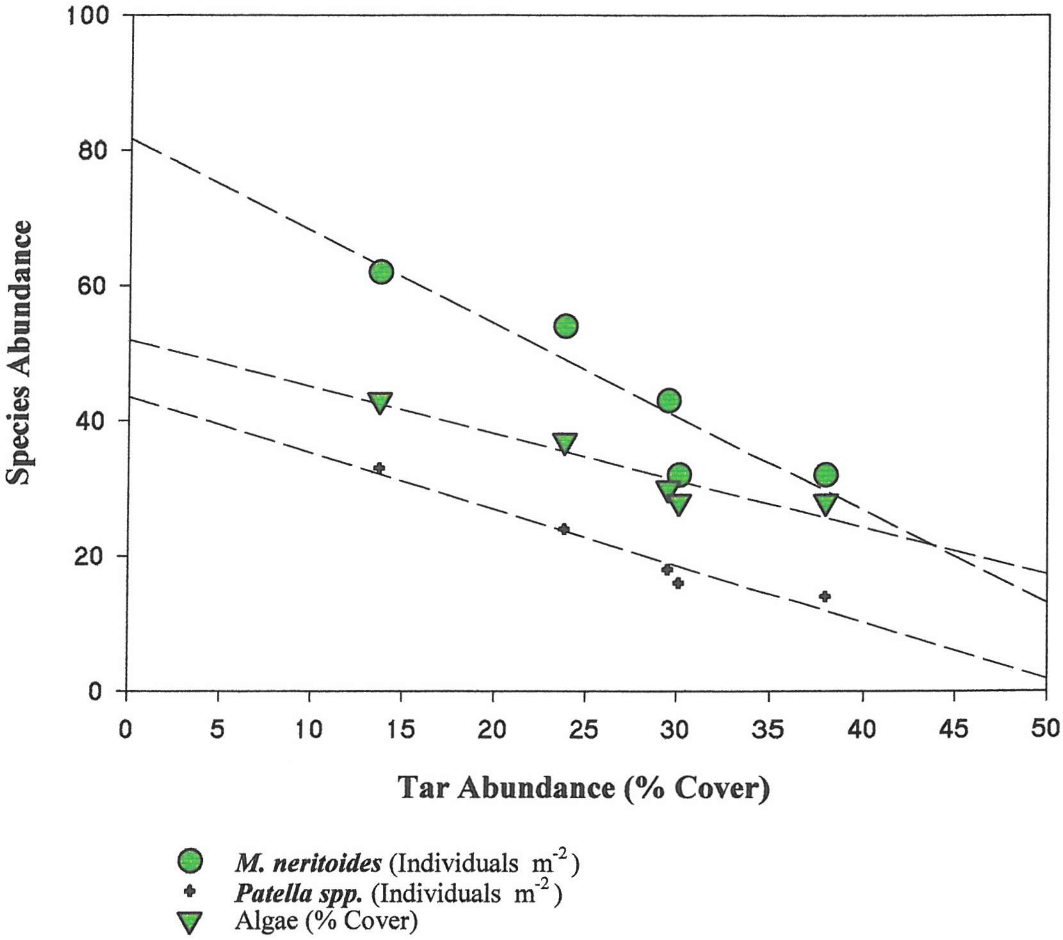


Figure 5.6 The relationship between the abundance of species and the abundance of tar on rocky shores of the study area.

This pattern is particularly clear in sites near to big cities such as Tripoli and Zawia where tar deposition rate is the highest (Fig. 5.1). This would suggest that the main effects of oil pollution on the existing species are probably the loss of. substratum and or smothering. Rocky shore communities, particularly the sessile species, can be affected directly by these factors (Forde, 2002; Hartnoll & Hawkins; Newey & Seed, 1995; Raffaelli & Hawkins, 1999; Suchanek, 1993; 1985; Terlizzi *et al*, 2002).

In all sites the number of individuals of ***Patella spp.*** was the lowest among other species (Fig. 5.1). This species is known as highly sensitive to oil pollution (Hawkins & Southward, 1992; Glegg *et al*, 1999; Hill, 2000; & Clark, 2001). ***Patella spp.*** have a particular high sensitivity to loss of substratum, smothering, and hydrocarbon contamination (Hill, 2000).

The lowest numbers of individuals of this species were recorded in the vicinity of big cites such as Tripoli, Zawai, and Misurata (Fig. 5.2) where oil pollution has the highest levels in the entire study area. As discussed in the previous chapters, the levels of oil pollution in these sites were the highest in all of the coastal habitats i.e. sediments, seawater, sandy beaches and rocky shores. The abundance values of ***Patella spp.*** probably indicate the extent of impact of oil pollution on these coastal habitats.

Results of the survey showed that ***Chthamalus spp.*** have a relatively high abundance among other species. Unlike the common limpet ***Patella spp.,*** the barnacle ***Chthamalus spp.*** is known to have low sensitivity to hydrocarbon contamination and intermediate sensitivity to smothering effects (Riley, 2002). Moreover, ***Chthamalus spp.*** as an opportunistic barnacle was reported to be very abundant in areas that previously suffered chronic oil spills (Peterson *et al*, 2001).

The fact that ***Chthamalus spp.*** has some degree of tolerance to hydrocarbon contamination and as an opportunistic barnacle probably explains the relatively high abundance of this species among other species in the study area. Nevertheless, the smothering effect and the loss of substrata that caused by tar deposition on the rocky shores of the sampling sites, probably has an effect on the abundance of this species.

Some algal species, particularly the red and green algae, are also known as highly sensitive to oil contamination (Glegg *et al*, 1999; Hawkins & Southward, 1992). Other algal species such as ***Corallina officcinalis*** have a low sensitivity to hydrocarbon contamination and intermediate sensitivity to smothering effects (Tyler-Walters, 2000).

No distinction was made between the individual algal species during the sampling, but the results showed that the percentage cover of the existing algae have decreased significantly in areas that receive greater pollution inputs. This probably indicates the impact of oil pollution on the rocky shores as an integrated habitat (Fig. 5.3).

All species including ***Melarhaphe neritoides*** and ***Osilinus turbinatus*** were found in lower numbers in all sampling sites compared with the control sites (Fig. 5.4, 5.6). The significant decrease in the abundance of species in areas such as Misurata, Zawia, Khmos and Tripoli compared with the control sites is consistent with the fact that these areas receive greater oil pollution inputs as discussed in the previous chapters.

Moreover, lower values of species abundance were recorded in sites that have higher oil pollution levels. This pattern is consistent with oil pollution levels that exist in the sites of the study area. Levels of hydrocarbon content in the sediments and seawater, and levels of oil deposited in form of tar in the sandy beaches and the rocky shores are adversely proportional to some degree with the species abundance in all sites (Figs. 2.6, 4.4, 4.1,5.1, 5.3, 5.6).

The decrease in species abundance on the rocky shores at the polluted sites is a clear indication of the extent of the impact that these habitats receive. The findings of this survey together with the findings that were discussed in the previous chapters have shown that the Libyan rocky shores, while acting as a natural shield for the rest of the coast, are receiving a greater impact as natural habitats.

CHAPTER SIX: GENERAL DISCUSSION

Chapter Six: General Discussion

6.1 Sources and distribution of oil pollution on the Libyan coast

The presence of dispersed and deposited hydrocarbons on the Libyan coast in the sea water and the sediments is probably a result of inputs from localised sources rather than trans-boundary pollution. The localised sources of oil pollution are mainly the seaports, the coastal refineries, and the municipal sewage discharge; but the trans-boundary oil pollution reaches the Libyan coast from the release of ballast water in the international discharge zone in the Mediterranean (Fig. 1.2) (El-Ghirani, 1981; Magazzu & Angot, 1981).

Oil released in areas far from the coast such as the international discharge zone in the Mediterranean sea, would lose much of its lighter components by evaporation and other natural processes before it reaches the coast (Sharma *et al*, 2002). Thus, only the heavier part in the form of mousse or pelagic tar may finally reach the coast (Shelton, 1971; Clark, 2001). Therefore, the dispersed and deposited hydrocarbons in the seawater and the sediments probably originated from localised sources such seaports, oil refineries, industrial effluents, and municipal sewage discharge.

However, the influence of the ballast water probably reaches the Libyan coast in form of pelagic tar that finally deposits on the rocky shores and the sandy beaches (El-Ghirani, 1981).

Many factors may influence the spatial distribution of tar on coastal habitats (Al-madfa *et al*, 1999; Irvine *et al*, 1999; Guidetti *et al*, 2000). The spatial distribution of oil deposited on rocky shores was different to that on sandy beaches. The main factors that influence these patterns are probably the physical and the geographical characteristics of the coastal habitats, such as topography and exposure to wave action.

Oil pollution in the Libyan coast is associated with the cities. Higher levels of oil pollution were found in the vicinity of the cities such Misurata, Khoms and Tripoli (Figs. 2.6, 4.4, 4.1,5.1, 5.3). Levels of oil pollution in such sites are high in the seawater, the sediments, the rocky shores, and the sandy beaches. This pattern is consistent with the low abundance of species on the more polluted rocky shores. The levels of pollution are adversely proportional to some degree with the species abundance on the rocky shores (Fig. 5.6).

6.2 Vulnerability of coastal habitats

Coastal ecosystems are both very productive and very vulnerable (Mann, 2000). The Libyan coast is particularly vulnerable to oil pollution compared with other coastlines in the Mediterranean Sea due to several factors. First, the Libyan coast being the second longest coastline in the Mediterranean, it is more exposed to oil transportation traffic. Second, there is no natural protection for this coastline such as islands that may act as natural shields. Third, Libya is the biggest oil producer and exporter in the Mediterranean.

The rocky shores in Libya represent less than 10% of the coast (Snoussi & Aoul, 2000) and are probably the most vulnerable to oil. Coastal habitats have a range of vulnerabilities to oil pollution (Table 6.1) as they vary in their exposure to wave action (Hawkins & Southward, 1992; Clark, 2001). The Libyan rocky shores, being sheltered or moderately exposed, may take many years to recover naturally (Table 6.1). Oil accumulates over time on these habitats due to their physical and geographical characteristics including the exposure to wave action and the topography. Therefore the natural recovery of these habitats may take a relatively long time (Al-madfa *et al*, 1999; Irvine *et al*, 1999; Guidetti *et al*, 2000).

Table 6.1 Vulnerability index for coastal habitats classification in order of vulnerability to oil-spill damage. Ranking starts from 1 that is the least vulnerable to 8 that is the most vulnerable (Gundlach, & Hayes, 1978).

Index	Coastal habitat	Persistence of stranded oil
1	Rocky shores (exposed)	Wave action keeps most of oil offshore. Clean up is not necessary
2	Eroding wave-cut platforms	Most of oil removed by natural process within weeks
3	Sandy beaches (Fine-grained)	Oil does not penetrate in the sediments. Oil may persist several months unless mechanical removal is used.
4	Sandy beaches (Coarse-grained)	Oil may penetrate in the sediments. Oil can be removed naturally in a relatively longer time.
5	Exposed tidal flats	Most of oil will not adhere to, nor penetrate into, the tidal flat.
6	Sand and gravel beaches	Oil may persist from many years under moderate to low-energy conditions.
7	Gravel beaches	Oil may persist from many years under moderate to low-energy conditions.
8	Rocky shores (Sheltered)	Oil may persist for many years.

6.3 The probability of oil spills

Oil pollution in the Libyan coast is a chronic problem caused mainly by frequent inputs from localised source boosted by the release of ballast water from international oil tankers in the Mediterranean Sea. However, catastrophic oil spills may occur at any time especially in areas such as the Libyan coast where oil exploration and exploitation activities have taken place since the 1950s.

The western region of the Libyan coast has been identified as one of five high risk areas in the Mediterranean in which oil pollution accidents may occur (World Bank, 1998). This area, as discussed in the previous chapters, accommodates a large number of oil exploitation activities including exploration, production and transportation. Two projects particularly have the highest probable risk: the new project which will link the Libyan coast with Italy through a sub-water pipeline to transfer gas and oil (DNV, 2001), and the "Bouri" offshore oil field which is the biggest offshore oil field in the Mediterranean Sea (SMI Group, 2000).

The Sicily-Malta channel was defined as a high-risk area as most of the oil that transported via the Mediterranean passes through this channel (World Bank, 1998). Any release of oil in the Sicily-Malta channel will have a direct impact on the Libyan western coast with a minimum drift time of 5-10 days to reach the Libyan coast (Fig. 6.1). Wind and surface currents are the main factors that govern the spread of released oil towards the area of influence (Magazzu & Angot, 1981; World Bank, 1998).

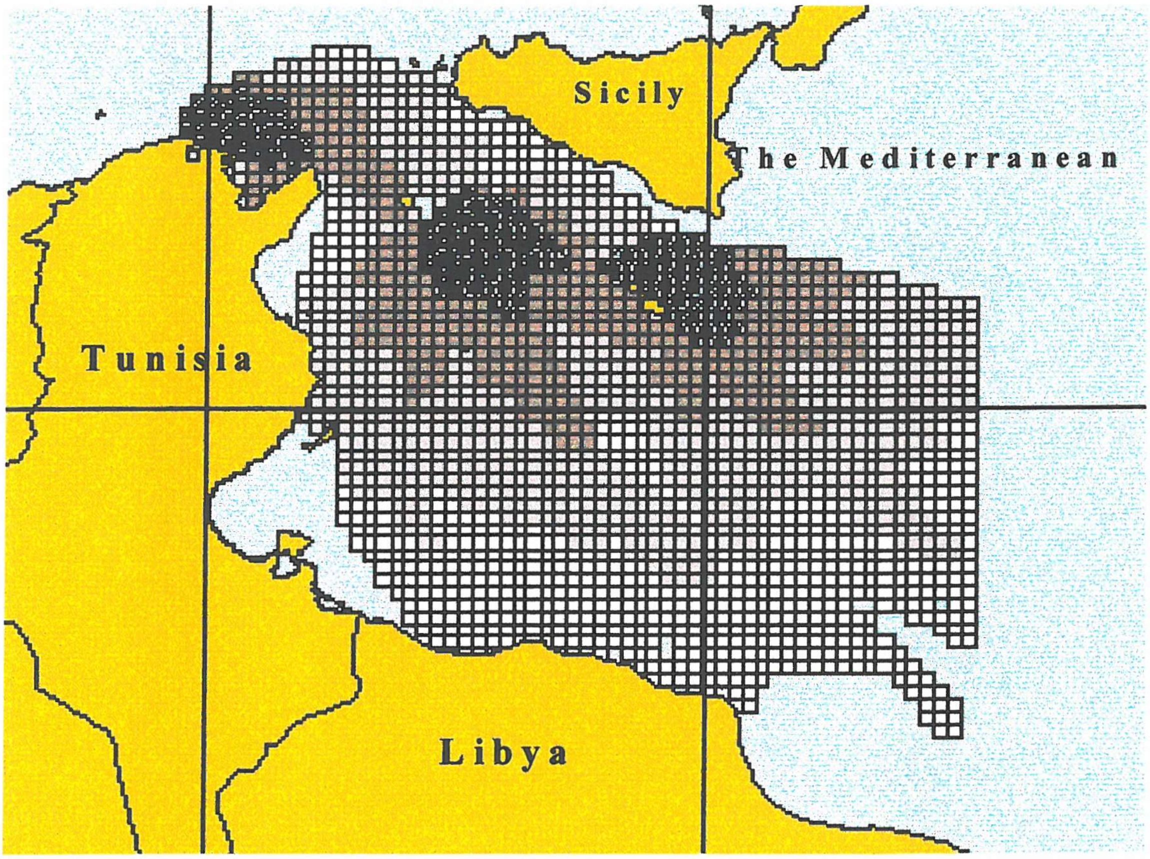


Figure 6.1 The area of influence of three simulated release sites in the Sicily- Malta channel (Not to scale)(World Bank, 1998).

The offshore oil field of "Bouri" is the centre of one of five areas of high risk in the Mediterranean (World Bank, 1998). The area of influence of oil spills from this location covers most of the western part of the Libyan coast (Fig. 6.2). The pollution probability at the coast extends to 50% while the minimum drift time to the coast ranges from 3 to 20 days (World Bank, 1998).

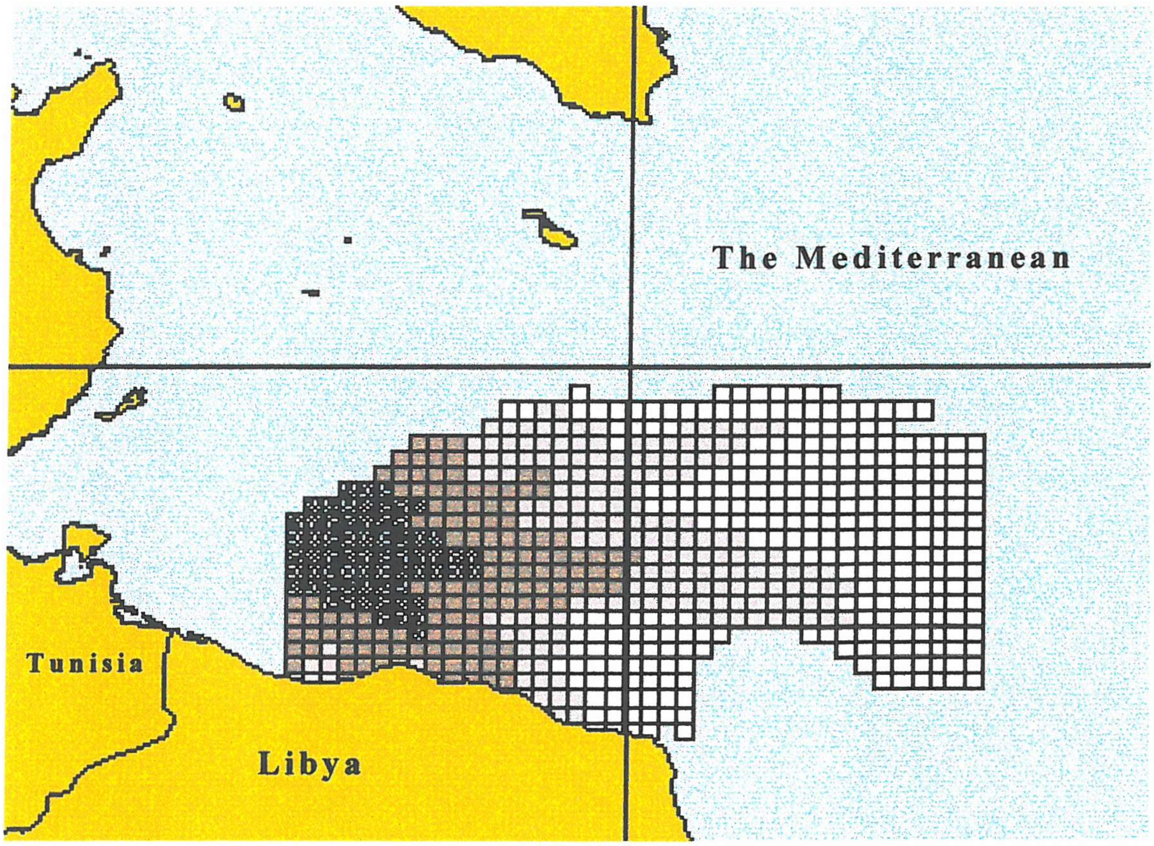


Figure 6.2 The area of influence of a simulated release site at Bouri oil field, Libya (Not to scale) (World Bank, 1998).

6.4 The impact of oil pollution on coastal resources

Coastal resources are vulnerable to adverse effects from chronic inputs of oil at sea particularly in areas such as the Libyan coast where coastal zone management (CZM) is poorly implemented (Snoussi & Aoul, 2000). The Libyan beaches are the most important nesting places for endangered species of marine turtles in the Mediterranean (Patel, 1995) which include the loggerhead turtle (***Caretta caretta***), the green turtle (***Chelonia mydas***), and the leatherback turtle (***Dermochelys coriacea***) (Laurent *et al.,* 1998). These species are regarded as rare in the Mediterranean region because of loss of nesting sites as a result of new developments and pollution (Laurent *et al.,* 1998; UNEP, 1990). There is evidence that oil pollution may cause significant damage to marine wildlife particularly the sea turtles (Bishop *et al*., 1998; Mignucci-Giannoni, 1999). Studies showed that residues of petroleum hydrocarbons were found in the tissues of sea turtles that have been exposed to oil spills (Hall *et al*, 1983).

As discussed in the previous chapters, oil residues are deposited in large quantities over considerable areas of the sandy beaches of the western region of Libya. The deposition of oil residues on sandy beaches, which are the nesting areas of these species, probably have significant effects on the sea turtles that can lead to the eviction of these animals from the area.

More than 20 bird species have been reported either as resident or migrant breeders in the western coastal region of Libya, and more than 100 other bird species are considered as seasonal visitors or passing migrants in this region (Bundy, 1976). Some of the locally breeding species are listed as threatened or endangered such as the Lesser-Crested Tern *(Sterna bengalensis*) (James, 1984). Chronic oil pollution can have significant adverse effects on seabirds (Camphysen & Heubeck, 2001). These effects range from skin damage to mortality (Boesch & Rabalais, 1987; Stephenson, 1997; Tseng, 1999). The frequent inputs of oil into the sea from various sources in the Libyan coastal waters probably have significant impact on the migratory and resident species of seabirds.

6.5 Protection of the Libyan coast against oil pollution

Periodic oil spill incidents can cause significant environmental damage, but chronic oil pollution may cause greater environmental damage than occasional extreme events (Dicks & Hartley, 1982; Baussant *et al*, 2001; Camphysen & Heubeck, 2001). In order to find a basis for managing this background pollution it is necessary for Libya to monitor the existing environmental quality status and use this to provide an indication of possible causes and response priorities. In some areas, oil pollution monitoring is an established operational procedure but elsewhere, such as the Libyan coast, a first is to undertake one-off surveys to indicate the overall status of the area.

The lack of well-defined strategies, long term plans, and co-ordination among authorities are the main factors that encounter the control of oil pollution in Libya (Tluba, 1991). The country has to develop new strategies to combat and prevent this problem. Plans and strategies should be designed to be flexible to respond efficiently to oil pollution as a chronic problem as well as in catastrophic events.

Certain steps should be taken to control and prevent this problem that should include:

- Increasing the awareness about the seriousness of oil pollution problems among the authorities as well as the general public.
- Enhancing marine pollution abatement and control in critical areas that are subject to industrial and land-based pollution.
- Strengthening the regional co-operation to respond to oil spills.
- Adoption of a national contingency plan, which would ensure that the country has consistent regulatory policies, methodologies, and equipment, and that they allocate resources and operate efficiently.

- Adoption of an action plan and implementation of its recommendations to ensure good coastal zone management and tackle marine pollution.
- Provision of a comprehensive monitoring system, both locally and regionally, to control maritime traffic and monitor compliance with local and international regulations.
- Implementation of appropriate alternatives for collecting and processing ballast water and oily wastes, including possible marketing of by-products and other options for final disposal.

6.5.1 The need for EIA from oil projects

Environmental Impact Assessment (EIA) in Libya has not obtained a full legal status and is still not defined by regulations that determine its scope and procedures (DNV, 2001). An EIA should evaluate the impact of a development on humans and on the whole surrounding environment. Existing regulations however do not give a sufficient basis for defining methods and procedures for estimating the impact on human health and on the ecosystem.

The existing regulations concerning EIA should be developed to include detailed guidelines on the preparation of EIAs for oil projects. Experts from the authorities should review the environmental statements before granting approval for any projects.

6.5.2 Possible improvement measures

Coastal oil refineries are contributing to oil inputs into the world's oceans with more than 0.10 million tonne $year^{-1}$ (Clark, 2001). Refineries in Libya are considered significant sources of chronic oil pollution. For example, particularly high levels of oil pollution were found near Zawia refinery as discussed in the previous chapters.

Possible improvement measures can be applied to the Libyan refineries by taking the Esso refinery in Fawley as an example. The measures that have been used to reduce hydrocarbon discharge in Southampton Water from the Esso refinery were effective and have improved the quality of the refinery's effluent considerably (ESSO & ExxonMobil, 2000).

In this context, improvement (Field Studies Council, 1994) may include:

- Training personnel on how to avoid leaks and spills that may occur during various operation activities.
- Modifying in the production processes to reduce the amount or toxicity of oil wastes.
- Improving the quality of the effluent water from the refinery by passing the process water and the cooling water through filtration plant.

6.6 Suggestions for Further work

The subject of marine oil pollution in Libya is still a new area for research and investigation. Very few studies can be found on this subject. Thus, this research can be used as a basis for many further studies to investigate the problem of oil pollution on the Libyan coast from various aspects. For example, the assessment of the impact of oil pollution on the coastal resources such as the fisheries and sea turtles, can be a subject for further investigation.

A further study on the possible measures and strategies for the protection of the Libyan coast from oil pollution is very important at the present time. Such study may include the design of reception facilities for ballast water in the Libyan seaports, and its technical and managerial aspects.

This research has studied the problem of oil pollution on the western part of the Libyan coast (Tripolitania) which is about 500 km. Considering the available time, it was not possible to study oil pollution on the entire Libyan coast (about 1770 km). The Gulf of Sirt and the eastern coast of Libya (Cyrenacia) is probably the most affected by the release of ballast water (Magazzu & Angot, 1981). A study on the assessment of the impact of ballast water on this region is, therefore, needed.

6.7 Conclusion

Oil pollution on the Libyan coast is caused by frequent inputs from localised sources such as seaports, coastal refineries, and municipal sewage discharge. Trans-boundary sources are also significant, i.e. the discharge of ballast water from international oil tankers in the Mediterranean (Magazzu & Angot, 1981).

Applying several technical and operational measures can reduce inputs from localised sources of pollution such as oil refineries. The measures taken to reduce hydrocarbon inputs into Southampton Water from the Fawley refinery can be applied to Zawia refinery in Libya. Based on the case of Southampton Water, results of any changes in Zawai refinery to reduce the inputs of oil into the sea may take several years before any improvements can be noticed.

Coastal habitats on the Libyan coast are affected considerably by deposition of oil. The rocky shores are particularly vulnerable to oil pollution due to the accumulation of tar that may take long time to recover in comparison with the sandy beaches (Gundlach, & Hayes, 1978; Al-madfa *et al*, 1999; Irvine *et al*, 1999; Guidetti *et al*, 2000). The Libyan rocky shores are acting as a natural shield for the rest of the coast, therefore they are probably the most vulnerable among other coastal habitats.

REFERENCES

REFERENCES

Abuodha P.A.W. & Kairo J.G. (2001). **Human-induced stresses on mangrove swamps along the Kenyan coast**. *Hydrobiologia,* **458:** 255-265.

Anonymous, (1963). **Mediterranean Pilot**. Vol. I. Hydrographic Department of the Admiralty, London.

Ali L. H., El-Jawashi S.A., Ejbali A.A., & Garbaj M. J., (1998). **Investigations on organics in the Libyan beach sand and water: extraction, spectroscopy and gas chromatography, Zwarah to east Tripoli coastline.** Oil and hydrocarbon spills modelling, analysis and control- Conference proceedings. Wessex Institute of Technology, Computational Mechanics Publications, Southampton.133-144.

Al-madfa H., Abdel-Moati M.A.R., & Al-Naama A., (1999). **Beach tar contamination on the Qatari coastline of the gulf.** *Environment International*, **25:** 505-513.

American Society for Testing and Materials (ASTM), (1996) **Standard test methods, D 4281, D 5368, D5369**. Annual book of ASTM standards - 1996.

Atia H.F., (1993). **Maritime safety conventions and maritime administration in Libya.** MPhil thesis, Dept. of Maritime studies and International transport, University of Wales College of Cardiff, April 1993.

Aybulatov N.A., Nemirovskaya I.A., Nesterova M.P.,(1981). **Oil pollution of the North African shelf of the Mediterranean Sea**. *Oceanology* **21**: 589-592

Baghni, et al. (1998). **Levels of heavy metals pollution along Tripoli beaches**. General Society of Engineers, Tripoli, Libya. *Al-handassi* **38**: 58-68

Barron M.G., Podrabsky T., Ogle S., Ricker R.W., (1999). **Are aromatic hydrocarbons the primary determinant of petroleum toxicity to aquatic organisms?** *Aquatic Toxicology,* **46:** 253-268.

Baussant T., Sanni S., Jonsson G., Skadsheim A., & Borseth J.F., (2001). **Bioaccumulation of polycyclic aromatic compounds: 1. Bioconcentration in two marine species and in semipermeable membrane devices during chronic exposure to dispersed crude oil.** *Environmental Toxicology and Chemistry,* **20:** 1175-1184.

Bishop C.A., Ng P., Pettit K.E., Kennedy S.W., Stegeman J.J., Norstrom R.J, & Brooks R.J, (1998). **Environmental contamination and developmental abnormalities in eggs and hatchlings of the common snapping turtle (*Chelydra serpentina serpentina*) from the Great Lakes-St Lawrence River basin (1989-91).** *Environmental pollution,* **101:**143-156

Boesch D.F. & Rabalais N.N., (1987). **Long-term environmental effects of offshore oil and gas development**. Elsevier applied science publishers Ltd.

Briggs K.T., Gershwin M.E., & Anderson D.W., (1997). **Consequences of petrochemical ingestion and stress on the immune system of seabirds**. *ICES Journal of Marine Science,* **54:** 718-725.

Bryan G.W., (1979). **Bioaccumulation of marine pollutants**. *Philosophical Transactions of the Royal Society of London, Series B.* **286**: 483-505.

Buisa A.A., Enbyah M., Huni A. A. D. & Aravindan C. M. (1985). **The ecology of some rocky shores of the Libyan coastal regions**. Proceedings of the symposium on marine biology of Arab countries, Aquaba, Jordan, 1985.

Bundy G., (1976). **The birds of Libya.** London, British Ornithologists' Union. B.O.U. Checklist No. 1. London.

Calabresi G., (1996). **ERS Thematic Workshop-Oil pollution monitoring in the Mediterranean: Summary report and conclusions.** *Spill Science and Technology Bulletin,* **3:** 83-96.

Campbell A.C., (1982). **The Hamlyn guide to the flora and fauna of the Mediterranean Sea**. The Hamlyn Publishing Group Ltd., London, the UK.

Camphysen C.J., & Heubeck M., (2001). **Marine oil pollution and beached bird surveys: the development of a sensitive monitoring instrument**. *Environmental Pollution,* **112:** 443-461.

Capuzzo J.M., (1981). **Predicting pollution effects in the marine environment**. *Oceanus* **24**: 25-33.

Day R.H., Murphy S.M., Wiens J.A., Hayward G.D., Harner E.J., & Smith L.N., (1997). **Effects of the Exxon Valdez oil spill on habitat use by birds in Prince William Sound, Alaska**. *Ecological Applications,* **7:** 593-613.

Clark R.B., (2001). **Marine Pollution**. 5th Ed. Oxford University Press Inc., New York.

Clemente A.R., Anazawa T.A., & Durrant L.R., (2001). **Biodegradation of polycyclic aromatic hydrocarbons by soil fungi.** *Brazilian Journal of Microbiology,* **32:** 255-261.

Daidola J.C., Reyling C.J., & Ameer P.G., (1997). **Oil outflow estimates for tankers and barges.** *Spill Science & Technology Bulletin,* **4:** 89-98.

Davies C.E. & Moss, D. (2002). **EUNIS Habitat Classification. Final Report to the European Topic Centre on Nature Protection and Biodiversity**, European Environment Agency.

Demetropoulos A., & Loizides L., (1986). **Baseline studies and monitoring of oil and petroleum hydrocarbons in marine waters** (MED POL I). MAP Technical reports series **1**:1-11

Dicks B., (1977). **Changes in the vegetation of an oiled Southampton Water salt marsh. Recovery and restoration of damaged ecosystems**. In: J. Cairns, Jr., K.L. Dickson, E.E. Herricks (eds.), University Press of Virginia, Charlottesville, VA, pp. 208-239.

Dicks B. & K. Iball, (1981)**. Ten years of salt marsh monitoring - the case history of a Southampton Water salt marsh and a changing refinery effluent discharge**. In:

Proceedings: 1981 Oil Spill Conference (Prevention, Behaviour, Control, Cleanup). API # 4334. Atlanta, Georgia. American Petroleum Inst., Washington, DC. pp. 361-373.

Dicks B., & Hartley J.P., (1982). **The effects of repeated small oil spillages and chronic discharges**. *Philosophical Transactions of the Royal Society of London, Series B*. **287**:285-307.

Dicks B. & Westwood S.S.C., (1987). **Oil and the mangroves of the northern Red Sea. In: Fate and Effects of Oil in Marine Ecosystems**. Martinus Nijhoff Publishers, pp. 187-200.

DNV (Det Norske Veritas), (2001). **Western Libya gas project environmental impact study-*Mellitah* coastal plants**. Report No. 2001-0733.

Domovic D., (1992). **The sources of marine oil pollution with special reference to accidental oil pollution in the Mediterranean.** *Bulletin of the Marine Biology Centre-Tripoli*, **9-B**: 180-203.

Duke N., Burns K., Swannell R., Dalhaus O., & Rupp R., (2000). **Dispersant use and a bioremediation strategy as alternate means of reducing impacts of large oil spills on mangroves: The Gladstone field trials.** *Marine Pollution Bulletin*, **41:** 403-412

Elazzabi A.M., (1992). **Oil pollution and marine transportation**. *Bulletin of the Marine Biology Centre-* Libya, **9-B**

El-Ghirani A.A., (1981). **Occurrence of tar balls on the Libyan beaches.** *Bulletin of the Marine Biology Centre*- Libya, **2:** 2-14.

Ellison A.M., (1999). **Cumulative effects of oil spills on mangroves**. *Ecological Applications,* **9:** 1490-1492.

Enbyah M. A., Buisa A. & Aravindan C.M. (1986). **Distribution and seasonal variations of organisms on wave exposed and sheltered stretches of rocky shores of Al-Khoms (SPLAJ)**. *Bulletin of the Marine Biology Centre*-Libya, **7:** 5-24.

ESSO Petroleum Co. Ltd. & ExxonMobil Chemical Ltd., (2000) **Progress at Fawley 2000**. Company Report. Fawley, Southampton.

Field Studies Council, Oil Pollution Research Unit (1994). **The recent history of the Fawley saltmarsh and the Esso refinery**. Report produced for Esso Petroleum Co. Ltd.

Forde S.E., (2002). **Modelling the effects of an oil spill on open populations of intertidal invertebrates**. *Journal of Applied Ecology,* **39:** 595-604.

Gallego A., CargilL L.H., Heath M.R., Hay S.J., & Knutsen T., (1995). **An assessment of the immediate effect of the Braer oil-spill on the growth of herring larvae using otolith microstructure analysis**. *Marine Pollution Bulletin*, **30:** 536-542.

Galt J.A., Lehr W.J., & Payton D.L., (1991). **Fate and transport of the *Exxon Valdez* oil spill**. Part 4. *Environmental Sciences Technology* **25:** 202-209.

Gamulin-Brida H., (1967). **The benthic fauna of the Adriatic Sea.** *Oceanographic Marine Biology Annual Review* **5:** 535-568.

Glegg G.A., Hickman L. & Rowland S.J. (1999). **Contamination of Limpets (*Patella vulgata*) following the *Sea Empress* oil spill**. *Marine Pollution Bulletin*, **38:** 119-125.

Goldberg E.D., (1972). **A guide to marine pollution**, FAO, Gordon and Breach Science Publishers Inc., New York.

Golik A., Weber K., Salihoglu I., Yilmaz A., & Loizides L., (1988). **Pelagic tar in the Mediterranean Sea**. *Marine Pollution Bulletin*, **19**: 567-572

Grant A. & Briggs A.D., (2002). **Toxicity of sediments from around a North Sea oil platform: are metals or hydrocarbons responsible for ecological impacts?**. *Marine Environmental Research*, **53**: 95-116

Guidetti P., Modena M., Lamesa G., & Vacchi M. (2000). **Composition, abundance and stratification of macrobenthos in the marine area impacted by tar aggregates derived from the *Haven* oil spill (Ligurian Sea, Italy).** *Marine Pollution Bulletin*, **40**: 1161-1166.

Guilbault G.G. (1990). **Practical Fluorescence**, 2nd Edition, Marcel Dekker, Inc., New York.

Gundlach, E.R., & Hayes M., (1978). **Classification of coastal environments in terms of potential vulnerability to oil spill damage**. *Marine Technology Society Journal*, **12:**18-27.

Guzzella L. & De Paolis A., (1994). **Polycyclic aromatic hydrocarbons in sediments of the Adriatic Sea**. *Marine Pollution Bulletin,* **28:** 159-165.

Hall R.J., Belisle A.A., Sileo L., (1983). **Residues of petroleum hydrocarbons in tissues of sea turtles exposed to the IXTOC-I oil-spill.** *Journal of Wildlife Diseases,* **19:** 106-109.

Hartnoll R. G. & Hawkins S. J., (1985). **Patchiness and fluctuations on moderately exposed shores**. Ophelia, **24:** 53-63.

Hawkins S. J. & Hartnoll R.G. (1983). **Changes in a rocky shore community: an evaluation of monitoring**. *Marine Environmental Research*, **9:** 131-181.

Hawkins S. J. & Jones H. D. (1992). **Marine field course guide 1: Rocky shores**. Marine Conservation Society. IMMEL Publishing, London.

Hawkins S. J. & Southward A.J. (1992). **The Torrey Canyon oil spill: Recovery of rocky shore communities**. In *Restoring the Nation's Marine Environment.* (Ed. G.W. Thayer). Maryland Sea Grant College, 583-632

Hawkins S.J., Allen J.R. & Bray S., (1999). **Restoration of temperate marine and coastal ecosystems: nudging nature**. *Aquatic Conservation: Marine and Freshwater Ecosystems*, **9**: 23-46

Hayes, M., Hoff, R., Michel, J., Scholz, D. & Shigenaka, G., (1992). **An Introduction to Coastal Habitats and Biological Resources for Oil Spill Response.** Hazardous Materials Response and Assessment Division, NOAA, USA.

Heintz R.A., Rice S.D., Wertheimer A.C., Bradshaw R.F., Thrower F.P., Joyce J.E., Short J.W., (2000). **Delayed effects on growth and marine survival of pink salmon *Oncorhynchus gorbuscha* after exposure to crude oil during embryonic development**. *Marine Ecology-Progress Series,* **208:** 205-216.

Hill J.M., (2000). ***Patella vulgata*. Common limpet**. *Marine Life Information Network: Biology and Sensitivity Key Information Sub-programme* [on-line]. Plymouth: Marine Biological Association of the United Kingdom. Available from: http://www.marlin.ac.uk

Horn M. H. (1970). **Petroleum lumps on the surface of the sea.** *Science* **168**: 245-246

Hughes J.B., (1999). **Cytological-cytogenetic analyses of winter flounder embryos collected from the benthos at the barge North Cape oil spill**. *Marine Pollution Bulletin,* **38:** 30-35.

Huni, A. A. D. & Aravindan C. M., (1984). **A preliminary study on the distribution of intertidal organisms on a rocky shore platform of the Libyan coast of the Mediterranean.** *The Libyan Journal of Sciences*, **13:** 1-8.

Irvine G. V., Mann D. H., & Short J.W. (1999). **Multi-year persistence of oil mousse on high energy beaches distant from**

***Exxon Valdez* spill origin**. *Marine Pollution Bulletin*, **38**: 572-584.

James P.C., (1984). **The status and conservation of seabirds in the Mediterranean Sea**. In: Croxall J.P., Evans P.G.H, & R.W. Schreiber, (eds.) **Status and conservation of the World's Seabirds**. ICBP Technical Publication No. 2. pp. 371-375.

Jenssen B.M., (1996). **An overview of exposure to, and effects of, petroleum oil and organochlorine pollution in grey seals (Halichoerus grypus).** *Science of the Total Environment,* **186:** 109-118.

Kator H., (1972). **Microbial degradation of oil: present status, problems, and perspectives**. Proceedings of the microbial degradation of oil pollutants, 47-65.

Kennish M. J., (1998). **Pollution impacts on marine biotic communities**. CRC Press LLC, Florida, USA.

Knap, A. H., (1978). **The fate of non-volatile petroleum hydrocarbons in refinery effluent entering Southampton Water** (1978). PhD thesis. Department of Oceanography. University of Southampton.

Lavecchia R. & Zugaro M., (2000). **Physicochemical characterization of crude oil fractions by artificial neural networks**. *Petroleum Science and Technology,* **18:** 233-247.

Laurent L., Casale P., Bradai M.N., Godley B.J., Gerosa G., Broderick A.C., Schroth W., Schierwater B., Levy A.M., Freggi D., Abd El-Mawla E.M., Hadoud D.A., Gomati H.E., Domingo M., Hadjichristophorou M., Kornaraky L., Demirayak F., &

Gautier CH., (1998). **Molecular resolution of marine turtle stock composition in fishery bycatch: a case study in the Mediterranean**. *Molecular Ecology,* **7:** 1529-1542

Law R. J., Fileman T. W. & Portmann J.E. (1988). **Aquatic Environment Protection: Analytical Methods**. Ministry of Agriculture Fisheries and Food. Directorate of Fisheries Research, Lowestoft, (2), 25 pp.

Lewis, J. R. (1964). **The ecology of rocky shores**. English Universities Press Ltd., London.

Lipiatou E., Tolosa I., Simo R., Bouloubassi I., Dachs J., Marti S., Sicre M.A., Bayona J.M., Grimalt J.O., Saliot A., & Albaiges J., (1997). **Mass budget and dynamics of polycyclic aromatic hydrocarbons in the Mediterranean Sea.** *Deep-sea Research Part II-Topical Studies in Oceanography*, **44:** 881-905.

Lockwood, A. P. M. (1986). **Southampton Water and the Solent: biological effects of the multi-use of an estuarine system**. Actes de Coll. No. 4 1986: 421-430.

Magazzu G., & Angot M., (1981). **Dissolved and dispersed petroleum hydrocarbons in Libyan coastal waters.** *Bulletin of the Marine Biology Centre- Tripoli,* **1**: 1-45.

Mann K.H., (2000). **Ecology of coastal waters: with applications for management**. Blackwell Science, Inc., the UK.

McLeod, C.R., (1996). Glossary of marine ecological terms, acronyms and abbreviations used in MNCR work. In *Marine Nature Conservation Review: rationale and methods,* (Ed. K.

Hiscock), *Appendix 1*. Peterborough: Joint Nature Conservation Committee. [Coasts and seas of the United Kingdom, MNCR Series].

Meadows P. S., (1992). **Pollution, conservation and the Mediterranean ecosystem: a perspective view.** *Bulletin of the Marine Biology Centre- Tripoli,* **9-B**: 270-297.

Meteorological Authority, (1994- 1998). Internal Meteorological reports for 1994- 1998. Tripoli- Libya.

Mignucci-Giannoni A.A., (1999). **Assessment and rehabilitation of wildlife affected by an oil spill in Puerto Rico.** *Environmental Pollution,* **104:** 323-333.

Nagelkerken I.A. & Debrot A.O., (1995). **Mollusc communities of tropical rubble shores of *Curacao* - long-term (7(+) years) impacts of oil pollution.** *Marine Pollution Bulletin*, **30:** 592-598.

National Academy of Scientific Research - Libya, (1991). **Environmental prospective of Libya: horizons of the years 2000-2025**. Unpublished report.

National Research Council, (1985). **Oil in the Sea: inputs, fates and effects**. National Academy Press, Washington, D.C.

Newey S. & Seed R., (1995). **The effects of the *Braer* oil spill on rocky intertidal communities in South Shetland, Scotland**. *Marine Pollution Bulletin,* **30:** 274-280.

Nielsen P., (1999). **Groundwater dynamics and salinity in coastal barriers.** *Journal of Coastal Research*, **15:** 732-740.

Noji T.T., Noji C.I.M., & Klungsoyr J., (2002). **The role of sedimentation and resuspension for the transport of sediments and contaminants in the Skagerrak**. *Hydrobiologia*, **469:** 99-108.

Oebius, H.U., (1999). **Physical properties and processes that influence the clean up of oil spills in the marine environment**. *Spill Science & Technology Bulletin*, **5:** 177-289

Oh Y.S., Sim D.S., & Kim S.J., (2001). **Effects of nutrients on crude oil biodegradation in the upper intertidal zone**. *Marine Pollution Bulletin,* **42:** 1367-1372.

Owens E.H., & Robilliard G.A., (1981). **Shoreline sensitivity and oil spills - a re-evaluation for the 1980s**, *Marine Pollution Bulletin,* **12:** 75-78.

Patel T., (1995). **Turtles find an unlikely ally**. *New Scientist*, **147:** 7

Peres J.M., (1967). **The Mediterranean benthos**. *World Oceanographic Marine Biology Annual Review*. **5:** 449-533

Peterson C.H., McDonald L.L., Green R. H. & Erickson W.P., (2001). **Sampling design begets conclusions: the statistical basis for detection of injury to and recovery of shoreline communities after the "Exxon Valdez" oil spill**. *Marine Ecology Progress series*, **210:** 255-283.

Petroleum Research Centre, (1984). **Internal reports** (Unpublished), Tripoli – 1984.

Petroleum Research Centre, (1987). **Internal reports** (Unpublished), Tripoli – 1987.

Pezeshki S.R., Hester M.W., Lin Q., & Nyman J.A., (2000). **The effects of oil spill and clean-up on dominant US Gulf coast marsh macrophytes: a review**. *Environmental Pollution,* **108:** 129-139.

Quinn M., Alotaibi A., Sethi P., Albahrani F. & Alameddine O., (1994). **Measurement and analysis procedures for remote identification of oil-spills using a laser fluorosensor.** *International Journal of Remote Sensing,* **15:** 2637-2658.

Raffaelli D., & Hawkins S. (1999). **Intertidal Ecology.** London: Kluwer Academic Pulishers

Ramamurthy V. D., (1991). **Effects of oil pollution on bio ecology and fisheries on certain enclosed coastal regions of Arabian Sea.** *Marine Pollution Bulletin*, **23:** 239-245

Riley G.A., (1985). **Oil in the sea: inputs, fates, and effects.** National Academy Press, Washington D.C.

Riley K., (2002). ***Chthamalus stellatus*. Poli's stellate barnacle**. *Marine Life Information Network: Biology and Sensitivity Key Information Sub-programme* [on-line]. Plymouth: Marine Biological Association of the United Kingdom. Available from: http://www.marlin.ac.uk

Roehl W.S. & Ditton R.B., (1993). **Impacts of the offshore marine industry on coastal tourism - the case of Padre Island national seashore.** *Coastal Management*, **21:** 75-89.

Ron E. Z., & Rosenberg E., (2002). Biosurfactants and oil bioredemdiation. *Current Opinion in Biotechnology*, **13:** 249-252.

Santas R. & Santas P., (2000). **Effects of wave action on the bioremediation of crude oil saturated hydrocarbons**. *Marine Pollution Bulletin,* **40:** 434-439.

Savari, A., (1988) **Ecophysiology of the common cockle (*Cerastoderma edule L.*) in Southampton Water, with particular reference to pollution**. PhD thesis, Dept. of Oceanography, University of Southampton.

Schmitz U., (2001). **Prospective area for onshore exploration and production in the Mediterranean region**. *Oil Gas-European Magazine*, **27:** 9-14.

Sharma V.K., Hicks S.D., Rivera W., & Vazquez F.G., (2002). **Characterization and degradation of petroleum hydrocarbons following an oil spill into a coastal environment of south Texas, USA**. *Water Air and Soil Pollution*, **134:** 111-127.

Shelton R. G. J., (1971) **Effects of oil and oil dispersants on the marine environment** *Proceedings of the Royal Society of London*. **177:** 411-422.

SMI Group, (2000). **The Libyan oil and gas report**. SMI Publishing, Ltd. London.

Snoussi M., & Aoul E. T., (2000). **Integrated coastal zone management programme: Northwest African region case.** *Ocean & Coastal Management*, **43:** 1033-1045.

Socialist Ports Co., Misurata, Libya. **Socialist Ports Co. Internal Reports.** The Libyan authorities.

Sogreah, (1977). **Trawl fishing ground survey off the Tripolitanian coast, Final report**. Unpublished report.

Stephenson, T. A., & Stephenson, A., (1972). **Life between tidemarks on rocky shores**. W. H. Freeman and Co., San Francisco.

Stephenson R., (1997). **Effects of oil and other surface-active organic pollutants on aquatic birds**. *Environmental Conservation,* **24:** 121-129.

Steuber T. & Loser H. (2000). **Species richness and abundance patterns of Tethyan Cretaceous rudist bivalves (Mollusca: Hippuritacea) in the central-estern Mediterranean and Middle East, analysed from a palaeontological database.** *Palaeogeography Palaeoclimatology Palaeoecology*. **162:** 75-104.

Suchanek T.H., (1993). **Oil impacts on marine invertebrate populations and communities**. *American Zoologist,* **33:** 510-523.

Tennyson E., (1990). **Results from selected oil-spill response research by the Minerals Management Service**. *Marine Technology Society Journal*, **24:** 27-32.

Terlizzi A., Fraschetti S., Guidetti P. & Boero F., (2002). **The effects of sewage discharge on shallow hard substrate sessile assemblages**. *Marine Pollution Bulletin*, **44:** 544-550.

Thorpe S.A., (2000). **Langmuir circulation and the dispersion of oil spills in shallow seas.** *Spill Science & Technology Bulletin*, **6:** 213-223.

Tluba B., (1991). **Pollution in the Libyan seaports**. The proceedings of the first conference on the Environment and pollution, Sebha-Libya, 1991

Tseng F.S., (1999). **Considerations in care for birds affected by oil spills**. *Seminars in Avian and Exotic Pet Medicine*, **8:** 21-31.

Tyler-Walters H., (2000). ***Corallina officinalis*. Coral weed**. *Marine Life Information Network: Biology and Sensitivity Key Information Sub-programme* [on-line]. Plymouth: Marine Biological Association of the United Kingdom. Available from: http://www.marlin.ac.uk

UNEP, (1978). **Report on pollutants from land-based sources in the Mediterranean** No. UNEP/IG.11/INF.5

UNEP, (1990). **Report on the status of Mediterranean marine turtles**. MAP Technical Reports Series No. 42 Athens, Greece.

UNEP, (1996). **State of the marine and coastal environment in the Mediterranean region**. MAP Technical Reports Series No. 100 Athens, Greece.

U.S. National Academy of Science, (1975). **Petroleum in the marine environment**. Workshop on Inputs, fates and effects of petroleum in the marine environment, May 21-25, 1973, Washington, D.C.

Vandermeulen J.H., & Singh J.G., (1994). **Arrow oil-spill, 1970-90 - persistence of 20-yr weathered bunker-c fuel-oil.** *Canadian Journal of Fisheries and Aquatic Sciences,* **51:** 845-855.

Walton P., Turner C.M.R., Austin G., Burns M.D., & Monaghan P., (1997). **Sub-lethal effects of an oil pollution incident on breeding kittiwakes *Rissa tridactyla*.** *Marine Ecology Progress Series,* **155:** 261-268

Williams, M. J. (1996). **Investigations into the effects of petroleum hydrocarbons on the immunocompetence of *Ostrea edulis* and the potential application for biological monitoring**. M.Phil./Ph.D. upgrading report, Oceanography Department, University of Southampton.

Witt G., (2002). **Occurrence and transport of polycyclic aromatic hydrocarbons in the water bodies of the Baltic Sea**. *Marine Chemistry,* **79:** 49-66.

World Bank, (1996). **Middle East and North Africa-Pollution Management, Abatement, and Control in the South Mediterranean Sea**. Project report, May 1996.

World Bank, (1998). **Oil Pollution Management Project for the South Mediterranean Sea**. Report No. 98-3100.

World Bank, (1998). **World development indicators.** World Bank reports.

World Resources Institute, (1994). **World Resources 94-95.** World Resources Institute reports 1994.

Zobell C. E., (1972). **Microbial degradation of oil: present status, problems, and perspectives**. Proceedings of the microbial degradation of oil pollutants, 3-16.

Zsolnay A., (1979). **Hydrocarbons in the Mediterranean Sea, 1974-1975.** *Marine Chemistry*, 7: 343-352

APPENDICES

APPENDIX (1)

CONCENTRATIONS OF HYDROCARBONS IN SEAWATER AND SEDIMENTS IN THE LIBYAN COAST

Appendix (1) Concentrations of Hydrocarbons in Seawater and Sediments on the Libyan coast (ppm)

Hydrocarbons concentrations in Misurata seawater

Location	Sample 1 Conc. (ppm)	Sample 2 Conc. (ppm)	Average Conc. (ppm)	Notes
40 km east	4	0	2	Control site
3km east (Iron and steel complex)	11.5	13.5	12.5	
Seaport	18	22	20	
Front of the city	9	10	9.5	
30 km west (Dafnia)	6.5	7.5	7	

Hydrocarbons concentrations in Misurata sea sediments

Location	Sample 1 Conc. (ppm)	Sample 2 Conc. (ppm)	Average Conc. (ppm)	Notes
40 km east	45	23	34	Comparison area
3km east (Iron and steel complex)	160	278	219	
Seaport	386	490	429	
Front of the city	128	154	141	
30 km west (Dafnia)	58	96	77	

Hydrocarbons concentrations in Zliten seawater

Location	Sample 1 Conc. (ppm)	Sample 2 Conc. (ppm)	Average Conc. (ppm)	Notes
3 km east	6	4	5	Comparison area
3 km west	5	0	2.5	

Hydrocarbons concentrations in Zliten sea sediments

Location	Sample 1 Conc. (ppm)	Sample 2 Conc. (ppm)	Average Conc. (ppm)	Notes
3 km east	122	146	134	Comparison area
3 km west	95	120	107.5	

Hydrocarbons concentrations in Khoms seawater

Location	Sample 1 Conc. (ppm)	Sample 2 Conc. (ppm)	Average Conc. (ppm)
3 km east	7.5	8.5	8
Seaport	8	10	9
3 km west	8	9	8.5

Hydrocarbons concentrations in Khoms sea sediments

Location	Sample 1 Conc. (ppm)	Sample 2 Conc. (ppm)	Average Conc. (ppm)
3 km east	988	875	931.5
Seaport	1359	1550	1454.5
3 km west	975	1100	1037.5

Hydrocarbons concentrations in Tajora seawater

Location	Sample 1 Conc. (ppm)	Sample 2 Conc. (ppm)	Average Conc. (ppm)
3 km east	7	8	7.5
3 km west	8.5	9.5	9

Hydrocarbons concentrations in Tajora sea sediments

Location	Sample 1 Conc. (ppm)	Sample 2 Conc. (ppm)	Average Conc. (ppm)
3 km east	112	126	119
3 km west	130	195	162.5

Hydrocarbons concentrations in Tripoli seawater

Location	Sample 1 Conc. (ppm)	Sample 2 Conc. (ppm)	Average Conc. (ppm)
3 km east	13.5	14.5	14
Seaport	23	22.5	22.75
3 km west	14	15	14.5
10 km west (Janzour)	6.5	7.5	7

Hydrocarbons concentrations in Tripoli sea sediments

Location	Sample 1 Conc. (ppm)	Sample 2 Conc. (ppm)	Average Conc. (ppm)
3 km east	270	219	224.5
Seaport	512	595	553.5
3 km west	228	210	219
10 km west (Janzour)	130	125	127.5

Hydrocarbons concentrations in Zawia seawater

Location	Sample 1 Conc. (ppm)	Sample 2 Conc. (ppm)	Average Conc. (ppm)
3 km east	35	32.5	33.75
Oil Refinery	32	33.5	32.75
3 km west	26	17.5	21.75

Hydrocarbons concentrations in Zawia sea sediments

Location	Sample 1 Conc. (ppm)	Sample 2 Conc. (ppm)	Average Conc. (ppm)
3 km east	415	390	402.5
Oil Refinery	620	695	657.5
3 km west	345	315	330

Hydrocarbons concentrations in Zwara seawater

Location	Sample 1 Conc. (ppm)	Sample 2 Conc. (ppm)	Average Conc. (ppm)
3 km east	25	17.5	21.25
3 km west	23	12.5	17.75
Abou-kammash chemical complex	27.5	23	25.25

Hydrocarbons concentrations in Zwara sea sediments

Location	Sample 1 Conc. (ppm)	Sample 2 Conc. (ppm)	Average Conc. (ppm)
3 km east	215	290	252.5
3 km west	320	370	345
Abou-kammash chemical complex	440	490	465

APPENDIX (2)

CONCENTRATIONS OF HYDROCARBONS IN THE SURFACE SEDIMENTS IN SOUTHAMPTON WATER

Appendix (2)

Concentrations of Hydrocarbons in the surface sediments in Southampton Water (ppm)

Site Name	Sample A	Sample B	Mean	Standard Difference
Marchwood	291	279	285	6
Dibden Bay	276	270	273	3.0
Hythe Pier	263	223	243	28.28
Hythe	341	359	350	9
Bird Pile	668	678	673	5
Lain's lake	1499	1481	1490	9
Fawley North	1429	1395	1412	17
Fawley Jetty	722	718	720	2
Fawley South	1194	1246	1220	26
Oil Jetty	669	611	640	29
Calshot	261	269	265	4
Beaulieu River	142	148	145	3

APPENDIX (3)

TAR ABUNDANCE RATE ON SANDY BEACHES

Appendix (3)
Tar abundance rate on the sandy beaches

Tar abundance for Misurata (Jannat Beach)- July 1999.

Distance from water edge (m)	Tar quantity (Line1) (g/m^2)	Tar quantity (Line2)(g/m^2)	Tar quantity (Line3)(g/m^2)	Tar quantity (Line4)(g/m^2)
1	0	0	0	0
2	0	0	0	0
3	210	150	20	150
4	70	30	40	85
5	20	25	16	20
6	10	15	15	15
7	12	10	15	15
8	7	0	10	10
9	25	30	40	25
10	10	25	15	6
11	15	7	5	10
12	20	13	15	16
13	25	25	30	0
14	0	0	0	0
15	0	0	0	0
16	0	0	0	0
17	0	0	0	0
18	0	0	0	0
19	0	0	0	0
20	0	0	0	0
21	0	0	0	0
22	0	0	0	0
23	0	0	0	0
24	0	0	0	0
25	0	0	0	0
Average (g/m^2)	13.27			
Total weight (g)	1327			
Average ball diameter (cm)	6			
Average ball weight (g)	20			
Distance of the nearest tar ball from water edge (m)	3			
Distance of the furthest tar ball from water edge (m)	13			
Range of tar balls distribution (m)	10			

Tar abundance for Zliten (Soug Et-tlat beach)- July 1999

Distance from water edge (m)	Tar quantity (Line1) (g/m^2)	Tar quantity (Line2)(g/m^2)	Tar quantity (Line3)(g/m^2)	Tar quantity (Line4)(g/m^2)
1	0	0	0	0
2	0	0	0	0
3	0	2	0	0
4	5	0	5	3
5	2	12	5	8
6	10	5	0	0
7	8	0	20	30
8	5	1	3	8
9	8	0	8	5
10	20	7	18	13
11	8	10	5	8
12	5	10	12	10
13	10	0	8	18
14	13	0	8	0
15	0	0	0	0
16	0	0	0	0
17	0	0	0	0
18	0	0	0	0
19	0	0	0	0
20	0	0	0	0
21	0	0	0	0
22	0	0	0	0
23	0	0	0	0
24	0	0	0	0
25	0	0	0	0
Average (g/m^2)	3.36			
Total weight (g)	336			
Average ball diameter (cm)	5			
Average ball weight (g)	15			
Distance of the nearest tar ball from water edge (m)	3			
Distance of the furthest tar ball from water edge (m)	14			
Range of tar balls distribution (m)	11			

Tar abundance for Khoms (3 km west) - July 1999.

Distance from water edge (m)	Tar quantity (Line1) (g/m²)	Tar quantity (Line2)(g/m²)	Tar quantity (Line3)(g/m²)	Tar quantity (Line4)(g/m²)
1	0	0	0	0
2	0	0	0	0
3	210	150	20	150
4	70	30	40	85
5	20	25	16	20
6	10	15	15	15
7	12	10	15	15
8	7	0	10	10
9	25	30	44	25
10	10	25	15	6
11	15	7	15	10
12	11	13	0	40
13	20	13	15	16
14	25	25	30	25
15	0	0	0	0
16	0	0	0	0
17	0	0	0	0
18	0	0	0	0
19	0	0	0	0
20	0	0	0	0
21	0	0	0	0
22	0	0	0	0
23	0	0	0	0
24	0	0	0	0
25	0	0	0	0
Average (g/m²)	14.30			
Total weight (g)	1430			
Average ball diameter (cm)	5			
Average ball weight (g)	16			
Distance of the nearest tar ball from water edge (m)	3			
Distance of the furthest tar ball from water edge (m)	14			
Range of tar balls distribution (m)	11			

Tar abundance for Tajora (3 km east) - July 1999.

Distance from water edge (m)	Tar quantity (Line1) (g/m^2)	Tar quantity (Line2)(g/m^2)	Tar quantity (Line3)(g/m^2)	Tar quantity (Line4)(g/m^2)
1	0	0	0	0
2	0	0	0	0
3	0	2	0	0
4	5	0	5	0
5	2	12	5	8
6	10	5	0	0
7	8	0	0	20
8	5	1	3	8
9	8	0	8	5
10	9	7	9	13
11	8	10	5	8
12	5	7	12	10
13	0	0	0	0
14	0	0	0	0
15	0	0	0	0
16	0	0	0	0
17	0	0	0	0
18	0	0	0	0
19	0	0	0	0
20	0	0	0	0
21	0	0	0	0
22	0	0	0	0
23	0	0	0	0
24	0	0	0	0
25	0	0	0	0
Average (g/m^2)	2.23			
Total weight (g)	223			
Average ball diameter (cm)	8			
Average ball weight (g)	27			
Distance of the nearest tar ball from water edge (m)	3			
Distance of the furthest tar ball from water edge (m)	12			
Range of tar balls distribution (m)	9			

Tar abundance for Tripoli (Textile Factory) - July 1999.

Distance from water edge (m)	Tar quantity (Line1) (g/m^2)	Tar quantity (Line2)(g/m^2)	Tar quantity (Line3)(g/m^2)	Tar quantity (Line4)(g/m^2)
1	0	0	0	0
2	0	0	0	0
3	210	165	120	150
4	170	130	140	185
5	120	125	116	120
6	10	15	15	15
7	12	10	15	30
8	14	13	20	10
9	25	30	44	25
10	10	25	15	6
11	15	7	15	10
12	11	13	0	40
13	0	10	0	0
14	0	7	0	23
15	20	13	15	16
16	25	25	30	25
17	0	0	0	0
18	0	0	0	0
19	0	0	0	0
20	0	0	0	0
21	0	0	0	0
22	0	0	0	0
23	0	0	0	0
24	0	0	0	0
25	0	0	0	0
Average (g/m^2)	24.45			
Total weight (g)	2445			
Average ball diameter (cm)	2			
Average ball weight (g)	8			
Distance of the nearest tar ball from water edge (m)	3			
Distance of the furthest tar ball from water edge (m)	16			
Range of tar balls distribution (m)	13			

Tar abundance for Zawia - July 1999.

Distance from water edge (m)	Tar quantity (Line1) (g/m²)	Tar quantity (Line2)(g/m²)	Tar quantity (Line3)(g/m²)	Tar quantity (Line4)(g/m²)
1	42	23	25	36
2	25	25	30	0
3	210	150	20	150
4	170	130	140	185
5	20	25	16	20
6	10	15	15	15
7	12	13	15	15
8	7	9	10	10
9	25	30	40	25
10	10	25	15	6
11	15	7	5	10
12	0	0	0	0
13	0	0	5	14
14	0	0	0	0
15	0	0	0	0
16	0	0	0	0
17	0	0	0	0
18	0	0	0	0
19	0	0	0	0
20	0	0	0	0
21	0	0	0	0
22	0	0	0	0
23	0	0	0	0
24	0	0	0	0
25	0	0	0	0
Average (g/m²)	18.40			
Total weight (g)	1840			
Average ball diameter (cm)	4			
Average ball weight (g)	10			
Distance of the nearest tar ball from water edge (m)	1			
Distance of the furthest tar ball from water edge (m)	13			
Range of tar balls distribution (m)	12			

Tar abundance for Zwara (3 km east) - July 1999.

Distance from water edge (m)	Tar quantity (Line1) (g/m^2)	Tar quantity (Line2)(g/m^2)	Tar quantity (Line3)(g/m^2)	Tar quantity (Line4)(g/m^2)
1	0	0	0	0
2	0	0	0	0
3	0	0	0	0
4	0	0	0	0
5	2	12	0	8
6	10	15	0	0
7	8	0	0	20
8	5	7	3	8
9	8	0	8	5
10	9	7	19	13
11	8	10	5	18
12	5	8	12	10
13	0	0	7	0
14	0	0	0	0
15	17	0	23	0
16	13	0	0	37
17	0	0	0	0
18	0	0	0	0
19	0	0	0	0
20	0	0	0	0
21	0	0	0	0
22	0	0	0	0
23	0	0	0	0
24	0	0	0	0
25	0	0	0	0
Average (g/m^2)	3.40			
Total weight (g)	340			
Average ball diameter (cm)	4			
Average ball weight (g)	10			
Distance of the nearest tar ball from water edge (m)	4			
Distance of the furthest tar ball from water edge (m)	16			
Range of tar balls distribution (m)	12			

APPENDIX (4)

TAR INCREMENT ON SANDY BEACHES

(ONE-MONTH PERIOD)

JULY–AUGUST 1999

Appendix (4)

Tar increment on the sandy beaches (one-month period) July–August 1999 (g m^{-2})

Site	Line 1 (g m^{-2})	Line 2 (g m^{-2})	Line 3 (g m^{-2})	Line 4 (g m^{-2})	Total (g m^{-2})	Distance from water edge (m)
Misurata	0	0	6	8	14	2
Zliten	0	0	0	0	0	0
Khoms	12	0	8	0	20	3
Tajora	0	0	0	0	0	0
Tripoli	4	3	0	0	7	2
Zawia	9	8	0	0	17	3
Zwara	4	0	0	0	4	3

APPENDIX (5)

TAR ABUNDANCE ON LIBYAN ROCKY SHORES

Appendix (5)

Tar abundance on the Libyan rocky shores (% cover)

Misurata

Quadrat No.	Line 1	Line 2	Line 3	Line 4
1	32	55	64	43
2	27	68	60	30
3	19	17	32	25
4	0	0	0	2
Average	29.6			

Zliten

Quadrat No.	Line 1	Line 2	Line 3	Line 4
1	25	34	53	28
2	16	11	11	10
3	9	8	0	5
4	0	8	0	2
Average	13.7			

Khoms

Quadrat No.	Line 1	Line 2	Line 3	Line 4
1	24	35	71	38
2	27	32	54	30
3	8	10	26	15
4	2	0	0	9
Average	23.8			

Tajora

Quadrat No.	Line 1	Line 2	Line 3	Line 4
1	21	38	48	17
2	15	10	32	15
3	0	6	9	4
4	0	2	0	0
Average	13.5			

Tripoli

Quadrat No.	Line 1	Line 2	Line 3	Line 4
1	62	45	72	54
2	38	43	69	44
3	23	34	43	28
4	8	26	3	15
Average	37.9			

Zawia

Quadrat No.	Line 1	Line 2	Line 3	Line 4
1	36	45	67	53
2	28	34	39	45
3	12	28	25	34
4	8	0	16	13
Average	30.1			

Zwara

Quadrat No.	Line 1	Line 2	Line 3	Line 4
1	21	39	42	25
2	16	18	24	18
3	5	12	11	0
4	3	0	0	0
Average	14.6			

APPENDIX (6)

SPECIES ABUNDANCE ON LIBYAN ROCKY SHORES

Appendix (6)

Species abundance on the Libyan rocky shores

Misurata- (30 km east)

Quadrat No.	*Melarhaphe neritoides*	*Osilinus turbinatus*	*Chthamalus sp.*	*Patella sp.*	Algae (% cover)
1	58	89	87	51	40
2	43	65	54	35	65
3	82	37	49	29	48
4	74	56	23	38	64
5	46	73	82	32	59
6	69	64	89	56	48
7	72	34	84	30	60
8	46	85	35	31	41
9	54	64	52	42	50
10	76	73	85	36	65
Average	62	64	64	38	54
SD	14.30	18.01	24.28	9.14	9.75

Misurata

Quadrat No.	*Melarhaphe neritoides*	*Osilinus turbinatus*	*Chthamalus sp.*	*Patella sp.*	Algae (% cover)
1	29	0	24	0	28
2	48	43	73	23	43
3	39	52	76	18	37
4	63	29	58	26	20
5	32	48	42	15	24
6	47	44	27	26	30
7	37	30	60	0	30
8	43	38	38	18	35
9	52	43	35	30	28
10	40	33	67	24	25
Average	43	36	50	18	30
SD	10	14.74	19.13	10.48	6.76

Zliten

Quadrat No.	*Melarhaphe neritoides*	*Osilinus turbinatus*	*Chthamalus sp.*	*Patella sp.*	Algae (% cover)
1	65	78	84	46	42
2	87	86	73	37	49
3	23	17	28	18	38
4	76	72	83	32	35
5	36	69	78	38	56
6	85	68	98	27	38
7	49	65	43	36	45
8	67	48	89	39	35
9	60	78	86	27	55
10	72	69	78	30	37
Average	62	65	74	33	43
SD	20.69	19.61	21.69	7.90	7.94

Khoms

Quadrat No.	*Melarhaphe neritoides*	*Osilinus turbinatus*	*Chthamalus sp.*	*Patella sp.*	Algae (% cover)
1	28	24	74	25	36
2	52	67	74	29	38
3	59	43	69	15	42
4	57	48	84	34	46
5	49	72	87	13	25
6	79	76	68	28	35
7	52	53	60	35	40
8	62	65	73	21	45
9	48	60	87	30	38
10	54	42	84	10	25
Average	54	55	76	24	37
SD	12.77	16.07	9.16	8.85	7.25

Tripoli

Quadrat No.	*Melarhaphe neritoides*	*Osilinus turbinatus*	*Chthamalus sp.*	*Patella sp.*	Algae (% cover)
1	31	0	32	0	28
2	34	32	37	25	36
3	39	39	29	27	42
4	26	24	12	13	25
5	21	29	5	0	15
6	41	26	23	19	22
7	32	19	26	12	32
8	37	35	16	6	25
9	14	21	19	23	25
10	45	25	31	15	30
Average	32	25	23	14	28
SD	9.48	10.74	9.97	9.76	7.54

Zawia

Quadrat No.	*Melarhaphe neritoides*	*Osilinus turbinatus*	*Chthamalus sp.*	*Patella sp.*	Algae (% cover)
1	34	30	. 25	32	58
2	0	9	0	19	25
3	36	32	33	12	25
4	48	34	14	6	40
5	32	42	71	19	10
6	42	27	67	8	10
7	23	22	30	23	25
8	45	32	48	22	22
9	35	26	40	15	30
10	25	36	22	4	35
Average	32	29	35	16	28
SD	13.77	8.96	22.30	8.71	14.17