Thesis 1394

## EFFECT OF TREATED BAPCO OIL REFINERY EFFLUENTS ON THE MARINE ENVIRONMENT IN BAHRAIN

Thesis submitted for the Degree of Doctor of Philosophy

> In the University of Stirling



Division of Ecology School of Molecular and Biological Sciences University of Stirling

February 1989

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The work presented in this thesis is the result of my own investigation, it has not been nor will be submitted for any other degree.

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### <u>A B S T R A C T</u>

The aim of this thesis was to study the effect of the treated oil refinery effluents of Bahrain Petroleum Company ( BAPCO ) on the marine environment.

The study has been carried out in seven chapters , the first dealing with general introduction about the physical environment of the Arabian Gulf and its oil industry in addition to marine pollution and fishery in Bahrain.

The second chapter was aimed at studying the quality of water at different areas in Bahrain to compare it with the quality of water at an area adjacent to the refinery outfalls.

The third chapter deals with the impact of the refinery on the marine environment. The research approach adopted was ecological and observational, involving water and sediment analysis.

The fourth chapter was aimed at studying the effects of the refinery effluents on the fish through toxicity tests and estimation of trace metals and hydrocarbons in the fish tissues. The studies were conducted with several effluents from the main and side streams of the refinery, outlets of the induced air flotation unit and Sitra separator.

The fifth chapter was aimed at studying the effect of Sitra oil storage tanks treated effluent on the intertidal fauna of the adjacent area.

The sixth chapter deals with a general discussion on the whole studies. While the seventh chapter deals with conclusions and recommendations.

From the study conducted , it could be said that in general the water quality of the western and northern regions of Bahrain is better than the water quality of the eastern region. The east has in general higher pH, higher ammonia , higher nitrite, lower nitrate, and higher phosphate levels than the other regions. The higher concentrations of all these substances reflects the urbanisation and industrialisation of this part of Bahrain and the consequent discharges of waste material.

The fish, safee, were tested with different concentrations of the refinery main stream effluent using both short and long term exposures. The same experiment was set up using effluents from the side stream, the I.A.F. discharge of the refinery and Sitra separator outlet . The results indicated a greater toxicity of pollutants in the I.A.F. and Sitar separator effluents than in the main and the side stream effluents. The lethal concentration of I.A.F. and Sitra separator effluents which brought death to fifty percent of the test population of fish (safee) within 96 hours was approximately twenty percent . Fish from the experimental media showed a higher concentration of heavy metals.

The study of the effect of Sitra oil storage tanks treated effluent on the intertidal fauna of the adjacent area revealed that no fauna was found at stations located just outside the effluent outlet. The sediment of these stations was black, slimy, heavily oiled with a bad smell and contains dead shells and turrets. Away from the effluent, a diverse fauna was found.

It is concluded that the BAPCO refinery has a measurable impact on the marine environment of the east coast of Bahrain , and recommendations are made for the development of future policies with regard to Bahraini coastal waters.

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## CHAPTER 1

# GENERAL INTRODUCTION

### 1.1 The Arabian Gulf:

### 1.1.1 Physical environment of the Gulf:

The Arabian Gulf (Figure 1.1) is a shallow semienclosed sea located in the Asian continent at longitude  $48^{\circ}$  to  $56^{\circ}$  2.0 `E and latitude 23.9° to  $30.25^{\circ}$ N, measuring about 1000 km in length and 200-300 km in width, covering an area of approximately 239,000 sq.km. It is surrounded by the arid land of Saudi Arabia peninsula on its south, Iranian sub-continent on the north and connected to the Indian Ocean by the 60 km. wide Strait of Hormuz.

The marine environment of the Gulf has very special geographical and meteorological conditions, and therefore is not comparable to any other sea areas, except perhaps the Red Sea and the Gulf of Aden (FA0,1981).

The Average depth of the Gulf is about 35m and the deepest part (100 m) is at the entrance near the Strait of Hormuz. In general, the depth is greatest near the Iranian coast and the bottom shows a slope from the southern to the northern coastline. The bottom is primarily sandy with extensive swampy areas nearer Iraq coast and isolated rock formations along the Saudi Arabian shores.

Surface salinity averages 37-40%. in the central part, 40-50%. in the shallow parts and 60-70%. in lagoons and bays such as the Gulf of Salwa (between Saudi Arabia and Qatar). Salinity increases by 2-4%. with depth in central part (Purser and Seibold, 1973). The salinity of the Gulf remains high as a result of little exchange with oceanic water and little precipitation in the region. The only freshwater influx is



## Figure:1.1

The Arabian Gulf.

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through the rivers Tigris and Euphrates in Iraq and flash floods from Zagros mountains in Iran. Further there is some replenishment of Gulf water through the Strait of Hormuz.

More rain falls on the Iranian coast than along the Arabian-coast and more in the northern region than in the central and southern regions. The mean annual rainfall close to Kuwait is 124mm; in Bushehr, Iran which is approximately in the same latitude, the mean annual rainfall is approximately 274mm; and in the central region in the vicinity of Bahrain the annual rainfall is less than 100mm (FAO, 1981).

Surface circulation appears to be counterclockwise, moving northwesterly along the Iranian coast and outflowing water moving southeasterly along the Arabian coast (Emery, 1956 and Nelson-Smith, 1980). Tidal ranges rarely exceed 3 m and average tidal current speeds in the Gulf are low (Jones, 1986).

The water temperature fluctuates greatly in the Gulf with a minimum of around  $10^{\circ}$ C in winter and summer maximum of around  $37^{\circ}$ C. The occurrence of a thermocline is possible only in summer during the period of no wind action when the sea is relatively calm. The difference between the surface and bottom temperatures can reach  $10^{\circ}$ C (FAO, 1981).

Dissolved oxygen has greater levels in winter due to mixing of water temperature, while in summer the oxygen level at the bottom drops to 1.5 - 3.5 mg/l (Alkhole and . Soloviov, 1978).

Along the coasts of Kuwait and Saudi Arabia, the bottom is generally sandy with some locations having extensive rock formations. Sand dominates the bottom around Bahrain, but there are also extensive coral reefs areas. The shores around United Arab Emirates are principally sandy. The bottom deposits along the Iranian coast are mainly mud, becoming sand-mud near Iraq.

The waters of the inner sea areas are more turbid than in the Red Sea or Indian Ocean generally, with a euphotic zone about 20 - 30 m deep which nevertheless includes a large area; of the bottom along the western side (Nelson-Smith, 1980).

Since the land surrounding the Gulf is largely desert, nutrients can enter the system only via Shat-al-Arab or, periodically, through the Strait of Hormuz; but intertidal micro-algae, sea grass beds in the shallows and, to a smaller extent, mangroves and other halophytes around sheltered bays apparently make a contribution sufficient to permit relatively high productivity (Nelson-Smith, 1980).

### 1.1.2 Oil industry:

Rapid industrialization and urbanization in the last couple of decades has subjected the Gulf to stressful environmental extremes. The Gulf, being the receiver of sewage, industrial, oil extraction and transportation discharges appears to be increasingly polluted.

The activity for which the Gulf is best known throughout the modern world is the production and export of petroleum. The extraction of oil began over sixty years ago; production has grown at an increasing rate during the last years and the exploration for new fields continues today. Many of the oil fields lie offshore, together with most terminals at which the larger tankers load, while most of the recent or planned oil-related industrial developments are located along the coastline.

The majority of this oil is carried from loading terminals throughout the Gulf through the Strait of Hormuz. Familiar overall statistics are that about one-third of the world's oil is produced around the sea area of the Gulf, which carries about two-thirds of all oil exports. Around 20 to 100 tankers may pass through the Strait in this trade during a single day to a wide range of destinations (Nelson-Smith, 1980).

About 57 per cent of the known world oil reserves and 82% of the OPEC reserves belong to the Gulf countries. Gulf countries' production of oil in 1979 was estimated to be about 20.69 million Barrels/day which constitutes about 68% of the total OPEC production (Khosravi, 1981).

It has been estimated that investment may reach 40 million US dollars per kilometre along southern and western shores (Anon., 1976; Newman, 1979) while a figure of 20 million \$ Km<sup>-1</sup> was projected for the Iranian coast.

Trends in such investment suggest a slow but steady increase in production, refining capacity and export, a slightly greater increase in oil-based fertilizer manufacture and a considerable increase in petrochemical production. Thus every activity, from exploratory drilling to by-product manufacture, may have a growing effect on the marine environment.

### 1.2 Bahrain:

Bahrain (Figure 1.2) is located in the Arabian Gulf at longitude  $48^{\circ} - 57$ ' and latitude  $24^{\circ} - 30$ ', it is an archipelago of more than 33 islands approximately fifteen miles off the east coast of the Arabian peninsula, one hundred and fifty miles off the coast of Persian and eighteen miles off the coast of the Qatar peninsula.

The total area of Bahrain is 265.61 square miles (687.7 square kilometers) (Ministry of Housing, pers.comm., 1985). Bahrain island (217.50 square miles) is the largest island with a population of about 417,210 persons (Central Statistics Organisation, Pers.Comm., 1985), it is 29.8 mile (48 km) long (N - S) and 9.9 mile (16 km) wide (E - W). On this island lies Manama, the capital, Mina-Sulman, the largest seaport, refinery in addition to the industrial and commercial community. The next islands being Muharreq (8 square miles), Sitra (5 square miles) where the petroleum port is found, followed by Umm-Nasan, Nabeeh Saleh and many other small islands.

The northern part of Bahrain, as well as a part of the western coast, is well irrigated and fertile. The remaining is desert.

Due to its geographical position in the Gulf, Bahrain has long very hot summers. It's temperature can exceed 35<sup>0</sup>C. Relative humidity is high all year around. The average rainfall is 75 mm per year.

The high summer temperatures and proximity to the sea result in high evaporation and relative humidity (48 - 83%).



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Wind velocities are lower around Bahrain than in many parts of the Gulf due to the lee effects offered by the Saudi Arabian mainland to the west. However, wind speed in excess of 10 m/s are not uncommon.

The waters around Bahrain and nearby Saudi Arabian coast have extensive coral reefs. Here, the depths being very shallow, often 20 m for several miles offshore, the vertical temperature profiles are more or less uniform.

### 1.2.1 Fishery:

A traditional fishery using fixed fishing gear (barrier and wire traps) for inshore fishery, in addition to gill-nets, seines, hand-lines and troll-lines for deep water fishing (>10m) was the major economic activity in Bahrain prior to the discovery of oil in the 1930s. The fisheries form an important economic sector of the country. This has been a traditional vocation of a large portion of local population and even to-day a sizable number of fishermen earn their livelihood from fishing and feed the population of this country with a protein rich diet .

In the early part of this century industrialization started and many people migrated from the agriculture and fishing sectors towards industrial employment.

In 1983, the total number of fishermen that were occupied with fishing was 1822 full-time, 1489 part-time and 292 amateur fishermen. The highest number of full-time fishermen was in the eastern province (653 fishermen), while the part-time fishermen were higher in Muharreq province (Anon., 1985).

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The total number of traditional dhows, wooden, fiberglass and steel boats operating in the artisanal sector during 1983 were 1429. However, the industrial sector consists of seven steel trawlers (Anon., 1985). The number of Artisanal shrimp trawlers were 59. The highest numbers of boats were in the Muharreq province, being 531. The next in order was the Eastern province with 485 boats. The third and fourth provinces were the Northern and Western. Here, the number of boats were 299 and 115 respectively (Anon., 1985).

During 1985, the total quantity of fish landed in Bahrain was 7762.6 metric tons (5850.6 mt fish,1869.9 mt crustaceans "1324.7 mt of this are shrimp", 42.1 mt molluscs) valued at BD6.13 million (BD4.65 million for fish, BD1.46 million for crustaceans "BD1.2 million for shrimp" and BD0.02 million for molluscs) (Anon.,1986).

Bahrain coastal ecosystems are not only diverse but are also very productive. Seagrass beds, coral reefs and tidal marshes are the most productive marine ecosystems, and their productivity can approach or exceed that of agricultural land (Mclusky, 1981). As might be expected, therefore, fish is an important component in the Bahraini diet. The per capita fish consumption in 1985 was 25.6 kg (Anon., 1986) which is comparatively high in international terms.

The fishery of Bahrain is primarily demersal i.e., the fishes are those living on the bottom of the sea. This is because of the existence of the vast stretches of sea-grass beds peculiar to Bahrain and biologically productive coral reefs which give shelter and food to the youngs of fishes. The fishing activity of the artisanal fishermen is largely confined to shallow reefs, sand flats and seagrass beds which surround the islands of Bahrain within a distance of 15 to 20 mile from the shore. Out of 11 landing sites of Artisanal sector, Sitra ranks first followed by Muharreq, Dair, Diraz and Manama. Sitra has more boats which fish on rich fishing grounds south of Fasht-al-Adum (Fugure12) and in Dawhat Salwa. The boats of Muharreq, Manama, Dair and Diraz fish on different fishing grounds mostly in the northern sea. For Industrial sector, Mina Sulman is the only landing place (Anon., 1985). The industrial fishing vessels fish the deeper waters to the north and south of Bahrain and out into the Gulf itself.

The vertebrate fish catch is composed of a wide variety of fish species because of the diversity of the inshore systems. Some fish are pelagic such as trevallies, barracudas and mackerels but the catch is dominated by reef fish such as groupers (16% of the vertebrate fish catch) perches (17%) and fish from sea-grass beds such as the rabbitfish (20%).

### 1.2.1.1. Shrimp fishery:

Shrimp is one of the most important species to the local market. Several species are landed but the dominant one is always found to be <u>Penaeus semisulcatus</u> which comprises 95% of local shrimp landings. Their populations are sensitive to depletion resulting from over-fishing, pollution, or destruction of their nursery area (Anon., 1980). The shrimping grounds around Bahrain are identified as the Northern and Eastern grounds (Figure 1.3). The industrial fleet operates mainly on the Northern ground,



Figure: 1.3 Bahrain shrimping grounds (based on interviews with skippers.



Common grounds. Seasonal or occasional grounds. Rarely fished grounds.

The dotted lines indicating the coral reefs (Fasht) and pearling grounds (Hayr) (after AbdulQader, 1986). while the Artisanal fleet is on the Eastern ground. These grounds have a soft bottom suitable for trawling operations. Trawling is generally carried out in relatively shallow areas compared with shrimp trawling grounds in other parts of the world.

The shrimping season starts in May/June and extends for a year until new recruits appear in the next season. In the beginning of the shrimping season, the shrimps usually found in the shallow waters near the eastern coast of Bahrain. The appearance of the shrimps at this stage in big quantities is a very attractive prospect for the fishermen who use small boats to operate in these areas.

During May and June 1979, few recruits appeared which was either the result of unsuccessful spawning or of mass post larvae (Juvenile) mortalities (Anon., 1980). This situation resulted in a very poor shrimping season during 1979 and the beginning of 1980. In response to this situation, a closed fishing season has been imposed since 1981(from1st of March to 30th of June)to protect the shrimp stock.

Like many animals, they occupy a range of habitats at various stages of their lives and damage to just one of these can affect the entire lifecycle of the species and bring about a collapse in its population. <u>Penaeus</u> <u>semisulcatus</u> breeds in early spring when spawning females discharge thousands of already fertilised eggs into the sea, generally under the protection of darkness. These drift in the plankton for about a day before hatching into pear-shaped nauplii larvae which are active swimmers. They develop via a series of moults into protozoa larvae feeding on phytoplankton. A further series

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of moults produced the carnivorous mysis larvae feeding on zooplankton. Three more moults bring the developing shrimp to the post mysis stage which eventually settle to the bottom to become juvenile shrimps. The whole planktonic phase lasts about three weeks (Vine, 1986).

Figure 1.4 shows the observed and probable shrimp nursery areas on the east coast of Bahrain (the numbers 1 and 2 are confirmed nursery areas.).

It is known that the new shrimp recruits have a great tendency to aggregate and migrate from place to place depending on environmental factors especially the wind. The stoppage of fishing during the recruitment period gives a better chance to the shrimp to migrate from the Eastern fishing ground to elsewhere and thus escape being caught.

The total shrimp catch from the Eastern ground during the season 1983-1984 is estimated as 176.7 metric tons which is lower by 48.0% than that of 1982 - 1983 season. It is believed that industrial expansion, dredging and land reclamation activities have contribution to a large extent in the decline of this valuable resource.

Shrimps consititute more than 70% of the crustaceans fishery. In 1985-1986 season, the total shrimp catch was 1324.7 metric tons valued at BD.1.2 million (Anon., 1986<sub>b</sub>)

### 1.2.1.2. Pearl:

Pearl oysters have been fished in the seas around Bahrain for at least four thousand years. Two species of commercial importance, <u>Pinctada margaritifera</u> and <u>Pinctada</u> radiata are bivalve molluscs living their adult lives



#### Figure: 1.4

The observed and probable shrimp nursery grounds (dark areas) on the east coast of Bahrain (the numbers 1 and 2 are confirmed nursery grounds). (After Anonymous, 1986).

coral

on the seabed, generally attached by byssus to some hard object. They possess a limited capability to change location by secreting new byssal threads which cling to an adjacent substrate. The oysters feed on diatoms and a range of other plankton such as <u>Coscinodiscus</u>; <u>Chaetocros</u>; <u>Trichodesmium</u>; <u>Skeletonema</u>; larvae of ostracods and even fish eggs. Their diets vary according to what plankton is available at any particular time. Food particles are trapped on the gill filaments and transferred to the labial palps where food is sorted prior to ingestion .

Reproduction of pearl oysters takes place by a process of synchronous spawning. This means that, as a result of some triggering factor, eggs and sperm are ejected into the water where fertilisation takes place and the eggs commence dividing to produce larvae. They have a relatively brief planktonic phase before attaching to some form of substrate. In Bahraini waters many young pearl oysters attach to brown algae. If the algae is dislodged during a storm there is a strong possibility that the Juvenile pearl oysters will be cast ashore and thus killed. There are sections of beach on Hawar island where small pearl oyster shells, form a recent recruitment period, can be collected in their tens of thousands indicating the intense spat settlement which must have occurred and the precarious nature of an oyster's life. The preferred settlement surface of the oyster spat in Bahrain waters seems to be on leaves of the sea-grass Halodule uninervis . Frequently a single blade have fifty to hundred young oysters attached to it and counts of several hundred spat per blade have been made. The main period for settlement is March-April and they grow rapidly during the summer months to a size of around 5 mm. During this phase they are an inconspicuous green color but by

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October, when the grass blades start to turn brown and die-off, the oysters transfer their grip to an adjacent upright blade. Then as that blade also dries they transfer again. The net result is that large clumps of darkshelled pearl oysters accumulate and are gradually transported into deeper water where they form dense aggregations wherever hard substrata are to be found near the base of the seagrass slopes. This relationship between Bahrian's pearl oysters and the sea-grass beds once again emphasises the vital importance of healthy sea-grass for the maintenance of productive marine-life in the region (Vine, 1986).

### 1.2.2. Marine pollution:

In Bahrain monitoring of pollution is inadequate. Regulations and standards for waste disposal have not yet been enacted. Most industrial wastes are carelessly dumped into the sea creating a potential marine pollution problem.

In the north part of Bahrain there is the capital Manama and the sea port Mina Sulman. All heavy industry is situated in this part and oil and gas are extracted there. The populated areas are in close proximity to the industrial activities.

The local aquatic and littoral environment consist of different important marine habitats such as intertidal flats, coral reefs, grassbeds and mangrove swamps. Fishery resources are almost the only existing natural resource of Bahrain.

Since 1930, the coastal waters have been exposed to man-made pollution. The marine enviornment receives wastes from different sources such as the refinery, dredging and land reclamation activities, sewage outfalls, aluminium industry, power stations, desalination plants, petrochemical industry, iron and steel company, ship building yards, asphalt and cement factories, agroindustry (lamb feedlots, dairy farms, layer houses), food manufacturing (slaughter houses, flour mill, soft drinks), plastic industries and photolaboratories. In the car service stations, no used-oil collection and recycling is practiced. Therefore, it may be assumed that most of the spent car lubricant oil finds its way into the sea. Table 1.1 shows analysis of some industrial effluents in Bahrain, their location is in Figure 1.5)

The above activities indicate the current need of controlling the toxic waste disposal into the sea.

### 1.2.2.1. Oil Spill

Petroleum became readily available about 100 years ago and has been in widespread use only within the present century but, even at the height of the recent so-called energy crisis, it was being shipped in greater quantities and larger carriers than any other product of commerce or industry.

Physical mixing of the water column can of course disperse a surface slick throughout the mixed layer if the turbulence is sufficiently great. By thus increasing the effective contact area between oil and water, mixing abets dissolution of the oil as well as simply dispersing small droplets of oil throughout the water column. Mixing thus tends to expose surface organisms, including even benthic organisms if the water column is shallow enough, to the impact of an oil discharge, whereas in calm weather the same organisms would feel little or no direct impact from the discharge.

Table: 1.1

Analysis of the main industrial effluents in Bahrain.

(From Environmental Protection Technical Secretariat. Personal communication)..

| EFFLUENT ANALYSIS                         | UNITS             | SI TRA<br>TREATMENT<br>PLANT | BAHRAIN<br>ALUMINIUM<br>EXTRUSION | SITRA<br>POWER &<br>DESALLNATION<br>PLANT | RAS ABU JARJOOR<br>R.O.DESALINATION<br>PLANT | AISCO<br>DESALINATION<br>& SEWAGE P<br>PLANT | BAHRA IN<br>PETROLEU<br>COMPANY | CENTRAL <sub>BI</sub><br>MBATTOIP | ARAB<br>SHIP<br>JILDIN<br>AND<br>YARD | GULF  | AL- C | GULF<br>PETRO-<br>HEMICAL<br>DUSTRIE<br>DUSTRIE | TUBLI<br>SEWAGE<br>TREATMENT<br>PLANT |
|---|-------------------|------------------------------|-----------------------------------|---|--|--|---------------------------------|-----------------------------------|---------------------------------------|-------|-------|---|---------------------------------------|
| Date                                      | Jen<br>L          | uary - Dec                   | ember 19                          | B6  |  |  |                                 |                                   |                                       |       |       |   | ·                                     |
| Flow                                      | m <sup>3</sup> /d | 250                          | 316                               | 1.840 <sup>6</sup>                        | 3785   | 15268  | 665000                          | 408.2                             | 1                                     | 105 1 | .08.7 | 552000  | 80000                                 |
| Physical properties<br>Floating particles |                   | IIN                          | White<br>Particles                | LIN                                       | 111  | N I I  | 1 I N                           | Green<br>Algae                    | 111                                   | N1 1  | 111   | 111   | 11N                                   |
| ¥   |                   | 6.18                         | 8.33                              | 8.3                                       | 7.0  | 8.2  | 8.21                            | 8.33                              | 7.5                                   | 7.8   | 9.69  | 8.0   | 16.7                                  |
| lemperature                               | •                 | 3                            | 26                                | 28  |  | 8  | 30.1                            | 20.16                             | 1                                     | 25    | 25    | 32  | 30                                    |
| Total suspended solids                    | mg/L              | 26.75                        | 922.285                           | 33.8                                      | 13.2   | 6.0  | 9.45                            | 95.6                              | 8.0                                   | 27.25 | 197.6 | 5.0   | 8.6                                   |
| Turbidity                                 | <b>JTN</b>        | 6.41                         | 1032.3                            | 5.68                                      | 0.95   | 0.5  | 2.87                            | 35.38                             | 1.95                                  | 12.5  | 27.4  | 2.0   | 3.098                                 |



### Figure: 1.5

Location of the main industries in Bahrain.
Ultimately most oil discharged into an aquatic system is presumably degraded by a combination of biological, physical and chemical processes, although actual degradation rates are poorly known.

There is no doubt that some bacteria can metabolize petroleum hydrocarbons, but no single bacterium can metabolize all the different hydrocarbons in crude oil. Hence a combination of bacteria would be needed to degrade all of the hydrocarbons in a crude oil spill.

The impact of a given oil discharge is thus determined very much by the nature of the hydrocarbons involved. However, other factors, including weather conditions and the distance of the discharge from shore, also play an important role in determining the extent of ecolological damage. This point is worth elaborating on. Because most components of oil are less dense than water, oil discharges usually tend to float on the surface. Thus organisms that come into contact with the surface are most likely to be affected by oil pollution. However, hydrocarbons do have a finite, although small, solubility in water, and some of the oil will therefore dissolve in the water rather than simply float on the surface. Unfortunately the low molecular weight hydrocarbons, which include the most toxic components of the oil, are also the most soluble in water. On the other hand, the low molecular weight hydrocarbons are also the most volatile, and therefore tend to evaporate from the surface most readily. Thus the characteristics of an oil slick are likely to change significantly within a day or so of the time the oil is released. Specifically, the percentage of toxic low molecular weight hydrocarbons is likely to be greatly reduced due to evaporation and

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dissolution of these compounds. Hence a slick that washes ashore a few days after discharge is probably much less toxic to intertidal organisms than a slick that is driven ashore immediately after discharge (Anon., 1986).

Offshore oil production is an important potential source of spills; although routine operations are carefully controlled, accidents can give rise to the release of very large volumes of oil which, because it passes through water immediately on its release, is a rich source of the lighter, more soluble and generally more toxic constituents which are removed during refining and may not even be loaded into crude tankers.

In Bahrain, relatively large oil spills have contaminated its coast during 1980 and 1983.

### 1.2.2.1 (i) First oil spill:

On 6 August 1980, large quantities of crude oil (about 2750 tons) from an area to the west of Bahrain ( $26^{\circ}$  6' North,  $50^{\circ}$  30' East) was spilled. During the night of 25 August, fishermen reported an oil slick off the northern shore of Bahrain and later oil had reached the northern and north-western shores as shown in Figures 1.6 and 1.7.

The initial impact of the spill was most serious in the upper interidal area where a high mortality of molluscs and crabs was apparent. The fishery most immediately affected was the barrier-trap fishery of the north and north-western shores where catches were apparently reduced and the fish samples found to be contaminated with petrogenic hydrocarbons (Al-Alawi, 1981).



Figure: 1.6 Oil slick movement during 25th August to 31st August 1980 (From Al-Alawi, 1982).

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Figure: 1.7 Oil slick movement during 2nd September to 8th September 1980 (From Al-Alawi, 1982).

Many fishing gears were affected. 305 barrier traps (haddrahs) were damaged in addition to 8048 wire traps (gargoors) and 162 gill nets.

On 9 September 1980, about 700 dead fish were seen at Al-Mamtalah coast (south-east of Bahrain).

#### (ii) Second oil spill:

On 8 October 1980, an explosion in the platform of Hasbah 6 well of the Arabian American Oil Company (ARAMCO) in an area  $27^{\circ}$  50' North,  $49^{\circ}$  40' East (Figure 1.8) lead to a release of 14,000 tons of crude oil at a rate of 2000 barrels per day for a period of eight days.

On 15 October 1980, the size of oil spill was twice the size of Bahrain (Figure 1.8).Large quantities of crude oil has contaminated Bahrain coast.

### (iii) Third oil spill:

In January 1983, about 200,000 tons of crude oil was released in the Gulf as a result of an explosion in the Iranian Noroz oil field. The spill continued for several months. Large quantities of the spilled oil reached Bahrain coast .

#### 1.2.2.1.1 Effect of oil on marine organisms:

Many commercially important species have planktonic eggs and larvae which are abundant in the uppermost surface layer and therefore exposed to the influence of oils.



# Figure:1.8

Position and size of the oil slick on 14th October 1980. (From Al-Alawi, 1982) . Oil may act physically to blanket organisms, causing death by preventing vital processes such as respiration, or in less severe cases hindering other processes such as movement and feeding. Organisms may be exposed to oil in the form of fine droplets, as components absorbed onto particulate material, or as soluble fractions in the water. At high concentrations, these could cause narcotization or death, while at lower levels they could interfere with physiological or behavioural processes that ultimately affect the survival or reproduction of the organisms (HMSO, 1976).

### 1.2.2.1.1 (i) The effect in the open sea:

The surface waters of the open sea contain the planktonic plants and animals which form the basis of most of the marine food chain, as well as the eggs or larvae of important commercial species of fish. These are particularly sensitive to the damaging effects of oil slick.

Bottom living organisms play a large part in the food chain of the sea as consumers and themselves often form food for bottom feeders such as fish and crustaceans. Oil carried to the sea bed could affect the eggs of bottom spawning fish such as herring, which are laid in limited spawning areas of hard gravelly bottoms (HMSO, 1976).

# (ii) The effect in the shallow water:

Shallow waters of large sandy bays and estuaries are valuable fish nursery grounds and important for their shell fisheries and as a source of bait. Nursery grounds in coastal waters and estuaries may be subject to accidental spills, single or repeated, and to the chronic discharge of oil from refinery and terminal operations. Fish appear to be able to tolerate intermittent small spills but where large or repeated spills, occur in restricted waters some mortality may results depending on the local circumstances (quantity and type of oil, depth of water etc.). In waters subjected to oil contamination fish are likely to take up oil by direct contact or through the food chain if they do not move away from the area. Tainting occurs when a very low level of certain oil components is present in the flesh and makes the fish inedible. However the taint is lost when ambient hydrocarbon levels return to normal (HMSO, 1976).

#### 1.2.2.2 Industry:

#### 1.2.2.2.1 BAPCO refinery:

The status of Bahrain as an oil producing country and as an oil refining centre, in addition to its proximity to major tanker routes, exposes it to a continuous risk of oil pollution.

Bahrain oil industry began when oil started to flow in 1932 at a rate of 9,600 barrels a day. A mining lease was granted to BAPCO on December 29th 1934 and this paved the way for the establishment of an integrated oil industry in Bahrain.

Oil refining began in 1935 and the processing of crude oil since the early stages of Bahrain's drilling programme has ensured that maximum economic benefits accrue to the country from its oil resources. From an initial level of 10,800 bpd the refining capacity has grown to more than quarter of a million barrels per day. Oil from both Bahrain and Saudi Arabia is processed into a wide range of products including diesel fuels (18 grades); gasoline (30 grades); naphthas (9 grades); fuel oils (16 grades) and liquified petroleum gas (LPG). In all there are 84 grades of products processed at the refinery. The oil from Saudi Arabia is carried via the 34 mile long Saudi Arabia-Bahrain pipeline, the fore-runner of which was a twelve inch bore, seventeen mile long pipe laid in 1945-at that time the world's longest commercial submarine pipeline.

BAPCO refinery is the oldest refinery in the Gulf and is the largest source of pollution into Bahrain seawater. It will be discussed in more detail in later chapters.

#### 1.2.2.2.2 Aluminium industry:

Aluminium Bahrain Smelter (ALBA) (Figure 1.5) is the largest non-oil industrial project on the Arab side of the Gulf. It is the biggest industry after oil. ALBA started operation in 1972. Its production capacity is approximately 174,000 tons of aluminium annually.

ALBA plant use distilled ground water for processing and cooling. This is discharged later to the sea without treatment at a maximum rate of 318,000 1/day (Al-Shoala, 1980). The untreated effluent might contain flourine compounds, oil, some mineral salts and is characterized by high temperature and alkalinity.

ALBA's production of raw aluminium has led to a number of satellite industries being established on Bahrain. Bahrain Atomisers with annual capacity of 3,000 tons of powder was the first of these, converting molten aluminium to fine grade aluminium powder to be utilised in a range of activities from paint production to explosives manufacture. Midal cables with a capacity of 1,000 tons /year, makes aluminium rod and insulated overhead conductors to a very high standard. It is also the largest single user of ALBA's aluminium production. A new associated project is that of the Gulf Aluminium Rolling Mill (GARMCO) with an annual capacity of 40,000 tons . The company hot-rolls aluminium provided by ALBA and produces 6 mm thick sheets of aluminium which are then cold-rolled into various products such as sheets, circles and corrugated sheets.

The liquid waste (150,000  $m^3/day$ ) from the mill is discharged into sewers and treated by North Sitra industrial treatment plant.

Another satellite industry which is based upon ALBA's production of aluminium is the Bahrain Aluminium Extrusion Company (BALEXCO) with a capacity of 6,000 MT/year producing doors, window frames, cladding etc. for the construction industry. It produces a number of fine quality products including some coated with polyester powder and available in a wide range of colours.

The liquid wastes overflows from the process are neutralised by sulphuric acid or caustic soda according to the pH of the flow and pumped to a settling pond where aluminium hydroxide settles at the bottom. The effluents which still contain a significant amount of aluminium due to problems in pH adjustment and inadequate settling are discharged to the sea at a rate of  $316 \text{ m}^3/\text{day}$ .

#### 1.2.2.2.3 Power stations:

Bahrain's first power station began operation in 1931. At present there are 4 Governmental power stations (Figure 1.9) the oldest being at Mahooz, a small station in Muharreq, a steam power station in Sitra and a gas turbine station at Rifa'a.

In 1984, electrical efficiency increased from 20.50% to 24.45% and the maximum peak demand, due to intense summer heat was 514 MW representing an increase of 4.9% over 1983.

In addition to these there are other power stations at the big industries such as BAPCO, ALBA and ASRY.

In 1961 the total production capacity of the power stations did not exceed 32 MW. By 1986 it increased to reach up to 900 MW.

The threat of destruction or alteration of marine communities by heated effluent from **p**ower plants and other industrial installations is greatest in the tropics. Unlike the biota of temperate and polar regions tropical organisms characteristically live at temperature only a few degrees below their upper lethal limit.Ferguson wood and Johannes ; 1975).

Increased temperatures can lead to oxygen depletion in the water. They can also cause excessive growth of deleterious organisms such as filamentous algae and dinoflagellates.

There is evidence that weight loss, lowered reproductive success, higher disease rates and increased mortality can result from prolonged exposure to temperatures only slightly higher than ambient (Bader <u>et al</u>, 1972).



# Figure: 1.9

Location of the power plants (from Columbus, 1978).

### 1.2.2.2.4 Desalination plants:

Bahrain has traditionally depended on spring and artesian wells to supply water for domestic and agricultural needs. However, with a marginal rainfall (about 75 mm) experienced every year and as more water is drawn from the underground aquifers, the supply of natural water is reaching its limits of exhaustion. Only 20% of the total amount of water being pumped out is for domestic use, the rest goes towards meeting the demands of agriculture and industry.

As demand exceeds the natural supply, the Government has embarked on an extensive programme of desalination to meet the State's growing need for water.

There are five main desalination plants (Sitra , Ras Abu-Jarjour, Al-Dour, BAPCO and ALBA) in Bahrain all situated along the eastern coast in addition to other small stations.

Sitra seawater desalination and power plant was constucted on a reclamined land to the north of Sitra island (Figure 1.5)It started production in 1976 with a capacity of 5 million gallons per day using the multi-stage flash system. In 1985, 3 additional units located at Sitra, each with a capacity of 5 million gallons per day was completed as an extension to the Sitra power and water station.

The brine effluent discharged to the sea from this plant is approximately 490 million gallon per day.

The desalination plant at Ras Abu-Jarjour (Figure 1.5) started production since 1984 with a capacity of 10 million gallons per day. The water is treated by the reverse osmosis method (RO), this water from Ras Abu-Jarjour is pumped to west Rifa'a blending station where the desalinated water is blended and then pumped on to various areas in Bahrain.

The quantity of brine effluent discharged to the sea is 66.7 million gallon per day at a distance of about 100 m away from the coast.

Al-Dour reverse osmosis sea water desalination plant is expected to start production in 1987.

Effluents from desalination plants are characterised by elevated levels of not only salinity but also temperature and toxic metals such as copper, zinc and nickel. They may also contain various chemicals added for pH and corrosion control and to prevent settlement of marine fouling organisms within the plant. These effluents are often sufficiently saline that, despite their elevated temperature, they sink and flow along or near the bottom where there is no loss of heat directly to the atmosphere and where their potential for damage to benthic communities is greatest.

# 1.2.2.2.5 Ship yards:

# 1.2.2.2.5 (i) ASRY:

The Arab Shipbuilding and Repair Yard (ASRY) owned by seven OAPEC member states is the biggest ship yard in Bahrain. It has a 500,000 dwt capacity drydock and facilities specially designed to handle VLCC (very large crude carrier) repairs. The yard occupy some 45,000 square meters of reclaimed land (Figure 1.5) and connected to the main land by approximtely seven kilometres long causeway constructed from dredged material. The drydock opened in late 1977 and is ideally positioned for taking on repairs to tankers sailing into the Gulf.

Between October 1977 and May 1978, the Yard docked 63 ships. Its annual capacity is 55 VLCCs (UNEP, 1980).

ASRY discharged about 2,900 tons of waste water annually This water might contain oil, solvents, cleaners, paints which contain heavy metals especially mercury and lead.

#### (ii) Bahrain Slipway Company:

Bahrain Slipway Company (Figure 1.5) was one of the first ship repair yards in the region and was established in the early 1950's near the Muharreq causeway. The slipway has three repair yards for vessels of up to about 250 feet. All kinds of repairs can be carried out on tankers and other vessels afloat, either alongside the slipway or at the Sitra Anchorage.

The company is also diversifying into steel fabrication to minimise the effects of world recession. An average of 180 vessels are repaired annually.

### (iii) <u>BASREC:</u>

Bahrain Ship Repairing and Engineering Company was established in 1983 on a reclaimed land at Mina Sulman (Figure 1.5), to provide a custom built service for offshore oil exploration vessels.

Areas of specialisation include hull repairs, propulsion and auxiliary repairs; electrical repairs of all types including motor rewinding up to 500 hp and marine boiler repairs. With two slipways the company can handle virtually any sort of repairs out of the water, on vessels up to 1,000 tons. The twin slipways can each accommodate a single vessel of up to 240 ft. or several vessels of a similar total length and a total displacement per ship of up to 1,000 tons.

The solid waste (steel scrap, 120 MT/year) is collected from the company by scrap dealers. The oily sludge (72 MT/year) is collected by waste disposal Co. and dumped at the Municipal site in Bahrain.

## 1.2.2.2.6 The petrochemical plant:

The Gulf Petrochemcial Industries Company(GPIC) was originally formed in 1979 at Manama.

The plant was built on 600,000 square metres of reclaimed land east of Sitra island (Figure 1.5). It started production on 1986. It produces 1,000 tons a day of ammonia and the same output of methanol using Khuff natural gas (81% methane) as feedstock and fuel-in total 95,000  $Nm^3$ /hour. Apart from certain chemicals, catalysts, air and power (~23 MW), the only other major resource input is a considerable quantity of sea water, 18,500 m<sup>3</sup>/hour, for cooling purposes and to provide process water.

Spent caustic wastes from desulphuriser caustic scrubber; approximately 5-100 tons /month spent caustic/sodium/ sulphide/sulphate solution (equivalent to 0.1m<sup>3</sup>/hour of 10-25% Na<sub>2</sub> SO<sub>4</sub>/NaOH solution) and higher alcohols/oils from methanol plant distillation unit; approximately 15-20 tons /month will be discharged directly to the sea. It is estimated that the total quantity of sanitary effluent discharge would be of the order of  $10m^3/hour$ , with total BOD of 50-100 ppm (Johnson, 1983).

The principal impact of the methanol effluent, with its associated BOD load, will also be at periods when the tide is out. The effect will be to gradually deoxygenate the surface sediment, which covers the anaerobic mud/ sand beneath the surface. The high temperature  $(84^{\circ}C)$ will tend to enhance this effect. The result will be a blackening of the sediment and disapearance of benthic fauna. This will be more pronounced in the summertime and there is the possibility of hydrogen sulphide emissions from the sediments (Johnson, 1983).

## 1.2.2.2.7 Iron and steel industry:

The Arabiron and Steel Company (AISCO) is situated on a reclaimed land approximately 800m wide by 1200m long and connected to ASRY causeway (Figure 1.5). The company was incorporated in 1980 as an offshore public shareholding company. The company has constructed an iron pelletising plant with a capacity of 4 million tons per year. It imports ore fines from several sources notably South America; Mauritania and India) and processes these into iron oxide pellets which are exported to Saudi Arabia; Qatar and other parts of the world. Once again however, the comapny is likely to spawn a number of satellite industries.

The rate of effluent discharge from the company desalination plant is  $632m^3$ /hour while the discharge from its two sewage treatment plants is  $100m^3$ /day.

### 1.2.2.2.8 Flour mill:

Bahrain flour mill companywas constructed on 1972 on a reclaimed land at Mina Sulman industrial area (Figure 1.5) It imports about 42346 MT of grain and produces about 32400 MT/year of various mixes of flour (1984). Emissions and effluents from the mill are insignificant.

### 1.2.2.2.9 The Central abattoir:

The central abattoir (Figure 1.5) has a capacity to process 1200 sheep and 100 cows a day. There is a treatment plant with facilities for blood and paunch removal and disposal. The treatment involves 1ry, 2ry and 3ry treatment involving aerobic and anaerobic ponds. The final effluent to the sea  $(408.2m^3/day)$  is of reasonably good quality but it has a high BOD (30 mg/l) and contain high nutrients-particularly phosphorus (approximately 30-70 mg/l) (Johnson, 1983). The final effluent (408.2  $m^3/day$  is discharged into the sea.

# 1.2.2.3 Dredging and land reclamation:

The increase in the human population of Bahrain and the need for new coastal industries brought the idea of land reclamation and dredging to its maxima in the 1970s without thinking about their effects on the marine environment.

The total land area of Bahrain in 1961 was 625 Km<sup>2</sup>. By 1986 it had increased to 687.7 Km<sup>2</sup> because of land reclamation activities. The total dredged area for use as land-fill and building till 1982 in Bahrain was more than  $13,500,000m^2$  and the overall quantity of dredged material is more than  $60,000,000m^2$  (Al-Alawi, 1982).

Dredging operations may increase turbidity, irritating or clogging fish gills and reduce primary productivity. It also cause the removal of the benthos which forms the main source of food for many demersal fish species, exposes anoxic sediment layers and releases toxic compounds previously buried in the sediment.

Action is needed to prevent too much damage to the marine environment by rapid unplanned development. It is much more economic, to correct for the side effects of a development plan before it is implemented than to wait until it is too late. Certain precautions should be followed to protect against irresponsible dredging and land reclamation projects which threaten fisheries, destroy the spawning and nursery grounds, damage the sea grass beds and the substrate on which fish live.

Land reclamation and dredging in Bahrain (Figure 1.10) have caused irreparable damage to the inshore biosystem with corals being killed. Some of the largest corals are over a hundred years old and will probably never manage to re-establish on a silted site.

In times past, Bahrain possessed large tracts of healthy mangroves but land reclamation has taken its toll and, despite evidence regarding the importance of the mangroves as high productivity and nursery areas, the vast majority of coastal mangrove systems have been destroyed (Vine, 1986).



Figure: 1.10

Dredging ( ) and land reclamation ( ) activities along Bahrain coast. ( Figure obtained from Al-Alawi, 1982). Complaints by the fishermen regarding the loss of their fishing gear because of these activities became common. Dredging and land reclamation activities at various areas along Bahrain coast during the last five years have caused a 44.9% decline in the number of barrier traps (haddras) from 971 in 1978 to 535 in 1983 (Anon., 1985).

Building solid jetties in certain configurations alters the natural flow of water and therefore causes sedimentation in small areas. Silting could be reduced by careful planning.

### 1.2.2.4 Sewage:

Very large quantities of untreated sewage reach Bahrain sea from many sewage outfalls around Bahrain coast as indicated in Figure 1.11. There are other outfalls e.g. from BAPCO, ALBA and private developments. Also there are many outfalls for storm water only from roads. Pipelines are used, but the waste is not discharged far enough from the coast and/or at sufficient depths (Figure 1.12) to avoid beaches being affected. In addition to this, many trucks dump the septic tanks water and other domestic effluents directly at the high water line irrespective of tide. As an example, Ras Zuwayed (Figure 1.11) has a sewage dumping area on south. On an average at least 30 trucks dump the septic tank water and other domestic liquid effluents directly at the high water line irrespective of tide. Each truck carries about 2000 gallons of sewage water.

At the end of 1979, Tubli sewage treatment plant was constructed on reclaimed land at Khor Maqta Tubli and started operation on 1982. In 1984, the average daily . flow of treated sewage from Tubli sewage treatment plant was 70,000m<sup>3</sup>/day. Less than 10% of this is used for irrigation while the rest is discharged to the sea.



# Figure:1.11

Position of some sewerage outfalls ( --- ) along Bahrain coast (From Al-Alawi, 1980).



Figure: 1.12

Ras Zuwayed sewage outfall (above). Sufalah sewage outfall (below). The disadvantage of the site of Tubli sewage treatment plant on fisheries is that Tubli is an area where mangroves grow, which with underwater springs, produce an environment similar to the estuarine conditions in which the shrimp breeds. It is believed that this area is an important nursery ground since both juveniles and subadults shrimps (<u>Penaeus semisulcatus</u>) were found

(Personal observation).

Components of sewage sludge such as trace metals, PCB's (polychlorinated biphenyls), pesticides and bacteria may affect the quality of species of fish and shellfish of commercial interest to man, either directly or through benthos or other organisms. Measurable changes in water quality can be expected to arise from the presence of organic substances, nutrients and suspended particulates in the sewage. The addition of sewage to natural water does increase the concentrations of phosphates and nitrates, which may ultimately stimulate the growth of algae. Excessive growths or blooms of algae can have public health significance as some algae produce toxins which can give rise to outbreaks of gastro-enteritis in man. Algae also commonly give rise to water treatment problems, so enumeration and identification of algae is a routine waterworks practice.

From the human stand point, viruses in the sewage can cause diseases at the bathing beaches near sewage outfall.

The estimated loads of sewage directly discharged to the sea in 1980 are 4000 tons total suspended solids, 2800 tons biological oxygen demand, 550 tons ammonia nitrogen and 45000 tons total dissolved solids (UNEP,  $1980_a$ ). It was noticed that ammonia level was very high near sewage outfalls and may reach up to 4430.0  $\mu$ g/l at Al-Manama sewage outfall (Al-Alawi, 1983).

Servizi <u>et al</u> (1978) measured the 96-h LC50 of effluent from a primary sewage treatment plant using sockeye salmon (<u>Oncorhynchus nerka</u>). They could attribute about 0.4 of the toxicity to anionic surfactants and cyanide, but further examination of their data suggests that the figure would rise to between 0.54 and 0.84 if contributions from un-ionized ammonia (0.01), zinc (0.05) and copper (0.38 to 0.08 depending upon the figure assumed for the toxicity of copper in the presence of organic matter), were also taken into account. CHAPTER 2

WATER QUALITY AT DIFFERENT LOCATIONS IN BAHRAIN COAST

#### 2.1. Introduction:

An ecosystem is a biological system composed of organisms, their physical environment, and the materials and energy they process. It is characterized by complex biogeochemical cycles and interrelationships which maintain the system in a dynamic, balanced state thereby delimiting the particular environmental quality.

Ecological criteria are requirements necessary to maintain the ecosystem at a defined level of dynamic balance taking into account certain deterioration due to pollution and practicable levels of protection (UNESCO/WHO, 1978).

The aquatic environment encompasses a wide variety of parameters, virtually all of which influence the maintenance of homeostasis, essential for growth and reproduction of fishes. These, if altered beyond acceptable limits, may predispose to, or actually cause, disease. Among the most important of them are physical factors such as the temperature, the intensity and periodicity of light (including shading and background of hue), the chemical composition of the water, its biological content, the availablility of space and food and the frequency of fright stimuli such as moving shadows.

Monitoring of water quality is not an activity which stands alone, but is instead an important part of any comprehensive water-quality management scheme. Waterquality data should therefore be compared to criteria and standards which are among the major elements leading to water-quality management decisions. Surface waters are also characterized by their contents of suspended matter, both organic and inorganic. Nutrients received by surface waters favour growth of aquatic plants, fish and other water fauna and flora. These in turn highly influence the oxygen content and the self-purification capacity of the water (UNESCO/ WHO, 1978).

The rate at which substances are degraded in natural environments depends on interactions among chemical, physical and microbiological factors as well as on the nature of each compound. The major limiting factors are the availability of nitrogen, phosphorus and, in particular, oxygen, since little degradation occurs anaerobically. Virtually all substances are biodegradable, many hydrocarbons, phenols, sulphides, cyanides and ammonia readily do so, certain high molecular weight hydrocarbons, trihydric phenols and porphyrine are examples of relatively persistent components which may be present in industrial effluents in very low concentrations and which are slow to degrade (Jenkins <u>et al</u>, 1979).

The physical and chemical properties of sea waters, are of primary importance in determining the occurrence of marine plants and animals. The fluctuations in the environmental conditions have a profound influence on the aperiodic and seasonal migrations and occurrence of fish. Furthermore, the conditions in the aquatic environment and their changes influence the recruitment, survival and growth of the fish. The environment also interfere with such biological activities as spawning and growth (Hela and Laevastu, 1961). Fish appear to respond to their oceanographic climate rather than to geographically fixed reference points during the spawning season (Ahlstrom, 1959). Fish have upper lower thermal tolerance limits and optimum temperatures for growth, egg incubation, food conversion and resistance to specific diseases. These optima may all be different and may change according to other parameter conditions such as oxygen tension and water pH (Roberts, 1978).

Water temperature also affects properties of the aquatic environment important for fish health. Surface waters are subject to temperature fluctuations of up to 40°C caused by latitude, season, altitude and time of day. The range of temperature change of sea water at depth is much less, due to water circulation in the seas and oceans and the large volumes of water involved. Dissolved gases generally decrease in solubility with increasing temperature whereas the solubility of toxic compounds which are only sparingly soluble in water, such as crude oil and pesticides, increases with temperature rise. The toxicity of some substances such as heavy metals increases with temperature (Roberts, 1978 and McLusky, 1986).

Therefore, abnormal temperatures on the spawning ground during the spawning season may force the fish to spawn in other areas than those to which they normally go for this purpose.

Every stock of fish has a "normal" temperature range, possibly with a seasonal cycle. At temperatures below this range the ripening of the sexual products is delayed, and the opposite is the case at higher temperatures (Hela and Laevastu, 1961). Actually, many fish make seasonal migrations towards the poles during the summer and towards the equator in winter. It may be that these migrations are directly influenced by temperature, or indirectly by the effect of temperature on the abundance of food. Besides the seasonal migrations, the shoaling connected with spawning, feeding, etc. must be controlled, either directly or indirectly, by temperature (Hela and Laevastu, 1961).

In common with land plants, marine phytoplankton require certain trace elements for their healthy growth. The most important of these micronutrients are nitrogen and phosphorus, which may be taken up by them from the water to such an extent that their further growth is inhibited.

In water quality management during recent years much attention has been paid to eutrophication problems. The increased discharge of nitrogen and phosphorus in the waste water of various pollution sources may cause a decreasing water quality, this is particularly significant in view of the increasing importance of recreation and nature conservation.

The transport, distribution and ultimate fate of pollutants in marine waters is controlled by physical, chemical and biological oceanography. Therefore, in order to understand the capacity of the marine environment to support pollutants without adverse effects, one must first understand the oceanography affecting them. Physical, chemical and biological oceanographic data can be used to determine and predict circulation and water residence time. This is most important because upon these two factors is based the ability of the sea area to flush itself clean of polluting substances. If the water residence time is very long i.e. slow exchange occurs then, polluting substances will have a tendency to build up over time. If exchange of water is rapid, then build up of substances will perhaps be less important.

Man's influence on the quality of water is quite apparent and is now a major economic and political concern. The main group of man-made changes consists of domestic, municipal and industrial sewage and waste water, followed by agriculturally-oriented activities such as irrigation, use of fertilizers, pesticides, herbicides, etc. Mining activities and power generation often cause substantial quality changes as does urbanization of new areas. Construction schemes, such as those connected with river training, flood control, low flow augmentation, reservoir management, etc., considerably influence the quality regime. Man-made changes of the hydrological cycle such as water transfer, artificial ground water recharge and artificial precipitation are supposed to be controlled, however, and water pollution resulting from these is unaviodable. Accidental pollution often imposes an insurmountable burden on a water body. Accidents which result from storage or transport of chemical substances, acids, salts, oil and oil products, and other substances harmful to micro-organisms, animals, plants, and man are also particularly noteworthy man-made changes. (UNESCO/WHO, 1978).

Urban development inevitably causes an intensification of water resources exploitation. The rapid growth of water consumption within the urban area due to industrial development, an increase of the urban population and an improvement of sanitary conditions is accompanied by the

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equally rapid increase of industrial and domestic wastes polluting all the components of the natural environment: the atmosphere, water bodies, soils and subsoils.

The pollution of natural water within urban areas as well as the pollution of the atmosphere are the most acute problems in the conservation of the normal state of the environment.

Sewage discharges may reduce water quality depending on the degree of dilution achieved, the degree of treatment of the original material, its composition and the response of the ecosystem. Oxygen depletion is the most common result of such discharges. It arises from insufficient dilution and microbial growth on its particulate and soluble organic content. Sewage-derived inorganic nutrients, such as phosphate, ammonia and nitrate, may stimulate excessive blooms of algae or attached weed with attendant oxygen depletion and toxin production. Sewage is also a potential source of heavy metals and toxic organic wastes such as PCBs. Although its presence is likely to be short-lived the highly toxic nitrite ion may also be present in sewage discharges.

Pesticides are chemicals designed to destroy plant or animal life. The major sources are run-off from treated farmlands, industrial and domestic sewage and spillage. A great variety of such compounds is currently in use and they may be contaminants of the food of both wild and cultured fish. Many are rapidly inactivated by microbial degradation or adsorption to benthic particulate matter but some, such as DDT or dieldrin, are highly resistant to degradation and are concentrated with little chemical alteration in the food web leading to fish.

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Considering the importance of oceanographic conditions, and because of the lack of such information about Bahrain waters, the study was carried out during the period January - December 1983 to determine the distributions of temperature, salinity, pH, phosphate, ammonia, nitrate and nitrite at different locations in Bahrain waters and their fluctuations at different seasons to compare it with the quality of water at an area adjacent to the refinery outfalls.

#### 2.1.1. Description of the study area:

The western region of Bahrain is characterized by three big islands Umm Nassan, Umm Sabban and Jeddah. There is an oil pipeline coming from Saudi Arabia. Down south is the newly constructed Saudi Arabia-Bahrain causeway. The northern extremity called Budia of this region has recently experienced extensive dredging and reclamation operations. The western region does not have any noticeable live-coral reefs nearer the shores or islands. The water circulation in this region is restricted and has developed eddies.

The northern region is more of open sea with the main watermass of the Gulf facing it on the north. The region has a major settlement of Bahrain on its coastline. The inshore waters are shallow for a considerable distance seawards and the intertidal and sub-tidal areas are studded with barrier traps (hadrahs). The large island called Muharreq is situated in this region. The region is important from fisheries point of view.

The eastern region is the most polluted area of Bahrain with majority of industries including an oil refinery, metal smelters, sand washing and sewage treatment plants, cement factory, raw sewage outfalls etc. are situated in this region. The port Mina Sulman and oil terminal of Sitra are also situated in this region. The eastern region is characterized by the presence of two major islands <u>viz</u>., Nabeeh Saleh and Sitra. In between these is a Tubli Bay, an extensive semi-enclosed sea area. This region also contains mangrove marshes and is supposed to have high fertility. The northern part of the eastern region faces the famous big coral reef Fasht Al-Adhum and seagrass beds. As such, this eastern coast is very important from fisheries point of view.

Due to the shape of Bahrain the eastern and western regions meet at the southern point of Ras Al-Bar.

The shallow marine habitats, or biotopes, of great significance around the Bahrain are as follows:

- (a) Intertidal areas including mud-flats, sand flats and tidal creeks.
- (b) Soft, sub-tidal sea-bed.
- (c) Sea grass beds.
- (d) Coral reefs.

Coral reefs or offshore banks are known as "Fasht" while the deeper areas are called "Hayr".

Intertidal areas in those regions where salinity is relatively low have high levels of benthic productivity and are exploited, during high tide, by many fish and shellfish. Despite the relatively high levels of productivity in the Gulf and its valuable fishery resources, the waters are not as rich in phytoplankton or zooplankton as one might expect. Chlorophyll concentrations in the water column are low (0.49 to 1.28 mg/cu.m) but this contrasts with levels in the sediments which may reach as much as 236 mg/cu.m. thus emphasising the importance of benthic productivity. This is further underlined by the presence of huge tracts of seagrasses (<u>Halophila</u> <u>ovalis</u> and <u>Halodule uninervis</u>) and benthic algae , sites of primary production which are key factors in the existence of several important species(Vine, 1986).

#### 2.2 Materials and Methods :

Seventeen sampling stations were fixed all around Bahrain (Figure 2.1 to 2.17) except the southern coast because it is a prohibited area . Surface water samples were collected during the period January - December 1983 at fortnightly intervals . The parameters studied were atmospheric and water temperatures, salinity (total dissolved solids), pH, ammonia, nitrite, nitrate and phosphate .

#### 2.2.1 Temperature :

The temperature was measured immediately after the collection of water samples using THL-490-030W general purpose thermometer (-10 to  $110X1^{\circ}C$ ).



# Figure: 2.1

Water sampling stations.


Figure: 2.2 Station 1 (Bilaj Al-Jazair).



Figure: 2.3 Station 3 (Jasra).



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Figure: 2.4 Station 4 (Budia).



Figure: 2.5 Station 5 (Portugese Fort).



Figure: 2.6 Station 6 (North the Muharreq Cause-way).



Figure: 2.7 Station 7 (Ras Rayyah).



Figure: 2.8 Station 8 (Hidd, East ASRY Cause-way)



Figure: 2.9 Station 9 (Hidd, opposite the Cement Factory).



Figure: 2.11 Station 11 (South the Muharreq Cause-way).



Figure: 2.12 Station 12 (Mina Sulman main jetty).



Figure: 2.13 Station 13 (Nabeeh Saleh)



Figure: 2.14 Station 14 (Ras Tubli, opposite Tublic Sewage Treatment Plant).



Figure: 2.15 Station 15 (Sitra, opposite Al-Ikr).



Figure: 2.16 Station 16 (Sitra jetty, Bander Al-Dar).



Figure: 2.17 Station 17 (Asker).

# 2.2.2. Total dissolved solids :

Total dissolved solids of water samples were determined using an Automatic Temperature Compensated Hand Refractometer Model 10419.

#### 2.2.3. pH value:

pH value was determined with a portable Digital pH/ Millivolt meter (GLI Model 819).

#### 2.2.4. Dissolved oxygen:

The dissolved oxygen was determined with a portable Digital Dissolved Oxygen Meter (GLI Model 867). Results are expressed as milligrammes of oxygen per litre.

## 2.2.5. Total ammonia - nitrogen:

Ammonia reacts with phenol and hypochlorite in alkaline solution catalyzed by nitroprusside (pentacyanonitrosyl ferrate) forming an intensely blue compound, indophenol (Strickland and Parsons, 1972). The absorbance was measured at 700 nm using a Unicam SP 600 UV Spectrophotometer.

Results are expressed as microgrammes of ammonia nitrogen per litre ( $\mu$ g NH<sub>3</sub> - N/1).

#### 2.2.6 Nitrate - nitrogen:

Nitrate is reduced to nitrite and determined as described for nitrite (Strickland and Parsons, 1972). Results are expressed as microgrammes of nitrate nitrogen per litre ( $\mu$ g NO<sub>3</sub> - N/1).

#### 2.2.7 Nitrite - nitrogen:

The nitrite is determined by diazotizing with sulphanilamide and coupling with N- (1 - naphthyl) - ethylenediamine to form a highly coloured azo dye which is measured at 543 nm (Strickland and Parsons, 1972) using a Unicam SP 600 UV Spectrophotometer.

Results are expressed as microgrammes of nitrite nitrogen per litre ( $\mu$ g NO<sub>2</sub> -N/1).

## 2.2.8 Phosphate - Phosphorus:

Orthophosphates react in an acid medium with ammonium molybdate and potassium antimonyl tartarate to form a heteropoly acid-phosphomolybdic acid - which is reduced to the intensely coloured molybdenium blue by ascorbic acid. The absorbance was measured at 880 nm (Strickland and Parsons,1972) using a Unicam SP 600 UV Spectrophotometer. Results are expressed as microgrammes of phosphate - phosphorus per litre ( $\mu$ g PO<sup>-3</sup><sub>L</sub> - P/1).

### 2.3 Results and Discussion:

## 2.3.1 Temperature

The temperature of water is one of the most important characteristics which determines, to a considerable extent, the trends and tendencies of changes in its quality. Temperature is an important factor affecting ion and phase equilibria, and influencing the rates of biochemical processes which accompany the changes of concentration and of content of organic and mineral substances. It is generally known that the rate of numerous chemical reactions including catalytic and enzymatic ones depends considerably on changes in temperature (on the average 2 to 3 times for every  $10^{\circ}$ C) (UNESCO/WHO, 1978). Consequently, when discussing parameters such as sedimentation, mobilization of undissolved substances, solution of gases and their escape from water into the atmosphere, the processes of chemical and biochemical self-purification, formation of secondary pollutants, and others, it is necessary to know the temperature of the water, air, and in some cases the bottom deposits.

Temperature data are also used when the degree of saturation of water by oxygen and other gases is calculated. The shifting of various dynamic equilibria such as concentrations of carbonates, sulphides, or degree of alkalinity, or electroconductivity, are also affected by temperature changes.

In some cases, temperature is the direct index of the influence of man-made factors on the quality of water (thermal pollution). Temperature measurements may also become useful in the studies of such parameters as the volume distribution of water or evaporation.

Fish and shellfish are cold - blooded animals and, unlike mammals and birds, their body temperature is not internally regulated but approximates to that of their surroundings. Therefore, because of the influence heat has upon chemical reactions (metabolism), environmental temperature has profound effects on the life processes of fish and shellfish, such as growth and development and swimming speed. Fish have the ability to perceive and select a limited thermal range in which they tend to congregate. This is usually the thermal range which offers them the opportunity for maximum expression of activity and is ultimately manifested in their abundance and distribution. The sense of temperature in fish seems to be well developed (Laevastu and Hayes, 1981).

Monthly mean atmospheric and water temperatures are shown in Tables 2.1 and 2.2 respectively. Table 2.1 shows that monthly mean atmospheric temperature ranged from  $15.5^{\circ}$ C at station 5 (Portugese Fort) during February to  $35.5^{\circ}$ C at station 9 (Hidd, ASRY causeway) during August. Generally, all the stations follow the same pattern.

Table 2.2 shows that montly mean water temperature ranged from  $14.0^{\circ}$ C at station 5 (Portugese Fort) during February to  $30.5^{\circ}$ C at the same station during July.

The overall maximum encountered monthly average atmospheric temperature (Figure 2.18) was  $34.4^{\circ}$ C in July, while the minimum encountered in February (18.1°C), a difference of 16.3°C. The maximum calculated overall monthly mean water temperature was 29.2°C during August, while the minimum (16.1°C) during February, a difference of 13.1°C (Figure 2.18). It is noticed from Figure 2.18 that water temperatures were always lower than that of atmospheric temperatures by an average of 3.8°C with a similar trend of high in summer and low in winter. The difference between atmospheric and water temperature during summer is higher than during winter.

Monthly mean atmospheric temperature (<sup>O</sup>C)

Table: 2.1

|                                  |          |      |      |      |      | IOM  | NTHS     |      |      |      |      |      |      | TANDARD  |
|----------------------------------|----------|------|------|------|------|------|----------|------|------|------|------|------|------|----------|
| STATIONS                         | <b>ר</b> | 4    | W    | v    | Σ    | ſ    | <b>٦</b> | V    | s    | 0    | z    | D    | 1EAN | EVIATION |
| 1-Bilaj Al-Jazair                | 20.0     | 18.0 | 17.0 | 27.0 | 33.5 | 32.0 | 35.8     | 35.0 | 32.0 | 28.0 | 26.3 | 24.5 | 27.4 | 6.5      |
| 2-Zallaq                         | 21.3     | 17.3 | 17.8 | 26.5 | 35.0 | 31.5 | 34.0     | 34.0 | 32.5 | 27.0 | 26.3 | 24.0 | 27.3 | 6.3      |
| 3-Jasra                          | 22.3     | 19.0 | 17.8 | 26.5 | 31.0 | 30.5 | 34.3     | 33.5 | 33.0 | 28.0 | 26.3 | 24.3 | 27.2 | 5.6      |
| 4-Budia                          | 19.5     | 16.8 | 17.3 | 27.5 | 32.5 | 31.3 | 34.3     | 32.8 | 32.0 | 27.5 | 26.3 | 24.5 | 26.9 | 6.2      |
| 5-Portug e se Fort               | 21.3     | 15.5 | 18.3 | 27.5 | 30.5 | 31.5 | 35.0     | 31.5 | 34.0 | 28.5 | 26.5 | 23.5 | 27.0 | 6.2      |
| 6-North the Muharreq Cause-way   | 20.0     | 16.3 | 17.0 | 27.5 | 32.3 | 33.3 | 34.5     | 33.0 | 32.0 | 28.0 | 26.0 | 23.0 | 26.9 | 6.5      |
| 7-Ras Rayyah                     | 20.3     | 19.5 | 21.5 | 26.0 | 29.5 | 34.5 | 33.8     | 34.5 | 34.5 | 28.5 | 27.0 | 20.7 | 27.5 | 6.0      |
| 8-Hidd(East ASRY Cause-way)      | 19.0     | 18.5 | 20.5 | 25.8 | 31.5 | 34.5 | 34.5     | 35.5 | 34.0 | 27.0 | 27.0 | 19.8 | 27.3 | 6.6      |
| 9-Hidd(Opp. the Cement Factory   | 19.0     | 20.0 | 19.0 | 27.3 | 31.0 | 34.5 | 34.0     | 35.3 | 34.0 | 27.0 | 27.0 | 20.0 | 27.3 | 6.5      |
| 10-Arad                          | 19.5     | 19.0 | 20.8 | 25.5 | 30.0 | 35.8 | 35.5     | 34.0 | 34.0 | 27.5 | 28.0 | 20.3 | 27.5 | 6.5      |
| 11-South the Muharreq Cause-way  | 20.3     | 16.8 | 17.8 | 27.0 | 33.0 | 33.3 | 34.5     | 33.5 | 32.0 | 28.0 | 26.0 | 23.3 | 27.1 | 6.4      |
| 12-Mina Sulman main jetty        | 24.0     | 19.8 | 21.3 | 27.0 | 30.0 | 33.0 | 35.0     | 33.5 | 33.0 | 28.0 | 27.5 | 20.5 | 27.7 | 5.4      |
| 13-Nabeeh Saleh                  | 19.3     | 19.0 | 16.8 | 26.0 | 31.5 | 34.3 | 32.5     | 32.0 | 33.0 | 28.0 | 26.8 | 25.0 | 27.0 | 6.0      |
| 14-Ras Tubli(opp.Sewage Trgament | 18.3     | 17.8 | 19.5 | 26.0 | 33.5 | 35.5 | 35.0     | 33.8 | 33.5 | 28.5 | 25.8 | 23.0 | 27.5 | 6.8      |
| 15-Sitra (Opposite Al-Ikr)       | 19.0     | 18.5 | 17.8 | 25.5 | 30.5 | 34.0 | 33.8     | 32.5 | 33.5 | 28.0 | 26.5 | 24.9 | 27.0 | 6.1      |
| 16-Sitra jetty(Bander Al-Dar)    | 18.5     | 18.0 | 17.0 | 26.5 | 29.0 | 35.3 | 34.0     | 33.5 | 34.5 | 28.0 | 26.8 | 25.0 | 27.2 | 6.6      |
| 17-Asker                         | 19.3     | 17.8 | 20.0 | 26.5 | 32.0 | 35.5 | 34.5     | 34.5 | 35.0 | 27.0 | 26.3 | 20.8 | 27.4 | 6.8      |
| MEAN                             | 20.1     | 18.1 | 18.7 | 26.6 | 31.5 | 33.5 | 34.4     | 33.7 | 33.3 | 27.8 | 26.6 | 22.8 | 1    |          |
| STANDARD DEVIATION               | 1.5      | 1.3  | 1.6  | 0.7  | 1.6  | 1.7  | 0.8      | 1.1  | 1.0  | 0.5  | 0.6  | 2.0  |      |          |

ı,

Monthly mean water temperature (<sup>O</sup>C)

Table: 2.2

|   |               |      |      |      |      |      |      |      |      |      |       |      | F        |          |
|---|---------------|------|------|------|------|------|------|------|------|------|-------|------|----------|----------|
|   |               |      |      |      |      | MOM  | ITHS |      |      |      |       |      | 4FAN     | TANDARD  |
| STATIONS                                    | -             | 6.   | Σ    | ۷    | Σ    | 2    | 7    | ۷    | S    | 0    | Z     | a    | <u>م</u> | EVIATION |
|   |               |      |      |      |      |      |      |      |      |      |       |      |          |          |
| 1-Rilai Al-Jazair                           | 17.5          | 16.0 | 16.3 | 24.5 | 29.3 | 28.0 | 29.0 | 29.0 | 27.0 | 23.5 | 23.5  | 20.0 | 23.6     | 5.1      |
|   | 18.5          | 16.3 | 16.8 | 24.5 | 29.8 | 27.0 | 29.0 | 29.0 | 25.0 | 24.0 | 23.5  | 20.0 | 23.6     | 4.8      |
|   | 18.5          | 16.3 | 16.5 | 24.5 | 28.3 | 26.5 | 29.8 | 29.8 | 25.0 | 25.0 | 23.0  | 20.0 | 23.6     | 4.8      |
|   | 16.5          | 15.0 | 15.8 | 25.5 | 28.3 | 27.0 | 29.0 | 28.8 | 26.0 | 24.5 | 23.3  | 20.0 | 23.3     | 5.2      |
|   | 19.8          | 14.0 | 16.0 | 25.5 | 28.3 | 26.5 | 30.5 | 28.5 | 24.0 | 25.0 | 23.8  | 19.0 | 23.4     | 5.2      |
| J-fultug ese fort                           | 18.0          | 14.5 | 16.0 | 24.5 | 28.0 | 28.5 | 29.8 | 30.0 | 25.5 | 26.5 | 23.3  | 19.5 | 23.7     | 5.4      |
|   | 17.5          | 17.5 | 20.5 | 24.0 | 26.0 | 30.0 | 27.3 | 29.5 | 27.0 | 25.5 | 23.8  | 16.8 | 23.8     | 4.7      |
| I-MAS NAYYAU<br>9 ULJAFFOET ASPY (AUSE-WAV) | 18.0          | 17.8 | 18.0 | 23.5 | 29.0 | 27.5 | 27.5 | 29.5 | 28.5 | 24.5 | 23.3  | 17.3 | 23.7     | 4.8      |
| G-NIGULERSE ASK CHERENE FACTORY             | 17.5          | 18.0 | 18.8 | 24.5 | 28.0 | 28.8 | 28.3 | 30.3 | 28.0 | 24.0 | 24.0. | 17.1 | 23.9     | 4.9      |
|   | 17.8          | 16.8 | 17.0 | 23.0 | 27.5 | 27.5 | 27.8 | 29.0 | 29.0 | 25.5 | 25.0  | 17.8 | 23.6     | 5.0      |
| 11-South the Muharred Cause-way             | 18.0          | 15.5 | 16.0 | 25.5 | 28.0 | 28.0 | 29.5 | 30.0 | 26.5 | 25.5 | 22.8  | 18.8 | 23.7     | 5.3      |
| 12-Mina Sulman main letty                   | 18.3          | 16.5 | 17.3 | 24.5 | 28.0 | 29.0 | 27.5 | 29.5 | 27.0 | 24.0 | 24.0  | 18.0 | 23.6     | 6.4      |
| 13-Nabeeh Saleh                             | 16.5          | 15.5 | 15.8 | 23.0 | 26.0 | 27.3 | 27.0 | 29.0 | 26.0 | 24.5 | 23.0  | 23.5 | 23.1     | 4.7      |
| 14-Pas Tubli (opp. Sewage Treatment         | <b>\$16.8</b> | 17.0 | 18.0 | 23.0 | 29.3 | 28.0 | 28.5 | 28.5 | 27.0 | 25.0 | 22.0  | 18.0 | 23.4     | 4.9      |
| 15_Stra (Annosite Al-Ikr)                   | 16.3          | 15.5 | 15.0 | 23.5 | 25.5 | 26.5 | 25.5 | 28.5 | 26.0 | 25.0 | 24.3  | 22.8 | 22.9     | 4.6      |
| 15-Sitre Sertv(Bander Al-Dar)               | 17.3          | 16.3 | 16.3 | 22.0 | 25.0 | 27.3 | 27.3 | 29.3 | 27.0 | 25.0 | 23.3  | 22.0 | 23.2     | 4.5      |
| 17-Asker                                    | 17.5          | 15.8 | 16.0 | 23.5 | 27.3 | 28.0 | 26.5 | 28.0 | 24.5 | 24.0 | 23.5  | 17.5 | 22.7     | 4.7      |
| MEAN  | 17.7          | 16.1 | 16.8 | 24.1 | 27.7 | 27.7 | 28.2 | 29.2 | 26.4 | 24.8 | 23.5  | 19.3 |          |          |
|   |               |      |      |      |      |      |      |      |      |      |       | ,    |          |          |
| STANDAKD DEVIATION                          | 6.0           | 1.1  | 1.4  | 1.0  | 1.4  | 1.0  | 1.3  | 0.6  | 1.4  | 0.8  | 0.7   | 0.2  |          |          |



## Figure: 2.18

Monthly mean atmospheric and water temperature over the year 1983 for the 17 stations. The bars represent the standard deviation. Monthly mean atmospheric and water temperature increased steadily from its minimum in February until it reached its maximum in July in the case of atmospheric temperature or in August in the case of water temperature and then decreased till December.

#### 2.3.2 Salinity:

Dissolved matter or total dissolved solids, sometimes referred to as salinity, is a measure of the total inorganic substances dissolved in water. These substances include the major chemical ions such as calcium, magnesium, sodium, potassium, carbonates, sulphates, and chlorides as well as the dissolved metals and metalloids (UNESCO/ WHO, 1978).

Salinity of the water affects the osmoregulation in fish and has a large influence on fertilization and development of the eggs. Different species are adapted to different salinities. Some species are euryhaline (adaptable to wider range of salinities), but most are stenohaline (with relatively narrow salinity tolerance limits) Laevastu and Hayes, 1981).

Table 2.3 indicate that monthly mean salinity fluctuated between 35.0% (station 14, Ras Tubli) to 55.9% (station 3, Jasra), a difference of 20.9%.

The overall mean of all the months in Figure 2.19 shows that the maximum observed salinity was 54.6% at both Al-Zallaq (station 2) and Jasra (station 3), while the minimum is 39.3% at station 14, Ras Tubli because it is opposite to Tubli sewage treatment plant which discharge about 70,000m<sup>3</sup>/day of treated sewage, followed by station 13, Table: 2.3 Monthly mean salinity (%.)

| 0 NC 1 T 1 T 3                    |             |      |      |      |      | MON      | ITHS |       |      |      |      |      |             | TANDARD  |
|-----------------------------------|-------------|------|------|------|------|----------|------|-------|------|------|------|------|-------------|----------|
| CNOTIVIC                          | 7           | ц.   | Σ    | ×    | Σ    | <b>_</b> | ſ    | ۷     | S    | 0    | z    | D    |             | EVIATION |
| 1-Bilaj Al-Jazair                 | 55.4        | 55.0 | 53.7 | 54.5 | S4.5 | 55.0     | 55.0 | \$4.5 | 0.42 | 55.0 | 0 75 | 52 D | 7 75        | 6 U      |
| 2-Zallaq                          | 55.5        | 55.0 | 53.9 | 53.5 | 55.0 | 55.0     | 53.5 | \$4.5 | 55.0 | 55.0 | 55.0 | 54.5 | <u>5</u> .6 | 0.7      |
| 3-Jasra                           | 53.6        | 55.9 | 55.3 | 53.4 | 55.0 | 52.5     | 50.4 | 57.0  | 57.0 | 57.0 | 52.5 | 55.0 | 54.6        | 2.1      |
| 4-Budia                           | 48.2        | 47.1 | 46.5 | 46.4 | 50.0 | 46.0     | 46.0 | 47.5  | 50.0 | 47.0 | 46.0 | 50.5 | 47.6        | 1.7      |
| 5-Portug e se Fort                | 43.8        | 45.0 | 46.0 | I    | 41.7 | 44.5     | 45.0 | 49.5  | 42.0 | 45.0 | 43.5 | 43.5 | 44.5        | 2.1      |
| 6-North the Muharreq Cause-way    | 43.5        | 43.4 | 43.7 | 43.5 | 44.5 | 47.5     | 43.5 | 44.5  | 45.0 | 42.0 | 41.5 | 42.5 | 43.8        | 1.6      |
| 7-Ras Rayyah                      | 43.0        | 42.4 | 42.7 | 41.4 | 42.1 | 42.0     | 0.44 | 43.3  | 42.0 | 42.0 | 40.5 | 67.0 | 42.5        | 1.0      |
| 8-Hidd(East ASRY Cause-way)       | 42.0        | 42.0 | 42.9 | 43.4 | 44.5 | 50.0     | 46.0 | 43.5  | 0.44 | 45.0 | 42.5 | 46.3 | 44.3        | 2.3      |
| 9-Hidd(Opp. the Cement Factory    | 42.0        | 42.3 | 42.1 | 42.7 | 43.5 | 42.0     | 42.0 | 41.5  | 47.0 | 42.0 | 42.0 | 43.3 | 42.7        | 1.5      |
| 10-Arad                           | 42.9        | 0.44 | 43.6 | 45.1 | 43.5 | 46.0     | 44.5 | 43.3  | 45.0 | 45.0 | 6.44 | 44.3 | 4.3         | 0.9      |
| 11-South the Muharreq Cause-way   | 42.1        | 43.4 | 43.1 | 43.4 | 43.9 | 45.0     | 41.5 | 41.8  | 42.0 | 42.0 | 42.0 | 43.0 | 42.8        | 1.0      |
| 12-Mina Sulman main jetty         | 42.1        | 42.0 | 42.1 | 42.6 | 42.0 | 42.0     | 42.0 | 40.8  | 42.0 | 42.0 | 42.5 | 42.8 | 42.1        | 0.5      |
| 13-Nabeeh Saleh                   | 42.1        | 41.4 | 40.4 | 42.1 | 42.9 | 43.5     | 41.5 | 41.0  | 42.0 | 42.0 | 41.5 | 42.3 | 41.9        | 0.8      |
| 14-Ras Tubli(opp. Sewage Trpament | 39.0        | ł    | 42.1 | 35.0 | 38.9 | 42.5     | 41.1 | 40.5  | 42.0 | 42.0 | 41.5 | 27.8 | 39.3        | 4.4      |
| 15-Sitra (Opposite Al-Ikr)        | 42.1        | 42.1 | 40.0 | 43.4 | 42.7 | 45.0     | 45.0 | 43.4  | 45.0 | 42.5 | 43.3 | 43.0 | 43.1        | 1.5      |
| 16-Sitra jetty(Bander Al-Dar)     | 42.1        | 41.5 | 41.5 | 43.9 | 45.0 | 45.0     | 41.5 | 42.0  | 42.0 | 42.0 | 41.5 | 42.5 | 42.5        | 1.3      |
| 17-Asker                          | 42.1        | 43.0 | 43.5 | 45.0 | 43.9 | 45.0     | 43.0 | 42.5  | 45.0 | 45.0 | 43.0 | 0.44 | 43.8        | 1.1      |
| MEAN                              | <b>64.8</b> | 45.3 | 4.9  | 45.0 | 45.5 | 46.4     | 45.0 | 45.4  | 45.9 | 45.4 | 44.5 | 44.8 |             |          |
| STANDARD DEVIATION                | 5.1         | 5.2  | 4.8  | 5.0  | 5.0  | 4.3      | 4.2  | 5.3   | 5.0  | 5.1  | 4.6  | 6.2  |             |          |
|                                   |             |      |      |      |      |          |      |       |      |      |      |      |             |          |



Distribution of salinity, based on average readings over the year 1983.

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Nabeeh Saleh (14.9%.) because it is near to station 14 which means that it is affected by the sewage effluent. At Arad, the monthly mean salinity (44.3%.) is slightly higher than the other adjacent northern stations (Figure 2.19). The probable cause for this is that Arad Bay is a large shallow water Bay with a maximum depth of about one meter during the high tide, where as its sand flats are exposed during the low tide. The Bay is connected to the main water by a narrow entrance of ca. 10m wide which allows water exchange during tidal movement.

In general, salinities of the western coast are the highest, followed by those of the northern and the eastern coasts respectively. This conclusion is supported by an earlier study during 1978 by the same author (Al-Alawi, 1983). This might be because the eastern coast facing the entrance of the Gulf, the Strait of Hormuz which opens to the Gulf of Oman and the Indian Ocean, while the western coast faces the closed side of the Gulf. The probable cause for the low salinity in the northern coast is the presence of open water mass of the main body of the Arabian Gulf and fresh water springs, industrial and sewage oufalls along the north eastern coastline. There are many submarine springs around the island of Bahrain. In the north east of the island there are more than twenty one submarine springs not far from the coast. Others are known further out to sea and it is not impossible that there are still others at present unknown which could be discovered later. The salinity of various springs range from 900 ppm to 1400ppm (Anon.,1969).

The highest encountered salinity was at the southern coast because it is the most enclosed one, it reached up to more than 65%.

It is found that salinity in summer is somewhat higher than in winter (Table 2.3).

#### 2.3.3 pH:

The pH value of natural water is an important index of acidity or alkalinity and is the resulting value of the acidic/basic interaction of a number of its mineral and organic components. In pure or slightly polluted water, the values of pH are determined mainly by the correlation between the concentrations of free carbon dioxide, bicarbonate, and carbonate ions . This correlation, in turn, depends substantially on the intensity of the process of photosynthesis and the biochemical oxidation of organic substances, as well as on the chemical conversions of some mineral substances (oxidation of ferrous iron, ammonia, oxidation and reduction of sulphurcontaining mineral substances, etc.). The pH value is affected by the increase in the content of coloured humus substances, i.e. humic acids and fulvic acids, a number of hydrolyzing compounds, as well as various acids and alkalis which can penetrate the body of water along with industrial waste waters (UNESCO/WHO, 1978).

Under natural conditions, the values of pH in the surface water range usually from 5.0 to 8.6; but in some cases, the range is considerably greater. Natural changes of the pH values must be considered when utilizing this index. When waters with an increased content of acids or alkalis are discharged into the bodies of water, the resulting pH may be used with other data for the establishment of the distribution of zones of pollution or the conditions for displacement of water, pH also serves as an auxiliary value when calculating a number of other characteristics of the quality of water such as free carbonic acid and free hydrogen sulphide. During the study period, it was found that pH ranged from 7.50 (station 5, Portugese Fort) during November to 8.51 (station 7, Ras Rayyah) during February, a difference of 1.01.

Monthly mean pH within the stations for the entire period of study (Table 2.4) indicate that Ras Tubli (station 14) has the lowest mean pH (7.88), probably because of the effect of the sewage discharge while Ras Rayyah (station 7) has the highest mean pH (8.20, followed by station 8, Hidd, east ASRY causeway (8.16) and then station 9, Hidd, opposite the cement factory (8.12).

It was noticed that pH of the fresh water is less than that of the sea water, as shown in the case of sewage discharge and fresh water springs.

In general the western coast has lower pH than the eastern and northern coasts. The probable cause for this is the industrial discharge, dredging and land reclamation activities along the north-eastern coastline.

Within the months, the maximum ecountered overall average pH (Figure 2.20) was 8.25 during March and the minimum was 7.83 during December.

#### 2.3.4 Chemical parameters:

Chemical parameters are the most important indices which characterize the quality of water. Their absolute values and correlations enable us to do the following:

(a) to classify the water by its mineralization, chemical composition (in particular, by the predominance of certain ions);

Monthly mean pH

Table:2.4

|   |      |      |      |      |      | MOM  | THS  |       |       |             |      |      |         | STANDARD    |
|---|------|------|------|------|------|------|------|-------|-------|-------------|------|------|---------|-------------|
| STATIONS                                    | ~    | ٤    | ¥    | <    | I    | ſ    | г,   | <     | s     | 0           | z    | ٩    | N 6 3 1 | DEVLATION   |
| 1-Bilai Al-Jazair                           | b.17 | 7.48 | 8.23 | 7.92 | 16.7 | 7.91 | 7.97 | 8.11  | 8.17  | 8.01        | 7.52 | 7.71 | 7.97    | 0.20        |
| 2-Zellau                                    | 8.19 | 8.11 | 8.16 | 16.7 | 7.95 | 7.87 | 8.00 | 8.10  | 8.06  | 8.04        | 7.78 | 7.83 | 8.00    | 0.13        |
| 1-2-2-2                                     | 8.15 | 7.98 | 8.18 | 7.98 | 7.95 | 7.86 | 8.00 | 8.11  | 8.06  | 8.08        | 7.63 | 7.92 | 2.99    | 0.15        |
| 4 - Budia                                   | 8.20 | 8.00 | 8.23 | 7.92 | 7.95 | 7.84 | 8.02 | 8.14  | 8.02  | 8.14        | 7.90 | 1.17 | 8.01    | 0.14        |
| S-Portue + se Fort                          | 8.10 | 8.06 | 8.14 | 7.65 | 7.91 | 7.85 | 1.11 | 8.14  | 8.05  | 8.16        | 7.50 | 7.86 | 1.93    | 0.21        |
| 6-North the Muharren Gause-way              | 8.21 | 7.95 | 8.27 | 7.86 | 7.8  | 7.88 | 8.01 | 8.20  | 7.99  | 8.21        | 7.83 | 1.11 | 10.8    | 0.17        |
|   | 8.35 | 8.51 | 8.53 | 8.12 | 8.01 | 7.98 | 8.09 | 8.37  | 8.20  | 8.17        | 7.98 | 8.07 | 8.20    | 0.20        |
| R-Mas MayJun<br>R-Widd(Fast ASRY Cause-wav) | 8.31 | 8.16 | 8.32 | 8.26 | 8.03 | 7.98 | 8.11 | 8.39  | 8.14  | 8.21        | 7.96 | 7.99 | 8.16    | 0.15        |
| Q-Hidd(One the Coment Factory               | 8.35 | 8.24 | 8.29 | 8.16 | 8.00 | 7.98 | 8.13 | 8.27  | н.01  | 8.26        | 7.82 | 7.89 | 8.12    | 0.17        |
|   | 8.27 | 8.05 | 8.35 | 8.08 | 7.96 | 7.89 | 8.09 | 8.32  | 7.93  | 8.21        | 7.98 | 7.72 | 8.07    | 0.19        |
| 11-South the Muharreo Cause-Vav             | 8.19 | 7.89 | 8.24 | 7.85 | 7.97 | 8.05 | 8.04 | 8.18  | 7.40  | 8.24        | 7.94 | 1.93 | 8.0     | 0.14        |
| 12-Mine Sulman main letty                   | 8.30 | 8.14 | 8.35 | 8.03 | 7.82 | 8.15 | 8.07 | 8.31  | 8.00  | 8.08        | 7.81 | 7.75 | 8.07    | 0.20        |
| 11_Neberh Salth                             | 8.19 | 8.23 | 8.24 | 8.06 | 7.94 | 8.08 | 8.14 | 8.35  | 7.93  | 8.21        | 7.80 | 7.81 | 80.8    | 0.18        |
| 12-Pas Tubli (opp. Sew age Treatment        | 8.23 | 16.7 | 8.12 | 7.89 | 7.73 | 7.78 | 7.82 | 8.03  | 7.99  | 11.1        | 7.72 | 7.59 | 7.88    | 0.18        |
| IS_SIFTA (Duussite Al-Ikr)                  | 8.36 | 1.72 | 8.32 | 7.96 | 7.95 | 7.99 | 8.08 | A. 32 | в. 32 | 8.16        | н.06 | 7.88 | 8.09    | 0.21        |
| 16-Stra iserv(Bander Al-Dar)                | 8.17 | 8.12 | 8.24 | 8.03 | 60.8 | 8.01 | 8.14 | 8.32  | 8.03  | <b>B.24</b> | 7.94 | 1.79 | 8.09    | <b>ሪ.</b> ይ |
| 17-Askar                                    | 8.23 | 8.19 | 8.20 | 8.10 | 8.00 | 7.89 | 8.17 | 8.23  | 8.08  | 8.19        | 7.96 | 7.81 | 8.09    | 0.14        |
|   |      |      |      |      |      |      |      |       |       |             |      |      |         |             |
| MEAN  | 8.23 | 8.07 | 8.26 | 7.99 | 1.%  | 7.94 | 8.04 | 8.23  | 8.05  | 8.14        | 7.83 | 7.83 |         |             |
| STANDARD DEVIATION                          | 0.08 | 0.18 | 0.10 | 0.14 | 0.08 | 0.10 | 0.11 | 0.11  | 0.11  | 0.12        | 0.16 | 0.11 |         |             |



#### Figure:2.20

Monthly mean pH over the year 1983 for the 17 stations.

The bars represent the standard deviation.

- (b) to evaluate the need to provide bodies of water with nourishing substances necessary for the development of aquatic organisms, such as compounds of nitrogen, phosphorus, silicon, iron, or trace elements;
- (c) to characterize the degree of water pollution and the nature of the prevalent pollutants; and
- (d) to record cases of sharp increase in the concentration of polluting substances and to pinpoint main sources of pollution.

Depending on the aim and the conditions of the observations, chemical parameters may be grouped by various features, among them substances which occur naturally in the body of water versus man-made wastes or other pollutants. There is no sharp boundary between these two groups of substances, since there are many which may be of both origins (i.e., phenols, organic acids, ammonium ions, etc.). Therefore, when, assessing the pollution of bodies of water, differences in concentration of such substances, not their absolute concentration, serve as better diagnostic indices. However, discovery of such substances as pesticides, does indicate the man-made pollution of the body of water (UNESCO/WHO, 1978).

The maintenance of natural composition and the minimizing of harmful toxic substances must meet various requirements when water is used by various branches of industry, agriculture, fisheries, etc. with the development of industry and the intensification of agriculture, the number of pollutants which affect the quality of water has been on a rapid increase. Every year the listed substances whose perimssible concentrations have been experimentally established is also lengthening.

#### 2.3.4.1 Nutrients:

The modern science of the sea pointed out the essential part played by plants in the economy of the sea. Plants are known to synthesize simple inorganic substances into highly complex organic forms. The nutrient salts of the sea are usually regarded as the dissolved mineral salts that have been shown to influence and, at times limit the production of phytoplankton in accordance with Leibig's law of minimum which states that growth is limited by the factor that is present in minimal quantity. The nutrient salts are characterized by being essential for plants growth together with their presence in small and variable quantities.

Phosphates and nitrates are considered to be the typical nutrient salts. However, other compounds of nitrogen and phosphorus are utilized by phytoplankton as nitrites, ammonia, urea, uric acid and dissolved organic phosphorus.

Certain other elements such as iron, manganese, copper, zinc, cobalt and molybdenum are essential to the growth of marine plants as they occur in their enzyme systems. It is unlikely that phytoplankton growth is ever limited by the total concentration of any of these trace metals, but in some waters an essential element may be present in which it is not assimilable by the organism. Thus, there is some evidence that certain ocean waters may be deficient in available iron and manganese (Harvey, 1955; Tranter and Newell, 1963). The very low requirements for the other trace metals makes it improbable that they ever limit marine photosynthesis. The nutrient salts are defined by certain characteristics other than their limiting factor:

a. <u>Vertical distribution</u>: The plant nutrients are not uniformly distributed through a vertical column of water. The fact that the existence of plants is limited to the upper lighted layer, results in a remarkable consumption of nutrients from the upper layers while the lower layer shows a remarkable high content due to absence of plant life and accumulation and disintegration of the falling bodies from the upper layers. The deep dark waters are regarded as the main store of nutrients.

b. <u>Seasonal fluctuations</u>: Fluctuations also take place with time in the upper lighted zone. It is well known that by the return of sunshine and increasing temperature during Spring in the temperate and higher latitudes, there is a remarkable outburst of phytoplankton in the surface waters which become subsequently more or less depleted of the nutritive salts. With the return of the unfavourable conditions of Winter there is a death of plants and waters become enriched again.

c. <u>Cycle in the sea:</u> The nutrient salts undergo a series of transformations in the sea. The main feature of the cycle is the consumption of the inorganic forms and their regeneration from the organically bound state in the disintegrating dead bodies. For example the principal steps in the nitrogen cycle are living organisms, dead organisms, ammonia, nitrite, nitrate, living organisms.

A thorough understanding of the circulation of nitrogen in the sea must be based on the quantitative relationships involved in these various steps. The soluble substances are the only ones which have received much attention. Phosphorus differs only in having one inorganic form; the orthophosphate.

d. <u>Nitrogen - Phosphorus Ratio</u>: Nitrogen and phosphorus are assimilated from sea water in an approximately constant proportion of 15:1 (by atoms) by phytoplankton as they grow. It is remarkable that ocean waters at all depths usually contain these elements in a similar ratio. However, there are a number of exceptions for example, English channel water has been found to have  $NO_3^-$ :  $PO_4^3$ ratio varying from 10.5:1 in Winter to 19:1 in Summer.

#### 2.3.4.1 (i) The physical processes of the nutrient cycle:

The general nutrient cycle is shown in the following figure after Barnes (1959). Since the diatoms are plants and utilise the sun's energy in their photosynthetic activity, the primary production must be limited to the upper layers where sufficient light penetrates for their activity. It is the diatoms that utilize the inorganic nutrients: herbivores feed on the diatoms and carnivores on the herbivores, and so begins the complex food chain. Dead organic matter will tend to sink and the products of decomposition will therefore be found in the deeper layers.

CONSUMPTION



Bacterial Action on Mud

Clearly there must exist mechanisms for the return of nutrients to the upper layers in order that production may be a continuing process. The most important of these mechanisms are:-

a. <u>The Process of Upwelling</u> which is observed particularly on the western coasts of the continents (e.g. California). As a result of prevailing winds carrying the lighter waters away from the coast and banking them up some 100 miles offshore, deep waters rise to the surface in the coastal region carrying with them their high content of the nutrients. Upwelling is not restricted to the coastal regions, it can occur in any region of divergences, even in midocean, where surface waters flow away from one another.

b. <u>Turbulent Currents</u>, however caused, will also tend to stir up the water and equalise the nutrient content throughout its depth. The tidal currents in the Bay of Fundy for example, result in effective mixing at all seasons. When such turbulence is very vigorous, it may be harmful to productivity, although it does keep the nutrient elements in the upper layer. This may be due to the large quantities of mud which may be stirred up, thus reducing the penetration of light with a reduction in photo-synthesis. Also the diatoms themselves may carried below the euphotic zone. c. <u>Eddy Diffusion</u>: In any moving body of water there exists turbulent motion within the water mass, and there will always be a tendency therefore to equalize concentrations within the body of water. The process is analogous to molecular diffusion brought about by molecular motion and is termed eddy diffusion. The magnitude of the vertical transfer by eddy diffusion depends upon the vertical eddy diffusion coefficient; in general it is greatest with low vertical stability , such as is present in the absence of density gradients and high velocity.

d. <u>Winter Convection</u>: In temperate zones, where there is a marked seasonal change in the climatic conditions, vertical convection arises as a result of the Winter cooling of surface waters, so that their density increases sufficiently to cause them to sink and to be replaced by an upward movement of the lower nutrient rich waters.

#### 2.3.4.1.1 Nitrogen:

Nitrogenisanessential constituent of all living organisms. It occurs as a component of all major classes of biochemical compounds and plays a unique role in the structure of proteins and enzymes. Nitrogen is present in organisms and in surface waters in various oxidation stages ranging from  $N^{+3}$  (ammonia and amino groups) to  $N^{+5}$  (nitrate). Most water analyses are restricted to ammonia (NH<sub>3</sub>), nitrate (NO<sub>3</sub>), nitrite (NO<sub>2</sub>), and Kjeldahl nitrogen (ammonia nitrogen plus organic nitrogen). Total nitrogen usually refers to the sum of nitrite nitrogen, nitrogen, and Kjeldahl nitrogen.

The principal inorganic forms of nitrogen are nitrate ion (usual range 1-500  $\mu$ g NO<sub>3</sub> -N/1), nitrite ion (usual range <0.1-50  $\mu$ g NO<sub>2</sub>-N/1) and ammonia (usual range <1-50  $\mu$ g NH<sub>3</sub> -N/1).

#### 2.3.4.1.1(i) Ammonia:

The presence of ammonium ions in unpolluted water is connected with the process of the biochemical decomposition of protein substances. An increase in the concentration of ammonium ions therefore, is observed when aquatic organisms are dying off, especially in the zone of the aggregation (the layers of increased density of phyto-and bacterioplankton). The amplitude of seasonal fluctuations of ammonium ions reflects the nutrition of the body water and its pollution by organic nitrogen-containing substances contained in household and industrial sewage (chiefly from the food industry). Ammonium ions can be formed during the anaerobic reduction of nitrates and nitrites. In oligotrophic bodies of water, characterized by pure water with a high content of dissolved oxygen and a high value of oxidationreduction potential, the content of ammonium ions is small.

The relationship between ammonium ion concentrations and free ammonia are determined by the pH value and may be determined from Table 2.5.

<u>Table 2.5</u>: Relationships between the percentage concentrations of  $NH_3$ ,  $NH_4^+$ , and the pH of the water (after UNESCO/WHO, 1978).

|                   |     | <sup>≉nh</sup> 3 | or NH <sup>+</sup> 4 | at pH |    |    |
|-------------------|-----|------------------|----------------------|-------|----|----|
|                   | 6   | 7                | 8                    | 9     | 10 | 11 |
| NH3               | 0   | 1                | 4                    | 25    | 78 | 96 |
| NH <sup>+</sup> 4 | 100 | 99               | 96                   | 75    | 22 | 4  |

During the study period, it was noticed that ammonia nitrogen exhibited the highest monthly average value of 739.0 µg/l in September at station 17 (Asker) and the lowest value of 1.1 µg/l in January at station 7 (Ras Rayyah). The overall maximum observed ammonia was 144.1 µg/l during September, while the minimum (15.6 µg/l) during January (Table 2.6).

The highest encountered overall monthly mean ammonia was at Asker (249.6 µg/1) followed by Ras Tubli (109.0 µg/1). Although Asker is an open sea area but it experiences a southerly drift coming from BAPCO refinery, untreated sewage outfalls at Ras Zuwayed and Al - Farsiyah and desalination plant at Ras Abu-Jarjoor. The highest ammonia at Ras Tubli is due to the discharge from the sewage treatment plant.

In general, it is found that ammonia is somewhat higher at the east coast followed by the north then the west coasts. This could probably due to the sewage and industrial discharges in the eastern and north-eastern regions.

High content of ammonia at Mina Sulman main jetty (overall monthly mean of  $77.2 \,\mu g/1$ ) could probably due to anchorage provided to large ships and vessels because it is the main port in the island. Also it is near to Mina-Sulman industrial area. At Sitra, opposite Al-Ikr, monthly mean ammonia concentration was  $75.4 \,\mu g/1$ . This might be attributed to the discharges of Sitra separator outlet and the new central abattoir.

Generally, ammonia increased gradually from its minimum during January to its maximum during September-December and then decreased again (Figures 2.21 to 2.29). Monthly mean ammonia nitrogen (Jug/l)

Table: 2.4

|                                     |      |       |       |       |      | W        | NTHS  |       |       |         |       |       |       | STANDARD  | <b></b> |
|-------------------------------------|------|-------|-------|-------|------|----------|-------|-------|-------|---------|-------|-------|-------|-----------|---------|
| SIATIONS                            | 7    | F     | Σ     | <     | Σ    | <b>「</b> | ſ     | ۲     | s     | 0       | z     | a     | MEAN  | DEVIATION |         |
| 1-Bílaj Al-Jazaír                   | 10.5 | 11.3  | 7.2   | 7.1   | 36.8 | 29.6     | 73.7  | 62.3  | 146.9 | 120.6   | 73.0  | 82.9  | 55.2  | 46.4      |         |
| 2-Zallaq                            | 18.5 | 33.0  | 15.3  | 28.8  | 43.5 | 86.1     | 64.8  | 88.7  | 68.3  | ł       | 73.1  | 113.3 | 57.6  | 32.0      |         |
| 3-Jasra                             | 12.2 | 22.1  | 22.9  | 34.4  | 44.4 | 54.2     | 119.0 | 69.7  | 146.9 | 96.1    | 86.2  | 110.1 | 68.2  | 43.5      |         |
| 4-Budia                             | 9.5  | 32.0  | 24.7  | 22.1  | 50.1 | 32.9     | 63.9  | 71.4  | 188.0 | 81.3    | 143.9 | 111.6 | 69.3  | 24.42     |         |
| 5-Portug e se fort                  | 9.4  | 30.4  | 8.8   | 66.6  | 27.0 | 40.2     | 50.0  | 62.6  | 128.8 | 210.0   | 101.8 | 123.9 | 71.6  | 59.6      |         |
| 6-North the Muharreq Cause-way      | 4.7  | 22.1  | 14.6  | 29.5  | 32.2 | 43.5     | 56.7  | 69.8  | 171.7 | 150.0   | 140.5 | 97.7  | 69.4  | 57.3      | -       |
| 7-Ras Rayyah                        | 1.1  | 33.3  | 18.7  | 13.8  | 32.0 | 41.9     | 76.4  | 78.8  | 48.6  | 63.3    | 165.7 | 64.1  | 53.1  | 43.2      |         |
| 8-Hidd(East ASRY Cause-way)         | 11.1 | 82.1  | 20.5  | 127.9 | 36.2 | 54.3     | 88.7  | 49.4  | 64.8  | 130.5   | 119.1 | 96.0  | 73.4  | 40.7      |         |
| 9-Hidd(Opp. the Cement Factory      | 6.1  | 21.3  | 8.0   | 4.8   | 23.8 | 33.0     | 75.6  | 27.0  | 48.6  | 96.1 ]  | 104.3 | 6.9   | 43.2  | 35.2      |         |
| 10-Arad                             | 4.4  | 20.3  | 20.5  | 67.9  | 31.2 | 46.8     | 89.6  | 123.2 | 97.6  | 142.1   | 129.0 | 112.7 | 73.5  | 48.3      | _       |
| 11-South the Muharreq Cause-way     | 3.7  | 11.1  | 15.6  | 31.2  | 28.7 | 56.7     | 49.3  | 77.1  | 165.2 | 220.0 1 | 112.5 | 110.7 | 73.5  | 67.1      | _       |
| 12-Mina Sulman main jetty           | 17.8 | 59.9  | 34.4  | 28.6  | 48.6 | 50.0     | 134.0 | 162.1 | 112.5 | 125.6   | 93.7  | 58.9  | 77.2  | 46.9      |         |
| 13-Nabeeh Saleh                     | 1.9  | 32.0  | 9.7   | 34.4  | 81.3 | 22.1     | 112.1 | 62.3  | 92.8  | 94.4    | 93.5  | 76.4  | 59.4  | 37.7      |         |
| 14-Ras Tubli (opp. Sewage Treatment | 28.6 | 179.3 | 6.9   | 109.4 | 87.9 | 160.3    | 226.0 | 136.1 | 72.9  | 97.7    | 101.8 | 102.6 | 109.1 | 60.9      | -       |
| 15-Sitra (Opposite Al-Ikr)          | 15.2 | 36.2  | 37.0  | 15.6  | 38.6 | 41.2     | 118.2 | 87.7  | 81.1  | 243.0 1 | 11.6  | 79.7  | 75.4  | 63.4      |         |
| 16-Sitra jetty(Bander Al-Dar)       | 17.8 | 39.1  | 100.8 | 10.4  | 90.5 | 33.6     | 86.3  | 61.6  | 76.4  | 147.1 1 | 6.10  | 82.3  | 70.7  | 39.8      |         |
| 17-Asker                            | 93.0 | 661.0 | 26.1  | 38.3  | 36.2 | 81.1     | 192.0 | 122.3 | 0.951 | 280.0 3 | 6.03  | 364.9 | 249.6 | 242.7     |         |
|                                     |      |       |       |       |      |          |       |       |       |         |       |       |       |           |         |
| MEAN                                | 15.6 | /8.0  | 23.0  | 39.3  | 45.2 | 53.4     | 98.6  | 83.1  | 144.1 | 143.6 ] | 124.3 | 109.3 |       |           |         |
| STANDARD DEVIATION                  | 21.2 | 155.3 | 22.0  | 34.6  | 21.1 | 32.3     | 748.8 | 34.3  | 159.5 | 62.8    | 65.8  | 68.7  |       |           |         |





Monthly mean ammonia nitrogen, nitrite nitrogen, nitrate nitrogen and phosphate phosphorus for stations 1 and 2.



Monthly mean ammonia nitrogen, nitrite nitrogen, nitrate nitrogen and phosphate phosphorus for stations 3 and 4 .

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#### Figure: 2.24

Monthly mean ammonia nitrogen, nitrite nitrogen, nitrate nitrogen and phosphate phosphorus for stations 7 and 8.


#### Figure:2.25

Monthly mean ammonia nitrogen, nitrite nitrogen, nitrate nitrogen and phosphate phosphorus for stations 9 and 10.



Monthly mean ammonia nitrogen, nitrite nitrogen, nitrate nitrogen and phosphate phosphorus for stations 11 and 12.



#### Figure:2.27

Monthly mean ammonia nitrogen, nitrite nitrogen, nitrate nitrogen and phosphate phosphorus for stations 13 and 14.



Figure:2.28

Monthly mean ammonia nitrogen, nitrite nitrogen, nitrate nitrogen and phosphate phosphorus for stations 15 and 16.



Figure: 2.29

Monthly mean ammonia nitrogen, nitrite nitrogen, nitrate nitrogen and phosphate phosphorus for station 17. The effect of ammonia is an important factor to be considered. Sewage effluent, effluents from certain industries and from agriculture are common sources of ammonia in water.

The harmful effects of ammonia on fish are related to the pH value and the temperature of the water owing to the fact that only the un-ionized fraction of ammonia is poisonous. The un-ionized fraction increases with rising pH value, and with rising temperature.

Fish differ slightly in their tolerance to ammonia, depending on species. However, the difference in tolerance is more significant for short periods of exposure, and is not great enough to justify different criteria for species.

The lowest lethal concentration found for salmonids is  $0.2 \text{ mg NH}_3/1$  (un-ionized), but other adverse effects caused by prolonged exposure are absent only at concentrations lower than  $0.025 \text{ mg NH}_3/1$  (un-ionized). Concentrations of total ammonia which contain this amount of un-ionized ammonia range from 19.6 mg/1 (pH 7.0, 5°C) to 0.12 mg/1 (pH 8.5,  $30^{\circ}$ C).

The criterion of 0.025 mg  $NH_3/1$  (un-ionized) should not be applied to temperatures below 5°C or to pH value 8.0 when other factors have to be taken into consideration (Alabaster and Lloyd 1982).

At Asker (station 17), the mean concentration of ammonia exceeded the criterion during February ( $661.0 \mu g/1$ ), September (739.0  $\mu g/1$ ), October (280.0  $\mu g/1$ ), November ( $360.9 \mu g/1$ ) and December ( $364.9 \mu g/1$ ) as shown in Table 2.6. The undissociated ammonia molecule,  $NH_3$ , is highly toxic for fish. It is a weak base. For example at pH 7.5 the percentage dissociation is represented by

$$NH_3 + H_20 = NH_4^+ + OH^-$$
  
1.3% 98.7%

Even low levels of ammonia  $(NH_3)$  can cause branchial hyperplasia (Smith and Piper, 1975). Levels above 0.02 mg/litre not recommended. Below pH 7 the amount of undissociated ammonia is small at any concentration of ammonia liable to be experienced in fish hatcheries but above pH 7 and especially in sea-water (pH 7.8 -8.2) its presence is always a potential danger to fish health (Roberts, 1978).

#### (ii) Nitrite:

Nitrites appear in the water chiefly as a result of biochemical oxidation of ammonia or the reduction of nitrates. In surface water with sufficient oxygen volume, at high values of oxidizing-reducing potential, processes of biochemical oxidations are predominant.

The reduction of nitrates with the formation of nitrites takes place under conditions where there is a deficit of oxygen in natural layers of the water and in bottom deposits. Together with other ingredients, the concentration of nitrates and its dynamics and distribution in the body of water serve as an important index of the processes mentioned above. The presence of nitrites in increased concentrations may indicate the pollution (including faecal) of the body of water (UNESCO/WHO,1978). In some industrial and biologically purified run off water, nitrites may be present in considerably larger amounts. Monthly mean nitrite-nitrogen is shown in Table 2.7. Figures 2.21 to 2.29 indicate that nearly all nitrite curves follow the same pattern. It was noticed during the study period that within nitrogen and phosphorus salts, nitrite-nitrogen has the lowest concentration at all the stations (Figures 2.21 to 2.29). This is because nitrite ion occur generally in seawater at low concentration as intermediates in oxidation of ammonia ions (nitrification). Its concentration ranged from  $1.4 \,\mu g/1$ during January at station 2 (Zallaq), station 6 (North the Muharreq causeway) and station 11 (South the Muharreq causeway) to 36.9  $\mu g/1$  during February at station 15 (Sitra, opposite Al-Ikr), a difference of 35.5  $\mu g/1$ (Table 2.7).

The maximum overall monthly mean concentration of nitrite  $(10.1 \ \mu g/l)$  was encountered during June while the minimum  $(3.1 \ \mu g/l)$  during January. Ammonia also has the lowest concentration during January. It appears that the trend of nitrite is somewhat higher in the eastern coast, followed by the northern and the western coasts respectively as in the case of ammonia.

Station 14 (Ras Tubli) has the highest monthly mean concentration (14.0  $\mu$ g/l) of nitrite reflecting the effect of Tubli sewage treatment plant. The high content of nitrite (11.1  $\mu$ g/l) in Portugese Fort (station 5) could be probably due to the presence of fresh water aquifer near the sampling station. It was noticed that its concentration at this station increased during the low tide and decreased during the high tide because the aquifer became more exposed at low tide and hence the percentage of freshwater to seawater is higher than during the high tide. That is why its concentrations are sometimes high and sometimes low. Monthly mean nitrite nitrogen (ug/l)

Table: 2.7

|                                    |      |      |     |      |      | MOM  | NTHS     |      |      |      |      |      |       | STANDARD  |
|------------------------------------|------|------|-----|------|------|------|----------|------|------|------|------|------|-------|-----------|
| STATIONS                           | ~    | لله  | Σ   | <    | Σ    | ~    | <b>「</b> | <    | s    | 0    | z    | a    | PIEAN | DEVIATION |
| 1-Bilai Al-Jazair                  | 1.7  | 4.6  | 4.2 | 2.7  | 7.3  | 7.5  | 7.4      | 4.5  | 5.2  | 6 4  | 6 7  | 8    | 5 1   | -<br>-    |
|                                    |      |      |     |      |      |      |          |      |      | 5    |      | 2    | ;     |           |
| 2-Zallaq                           | 1.4  | 5.4  | 4.9 | 4.4  | 7.5  | 7.8  | 0.6      | 3.1  | 5.2  | 2.8  | 6.9  | 4.5  | 5.2   | 2.2       |
| 3-Jasra                            | 2.5  | 3.9  | 3.7 | 4.3  | 8.3  | 8.3  | 5.8      | 4.6  | 4.0  | 16.7 | 6.5  | 4.5  | 6.1   | 3.8       |
| 4-Budia                            | 3.0  | 4.3  | 6.6 | 4.2  | 9.6  | 10.2 | 5.8      | 5.0  | 4.3  | 9.2  | 9.4  | 4.8  | 6.4   | 2.6       |
| 5-Portug e se Fort                 | 2.5  | 5.9  | 8.6 | 13.6 | 7.0  | 32.8 | 6.1      | 5.9  | 12.0 | 23.6 | 1.7  | 8.0  | 11.1  | 8.7       |
| 6-North the Muharreq Cause-way     | 1.4  | 4.2  | 3.4 | 3.0  | 6.7  | 7.8  | 6.0      | 5.1  | 4.0  | 14.1 | 5.3  | 4.8  | 5.5   | 3.2       |
| 7-Ras Rayyah                       | 2.2  | 5.9  | 5.4 | 4.4  | 8.8  | 10.0 | 6.1      | 4.2  | 10.1 | 4.6  | 8.1  | 6.1  | 6.3   | 2.5       |
| 8-Hidd(East ASRY Cause-way)        | 1.7  | 4.0  | 4.5 | 3.9  | 7.1  | 8.3  | 6.4      | 4.5  | 3.8  | 4.9  | 5.4  | 4.6  | 4.9   | 1.7       |
| 9-Hidd(Opp. the Cement Factory     | 2.0  | 4.5  | 4.5 | 2.8  | 6.6  | 7.9  | 6.0      | 2.8  | 3.4  | 10.4 | 5.9  | 5.0  | 5.2   | 2.4       |
| 10-Arad                            | 1.9  | 6.8  | 8.2 | 6.0  | 7.8  | 9.1  | 6.5      | 9.4  | 5.6  | 7.0  | 7.8  | 4.9  | 6.4   | 1.9       |
| 11-South the Muharreq Cause-way    | 1.4  | 3.6  | 3.7 | 3.5  | 8.2  | 8.9  | 5.3      | 4.1  | 4.0  | 13.6 | 4.9  | 4.6  | 5.5   | 3.3       |
| 12-Mina Sulman main jetty          | 1.6  | 4.4  | 4.9 | 2.3  | 6.8  | 9.2  | 5.4      | 6.3  | 4.3  | 14.5 | 5.9  | 4.3  | 5.8   | 3.4       |
| 13-Nabeeh Saleh                    | 2.6  | 3.9  | 5.4 | 3.4  | 18.9 | 7.4  | 6.3      | 5.1  | 12.3 | 5.9  | 8.0  | 7.2  | 7.2   | 4.5       |
| 14-Ras Tubli (opp.Sewage Treatment | 4.8  | 15.6 | 5.7 | 21.7 | 30.4 | 12.3 | 8.0      | 15.2 | 13.2 | 4.9  | 7.5  | 28.8 | 14.0  | 8.9       |
| 15-Sitra (Opposite Al-Ikr)         | 3.0  | 36.9 | 8.1 | 4.1  | 7.0  | 8.6  | 7.5      | 4.0  | 4.9  | 15.3 | 7.0  | 4.8  | 9.3   | 9.3       |
| 16-Sitra jetty(Bander Al-Dar)      | 3.7  | 4.4  | 4.6 | 4.2  | 11.5 | 7.3  | 10.9     | 4.3  | 5.2  | 5.9  | 8.1  | 5.4  | 6.3   | 2.6       |
| 17-Asker                           | 14.5 | 18.9 | 7.1 | 5.2  | 7.4  | 8.3  | 8.0      | 10.3 | 7.3  | 6.1  | 10.6 | 5.4  | 9.1   | 4.0       |
| MEAN                               | 3.1  | 8.1  | 5.5 | 5.5  | 9.8  | 10.1 | 6.9      | 5.5  | 6.3  | 9.8  | 7.1  | 6.6  | ·     |           |
| STANDARD DEVIATION                 | 3.1  | 8.6  | 1.7 | 4.9  | 6.1  | 6.0  | 1.5      | 3.0  | 3.3  | 5.7  | 1.5  | 5.8  |       |           |

#### (iii) Nitrate:

Nitrates are the end product of the biochemical oxidation of ammonia which is formed chiefly as a result of the breaking up of protein substances. Increased concentrations of nitrates may indicate faecal pollution of the body of water in the preceding period. High content in potable water is also harmful for children and causes anaemia (methaemoglobanaemia) (UNESCO/WHO, 1987).

Information on changes in the concentration of nitrates and the concentrations of other nitrogen forms may be used to characterize the rate of the process of selfpurification and the self-purifiying capacity of the bodies of water.

Monthly mean nitrate-nitrogen is shown in Table 2.8. Unlike nitrite, there is somewhat a high range between nitrate-nitrogen concentrations, with a maximum observed monthly average of 1188.0 µg/1 during February at station 14 (Ras Tubli) because of the sewage treatment plant and a minimum of zero during September and October at different stations. This could be probably due to increase in plankton biomass during these months which feed on such nutrient and cause depletion in its concentration. As a rule, nitrates are present in appreciable amounts in surface water, exceptfor periods of intensive development of phytoplankton in bodies of water, at which time the content of nitrates may drop to negligible levels (UNESCO/WHO,1978). Monthly mean nitrate nitrogen ( $\mu g/l$ ).

**Table: 2.8** 

|                                    |       |        |       |       |       | NOM   | THS  |       |     |      |      |       |        | STANDARD  |
|------------------------------------|-------|--------|-------|-------|-------|-------|------|-------|-----|------|------|-------|--------|-----------|
| STATIONS                           | ~     | ٤.,    | Σ     | <     | Σ     | 7     | ~    | <     | S   | 0    | z    | ٩     |        | DEVIATION |
| l-Bilai Al-Jazair                  | 51.3  | 60.09  | 56.9  | 45.3  | 41.5  | 73.9  | 30.9 | 22.1  | 0.0 | 2.2  | 9.8  | 5.1   | 33.3   | 25.2      |
| 2-Zallaq                           | 82.4  | 80.0   | 49.3  | 64.3  | 45.4  | 81.8  | 21.5 | 30.5  | 0.0 | 25.3 | 11.5 | 26.4  | 43.2   | 28.6      |
| 3-Jasra                            | 40.3  | 48.1   | 44.4  | 49.4  | 59.7  | 70.9  | 19.1 | 26.0  | 0.0 | 5.7  | 7.0  | 12.8  | 32.0   | 23.3      |
| 4-Budia                            | 73.0  | 53.8   | 120.4 | 58.2  | 84.2  | 83.2  | 48.0 | 42.7  | 0.0 | 4.7  | 21.5 | 21.2  | 50.9   | 35.8      |
| 5-Portuge se Fort                  | 325.5 | 60.1   | 89.1  | 1     | 57.7  | 262.2 | 26.1 | 95.5  | 0.0 | 81.7 | 20.3 | 34.4  | 95.7   | 103.4     |
| 6-North the Muharreq Cause-way     | 74.7  | 72.6   | 55.7  | 82.0  | 51.9  | 73.6  | 31.8 | 17.6  | 0.0 | 12.6 | 27.2 | 6.0   | 41.7   | 30.3      |
| 7-Ras Rayyah                       | 61.6  | 52.6   | 91.4  | 36.6  | 51.4  | 183.9 | 18.2 | 31.8  | 0.0 | 2.4  | 28.4 | 44.8  | 50.3   | 49.1      |
| 8-Hidd(East ASRY Cause-way)        | 6.14  | 27.8   | 89.9  | 63.4  | 35.7  | 82.9  | 12.5 | 35.4  | 0.0 | 0.0  | 6.9  | 8.9   | 34.0   | 31.2      |
| 9-Hidd(Opp. the Cement Factory     | 35.9  | 35.6   | 100.4 | 34.1  | 48.1  | 117.3 | 20.0 | 25.0  | 0.0 | 6.4  | 16.4 | 26.1  | 38.8   | 35.5      |
| 10-Arad                            | 43.4  | 48.3   | 125.0 | 94.7  | 61.2  | 112.8 | 30.0 | 32.3  | 0.0 | 45.2 | 22.2 | 32.6  | 54.0   | 38.0      |
| 11-South the Muharreq Cause-way    | 32.7  | 47.2   | 102.9 | 52.1  | 62.3  | 76.6  | 36.9 | 30.0  | 0.6 | 13.7 | 19.2 | 1.7   | 39.7   | 30.6      |
| 12-Mina Sulman main jetty          | 84.5  | 63.6   | 73.4  | 117.4 | 55.0  | 132.3 | 36.7 | 95.1  | 0.0 | 2.7  | 15.2 | 32.6  | 59.0   | 43.4      |
| 13-Nabeeh Saleh                    | 39.8  | 23.5   | 68.0  | 30.6  | 130.3 | 104.5 | 34.9 | 63.3  | 0.0 | 2.4  | 21.5 | 22.7  | 45.1   | 39.7      |
| 14-Ras Tublí (opp.Sewage Treatment | 251.7 | 1188.0 | 146.9 | 639.3 | 416.3 | 231.2 | 36.6 | 295.3 | 2.4 | 0.0  | 10.0 | 730.1 | 329. d | 363.7     |
| 15-Sitra (Opposite Al-Ikr)         | 50.2  | 9.8    | 124.9 | 70.4  | 51.0  | 78.3  | 23.8 | 28.9  | 0.0 | i    | 25.4 | 18.9  | 43.8   | 36.4      |
| 16-Sitra jetty(Bander Al-Dar)      | 41.6  | 21.9   | 48.8  | 54.3  | \$4.0 | 93.8  | 17.6 | 41.7  | 0.0 | 0.0  | 15.2 | 27.4  | 34.7   | 26.7      |
| 17-Asker                           | 67.7  | 51.2   | 53.2  | 21.3  | 45.7  | 87.2  | 16.6 | 45.7  | 0.0 | 0.0  | 12.8 | 14.3  | 34.6   | 27.8      |
| MEAN                               | 82.4  | 114.4  | 84.7  | 94.6  | 79.5  | 114.5 | 27.1 | 56.4  | 0.2 | 12.8 | 17.1 | 62.4  |        | *         |
| STANDARD DEVIATION                 | 80.4  | 277.3  | 31.9  | 147.3 | 89.4  | 57.5  | 9.6  | 65.7  | 0.6 | 21.9 | 6.8  | 172.5 |        |           |

The overall monthly mean nitrate shows that Ras Tubli (station 14) again has the highest concentration (329.0 µg/1) followed by Portugese Fort (95.7 µg/1) because of the agricultural discharge from the onshore gardens and the presence of the submarine spring. The next station being Arad (54.0 µg/1) probably because of a sewage outfall and also it contains algae in abundant quantities. Fishermen from villages throughout Muharreq island (Dair, Hidd, Qalali, Samaheej and Busaitain) collect these algae for use as bait to catch fish, mainly safee, by gargoors (wire traps). Jasra (station 3) which lie on the west coast has the lowest concentration (32.0 µg/1). The maximum overall monthly mean was encountered during June and the minimum during October (Table 2.8).

It could be noticed from Figures 2.27 and 2.29 that nitrate level is higher than ammonia level at station 14 (Ras Tubli), while the reverse is true at station 17 (Asker). This might be because the treatment of sewage at Tulbi allow the ammonia to be converted to nitrate during the aeration process. On the contrast, Asker experience a southerly drift coming from the untreated sewage oufalls at Ras-Zuwayed (Figure 1.12) and Al-Farsiyah which resulted in higher concentration of ammonia than nitrate.

Generally, all the nitrate and ammonia curves in Figures 2.21 to 2.29 follow the same pattern and show an interesting relationship, since as ammonia increases, nitrate decreases and vice versa.

## 2.3.4.1.2 Phosphate:

In unpolluted bodies of water, phosphates are formed mainly during certain biological processes of transformation of organic substances to inorganic phosphates. A considerable amount may be introduced with the incoming waters from the drainage collection system. While draining the soil, these waters wash away the soluble phosphates as well as other salts. Some phosphates enter the water in suspension and may be dissolved later under favourable conditions.

Phosphates belong to a group of nutrient substances which are often the limiting factor in fresh water in the processes of photosynthesis, and which are utilized to a point where insignificant, small concentrations are left. During the vegetation period, the phosphates are used up rapidly by aqueous plant organisms, mainly phytoplankton. The main users of organic phosphorous are zooplankton and bacteria (UNESCO/WHO, 1978). It is the rate of the active life of these groups of organisms which determines the seasonal (and diurnal) dynamics of phosphate content under natural conditions. The pH value of the water also determines the type of phosphates present. Content of phosphates in ground waters, for example, is usually not significant.

Considerable irregular increases in the concentration of phosphates may indicate a presence of pollutants. The latter may be in the form of phosphates, organophosphates, or polyphosphates. Polyphosphates, as washing or flotation agents, are used in a number of enterprises. They may enter the bodies of water along with the run off waters in quite large amounts.

Inorganic phosphate exists in the sea practically entirely in the form of orthophosphate ions. Kester and Pytkowicz (1967) have shown that in a sea water of average salinity (pH 8.0) at  $20^{\circ}$ C, 87% of the phosphate occurs as HPO<sub>4</sub><sup>2-</sup>, 12% as PO<sub>4</sub><sup>3-</sup> and 1.0% as H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, and that 99.6% pf the PO<sub>4</sub><sup>3</sup> and 44% of the HPO<sub>4</sub><sup>2-</sup> is in the form of ion pairs, presumably with calcium and magnesium.

During the study period, it was noticed that monthly mean phosphate-phosphorus (Table 2.9) fluctuated between zero at station 11 (South the Muharreq causeway) during January, station 9 (Hidd, opposite the cement factory) and station 15 (Sitra, opposite Al-Ikr) during April to 2295.0  $\mu$ g/l at station 14 (Ras Tubli) during February reflecting the effect of the sewage. In general, phosphate concentration in the northern coast remained the lowest in comparison with that of the western and eastern coasts.

The highest recorded overall monthly mean was at Ras Tubli (667.1  $\mu$ g/l) due to its proximity to Tubli sewage treatment plant followed by Asker (80.5  $\mu$ g/l) because of its proximity to Ras Zuwayed and Al-Farsiyah sewage outfalls. Ammonia and nitrate were also high at these stations (stations 14 and 17).

The maximum encountered overall monthly mean phosphate was during February (170.8  $\mu$ g/l) while the minimum (23.2  $\mu$ g/l) during January (Table 2.9), but the highest encountered phosphate in most stations was during August.

#### 2.4 Conclusion:

From the study conducted, it could be said that in general the water quality of the western and northern regions of Bahrain is better than the water quality of the eastern region. The east has in general higher pH, higher ammonia, higher nitrite, and higher phosphate levels than the other regions reflects the urbanisation and industrialisation of Monthly mean phosphate phosphorus (Jg/l)

**Table: 2.9** 

| 04017170                           |       |        |      |       |       | NOM   | ITHS   |       |       |      |       |         | S    | TANDARD  |
|------------------------------------|-------|--------|------|-------|-------|-------|--------|-------|-------|------|-------|---------|------|----------|
| SNUTIAIS                           | ſ     | Ŀ      | Σ    | <     | Σ     | ٦,    | ſ      | <     | s     | 0    | z     | D       | EAN  | EVIATION |
| 1-Bilaj Al-Jazair                  | 2.7   | 14.6   | 12.0 | 2.0   | 3.4   | 11.1  | 8.5    | 57.2  | 23.3  | 12.0 | 37.3  | 16.0    | 16.7 | 16.1     |
| 2-Zallaq                           | 4.3   | 66.2   | 16.8 | 2.0   | 13.6  | 10.2  | 11.1   | 42.3  | 26.6  | 87.6 | 32.5  | 29.9    | 28.6 | 26.0     |
| 3-Jasra                            | 3.4   | 17.7   | 2.7  | 2.7   | 13.6  | 27.5  | 16.8   | 53.0  | 10.2  | 20.1 | 27.5  | 13.6    | 17.4 | 14.1     |
| 4-Budia                            | 15.0  | 13.3   | 12.6 | 3.4   | 6.8   | 12.8  | 7.8    | 13.5  | 20.1  | ı    | 34.2  | 13.5    | 3.9  | 8.1      |
| 5-Portug e se Fort                 | 10.1  | 8.5    | 13.5 | 12.0  | 12.0  | 16.0  | 12.0   | 31.6  | 10.2  | 16.7 | 17.7  | 11.8    | 4.3  | 6.1      |
| 6-North the Muharreq Cause-way     | 5.3   | 36.7   | 17.5 | 3.4   | 6.8   | 23.3  | 19.3   | 38.2  | 23.3  | 31.6 | 26.7  | 16.8    | 0.7  | 11.6     |
| 7-Ras Rayyah                       | 5.1   | 9.4    | 29.9 | 7.6   | 8.4   | 30.8  | 9.4    | 29.2  | 13.5  | 23.3 | 37.3  | 25.81   | 9.1  | 11.3     |
| 8-Hidd(East ASRY Cause-way)        | 4.3   | 28.4   | 39.0 | 0.9   | 2.7   | 16.7  | 15.1   | 23.4  | 15.1  | 31.6 | 27.4  | 16.4 1  | 8.4  | 12.0     |
| 9-Hidd(Opp. the Cement Factory     | 13.3  | 14.3   | 11.2 | 0.0   | 17.6  | 11.0  | 7.7    | 46.4  | 21.8  | 12.0 | 13.6. | 22.6    | 6.0  | 11.3     |
| 10-Arad                            | 2.0   | 2.1    | 16.9 | 6.8   | 11.9  | 17.6  | 12.8   | 37.3  | 21.8  | 20.1 | 21.0  | 17.6 1  | 5.7  | 9.7      |
| 11-South the Muharreq Cause-way    | 0.0   | 4.0    | 7.6  | 2.0   | 18.3  | 13.5  | 12.0   | 15.9  | 36.5  | 12.0 | 29.2  | 21.7    | 4.4  | 10.9     |
| 12-Mina Sulman main jetty          | 7.6   | 28.3   | 34.0 | 2.0   | 18.4  | 23.3  | 24.1   | 43.1  | I     | 74.4 | 28.3  | 20.92   | 7.7  | 19.2     |
| 13-Nabeeh Saleh                    | 7.6   | 38.1   | 53.0 | 57.1  | 63.1  | 24.9  | 28.3   | 51.3  | 36.5  | 30.0 | 27.5  | 53.83   | 9.3  | 16.5     |
| 14-Ras Tubli (opp.Sewage Treatment | 220.4 | 2295.0 | 67.8 | 600.0 | 328.3 | 215.1 | 2230.0 | 328.6 | 38.1  | 36.5 | 67.7  | 1577.86 | 67.1 | 856.6    |
| 15-Sitra (Opposite Al-Ikr)         | 2.0   | 19.2   | 11.0 | 0.0   | 11.8  | 57.1  | 10.2   | 12.7  | 31.6  | 20.1 | 34.0  | 35.72   | 0.5  | 16.4     |
| 16-Sitra jetty(Bander Al-Dar)      | 24.0  | 6.3    | 47.9 | 2.0   | 7.1   | 12.6  | 8.5    | 26.6  | 21.8  | 18.4 | 12.6  | 16.8 1  | 7.1  | 12.3     |
| 17-Asker                           | 67.8  | 298.4  | 20.1 | 6.0   | 9.4   | 20.1  | 0.44   | 59.8  | 210.0 | 30.0 | 120.1 | 85.98   | 0.5  | 0.06     |
| MEAN                               | 23.2  | 170.8  | 24.3 | 41.5  | 32.5  | 32.0  | 145.7  | 53.5  | 35.0  | 29.8 | 35.0  | 117.5   |      |          |
| STANDARD DEVIATION                 | 53.2  | 551.8  | 18.2 | 144.6 | 77.4  | 48.5  | 537.2  | 72.4  | 47.5  | 21.5 | 25.1  | 376.8   |      |          |

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this part of Bahrain, and the consequent discharges of waste material. Within the east the areas most affected are Ras Tubli and Asker which are close to sewage discharges. Notice that there are no stations at BAPCO area in this study. If the stations in the vicinity of BAPCO which were shown in chapter 3 are compared with this study, one can conclude that BAPCO area is worse than both Ras Tubli and Asker.

The concentration of material liable to cause deterioration show a fluctuation throughout the year with no consistent annual pattern shown at all stations. The fluctuations observed appear to be related to variations in discharge of contaminants from sewage works... etc. The concentration of ammonia seemed to be inversely related to the concentration of nitrate reflecting the known chemical changes in nitrogen cycle in the sea. The results for the latter half of 1983 may show disturbance due to the long distance effect of the Iranian Noroz oil spill which occured in January 1983. About 200,000 tonnes of crude oil was released in the Gulf as a result of an explosion in the Iranian Noroz oil field. The spill continued for several months. Large quantities of the spilled oil reached Bahrain coast and the first material from this disaster reached Bahrain later in 1983. The oil spillage from this incidence continued throughout 1983.

UNESCO/WHO, 1978 report that petroleum and its derivations are a complex and varied mixture of substances composed of various hydrocarbons, numerous oxygen containing compounds, nitrogen, sulphur, as well as high molecularweight unsaturated heterocyclic compounds whose structure have not accurately been established and which are divided into neutral resins, asphalt acids, and asphaltenes. Hence, nitrogen compounds which are present in the oil could have caused elevations in these parameters in late 1983 samples.

The results of the present study could be used to study the relationships between the various measured parameters, and the presence and absence of different fish species in certain areas and in various seasons. For example, the diversity of fish in Bahrain has been shown to be seasonly variable with a greater diversity in September to December (Abdul-Qader, 1986).

Fish landing in the adjacent state of U.A.E. was studied by Ali and Cherian (1983) in relation to water temperature. A temperature oriented landing was observed in some of the common species. Queen fish, snapper and scad recorded the maximum percentage of landing (>70%) during May to October (warm water period) whereas major percentage (>70%) of landings of sardines, mackerel and king fish was during low temperature period(December - March). A more elaborate study is required to draw authentic conclusions regarding the relationships between the catch composition and prevailing water temperature of the region.

The abundance of shrimps appears to be related to salinity with more juveniles shrimps found in low salinty areas. CHAPTER 3

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# IMPACT OF THE REFINERY ON THE MARINE ENVIRONMENT

#### 3.1 Introduction:

The wide spread use of petroleum and petroleum products has inevitably resulted in the discharge of oil to the environment. With respect to the aquatic systems, it is the marine environment that has received the greatest attention, since the majority of the more noteworthy oil spills have involved accidents at sea.

In many cases, pollutants are much more dangerous not only because they poison fish and other marine life but because, by entering the food cycle, they can ultimately threaten human life as well.

It has been estimated by the National Academy of Science of the United States that in 1980 as much as 3.54 million tons of oil entered the oceans of the world. More than 2 million tons of this, it was estimated, got into the sea as a result of land-based activities. These included the waste products of industry: municipal and urban runoff; natural seeps and atmospheric rain-out.

The Remaining 1.5 million tons was estimated to be the result of the transport of oil by sea (IMO, 1983).

Crude oil is an extremely complex mixture of hydrocarbons. Although compounds made up of hydrogen and carbon predominate, small traces of sulphur, nitrogen and oxygen also are present. Every separate accumulation of oil is a unique mixture not matched exactly in composition or properties by any other place of origin. A very wide range of analytical techniques has been, and is being, applied to elucidate the chemical composition of petroleum. Because of this complex chemical composition, crude oils, and indeed petroleum products, are characterised by empirical parameters such as boiling range. specific gravity and viscosity, or more specific properties related to application, e.g. anti-knock properties for motor gasoline and pour point for fuel oils.

The bulk of compounds present in petroleum comprises hydrogen and carbon. These hydrocarbons can be divided into three main chemical groups: paraffins (alkanes), naphtenes (cycloalkanes), and aromatics, and they range from simple, highly volatile substances to complex waxy and asphaltic compounds which cannot be distilled. In addition to these pure hydrocarbons, crude oils also contain a few percent by weight of sulphur organically combined and nitrogen, oxygen, vanadium and nickel containing compounds at the parts per million (ppm) level. Many other elements may be present at the parts per billion level (ppb).

The gross composition of the Kuwait crude oil, as determined by silica-gel fractionation, was 39% paraffinic, 40% aromatic, 6% asphaltic with an overall recovery of 85% (Della Venezia and Fossato, 1977). There is general agreement that the toxicity of crude oil increases along the hydrocarbon series: from paraffins to naphthenes and olefins, to aromatics. Ryan (1977) observed that within each series of hydrocarbons, the smaller molecules are more toxic than the larger. Even though many of the toxic compounds are removed during the refining process by treatment with sulphuric acid, in many cases the final product is still toxic.

A refinery is a rather complex plant where different crude oils are processed by different treatments to produce different refined products. As a consequence of this activity waste effluents are produced and collected in one or different streams. These effluents are treated by different processes including decantation, biological treatments, flotation, flocculation, and then are discharged into the environment.

The total effluent from a petroleum refinery has several origins , i.e. streams from desalting facilities, striping of undesirable chemicals, cooling units, etc. Furthermore, ballast water from tankers often make a considerable contribution to the total amount of waste water to be treated. The chemical composition of these streams may vary considerably depending on both the fracturing processes and chemical additions used and also on the characteristics of the crude oil stock (Cadron and Klein, 1977; Snider and Manning, 1982).

However, besides having different effluent streams, refineries also use different treatments. In a recent Concawe study of 105 refineries (DeRoocker <u>et al</u>, 1984) it was shown that 30% had only gravity separation (primary treatment), whereas 18% had both primary and secondary treatment. 52% of the investigated refineries in 1984 had three treatment steps, i.e. also some form of final biological treatment, in comparison with only 23% in 1969. Furthermore, recirculation of process streams is getting increasingly common thus decreasing the total amount of aqueous effluent.

Because of the improved treatment, this recirculation has not necessarily lead to an accumulation of hydrocarbons in the effluent. Instead, the total amount of oil discharged from Western European oil refineries decreased

In spite of the oil recovery techniques applied in the refineries, the effluent may contain a large number of hydrocarbon (alkanes, cycloalkanes, aromatics and polycyclic aromatics) in the final discharge in addition to residues of other chemicals used in the processing of that oil (i.e., caustic liquor and spent hydrochloric acid). The refinery effluents also contain phenols, ammonia, sulphides, cyanide, some heavy metals and suspended solids . The concentrations of these pollutants are very variable and few comparative data are available (Jenkins et al, 1979). The waste-water containing all these pollutants when released to the sea brings about both localized and wide destruction of the marine biota and disruption of the ecology through the release of harmful pollutants. The petroleum hydrocarbons, metals and other elements get adsorbed to bottom deposits. The biodegradability of some of these is dependent on several factors. It is generally considered that nearly all organic substances derived from biosynthesis (i.e. crude oil) can be degraded by micro-organisms. In addition, chemicals may be removed from the aqueous environment by photochemical reactions, etc. The rate at which a particular chemical is biodegraded depends not only upon its chemical structure but also upon physical conditions, such as pH, temperature, oxygen availability and salinity; the availability of sources of energy and nutrients and the presence of suitable organisms (Jenkins et al, 1979).

discharged by 1983 (Lehtinen, 1986).

In most cases, such polluted areas become unfit for fisheries use and the fishes collected here may have oiltaints. Incessant sinking of residual hydrocarbons and emulsifying agents used in the refining processes cause localized eutrophication.

Older (pre-1960) refineries were not usually designed with water economy/treatment in minds. They use water cooling rather than air cooling, and polluted and clean water streams are often intermixed in a combined sewer system. This results in higher waste water flows and most often in higher pollutant loads per ton of crude oil handled than in modern refineries (Baker, 1979).

In Bahrain, such a situation exists in Salba Bay on the western side of Sitra island where the Bahrain Petroleum Company's (BAPCO) refinery is located and also at the nearby Sitra oil terminal. The BAPCO refinery is the oldest in the Gulf, and is the major source of pollution in Bahraini waters. The present study was conducted at those two localities with the objective of assessing the impact of the discharge on the local marine environment with special reference to the commercial fish species occurring there.

The ecological approach represents the most direct method of monitoring the impact of refinery effluents on the environment. It makes use of the environment itself or parts of it in the monitoring process. It requires that one is able to describe the ecosystem involved so precisely that changes caused by refinery effluents can be separated from the natural background variations in the system.

Although there is a vast literature on effects of petroleum hydrocarbons on marine organisms, the understanding of the impact of the complex effluents from refineries is poor (Mattsson and Notini, 1981). Comparatively little information is available on sublittoral ecological effects of refinery effluents, and the effluent quality data are very far from complete (Baker, 1979).

This chapter contains three studies. The first dealing with water quality at different stages of BAPCO effluent treatment during 1983 to compare it with the quality of water at different locations in Bahrain coast which was conducted during 1983 and given in chapter 2.

The second study aimed at studying water quality at different stages of BAPCO effluent treatment during 1984 to compare it with the study of the quality of water at an area adjacent to the refinery outfalls which was conducted during 1984.

The third study dealing with water quality at an area adjacent to the refinery and oil storage tanks outfalls.

# 3.2 <u>Effects of the Refinery Effluent Constituents on the</u> Marine Environment:

### 3.2.1 Temperature:

Water temperature is one of the most important characteristics of marine environments. Temperature and temperature changes affect metabolism and other processes in marine plants and animals (Hebert et al, 1977).

Tropical fish often live at environemtnal temperatures closer to their upper thermal limits than fish living in temperate waters, an important factor when assessing the significance of thermal pollution in the tropics. Temperature modifies the impact of pollutants. Many are more toxic in warmer waters and since they are also more soluble at higher temperatures may also reach higher concentrations.

The lowest and highest temperatures at which a fish may survive depend upon its previous acclimatization. Therefore, sudden changes of temperature are normally much more dangerous to fish than slower changes during which they have time to become acclimatized.

There is evidence that weight loss, lowered reproductive success, higher disease rates and increased mortality can result from prolonged exposure to temperatures only slightly higher than ambient. Increased temperature can lead to oxygen depletion in the water. They can also cause excessive growth of deleterious organisms such as filamentous algae and dinoflagellates.

Mass mortalities can be caused by a change of as little as 5°C in less than a few days. The toxicity of pollutants such as cyanide, heavy metals, detergents and insecticides have been shown to increase with increasing temperature (Desylva, 1969). The common theme that is apparent from almost every heavy metal reviewed by McLusky (1986) is that toxicity increases as salinity decreases, and that toxicity increases as temperature increases.

In view of the requirements for the well-being and production of marine organisms, it is maintained that the discharge of any heated waste into any coastal or estuarine waters should be closely managed. Monthly means of the maximum daily temperatures recorded at the site in question and before the addition of heat of artificial origin should not be raised by more that  $2^{\circ}C$  during autumn, winter and spring, nor by more than  $1^{\circ}C$  during the summer. The imposed rate of temperature change should not exceed  $0.5^{\circ}C/h$  above ambient (Perkins, 1976).

# 3.2.2 Salinity:

The variations of salinity affect the osmotic regulation of fish , determine the buoyancy of the pelagic eggs, and very often indicate the change in water masses or in their stability conditions. Freshwater is clearly a pollutant when introduced into marine environment. Exposure to freshwater for 30 minutes kill most species (Edmondson, 1982). Calcification in corals decreases with decreasing salinity (Yamazato, 1970).

For the protection of estuarine organisms, no changes in channels, in the basin geometry of the area, or in freshwater inflow should be made that would cause permanent changes in isohaline patterns of more than  $\pm$  10% of the natural variation (Perkins, 1976). Salinity affects the toxicity of most metals. In general, for estuarine animals heavy metal toxicity increases as salinity decreases and as temperature increases (McLusky, 1986).

# 3.2.3 <u>Hydrogen ion cencentration (pH)</u>:

pH may influence seawater chemistry in several important ways, notably the carbonic acid equilibrium, chemical form of metals, and the characteristics of dissolved substances. In principle, these are important in relation to both toxicity and bioaccumulation. The acid and alkaline death points on warm water pond fish are approximately pH 4 and pH 11 (Swingle, 1961). Reproduction diminishes at pH values below 6.5 (Mount, 1973).

Materials that extend normal ranges of pH at any location by more than  $\pm$  0.1 pH unit should not be introduced into saltwater portions of tidal tributaries or coastal waters. At no time should the introduction of foreign materials cause the pH in a saltwater regime to be less than 6.7 or greater than 8.5 (Perkins, 1976).

## 3.2.4 Dissolved oxygen:

The oxygen content of water depends on a number of physical, chemical, biological, and microbiological processes. The water which is in contact with air contains a quantity of oxygen depending on, or according to, atmospheric pressure (the partial oxygen pressure), the temperature, and the content of dissolved salts. Deviations in the concentration of oxygen from the equilibrium may be caused by:

sharp changes in barometric pressure, the temperature of water, or the aeration of water in various hydrotechnical structures; physicochemical and chemical processes, such as the use of oxygen for chemical oxidation of the substances or absorption of oxygen during the corrosion of metals; and biochemical processes, such as the aerobic biochemical oxidation of organic substances, the breathing of aquatic organisms, or the production of oxygen during the process of photosynthesis (UNESCO/WHO, 1978). The content of oxygen is an important indicator of the pollution of a water body, indicating its biological state, the predominant processes in it, the destruction of organic substances, and the intensity of selfpurification. The study of the oxygen content plays quite an important role, when evaluating the conditions of the habitation of the flora and fauna in a body of water.

Oxygen is readily soluble in water. Its solubility rate varies inversely with water temperature and directly with atmospheric pressure. At normal atmospheric pressures, solubility rates of oxygen in water range from 14.5 mg/l at  $0^{\circ}$ C to 7.8 mg/l at  $30^{\circ}$ C. Dissolved oxygen concentrations may be expressed in milligrammes per litre (mg/l) or as a percentage of saturation.

The main source of oxygen in water is from the atmosphere. Oxygen is dissolved into the upper layer of the water body through the air-water interface and is dispersed throughout the water body by wind and wave action, vertical mixing and other forms of agitation. Another important source of oxygen is from the well Known photosynthetic process in water may be summarized by the equation:

$$6 \text{ CO}_2 + 6 \text{ H}_2 \text{O} \xrightarrow{\text{Light}} \text{C}_6 \text{H}_{12} \text{O}_6 + 6 \text{ O}_2$$

Carbon dioxide and water react chemically in the presence of light (solar energy) to produce sugar and oxygen. This oxygen becomes dissolved in the water body and enters the organic cycle of the water. Often, when water is in a stagnant condition, photosynthesis is the main source of oxygen. Photosynthesis is also an important source of oxygen in tropical waters which have long periods of intense sunlight and infrequent turnovers (Lane, 1974).

Sensitivity of fish to low concentrations of dissolved oxygen (DO) differs between species, between the various life stages (eggs, larvae, and adults), and between the different life processes (feeding, growth, and reproduction, which in turn may depend on swimming ability, and specialized behaviour which may also be influenced by DO).

Providing other environmental factors (including the absence of poisons) are favourable, a minimum constant value of 5 mg/l would be satisfactory for most stages and activities in the life cycle in that some processes, such as juvenile growth, fecundity, hatch of eggs, larval morphology and survival, upstream movement of migratory salmon, and schooling behaviour of some species, including shad, are not particularly susceptible to levels of DO above 5 mg/l.

Fluctuations about 5 mg/l of DO or any reduction below 5 mg/l could have a greater effect on some processes than on other. Fluctuations in DO on juvenile growth is greater than that on growth of larvae, but clearly fecundity, hatch of eggs, and larval morphology and survival, as well as the upstream movement of migratory salmon and schooling behaviour of some species, including shad, would also be adversely affected by levels below 5 mg/l that would not necessarily affect either the survival of individuals of the upstream migration of shad. This is consistent with the mere presence of fish observed in polluted rivers and estuaries where the DO is well below saturation and exhibits a wide variation within a year (Alabaster and Lloyd, 1982).

Probably the most important measure of water quality is the dissolved oxygen. Oxygen, although poorly soluble in water, is fundamental to aquatic life. Without free dissolved oxygen, streams and lakes become uninhabitable to most desirable aquatic life. Yet, the maximum oxygen that

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can possibly be dissolved in water at normal temperatures (e.g.  $10^{\circ}$ C in U.K.) is about 9 mg/l, and this saturation value decreases rapidly with increasing water temperature (Vesilind and Peirce, 1981). This is especially important in the Gulf which is characterized by high temperature.

For the protection of marine resources, it is essential that  $0_2$  concentrations be sufficient for survival, growth, vigour, reproduction and production of suitable crop. To attain this objective, it is recommended that surface dissolved  $0_2$  concentrations in coastal waters should not be less than 5.0 mg dm<sup>-3</sup>(ppm), except when natural phenomena cause this value to be depressed (Perkins, 1976).

# 3.2.5 Biochemical oxygen demand:

The amount of oxygen dissolved in the water necessary for the aerobic biochemical oxidation of organic substances present in water during a certain period of time is called the biochemical oxygen demand (BOD).

Perhaps even more important than the determination of dissolved oxygen is the measurement of the rate at which this oxygen is used. A very low rate of use would indicate clean water. The rate of oxygen use is commonly referred to as biochemical oxygen demand (BOD) (Vesilind and Peirce , 1981).

The BOD is useful in water pollution investigations because the amount of oxygen required to stabilize an effluent may be calculated from the BOD and the volume of the effluent (Boyd, 1982).

#### 3.2.6 Ammonia:

Free ammonia  $(NH_3)$  and undissociated ammonium hydroxide  $(NH_4OH)$  are relatively toxic: the dissociated ammonium ion  $NH_4^+$  has relatively low toxicity. High temperatures lead to greater proportions of un-ionised ammonia, and therefore an increase of toxicity (Cairns <u>et al</u>, 1975). Most available toxicity information is for freshwater organisms; however, because of the slightly higher alkalinity of seawater and the resulting relatively large proportion of un-ionised ammonium hydroxide, ammonia may be more toxic in seawater than in fresh water (Doudoroff and Katz, 1961). Ellis (1937) found that the toxic action of an ammonium salt increase by 200% when the pH was raised from 7.4 to 8.0.

Ammonia is formed in the water as a product of fish metabolism and decomposition of organic matter by bacteria. As ammonia concentration increases in the water, ammonia excretion by fish diminishes and levels of ammonia in the blood and other tissues increases. The result is an elevation in blood pH. Ammonia increases oxygen consumption by tissues, damages gills, and reduces the ability of blood to transport oxygen. The tolerance of fish to ammonia varies with species, physiological and environmental conditions. Most clean water fish, aquatic invertebrates and microorganisms cannot tolerate over 0.1 mg/l ammonia (Environmental Protection Technical Secretariat (EPTS), Personal Communication).

The European Inland Fisheries Advisory Commission (EIFAC, 1973), stated that toxic levels of  $NH_3$  for short-term exposure usually lie between 0.6 and 2.0 mg/l. Un-ionized ammonia is more toxic when dissolved oxygen concentration is low (Merken and Downing, 1957).

A number of workers demonstrated that sublethal concentrations of  $NH_3$  cause pathological changes in fish organs and tissues (Smith and Piper, 1975). Poor growth of fish in culture tanks has also been attributed to accumulation of  $NH_3$  (Smith and Piper, 1975). It was reported that 0.12 mg/l  $NH_3$  caused reduced growth and caused gill damage in channel catfish (Robinette, 1976).

The lowest lethal (96 hr LC50) concentration of unionised ammonia reviewed by Côté (1976) is 0.2 ppm for young fish (<u>Salmo gairdnerii</u>). Other literature has been difficult to assess because the relative proportions of ionised and un-ionised ammonia in seawater were not accurately known.

The environmental protection agency (EPA, 1976) water quality criterion is 0.02 mg/l of unionized ammonia for fresh water, no criterion is given for sea water.

### 3.2.7 Nitrite:

Nitrite ions occur generally in sea water as intermediates in the oxidation of ammonium ions to nitrate ions (nitrification). In oxygen-depleted environments they may occur as a stage in nitrate reduction (denitrification). In most sea waters the concentration is very low. High concentration can occur in coastal waters receiving sewage or industrial wastes.

It was reported that the 96 hour LC50 at  $21^{\circ}$ C nitritenitrogen (NO<sub>2</sub>-N) to channel catfish was 4.6 mg/l (Konikoff, 1975). More recent evidence indicates that nitrite may be a significant limiting factor in channel catfish production ponds. During the fall of 1978 a number of fish kills were reported in Mississipi and Alabama in which fish mortality could not be attributed to low dissolved oxygen, parasites, diseases or other common causes. All dead or dying fish had "ohocolate" colored blood which indicated that hemoglobin had been converted to methemoglobin.

Nitrite poisoning results in methemoglobin formation, so nitrite toxicity was suspected as the cause of the fish kills. Further investigations of nitrite toxicity to warmwater pond fish, and especially channel catfish, appear warranted. Nitrite concentrations as low as 0.5 mg/l were toxic to certain cold water species (Crawford and Allen, 1977).

#### 3.2.8 Nitrate and phosphate:

One result of pollutional enrichment of waters by the ions NO<sub>3</sub>, PO<sub>L</sub><sup>3-</sup> and other plant nutrients is eutrophication.</sub>It has been reported that with enrichment of water the whitefish Coregonus wartmanni, grows faster so that at any given size the gonads and the eggs are smaller. Therefore, the existing fishery removes the immatures and prevents adequate spawning. Also, the mortality of the embryos was greater (50 percent) than before (20 percent). In addition, eutrophication has caused the migration of perch from shore into the pelagial (Nümann, 1964). It seems probable that phosphorus is the main cause of such eutrophication in freshwater, since even in the absence of combined inorganic nitrogen, nitrogen-fixing algae will continue to flourish, provided that sufficient phosphate is available. But in sea N not P is important for eutrophication.

### 3.2.9 Phenols:

In hydrochemistry, the term phenols is usually restricted to the simplest hydroxy derivatives of benzene, whose hydrogen atoms have been substituted by one to three hydroxyl and a few simple alkyl and alkoxy groups. However, even with such restrictions, the composition of phenols present in water is so complex and varied that the accuracy and reliability of their determination by any known methods is quite low. The properties of phenols and their influence on organisms also differ considerably. All this hinders the control and the evaluation of the quality of phenols-containing waters.

When the phenols concentration is several milligrammes or more per litre, the phenols may exert an osmotic pressure effect on the aquatic organisms and become dangerous for warm-blooded animals and man.

Under natural conditions, phenols are formed during metabolic processes of aquatic organisms, particularly during the biochemical breakdown and transformation of organic substances from dead algae. Phenols may also enter the water during the decomposition of some species of higher plants. For instance, phenols are often detected in waters in contact with fallen leaves of some species of trees, such as oak, or in the overgrowth of reeds. It is known that some of these phenols also form compounds which impart the chlorophenol during chlorination, However, in unpolluted surface water the content of phenols is, as a rule, small. In ground water, particularly in the oil-bearing areas, the concentration of phenols is often increased (a fact which is used as one of the indices during the prospecting for oil). The increase in the concentration of phenols in surface water is usually connected with the pollution of the bodies of water by drainage waters from coal, chemical, and oil-producing industries.

A considerable, often predominant part of phenols in water comprises volatile phenols (carbolic acid, cresols, xylenols, thymol, quaiacol, etc.) They may be separated from the remaining phenols and many other substances contained in the water by means of steam distillation.

At moderate and low concentrations, phenols are biochemically unstable, hence conducting the determination soon after the sample is taken is recommended.

Phenolic wastes can contain monohydric phenols, including phenol, the three cresol isomers, and the six xylenol isomers, together with other substances. They may adversely affect fisheries by their direct toxicity to fish and fishfood organisms, by their high oxygen demand resulting in oxygen depletion of the receiving water, and by the production of undesirable flavours in the edible flesh of fish.

Laboratory tests show that the toxicity of phenol is increased by decrease in dissolved-oxygen concentration, increase in salinity, and decrease in temperature. Salmonids and newly hatched fish are more sensitive than coarse fish and adults respectively. Cresols, xylenols, and phenols are of similar toxicity, and the toxicity of mixtures of phenols is apparently additive, although the toxicity of phenolic wastes may be greater than expected from chemical analyses, since these may not be equally sensitive to all phenols and may neglect the contribution from other poisons (Alabaster and Lloyd, 1982).

In oil refineries, phenolic compounds are produced through thermal and catalytic cracking of crude oil. According to Portmann (1975), the toxicity of phenol to aquatic life has been variously reported within the range 1-100 mg/l, depending on species, temperature and salinity.

In acute poisoning phenol acts as a nerve poison (Havelka and Effenberger, 1957) causing death by paralysis. In subacute poisoning a general intoxication of fish occurs followed by inflammatory and necrotic changes of vital organs, gill, circulatory system, brain, liver, kidney, spleen and gonads (Mitrovic <u>et al</u>, 1968). As early as 1935, it was concluded from the results of a field study that fish would not inhabit parts of the river with phenol content more than 0.2 mg/l (Kalabina, 1935). At concentration range as low as 0.05 - 0.06 mg/l, chlorophenols give fish an unpleasant taste after an exposure time of a few days and render them unfit for human consumption (Schulze, 1961).

Phenolic substances produce undesirable tainting in fish flesh at concentrations well below the lethal level and this aspect of pollution should be investigated where commercially important species are at risk.

The U.S. Environmental Protection Agency (EPA, 1976) water quality criterion is  $1 \mu g/l$  phenol for domestic
water supplies and to protect against fish tainting. No criterion is given for sea water.

With controls imposed on discharges of phenol at about 0.5 mg/l, the risk of acute toxic action on marine life is not very great (Portmann, 1975).

# 3.2.10 Sulphur compounds:

Hydrogen sulphide is caused by reducing processes which may develop in subsurface water and in benthic layers of bodies of water where the water masses are mixing slowly under oxygen deficient conditions. Such processes often occur when bacteria decompose rapidly and when the biochemical oxidation of organic substances is intensive. In lakes and other waters characterized by high biological activity, such processes occur most frequently during summer (when phytoplankton die off in great numbers), during the winter (after the ice is formed) when water is isolated from the atmospheric oxygen, and also during a weak wind mixing. Hydrogen sulphide is also formed when organic substances introduced into the water with waste waters (household sewage, food industry, metallurgy, chemical and paper industries wastes) become decomposed. Some sewage waters contain considerable amounts of hydrogen sulphide and other sulphides. Hence, its presence in surface water and the water close to the surface may indicate the presence of pollution by sewage.

Hydrogen sulphide is toxic and considerably deteriorates the organoleptic properties of water. Water bodies used for sanitary and hygienic purposes and fisheries should be rigidly regulated for hydrogen sulphide content.

Hydrogen sulpide is present in water in the form of undissociated molecules of  $H_2S$ , ions of  $HS^-$ , and

occasionally  $S^{2-}$ . The correlations between the concentrations of these forms are determined by the pH value of the water. When pH is below 10 the  $S^{2-}$  sulphide content may be disregarded. The remaining forms of hydrogen sulphide are present in the correlations as indicated in Table 3.1.

TABLE 3.1: Correlations of the forms of hydrogen sulphide at various pH values of water(From UNESCO/WHO,1978).

| Forms of<br>hydrogen<br>sulphide | % hydrogen sulphide at pH |      |      |      |      |      |       |  |
|----------------------------------|---------------------------|------|------|------|------|------|-------|--|
|                                  | 4                         | 5    | 6    | 7    | 8    | 9    | 10    |  |
| H <sub>2</sub> S                 | 99.8                      | 98.8 | 78.3 | 43.9 | 7.3  | 0.8  | 0.09  |  |
| HS                               | 0.2                       | 1.2  | 21.7 | 56.1 | 92.7 | 92.2 | 99.01 |  |

The stability of the various forms of sulphide depends also on the value of the oxidizing-reducing potential(UNESCO/WHO, 1978).

According to Côtè (1976). The toxic effect of sulphides is influenced by pH. In cases of low pH effluent, the sulphide may become undissociated hydrogen sulphide and the toxicity increases. The principal effect of hydrogen sulphide at low concentrations is believed to be inhibition of the iron-containing oxidative enzymes (Smith and Gosselin , 1966).

Under anaerobic conditions, certain heterotrophic bacteria can use sulphate and other oxidized sulphur compounds as terminal electron acceptors in metabolism and excrete sulphide.

Un-ionized hydrogen sulphide is toxic to fish, but the ions resulting from its dissociation are not appreciably toxic. The proportion of un-ionized hydrogen sulphide decreases with increasing pH (Boyd, 1982).

Like hydrocyanic acid, hydrogen sulphide, is a respiratory poison, which causes blocking of the corresponding enzymes (Huber, 1979).

Caldwell (1975) examined six species of marine invertebrates for their tolerance to dissolved hydrogen sulphide in seawater. In tests lasting up to four days, the hydrogen sulphide tolerances of organisms ranged from 0.2 mg/l to 6.0 mg/l. Petpiroon (1976) tested the effects of sodium sulphide/seawater solutions containing 15,10,5,2.5,1 and 0.5 ppm of S on the activity of winkles (Littorina saxatilis) using 2 hr static tests, and found that with 15 and 10 ppm activity was lower than the controls.

Hydrogen sulphide is given off when organic matter decomposes in estuarine sediments. If oxygen is deficient, iron salts are converted to ferrous sulphide, which colours the sediment black. If the amount of hydrogen sulphide is in excess of the amount of iron available, then free hydrogen sulphide permeates the interstitial water and may extend into the water above (Baker, 1979).

Egg survival and fry development in northern pike (Esox lucius) were limited by 0.006 mg/l of  $H_2S$  (Adelman and Smith, 1979). It was reported that the 96-h LC50 for adult bluegill at 20°C was 0.045 mg/l (Adelman and Smith, 1979).

Bioassays of bluegill and certain other species (Smith et al, 1976) suggest that any detectable concentration of hydrogen sulphide should be considered deterimental to fish production. The maximum acceptable level of undissociated hydrogen sulphide is 0.002 mg/litre. The toxicity of many heavy metals decreases as the pH increases due to pH related effects including decreased solubility or increased complexing with other compounds or ions (Roberts, 1978).

The Environmental Protection Agency (EPA, 1976) water quality criterion is 2  $\mu$ g/l undissociated H<sub>2</sub>S for both fresh and sea water. This criterion is based mainly on tests with fresh water fish eggs and with young and adult fish.

#### 3.2.11 Suspended solids:

All natural waters contain a certain ammount of naturally occurring suspended solids. During spates and flooding suspended solids levels may rise considerably but fish usually survive these episodes reasonably well despite mechanical gill damage. Fish eggs, however, are very vulnerable to silt deposits which inhibit respiration through the chorial membrane and encourage microbial growth.

Sand and gravel extraction, mining, paper-and paintmaking, and surface disturbance from civil engineering can introduce large amounts of particulate matter whose effects on fish health may be observed many miles downstream from their source. As well as its effects on the gills, it also reduces the light penetration into water resulting in less energy in the food web leading to fish production (European Inland Fisheries Advisory Committee " EIFAC " 1965).

Suspended solids in lake waters are, for the most part, finely suspended particles of insoluble materials

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including sand, silts, clay, debris from vegetational growth, algae, chlorophyll and other buoyant type substances. These maerials originate from shore erosion through wind and wave action, tributary inputs, biologiocal activities, and from pollution sources. Suspended solids reduce the transparency of lake waters and inhibit the penetration of light thereby reducing the photosynthetic processes, and the production of oxygen. Photosynthesis is important source of oxygen in aquatic ecosystem and the quantity of suspended solids in aquatic ecosystem is an important factor in the organic cycle of aquatic ecosystem (UNESCO/WHO 1978).

Sufficiently high concentrations of suspended solids can kill fish directly, increase their susceptibility to disease, reduce their rate of growth, modify their rate of growth, modify their normal movements within fresh water, reduce the area suitable for spawning, and kill developing eggs. In addition, the quantity of natural food available to fish can be reduced. When a fishery is harmed by excessive quantities of finely divided solid matter, it is likely that many of these factors will be operating, although the relative importance of each one will probably not be the same in every case (Alabaster and Lloyd, 1982).

Since it is known that even minor deposits may reduce productivity and later the benthic environment, it is generally recommended that no materials containing settleable solids or substances that may precipitate out in quantities that adversely affect the biota should be introduced into estuarine or coastal waters (Perkins, 1976).

#### 3.2.12 Organic matter:

The content of organic carbon in water is one of the most important parameters of the quality of water, and is the most reliable characteristic of the total content of organic substances. The sum total of organic sustances, which is represented by the concentration of organic carbon above and below the sources of pollutions, may serve as quite a useful pollution index of a body of water. This value is used when establishing the pollution zone and the zone of influence of drainage waters. The primary effect of organic matter in an aquatic system is the change of colour, the decreased transparancy of the water and increased turbidity. The properties decrease the light penetration and therefore decrease the assimilation of the green plants. Some organic compounds may be directly poisonous, or toxic matter may be formed in the water. A large part of the organic matter discharged to water is, however, precipitated in the neighbourhood of the discharge point, especially when the discharge occurs into sea water with a high salinity. This can lead to local de-oxygenation problems (Fonselius, 1978).

# 3.2.13 <u>Oil</u>:

Petroleum products enter the natural water along with the drainage water of oil-producing, oil-processing, petroleum, and chemical industries, and in various marine operations as fuel by-products and cargo waste.

The main feature of petroleum products determining their behaviour is their low solubility in water and the considerable differences in the values of the specific gravity. Hence petroleum, which finds its way into the water, is subject to fractionation forming a surface film, an emulsion, and a solution. Furthermore it is absorbed by the bottom deposits. Usually only a small part of petroleum products is found dissolved; most of them are present in suspension, as a stable emulsion. Heavy hydrocarbons settle to the bottom, on the shore, and on the aqueous vegetation. Lighter fractions emerge to the surface and form a film.

The quantitative correlations between individual forms of petroleum vary. They depend on a number of factors which are connected both with the conditions of the inflow of the petroleum products into a body of water and with the specific character of the aqueous body.

Polynuclear aromatic hydrocarbons (PAH), some of which are known to be carcinogenic to man (e.g. 3.4, benzopyrene), occur in crude oils, and especially in refined oils. These compounds can be stored unchanged in the body fat of some marine organisms, especially in molluscan shellfish. Huber (1979) considers that only high molecular weight polynuclear aromatics (PNAs) containing more than three rings should be regarded as "relatively persistent". Localised inputs of oil from sewage and refineries are thought to contribute significantly to background levels of PAH. Consumption of contaminated tissues by man may be a serious health hazard, especially in heavily industrialised regions (UNEP, 1978). It is found that green algae, such as <u>Scenedesmus</u> <u>acutus</u>, accumulate to a much greater extent in an environment containing polycyclic hydrocarbons than in an uncontaminated environment (Payer and Soeder, 1975).

Reviews of current literature indicate that to sensitive marine species (larval fish and crustacea) the 96 h LC50 of oil hydrocarbons is equivalent to an oil-in-water concentration producing death or gross damage to larvae appears to be about 100ppb (0.1 ppm), while behavioural effects on adult organisms and zooplankton and stimulation of growth and photosynthesis in phytoplankton, may occur in the range 60-100 ppb. Thus, in setting an environmental quality objective it was specified that, outside a given area around a discharging platform the water concentrations of oil hydrocarbons should not exceed 50 ppb above background (Reed, 1984).

The sublethal effects of oil reduces the viability of salmon fry in nature which then become extremely vulnerable to predation by other fishes (Malins et al, 1980). The avoidance reflex is the most common response of fish to sublethal toxicant concentrations and this becames an important factor in evaluating the impact of pollution (Westlake et al, 1983). The flag fish Jordanella floridae when exposed to 28% of refinery effluent continuously developed hemorrhaged fins and spinal curvatures (Rowe et al, 1983). The most vital affliction was to gonads resulting into delayed and infrequent spawning with fewer eggs per spawn. In the case of rainbow trout, impaired growth even with concentration as low as 10% was noticed (Rowe et al, 1983)) The long-term toxic effects of oil pollution are known to find entry in the marine food chain. It was found

that once hydrocarbons get incorporated in the body systems of an organism, it remains stable and enters the successive links of the food chain without alteration (Blumer and Thomas, 1965; Blumer, 1976).

Marine larvae are intolerant of concentrations as low as 100  $\mu$ g/l of polynuclear aromatic hydrocarbons, and sublethal effects, on feeding behaviour for example, are felt at concentrations as low as 10-100 $\mu$ g/l (EPA, 1976).

In the organism, oil may be stored, metabolised, or excreted. Lipid storage of hydrocarbons occurs in many marine organisms, leading to cocentration factors of 2000-3000 in oysters after 49 days of exposure to a fuel oil. Even after being returned to "clean" water, the concentration factor remained 3000 after four weeks (CEC, 1976).

It has been alleged that oil discharges have induced carcinomas in marine products (IMCO <u>et al</u>, 1977). No amount of carcinogen can be regarded "as safe", although the dose which will induce cancer in practice varies enormously with the way in which it is taken and the physical condition of the recipient (Nelson - Smith, 1972). Changes in taste and odour in fish, as a consequence of bioaccumulative processes, are regarded as one of the most important effects of the discharge of waste-water from refineries and petrochemical plants without biological purification, or when there are oil spills (Huber <u>et al</u>, 1979).

Mann (1965) demonstrated that food fish, such as eels, show definite impairment of flavour after being kept for eight days in oil-polluted water (5\_14 mg/l oil: 0.12-0.8 mg/l phenol).

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Tainting of commercial fish and shellfish is of serious economic concern in the mediterranean. Concentrations as low as 1\_10 µg/l of poly cyclic aromatic hydrocarbons have been reported to cause tainting in oyster (EPA, 1976). It is reported that a standard of 1 µg/kg Benzo-(a) pyrene (BaP) has been adopted by the Federal Republic of Germany for smoked foods (Stich, 1975).

Some badly dispersed primary-treated effluents in estuaries have produced easily observed localised effects such as death of salt-marsh vegetation, reduction of shore molluscs populations, increase in some species of algae, and visible oil residues in mud (Baker, 1979).

French regulations on refineries effluents is 5 ppm hydrocarbons (hexane extraction), 20 ppm hydrocarbons (infrared method) (CEC, 1976).

There is little information on the fate and effects of oil in refinery effluents. However, literature concerning the biological effects of oil spills is extensive, and though this cannot be used directly to make predictions about refinery effluents, relevant information can be gained on a variety of topics. Oil type is one of the many factors determining degree of products such as gasoline and No.2 fuel oil (diesel oil or light gasoil) appear to have relatively severe toxic effects (Baker, 1979).

UNESCO/WHO (1978) indicated that the maximum permissible concentration of petroleum products in water used for sanitary and hygienic purposes is 0.3 mg/l and in water used for fishing purposes it is 0.05 mg/l. The presence of petroleum products in a body of water in concentrations of 0.5 to 1 mg/l, imparts to the water an unpleasant odour and taste. With increased content of petroleum, the atmospheric gas exchange of the water becomes disrupted, the dissolved oxygen content decrease, the colour index and the normal life of the body of water becomes disrupted.

#### 3.2.14 Heavy metals:

Metals and metalloids, including copper, zinc, lead, aluminium, nickel, cadmium, strontium, vanadium, sulphur, mercury, and also asbestos, when present in waters above acceptable levels, may be toxic to the aquatic ecosystem or may accumulate in the food chain as part of the biogeochemical cycle in the ecosystem. The presence of these elements may be due to natural causes or may be due to industrial, municipal, agricultural, and mining wastes being discharged into the lake system. These substances may be the cause of serious ecological problems in many of the world's aquatic ecosystems.

Most metals are found in natural water in quite small micromolar concentrations and, in accordance with the classification accepted by hydrochemistry, are regarded as trace components. In natural conditions, they appear in water as a result of the interaction of the water with the minerals in it. Water draining from the soil may also become enriched in metal compounds. Numerous metals, especially polyvalent and transition metals are strong complex-formers; hence, they are present in the water mainly as complexes with organic or inorganic ligands. The properties of the most stable and predominant complexes determine, on the whole, the behaviour of the element in the water.

Most of the metals actively participate in biochemical processes. In accordance with the direction and the intensity of these processes, the concentration of the metals is subject to regular seasonal changes. For instance, during the periods of intense development of phytoplankton, metal compounds are used by these organisms until very low concentrations remain. This is followed by mass mortality of algae, whose accumulated metals then dissolve into the water, causing a renewed increase in metal content. Such processes are often superimposed on other processes; for instance, the consumption of the phytoplankton by other organisms, the sorption of the metals onto plant and rock surfaces, and the changes in the flow rate of the feeding bodies of water, such as the surface and subsurface waters containing metals.

A considerable increase in the concentration of metals serves as one of the important indices of the pollution of a body of water. Such an increase in the concentration of certain metals is usually observed in the areas where the water is discharged from mine pits, ore-enriching factories, the iron and steel industry, the industry of non-ferrous minerals, metalworking plants, and also some other industries.

Table 3.2 shows the frequency and concentration range of trace elements in refinery final effluents from nine refineries in the U.S.A. Heavy metal content in some European refinery effluents outside West Germany are given in Table 3.3.

# Table: 3.2

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Frequency and concentration of trace elements in refinery final effluents<sup>1</sup> (From CONCAWE, 1979).

|           | Frequency of           | Concentratio  | Number of     |                              |  |  |
|-----------|------------------------|---------------|---------------|------------------------------|--|--|
| Element   | Detection <sup>2</sup> | Minimum Value | Maximum Value | Reported Values <sup>3</sup> |  |  |
| Zinc      | 7                      | 10            | 190           | 12                           |  |  |
| Chromium  | 9                      | 11            | 1,100         | 20                           |  |  |
| Copper    | 6                      | 10            | 130           | 11                           |  |  |
| Lead      | 7                      | 2             | 30            | 10                           |  |  |
| Beryllium | 2                      | 0.2           | 2.1           | 4                            |  |  |
| Antimony  | 5                      | 5.3           | 190           | 9 n.d.                       |  |  |
| Thallium  | 2                      | 4.8           | 6.8           | 2                            |  |  |
| Nickel    | 6                      | 0.9           | 82            | 10                           |  |  |
| Arsenic   | 5                      | 2             | 70            | 8.831 7                      |  |  |
| Selenium  | 4                      | 9             | 74            | 8                            |  |  |
| Silver    | 3                      | 1.3           | 174           | 4                            |  |  |
| Cadmium   | 3                      | 1.1           | 16            | 5                            |  |  |
| Mercury   | 3                      | 0.1           | 0.8           | 3                            |  |  |

<sup>1</sup> Data from nine refineries in the U.S.A.

<sup>2</sup> Number of refineries where the element was detected by one or more of the reporting laboratories.

<sup>3</sup> Does not include duplicate determinations.

ppb = perts per billion (equivalent to micrograms/kg or 10"g)

# Table: 3.3

Heavy metal content in some European refinery effluents and outside W. Germany.

| Refinery | Mercury<br>ppb             | Cadmium<br>ppb                            | Lead<br>ppb                         | Chromium<br>ppb       |
|----------|----------------------------|---|-------------------------------------|-----------------------|
| quatic   | n.d.                       | Creak Con                                 | auto Loan                           | -                     |
| 2        | 0.2                        |   |                                     | -                     |
| 3        |                            |   |                                     | n.d.                  |
| 4        | (*)                        | 전학권 이 이 이 이 이 이 이 이 이 이 이 이 이 이 이 이 이 이 이 | for con                             | < 0.05                |
| 5        | < 10                       | range: 0.8-14.8<br>ave. 7.5               | range. 8.8-31                       | an Lem                |
| 6        |                            | range: 1-2<br>ave. 2                      | < 1                                 | ng/ <del>1</del>      |
| 7-024    | range: 1.4-2.1<br>ave. 1.8 | range: 0.2-1.2<br>ave. 0 6                | range 1-6<br>ave. 3                 | ug/14                 |
| 8        | n.d.                       | < 5                                       | < 20                                | -                     |
| 9        | -                          | 2-5                                       | 2-4                                 | -                     |
| 10       | che pangi                  | -   | ail samples < 100<br>ave. 20 (n=57) | rest <u>i</u> tt<br>a |
| 11. 03   | 107 0-1100                 | 2 800 <b>-</b> 2080                       | all samples < 20<br>(n=12)          | d in                  |

#### (Information from CONCAWE 1977)

n.d. = not detectable

(\*) effluents containing mercury are stored for special treatment

ave. = average

n = number of samples examined

Waste water treatment plants have, until now, been installed to improve the quality of the effluent water from refineries in terms of oil content, biological, oxygen demand, concentration of suspended solids, or acute toxicity. These treatments have at the same time reduced the concentration of cadmium and mercury down to prevailing levels in the natural environment, as shown in Table 3.4.

# Table 3.4

Concentrations of cadmium(Cd) and mercury (Hg) in treated refinery effluents and in unpolluted surface waters compared to toxic concentrations for common aquatic organisms (From CONCAWE, 1980).

| Metals | In treated<br>refinery effluents | In unpolluted<br>surface water | LC <sub>50</sub><br>24-96 h exposure<br>for common<br>aquatic organisms |
|--------|----------------------------------|--------------------------------|---|
| Cd     | 0.002-0.005 mg/l                 | 0.001 mg/1                     | 0.05-50 mg/1  |
| Hg     | 1/gµg 0.2-0.4                    | 1/gµg 0.10 µg                  | 100-5000 µg/1   |

 $LC_{50}$  stands for Medium Lethal Concentration which results in death of 50% of the sample of test organisms in a specified time, under defined conditions (expressed in mg/kg or litre).

The levels of these metals in treated refinery effluents are well below the toxic levels  $(24-96 \ h \ LC_{50})$  for common aquatic organisms which range from 0.05 to 50 mg/l for cadmium and from 0.1 to 5 mg/l for mercury as shown in Table 3.4. In addition, refinery effluents are generally rapidly diluted in receiving waters which still further reduces possible toxic effects . At increased concentrations, compounds of numerous metals suppress or inhibit the development of aquatic organisms and adversely affect warm-blooded animals including man. Hence, the metal content of water used for sanitary and hygienic purposes should be strongly limited.

Huber (1977) has pointed out that dissolved heavy metals do not exist in water in purely ionic form but as hydroxy, oxy, halogen or other complexes with strong pH dependence.

Toxicity is affected by temperature, though not consistently-according to Cairns <u>et al</u> (1975), mercury compounds are more acutely toxic to freshwater fish at high temperature accentuated the toxicity of mercuric chloride to fiddler crabs(Uca pugilator).

Marine organisms tend to accumulate heavy metals from the environment and are adapted to handle natural fluctuations in intake brought about by slight changes in their availability in water or food. In the sea the concentrations of most heavy metals are so low that they can easily be increased by local contamination to levels which organisms have never previously encountered (Bryan, 1976).

An idea of the relative toxicities of the rarer metals may be gained from the results of a study on their effects on the fathead minnow <u>Pimephales</u> promelas in hard fresh water (Tarzwell and Henderson, 1960). The following order was found for fresh water: Cu>Cd>Be>Sb>Ni>V>Pb>Ti>U>Zn>Mo (Bryan, 1976) and Hg>Cd>Cu>Zn>Cr>Ni>Pb>As for marine water (McLusky, 1986). Occupational hazards involving heavy metals are well known (Browning, 1969), but it is evident that much lower levels of metals in the diet may be implicated in human diseases (Warren et al, 1967). Studies about a relationship between the incidence of stomach cancer and the Zinc/Copper ratio in solids, have suggested that long exposure to an imbalance of heavy metals in the diet can eventually lead to disease (Stocks and Davies, 1963). It is generally true that concentrations of the more toxic metals such as mercury, cadmium, lead, arsenic and selenium are high in foodstuffs of marine origin (Bryan, 1976). The provisional tolerable weekly intake rates for mercury, cadmium and lead are so low that persons eating contaminated seafood regularly could easily exceed them. Persons at risk from metal contamination of marine origin are obviously those who eat large amounts of fish or shellfish from estuarine or coastal areas which are associated with industry.

Information on allowable levels of trace metals in fish is somewhat sparse, and varies depending on the country concerned. The status of the allowable level also varies from an administrative guideline to a legal requirement

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and in some countries the guidelines are presently under review.

Environmental Protection Agency water quality criteria for a number of heavy metals are given in Table 3.5.

#### 3.2.14.1 Mercury (Hg):

Mercury compounds are converted to methylmercury by the action of aerobic or unaerobic microorganisms which is believed to be highly toxic to human.

Mercury, is toxic at very low concentrations and bioaccummulate along food chain. Concentrations down to 4ppb of inorganic mercury in water are lethal to some fish, and 0.4 ppb has been reported to kill 50% of Daphnia in 64 hrs. Photosynthesis in marine diatoms has been reported to be inhibited by as little as 0.1 ppb of some organic mercury compounds (Evidence reviewed by Water Pollution Research Laboratory, 1971). Acute toxicity to fish has been found to occur at methyl mercury conentrations in the tissues of 20 µg/g (Jernelöv, 1975). Jernelöv points out that methyl mercury in fish is bound to protein and is not dissolved in the fat as are chlorinated hydrocarbons. Therefore, mercury content of fish is not very fatdependent but more related to trophic level, size and age of fish. The highest mercury content is found in large predators such as swordfish and tuna. Many of these fish have mercury contents above the permissible levels in North America  $(0.5\mu g/g)$ .

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# Table: 3.5

Water quality criteria for some heavy metals (extracted from EPA,1976).

| Chromium | 100 Jg/l in fresh water; it is suggested that<br>100 Jg/l is appropriate for sea water   |
|----------|--|
| Copper   | For fresh and sea water organisms:0.1 times<br>the 96 h<br>LC50as determined by non-aerated bio-assay<br>using a sensitive aquatic resident species.   |
| Iron     | 1.0 mg/l for fresh water. The effect on marine<br>life has not been investigated adequately but<br>fears have been expressed about precipitation<br>of dissolved iron and the settling of iron<br>flocs. |
| Lead     | 0.01 times the 96 h.LC50 for sensitive fresh<br>water resident species.There is insufficient<br>evidence for a sea water criterion .   |
| Mercury  | 0.05 AJg/l for fresh water; 0.10 AJg/l for sea water .   |
| Nickel   | 0.01 times the 96 h.LC50 for appropriate fresh and sea water organisms .   |

Consumption of contaminated fish containing methylmercury has been shown to correlate with the total blood mercury and also with the mercury content of erythrocytes (Parvaneh, 1977).

With a few exceptions, fish are the most significant source of methylmercury in the diet and Minamata disease, which has the symptoms of methylmercury poisoning, occurred in persons such as fishermen who had consumed large quantities of fish and shellfish containing 5-20 ppm (wet) of Hg (Tarzwell and Henderson, 1960). The symptoms of Minamata disease include mental disturbance, ataxia and impairment of gait, speech and hearing. In severe cases, patients eventually died and it was also found that children having the disease were born of mothers who were unaffected. It has been shown that newly born children contain appreciably more Hg than their mothers as a result of placental transfer (Tejning, 1968).

Fish containing as much as 7 ppm (wet) of methylmercury had been eaten by some people and cats fed exclusively on fish diet of this type were found to be suffering from methylmercury poisoning after 60-83 days (Alabanus et al, 1972). Concentrations of methylmercury which are insufficiently large to produce obvious symptoms, may have detrimental effects on brain capacity later in life (Löfroth, 1970). The F.A.O./W.H.O (1972) (Bryan, 1976) provisional weekly intake of Hg is 300 ug of which no more than 200 ug (~ 30 ug/day) should be methylmercury. Regarding the acceptable amount of mercury, a limit of 500 µg/kg (wet weight) is now acceptable for fish and sea foods (Parvaneh, 1977). The following guidelines and decrees (Huber et al, 1979) on the maximum allowable mercury content in fish and fish products have been established in different countries :

| USA and Canada               | : | max. | 0.5 | ppm |
|------------------------------|---|------|-----|-----|
| Italy                        | : | max. | 0.7 | ppm |
| Sweden and Finland           | : | max. | 1.0 | ppm |
| Ferderal Republic of Germany | : | max. | 1.0 | ppm |

Bacteria and higher aquatic plants are capable of accumulating heavy metals such as Hg and passing them on in the food chain (Patric and Loutit, 1976).

# 3.2.14.2 Cadmium(Cd):

Cadmium is widely used in industry and small quantities are discharged to surface fresh waters; natural background concentrations are usually below 1 µg/1 and higher levels have been found in polluted waters. A substantial proportion of the cadmium in a river water is adsorbed onto solids in suspension but only the soluble forms of cadmium are toxic to fish. The concentrations at which soluble cadmium is present in natural and polluted waters are close to the limits of measure and this causes difficulties in defining and interpreting field data. Little is known of the toxic action of cadmium to fish. The metal is accumulated predominantly in the gills, liver and kidney, but the significance of the levels found to the functioning of these organs is not clear, although there is some evidence that the osmoregulatory role of the gills and kidney may be impaired. Cadmium is slowly lost from the tissues when fish previously exposed to cadmium are returned to clean water, but loading can occur in a short period of time, causing death several days later (Alabaster and Lloyd, 1982) .

Acute and chronic toxicity tests with sensitive species of fish have given conflicting results which may have been caused by the variable and unusual concentrationresponse curve or errors in measuring concentrations of soluble cadmium. Concentrations lethal after at least 10 days exposure can be up to 100-fold less than those lethal in 2-4 days, and if a threshold lethal concentration exists, it is ill-defined. Several environmental factors influence the position and shape of the concentration-response curve. A decrease in water hardness and dissolved oxygen and possibly in pH value produces a lower LC50; changes in temperature and salinity may also affect cadmium toxicity (Alabaster and Lloyd, 1982).

The interspecific sensitivity of fish is more variable for cadmium than for other common pollutants but comparisons between data are difficult to make because of differences in water quality and exposure times. However, of the species tested, salmonids are more sensitive than cyprinids (with the possible exception of carp), with pike occupying an intermediate position . Juvenile stages appear to be more sensitive (Alabaster and Lloyd, 1982) .

Few sublethal effects of cadmium have been observed . Minnow have been shown to develop spinal deformities and in rainbow trout the development of ova can be impaired. Increased activity of male brook trout during spawning in low concentrations of cadmium had led to increased mortality .

Salmonid fish appear to be more sensitive than those other components of the aquatic biota which have been tested. Some species of invertebrates such as <u>Daphnia</u> <u>magna</u> and <u>Gammarus</u> fossarum appear to be as sensitive as salmonids, but most others are much more resistant. Some species of aquatic plants grow more slowly in concentrations of cadmium which are close to the limits for the survival of fish, but the majority of plants appear to be very resistant. Few data exist on the status of the fish fauna in surface waters polluted with cadmium, although there is some evidence that brown trout were absent from waters where the cadmium concentration was predicted to be harmful on the basis of laboratory experiments. Minnows were also found at concentrations predicted to be harmless to rainbow trout. However, rivers polluted with cadmium also contain other pollutants, especially heavy metals, and although some of these have been shown to be additive with cadmium in their joint toxic action, there is some evidence that zinc may have an antagonistic effect (Alabaster and Lloyd, 1982).

The concentration of cadmium in the muscle of fish exposed for long periods to low concentrations of cadmium in the water under either laboratory or field conditions is highly variable and can be 1-100 times higher (on a dry weight basis) and 0.1-100 times higher (on a wet weight basis) than that in the water, i.e., <1 mg Cd/kg muscle (dry weight) or < 0.1 mg Cd/kg muscle (wet weight) of fish from water containing 1  $\mu$ g Cd/1. The reasons for these wide differences are not all known nor fully understood.

Many years of systematic investigations on Bavarian surface waters (Wachs, 1977) have shown that the cadmium content (background level) averages < 0.9 ppb Cd.

High concentrations of Cd and Zn in some Tasmanian oysters appear to have caused nausea and vomiting (Ratkowsky <u>et al</u>, 1974). However, there is a general feeling that, since it is a cumulative poison, levels of intake should be kept as low as possible. In U.K. the daily intake of Cd is 15-30  $\mu$ g (MAFF, 1973<sub>a</sub>).

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Itai-itai disease seems to have been caused by eating rice from Cd contaminated soil and the symptoms include pains in the back and joints, duck gait, decrease in stature and changes in the bones, including decalcification and a tendency to fracture easily. Apart from this disease, many other symptoms attributable to Cd have been detected in occupationally exposed workers and experimental animals, including damage to liver and kidneys (Nilsson, 1970). At lower levels of exposure, there is now some evidence that Cd is in some way implicated in the incidence of cardiovascular disease (Schroeder, 1971). Kumuda et al (1972) established a concentration factor of about 300 in rainbow trout, kept in a solution with a Cd content of 0.001 ppm; at the same initial concentration of cadmium, Pasco and Matthey (1977) determined 900-times accumulation relative to the starting

water, for Gasterosteus aculeatus .

The draft of a decree on permissible limits of heavy metals in fish used as foodstuff, stipulates a limit for cadmium of 0.02 ppm wet weight (Huber, et al 1979).

Certain types of algae such as <u>Cladophora glomerata</u> have been proposed as biological indicators of metal pollution of surface water, on account of their ability to accumulated heavy metals. For cadmium and lead, concentration factors up to 49 x  $10^3$  and 20 x  $10^3$ , respectively, have been observed. This corresponds to cadmium contents of 3.9 µg/g and lead contents of 12.2 µg/g (Keeney <u>et al.</u>, 1976).

# 3.2.14.3 Lead (Pb):

Lead is a metal with cumulative toxic properties, which does not display any recognisable useful value, e.g. as trace element, in natural waters. It is accumulated in bones and tissues, and can impair liver, kidney and spleen function in fish (Haider, 1964). In the U.K. the average daily intake of Pb in food is about 200  $\mu$ g (MAFF, 1973<sub>b</sub>). The F.A.O./W.H.O. (1972) provisional tolerable weekly intake is 300  $\mu$ g for adults, but does not apply to children since they are thought to be at greater risk .

A concentration of 600 µg/day has been suggested as an upper limit for intake and a level of 1200 µg may be injurious over a long period of exposure (Kehoe,1961). Nearly half of the Pb absorbed by town-dwellers comes from air pollution (Schroeder, 1971) . The "maximum acceptable toxicant concentrations" (MATC) were 18.2-31.6 µg dissolved lead/litre in these tests in hard water; in soft water, 7.2-14.6 µg dissolved lead/ litre was regarded as permissible (Huber, 1979) The draft of a decree on maximum permitted concentrations in fish stipulates a maximum lead content of 0.5 ppm wet weight (Huber, et al, 1979).

### 3.2.14.4 Chromium (Cr):

Lower forms of aquatic life are sensitive to chromium, and it can accumulate at all trophic levels (EPA,1972). Oshida (1977) carried out a series of long-term experiments which suggested that trivalent chromium was not toxic to the marine polychaete worm <u>Neanthes arenaceodentata</u>, but that at concentrations of  $12.5-50 \ \mu g/g$ hexavalent chromium began to cause detrimental effects on reproduction .

Some chromium compounds are extremely irritating corrosive and carcinogenic (Von Oettingen, 1958). The lethal concentration of chromium varies with the valency state of the element and may range from 18 to more than 200 ppm. There is apparently a growing incidence of cancerous growth and skin ulcers on marine fishes taken near industrial outfall areas in the United States, and it is suspected that chromium compounds are contributing factors (Dvizhkov, 1967)

# 3.2.14.5 Copper (Cu):

Copper is a common pollutant in surface waters; its mode of action on aquatic organisms is not clear but toxicity is largely attributable to  $Cu^{2+}$ . The cupric form of copper (which is the species commonly found) is readily complexed by inorganic and organic substances and is adsorbed on to particulate matter. For this reason, the free ion rarely occurs except in pure acidic soft water .

Toxicity is increased (median lethal concentrations, or LC50 values, are decreased) by reduction in water hardness, temperature, and dissolved oxygen, and decreased in the presence of chelating agents such as EDTA (ethylene diamine tetra acetic acid) and NTA (nitrilotriacetic acid), humic acid, amino acids, and suspended solids, but little is known of the effects of pH and alkalinity.

Only tentative water quality criteria can be formulated at present because there are virtually no field observations that indicate unequivocally the concentrations of copper that are not inimical to fish populations or fisheries. This is mainly because analytical methods for determining low concentrations are inadequate and the methods commonly used do not distinguish between toxic and non-toxic soluble forms. Also, quantitative data on the size and structure of the fish populations are not available and other poisons are frequently present with copper. Only meagre qualitative data are available for non-salmonid species. In the absence of data on the precise effects of copper on natural fish populations, considerable reliance has to be placed on laboratory data; it is suggested that the maximum safe concentrations should be based on annual 50 and 95 percentile values of soluble copper of 0.05 and 0.2 respectively of the threshold LC50 to rainbow trout, taking into account the effect of water hardness. Peak concentrations (>0.5 of the threshold LC50) may be more damaging in the winter than in the summer .

The sublethal effects measured in copper solutions are transitory and persist for a few days only,which could imply that some acclimation takes place. Except for work on the long-term effects of copper solutions on the fathead minnow (Mount, 1968) and bluegill (Benoit, 1975) in hard waters, concentrations below 0.1 of the threshold or 4-days LC50 appear to exert no measurable effect (Alabaster and Lloyd, 1982).

Acutely lethal concentrations (i.e., 2-or 4-day LC50s) of copper to European species of fish in hard water range over 1½ orders of magnitude. No reliable comparative data are available for different species in soft water, for the young stages, or for sublethal effects .

Significant adverse effects on growth of some species, including rainbow trout, occur at about 0.1 of the 4-day LC50 .

Aquatic plants and algae and invertebrates are generally more resistant than fish and there is no evidence that fisheries in waters containing copper have been adversely affected because of a reduction in food organisms . - 156 -

The toxicity of copper in natural waters, except soft water free from organic matter and suspended solids , is less than that predicted from laboratory tests in clean water, probably because of the presence of nontoxic complexes and insoluble precipitates . Sewage effluents containing copper are also less toxic than would be predicted from laboratory data. The presence of non-toxic complexes may partly explain the existence of brown trout populations where the annual 50 and 95 percentile values of soluble copper were 0.17 and 0.38 of the 2-day LC50 to rainbow trout and of some non salmonid species where the corresponding values were 0.17 and 0.66 respectively (Alabaster and Lloyd, 1982).

Copper is toxic to man in quantities of 100 mg (Mckee and Wolfe, 1963). However, copper poisoning as a result of eating copper contaminated marine organisms is unlikely because their taste renders them unpalatable. Human taste threshold is about 5-7 ppm (Portmann, 1970).

Haemopathological changes attributed to heavy metal poisoning were observed in blood smears of <u>Liza</u> <u>macrolepis</u> taken after exposures of 96 h to graded doses (mg/l) of copper (0.11-1.80), lead (1.15-18.36), and mercury (0.04-0.59), in a flow-through marine bioassay system (Helmy <u>et al.</u>, 1978) . The maximum permissible level of copper in fish in spain is 20 ppm (MAFF, Personal communication) .

# 3.2.14.6 Zinc (Zn):

The toxicity of solutions containing zinc is mainly attributable to the zinc ion and perhaps also to particulate zinc present as the basic carbonate or the hydroxide held in suspension. It is modified by water quality, being reduced in particular by an increase in hardness and also temperature, salinity and suspended solids, and increased by a decrease in dissolved oxygen .

The acute toxicity of zinc in the presence of other heavy metals and other common pollutants seems to be largely simply additive but there is no evidence that the chronic toxicity of different poisons in a mixture is also additive. The effect of zinc is modified, and can be reduced, by acclimation and by the age of the fish .

A low but significant mortality has been found among rainbow trout exposed continuously for 4 months to constant concentrations of 0.2 of the 5-day LC50 and among rudd exposed for 8% months to 0.3 of the 7-day LC50.

Laboratory studies of avoidance reactions have shown that Atlantic salmon and rainbow trout may avoid concentrations of zinc in soft water which are 0.14-0.01 of the 7-day LC50.Avoidance reactions have also been observed at 0.35-0.43 of the 7-day LC50 by migrating Atlantic salmon in a river polluted with copper and zinc (Alabaster and Lloyd, 1982).

Carp and goldfish show avoidance of 0.3-0.45 of lethal concentrations under laboratory conditions .

Alabaster and Lloyd (1982) found that field observations show that brown trout populations were present when the concentration of zinc was less than 0.06 of the 2-day LC50 to rainbow trout or when the annual 50 and 95 percentiles were up to 0.05 and 0.19 of the LC50 respectively; coarse fish were present when the corresponding percentiles were 0.02 and 0.11 of the 5-day LC50 to roach . It is tentatively recommended that for the maintenance of thriving populations of fish the annual 95 percentile of concentration of zinc should be no greater than 0.1 of the appropriate 7-day LC50 at  $15^{\circ}$ C; thus the criteria in terms of concentration of zinc would depend upon water hardness and type of fish .

The concentration of 0.03 mg Zn/1 for salmonids in very soft water may be too severe if brown trout only are present, since this species appears to survive successfully at higher concentrations; in such cases a 95-percentile concentration of 0.2 of the 7-day LC50 (0.06 mg Zn/1) may be more appropriate .

The values of the corresponding annual 50 percentiles would be approximately 0.25 of the proposed 95 percentiles unless the distribution was much wider in range than has hitherto been found or was not lognormal, resulting in a larger ratio between the 95 percentile and dissolved oxygen concentrations are below the airsaturation value, allowance should also be made for their contribution to the toxicity .

Concentrations of up to 0.4 mg/1 have been reported in some estuarine waters (Portmann, 1968). Concentrations at this level are lethal to molluscs larvae. Toxic levels for adult shellfish and fish are about 10 ppm (Portmann, 1968). High zinc concentrations may have a deleterious effect on larval fish and shellfish (Portmann, 1970).

### 3.2.14.7 Nickel (Ni):

Human fatalities have been caused by nickel carbonyl in the production of nickel by Mond process (Von Oettingen, 1958). To what extent this contaminant is dangerous is not known. Nickel is reported to have carcinogenic properties in laboratory animals (Hueper, 1963).

# 3.2.14.8 Vanadium (V):

Vanadium is known to have very high accumulation factors from seawater to some marine organisms. The extent of man's impact on vanadium concentrations in marine organisms is unknown, and so are the biological and ecological effects of vanadium contamination (Jernelöv, 1975).

### 3.2.14.9 Iron (Fe):

Iron is present in most surface and subsurface water. In polluted surface water, the concentration of iron varies from several micrograms to hundreds of micrograms per litre. In subsurface water, it may be in the magnitude of grammes per litre. The concentration of iron is determined by geological structure, hydrological conditions of the basin and also by complex physiochemical and biochemical factors the most important being :

- (a) pH;
- (b) the oxidizing-reducting potential;
- (c) the content of oxygen, carbonic acid, hydrogen sulphide, and other mineral components .
- (d) organic substances with a high capacity to form complexes including humic substances; and
- (e) the content and the composition of microflora .

These same factors also affect the correlation between the concentrations of various forms of iron occurrence in natural water .

Iron is found in a great variety of forms: in solutions, colloids, and suspensions, and in organic and mineral complexes in various states of valence. When organic substances are present in small amounts, a large amount of dissolved oxidized iron is found in a non-dissociated state. When the content of organic substances is increased, for instance, in coloured water, a considerable amount of iron is found in it as complex compounds, in particular as humates. Organic substances also facilitate the peptization of colloidal forms of iron .

The correlations between the content of ferric and ferrous iron determined chiefly by the values of the oxidizingreducing potential and the pH of the water. When their values increase, the stability of the oxidized form also increase, and when eH and pH decrease, that of the ferrous forms increase. The concentration of iron as a biologically active element is subject to regular seasonal fluctuations depending on the rate of biochemical processes of active aquatic organisms. Irregular increases in the concentration of iron indicate a possible pollution by waste waters of metallurgical and metal-processing industries and some mine waters containing large amounts of iron (UNESCO/WHO, 1978).

# 3.2.15 Cyanide:

Cyanide hydrolyses in water, forming toxic hydrocyanic acid. Hydrolysis, and therefore toxicity, increases with a decrease of pH (Cairns <u>et al</u>, 1975). Most of the available toxicity information is for freshwater organisms, for example cyanide levels of 0.06 mg/l are reported to be lethal to trout in five days (Mckee and Wolfe,1963). The Environmental Protection Agency (EPA, 1976) water quality criterion is 5.0  $\mu$ g/l for both fresh and seawater. The effect of cyanide on marine life has not been investigated adequately.

# 3.3 Importance of the East Coast Habitat :

The fishing villages of Bahrain are restricted to the northern half of the island. Fishing in the west coast is relatively unproductive and provides less than 5% of total landings by weight, 95% of which is large hamour (grouper, <u>Epinephelus spp</u>.). This is attributed to the low effort and also probably to the bottom type and comparatively poor water circulation off the west coast. Consequently, fishing effort is concentrated on the more productive northern and eastern grounds .

The east coast provides a base for one third of Bahrain's fishing fleet, including the industrial fishing vessels . Some of these boats based inside the Sitra causeway such as Nabeeh Saleh, Al-Qariah and Al-Kharjeyah and are restricted to fishing within Tubli Bay. The main ports for boats fishing Fasht Al-Adum and areas to the south are based on Sitra . The east coast (excluding Muharreq)provides a livelihood for 36% of Bahrain's full-time fishermen and 26% of the part-time and amateur fishermen .

The productivity of the east coast is demonstrated by the fish landings. Sitra alone which lies on the east coast (Figure 3.1) is the largest artisanal landing point and contributes 20-30% annually of Bahrain's artisanal catch by weight and more important landings are also made at Asker and Jaw which lie on the east coast . Almost all of the artisanal shrimp catch, i-e. 445 tonnes valued at BD 635,000 (1983), is taken from the east coast and most of this is landed at Sitra. Most of the vertebrate fish taken by artisanal fishing off the east coast are caught in large wire pot types ( local name: gargoor), set either on the reefs or sea grassbeds. On Fasht Al-Adhum these traps take a mixture of reef fish dominated by grouper. During 1983, 115 metric tonnes of hamour from the Fasht were landed at Sitra and Jaw, i.e. 27% of the artisanal grouper catch or 20% of the total grouper catch. On the sea grassbeds gargoor catches are dominated by safee (Siganus spp.), 168 tonnes per annum of which are landed at Sitra which represents 25% of the artisanal rabbitfish catch and 22% of the total rabbitfish catch .





# Figure: 3.1

The aquatic and littors

Offshore habitat areas in the vicinity of BAPCO. (From Johnson, 1983).

An important traditional method of artisanal fishing in Bahrain is the permanently fixed fish trap (local name : haddrah) which fishes tidal currents or longshore drift on the ebb. These take about 14% of the vertebrate fish catch. i.e. about 12% of the total catch. In 1983, there are 535 haddrahs (Anon., 1984) in operation concentrated in the Muharreq / Manama area were the coastal topography produces the tidal currents necessary for the effective operation of these fixed traps. 45 (8.8%) haddrahs are operated on the east coast (excluding Muharreq), and an additional 20 haddrahs operated offshore on Fasht A1-Adhum .

The diverse east coast grounds produce a variety of commercial fish species. In 1983, the cuttlefish (local name: Khathag,<u>Sepia spp</u>.) was 53 tonnes valued at BD 32,000.The winter by\_catch of cuttlefish is taken by artisanal shrimpers over the sea grassbeds between the southern east coast and the small Gabbari reef. Spanish mackerel (local name: Chana'ad, <u>Scomberomorus commerson</u>) are also taken in water from the south eastern coast grounds by gill-netting. In 1983, the spanish mackerel catch was 190 tonnes valued at BD 260,000.

# 3.3.1 The BAPCO refinery area :

The aquatic and littoral environment in an areaadjacent to BAPCO refinery is divided into three areas; the intertidal mudflats, coral reefs and sub-tidal soft-bottomed grassbed areas (Figure 3.1).

The inter-tidal sand and mudflats are characterised by mud sediments containing organic matter which support a wide variety of gastropods, worms, snails, molluscs, bivalves and certain species of crabs (Johnson, 1983); and by an area of coarse sands which are rather less productive. Intertidal flats have algal mat zones whose growth is stimulated by the nutrients of the tidal pools formed at low tide, and by the vigorous photosynthesis of the shallow waters . The intertidal areas are biologically important as a

feeding ground for fish and other larger aquatic species which swim in when the tide covers the sediment. They are also main feeding grounds for a large number of seabirds and waders .

The coral reef is of great importance to the aquatic ecology of eastern Bahrain, indeed for the whole of that region of the Gulf between Bahrain and Qatar. Most of the coral (Fasht Al-Adhum) is reported to be in good condition except the north west tip and parts of the western edge of the reef, which is closest to BAPCO. Much of the dead coral (particularly staghorn) is covered with blue-green and other algae, bacteria and detritus (Johnson, 1983).

The Fasht has also been the fishing ground for some of our best commercial fishes . The principal amongst them are safee (<u>Siganus canaliculatus</u>), hamour (<u>Epinephelus suillus</u>), sharee (<u>Lethrinus lentjan</u>) and gorgofan (<u>Rhabdosargus sarba</u>). The total annual finfish catch here is 970 tonnes worth BD 856,510 .

The shrimp catch from the areas over and south of Fasht is around 340 tonnes. Along with the fish catch, the total fish-shrimp inflow in Bahrain from the area on and around Fasht Al-Adhum is 1290 tonnes of the total value of 1.65 million dinars per annum .

There are 819 fishermen depending on this fishery. The family members and the marketing personnel are in addition. Besides,
the fishermen from other places in Bahrain and some foreign vessels also fish here. Thus the total fishing population including families depending on the fishery on and around Fasht Al-Adhum will be above 2500.

Grassbeds are an extremely important hatching, nursery and feeding ground for smaller species, which in turn are the prey for larger fish . Sea grasses grow in strips, parallel to the current, in 3-7 metre water depths all along the sandy area between the inter-tidal flats and the coral south of Sitra Island. In amongst , the seagrass grow mats of large algae (<u>Hormophysa</u> and <u>Sargassum</u>).

Rabbitfish (safee) and grouper (hamour) are two species of commercial importance in this area. Probably the most economically significant of the smaller species is the commercial shrimp (<u>Penaeus semisulcatus</u>), which feed on bivalves and polychaetes in the bottom sediment. The grassbed area along the east coast of Bahrain (Figure 3.1) is probably one, if not the most important shrimp nursery of the whole Island. Figure 3.2 shows the known shrimping grounds on the east coast of Bahrain. The area immediately to the south of Sitra inter-tidal flats is somewhat less productive than areas further south, such as to be found off Asker (Johnson, 1983).

This lower productivity is as a result of the impact of the large effluent discharge of the BAPCO oil refinery at the northerly point of this area (Johnson, 1983) .

## 3.4 Description of the Refinery Processes :

Although the processing system of oil refineries have various degrees of sophistication, they all have the common task of splitting crude oil into the range of petroleum products such



Known Shrimping grounds(dark areas) on the east coast of Bahrain (From Anonymous, 1986<sub>b</sub>) as gas, gasoline, kerosine, gas oil, and fuel oil required by a modern industrialised economy. Crude oils are mixtures of a very large number of complex compounds - mainly hydrocarbons (i.e. composed of hydrogen and carbon atoms only) and the first processing step in every refinery consists in separating crude oil into a number of fractions in a distillation unit .

Reforming and hydrotreating units are used to modify or improve the quality of the products. The correct balance of supply and demand for each product, which cannot always be achieved by distillation, is obtained by the use of further conversion processes. An example of a conversion unit is a catalytic cracker which is used for producing gasoline blending components by breaking down heavier fractions. Before they are blended into finished products, the components are subjected to treatments to remove compounds which could impair the properties of the final products. The more complex refineries also need a vacuum distillation plant and other units such as polymerisation plants. Further processes can be added as required so that the full range of petroleum products may be produced, including lubricating oils and bitumen .

In addition to the process units, a refinery also includes tank farms for storage of crude oil and products , blending and loading facilities, systems for the generation and distribution of utilities like fuel, steam, electricity and cooling water, waste treatment units , etc. (Pauluis, 1979; Cadron and Klein, 1977) .

The pollutants emitted into the air from the oil refineries are sulphur dioxide, carbon monoxide, hydrocarbons, nitrogen oxides, particulates and odorous compounds (Cadron and Klein, 1977). Water is used for various purposes at a refinery. Before the crude oil is processed, it is often washed with water to remove inorganic salts. Typically 3-5% weight water on crude is used. In further processing, the main use of water is as stripping steam to reduce the partial pressure of hydro-carbons. Water is also used for cooling products as they come from the process plants prior to blending and shipping. Refineries also have to make provision for handling drainage and rainwater which may come contaminated with oil .

The volume of water discharged from a refinery varies considerably and is dependent on the type of cooling used during processing and the location of a refinery. In the older refineries with once-through cooling the water requirement can be as high as 20 times the crude throughput . However, water demand can be lowered considerably by recycling, through cooling towers or by making use of air cooling .

## 3.5 Composition of Crude Oil :

Crude oils are complex mixtures of a variety of hydrocarbons displaying a wide range of physical characteristics . In addition to pure hydrocarbon, crude oils also contain a few percent of sulphur and some parts per million of nitrogen, vanadium and nickel combined with hydrocarbons. Every oilfield produces an oil unique in composition and properties, and sometimes a change of properties can be noticed with time (Pauluis, 1979).

#### 3.6 Composition of Coastal Refinery Effluents :

Treated refinery effluents comprise varying proportions of process, cooling, storm and ballast water and may contain oil, phenols, sulphides, mercaptans, cyanides, ammonia, some heavy metals and suspended solids, and possibly other compounds. Variation in concentration of these components occurs both between refineries and within any particular refinery over a period of time. The 'oil' component includes hundreds of different compounds. Relatively little information is available on the detailed composition of the 'oil'component. There have been cases of compounds other than those listed above being intermittently present in effluents, such as cleaning products and herbicides used within the refinery (Côté, 1979).

## 3.6.1 Oil and hydrocarbons :

Oil is the most obvious pollutant in refinery effluent. Most of its components are insoluble in water and will be present as a dispersion/film easy to separate or as a more or less stable emulsion of oil in water which will require destabilisation before breaking up into a separable phase .

## 3.6.2 Oxygen Demand (OD) :

The oxygen demand of an effluent gives an idea of the oxygen depleting stress imposed on a receiving water. In refinery waste-water the main pollutants exerting an OD are dissolved organics, ammonium salts and sulphides. The OD of an effluent can be reduced by submitting the waste-water streams to various treatments .

## 3.6.3 Toxic substances :

Substances like sulphides, mercaptans, cyanides, ammonia and phenols are acutely toxic when present in water above a given concentration. These pollutants can be eliminated or their concentration reduced to a safe level through physical/chemical/biochemical treatment.

## 3.6.4 Heavy metals :

The release of heavy metals in the environment is a matter for concern because some of them are acutely toxic at low concentration and could accumulate through the food chain mechanism (biomagnification) .

Some heavy metals in refinery waters may have their origin:

- in crude oil (Ni,V);
- in the raw water and the chemicals used to produce steam or cooling water (Fe, Mn);
- in the chemicals used for conditioning cooling water (Zn, Cr);
- in losses of process catalyst (Cu, Co);
- in corrosion products of process equipment (Fe, Cr,Cu,Ni);
- in additives used for blending motor gasolines (Pb) or lubricating oils .

## 3.6.4.1 Vanadium :

Vanadium is present in organic form at various concentration in most crude oils. After distillation, it remains associated with the residues. A limited number of analyses indicate levels of 10 to 100 micrograms per litre (ppb) in biotreated effluent .

#### 3.6.4.2 Lead alkyls :

Although lead alkyls are used in refineries as gasoline additives they do not appear in aqueous effluent since, owing to their very toxic nature, exhaustive precautions are taken covering all aspects of handling, storing and blending. Opportunities for these products to reach surface waters are further reduced by their very volatile character, so that a small accidental spill has little chance of being washed away, and also because being practically insoluble in water, they hardly appear in the small amount of water drained from leaded gasoline tanks .

## 3.6.5 Sources of pollutants in the refinery effluents :

Pollutants in an oil refinery originates from various sources :

3.6.5.1 Cooling water :

Large amounts of heat has to be removed from the hydrocarbon streams. In older coastal refineries, this is frequently done by a"once-through" cooling water system; the flow of water discharged can be as high as 30 m<sup>3</sup>/tonne of crude processed, depending on the complexity of the refinery. New refineries have either air cooling and/or a recirculating cooling water system, thus their discharge may be reduced to as low as  $0.05 \text{ m}^3$ /tonne of crude processed (Pauluis, 1979). Cooling water is normally uncontaminated with oil-except in the event of heat exchanger tube failure. The waste from a cooling tower may contain low concentrations of conditioning chemicals .

For many years the tendency has been to eliminate or to minimise the use of cooling water by using air cooling for example, but even the most modern refineries still have to deal with a certain number of streams of water. These streams differ in composition and wholly or partially segregated systems are commonly used to effect the most economic overall disposal . - 172 -

Streams are :

- (a) Cooling water
- (b) process water, storage tank drainage and steam generation
- (c) ballast water i.e. water discharged by tankers arriving at the refinery
- (d) rainwater
- (e) sanitary/domestic waste etc.

## 3.6.5.2 Steam generation :

Refineries require large amounts of steam for processing and sometimes for power generation.After condensation some streams of clean condensates are returned to the boiler feed water tank, but the balance which is lost to the effluent as sour condensate or oily water must be made up with treated water. The backwash water from the demineralisation or softening plants together with the boiler blowdown is a small flow of water containing mainly inorganic salts; after neutralisation it may be discharged directly into surface water .

## 3.6.5.3 Waste water from process units :

The water has been in intimate contact with the hydrocarbons of the process streams. It originates from the drainage of crude and product tanks, from steam used in distillation and conversion units, from wet chemical treatment or from water-washing of crude and products. This stream is always the most heavily loaded with impurities in a refinery. It may contain variable amounts of oil (in dissolved, suspended or emulsified state) , dissolved inorganic salts and dissolved organic compounds (light hydrocarbons, phenols, thiophenols and other oxygenated products like organic acids) . During further distillation and convertion processes, water is also introduced as stripping steam to reduce the partial pressure of hydrocarbons.After condensation and separation from the hydrocarbon layer , a " sour condensate" is produced containing  $NH_3$ ,  $H_2S$ , oil and soluble organic material such as phenols, mercaptans and organic acids . This condensate is often stripped with steam to reduce its  $H_2S$  concentration to below 20 ppm wt., and to remove part of the ammonia and volatile organic impurities .

In modern refineries, considerable attention has been devoted to designs which eliminate or reduce contact of water with hydrocarbon streams. Processes have been selected because they produce no waste, or produce it in reduced volume or improved quality. Improved designs of equipment have reduced the quantity and the contamination of water while operating conditions and procedures have also been implemented to minimise the production of process water .

## 3.6.5.4 Ballast Water :

Product tankers arriving at the refinery in ballast usually discharge their ballast water containing dispersed oil which can be skimmed off in reception tanks. The ballast water contribution to the total refinery waste water may be negligible at inland refineries , but at coastal refineries, moving most of their products by sea, it can be a significant amount .

## 3.6.5.5 Rainwater :

The rainwater runoff from paved areas in the processing units or the product loading stations, generally contains some oil due to small spillages.Rainwater runoff from other areas such as the tank farm can be contaminated only in the event of accidental spillage. The rainwater from undeveloped areas is free of oil .

# 3.7 Waste-Water Treatment Technology in Modern Refinereis :

Until the end of the fifties, the waste-water treatment facilities in most refineries merely consisted of gravity separators for the recovery of free oil and sometimes steam strippers for the reduction of odour of sour condensates. Then, in the early sixties, several new refineries were built inland, and in order to meet the much stricter standards for discharge into the aquatic ecosystem a new approach to waste-water management was developed (Pauluis, 1979).

Nowadays, if a new refinery had to be built in a sensitive area where severe discharge specifications applied, its wastewater treatment programme would probably include both inplant control measures and modern "end-of-pipe" wastewater treatment units .

#### 3.7.1 In-plant control :

In-plant control might include the following steps :

## 3.7.1.1 Pre-treatment of sour condensates :

Sour condensates containing volatile malodorous impurities like phenols, sulphides, mercaptans, ammonia and light hydrocarbons are collected in a closed sewer system and are countercurrently stripped, most often with steam, before joining other contaminated streams.

# 3.7.1.2 Reduction of the flow of waste-water and of the load of impurities :

A new refinery could be designed for minimal water consumption e.g. by applying air and recirculating water cooling and selecting processes which do not produce so much waste water. The effluent or the spent chemicals from one unit could be recycled in the same unit or re-used in another unit, e.g. spent caustic can be re-used for crude neutralisation, sour condensates re-used for crude desalting. Equipment and operating procedures have also been modified to reduce the concentration of impurities in the water.

#### 3.7.1.3 <u>Segregated sewer system</u> :

Idealy, each category of waste-water should be collected in a separate sewer system. This is of importance to prevent the most contaminated streams (mainly process water) becoming unduly diluted with relatively "clean" water, which would reduce the efficiency of the endof-pipe treatment units, particularly of the biotreater. It is indeed often observed that activated sludge units in refineries experience unstable operation owing to the low concembration of biodegradable impurities in their influent (inadequate BOD of the feed).

#### 3.7.2. End-of-pipe treatment units :

The end-of-pipe treatment includes the following steps:

## 3.7.2.1 Primary treatment and equalisation :

Primary treatment comprises the removal by gravity separation of oil dispersions and coarse particulate matter. In modern refineries this is often performed in plate type interceptors. Provided the oil at the inlet is not emulsified, the oil content of the effluent water may be below 50 mg/1. Oil and solids in a colloidal or dissolved state are not removed.

When further treatment is required, it is important to avoid wide variations in the water flow and in the concentration of impurities. Storage tanks can be used to provide buffering and equalisation for oily water and storm water . The tanks can be equipped with skimmers for further deoiling .

## 3.7.2.2 Deep removal of emulsified oil and colloidal solids:

Waste-water that has passed through a gravity separator can still contain appreciable amounts of oil, mostly in the form of small droplets or attached to suspended solids. In new refineries these finely dispersed materials are separated in a dedicated treatment unit to meet the effluent discharge specifications or to protect the biotreater against an excessive ingress of oil .

This can be done in a flocculation unit by addition of flocculant chemicals under controlled conditions. The flocculant can produce any of the following effects :

- destabilize the colloids/emulsions allowing them to coalesce .
- generate a dense precipitate which adsorbs and enmeshes the contaminants .
- form bridges between the particles/droplets which then agglomerate .

The resultant large aggregate can then be separated from the water by either sedimentation, filtration or flotation. Flotation, and more specifically "dissolved air flotation", is a good choice for refinery waste-water. In this process the water is saturated with air under pressure; upon release of the pressure the air in excess of the atmospheric saturation concentration is released from solution,forming very small bubbles which attach and grow on the surfaces of the flocs and bring them to the surface of the water, where they are skimmed off and collected for disposal. The contents of oil and suspended solids in the effluent of a flocculation-flotation unit are less than 20 mg/l (oil measured by infra-red analysis) (Pauluis, 1979).

## 3.7.2.3 <u>Removal of dissolved organic material by biological</u> oxidation :

In a biological treatment unit, the waste-water is contacted with a high concentration of active microorganisms under intensive aeration. 10-50% of the soluble convertible organics having a BOD are converted into insoluble material (biomass), the balance being carbon dioxide , water and some waste energy. These micro-organisms are sensitive living creatures which will die or at least become inactive if a suitable environment is not maintained .Experience has shown that they are particulary sensitive .

- to rapid fluctuations in the quality of the feed water (BOD,pH,temperature), which is why efficient equalisation is desirable;
- to the presence of hydrogen sulphide, which is why steam stripping of all sour streams is so important;
- to the presence of an excess of oil,or suspended solids ,which is why deep deoiling is often performed prior to biological treatment .

There are three main versions of biological treatment for waste water purification, namely :

- the activated sludge process
- the trickling filter
- the aerated lagoon

for refinery effluent treatment the completely mixed activated sludge process is often used.

#### 3.7.2.4 After-treatment :

After-treatment (polishing) of the biotreater effluent is generally limited to an after-aeration step prior to final discharge. When the treated effluent is to be reused as make-up for a circulating cooling system, a filtration step is advisable .

## 3.7.2.5 Sludge dewatering and disposal :

Several sludges are produced in this treatment sequence:
bottom sludges in the oil/water separators
scum and sludge in the flocculation unit
excess biological sludge in the biotreater
They are characterised by a high water content and a low calorific value. After collection, homogenisation and primary dewatering in a thickener, the sludges can be mechanically dewatered, e.g. in centrifuges, and incinerated, e.g. in a fluid bed type of incinerator .

To avoid the high operating costs associated with incineration, other disposal routes can be envisaged such as disposal on land ("Sludge Farming") .

## 3.7.3 Water pollution abatement in established refineries :

Generally speaking, older refineries were not designed with water economy/treatment in mind: their water consumption is high and polluted and clean water streams are often intermixed in a combined sewer system. This results in higher waste-water flows and most often in higher pollutant loads per tonne of crude than in modern refineries (Pauluis, 1979).

## 3.8 <u>Description of Waste-Water Segregation and Effluent Treating</u> System of BAPCO Refinery :

The complex operation at the refinery involves a large fluid catalytic cracking unit (FCCU), a sulphur recovery plant, and a large number of process heaters ( $\sim 29$ ). In addition to that, BAPCO has its own power plant which provides electricity to the whole complex .

BAPCO refinery produces liquified petroleum gas, naphtha, motor gasoline, jet fuel, kerosine, diesel oil, heavy gas oil,fuel oil, asphalt and sulphur.Since the 1960's,it has had a daily production capacity of approximately 255,000 barrels (~ 40,000 tonnes per day) including the refined products with the exception of lubricants.The main waste product is oily water, spent caustic liquor and hydrochloric acid, besides sanitary wastes. The quantity of spent caustic liquor discharged into the sea is approximately 7,000 USG/day (26,500 l/day) originating from the use of 3.5 tonnes/day of caustic soda. While that of spent hydrochloric acid is 40,000 USG/Year (151,000 l/year) orgininating from the use of about 145,000 lbs/year (65,700 kg/year) of hydrochloric acid. Alkyl lead is used for gasoline production.

The refinery requires water for the processing of oil and cooling the refinery machinery. This water is pumped at a rate of 100,000 G.P.M. (380,000 l/m) from the Gulf sea and brought to the refinery through two inlet channels of about 20 feet width (Figure 3.3).These channels are earthen and bring in water almost 24 hours/day . In the oil processing and cooling procedures, this water is mixed with a variety of chemicals along with the oil, thereby forming effluents.Figure 3.4 shows a simplified flow diagram of waste water segregation and effluent treating system (Symbols A,B and C indicate the position of the outlets used in the toxicity tests). The effluents are of five types depending upon the use of the inlet sea water in the factory.The five types of effluents are given below along with their discharge rates .

| 1. | Oily process | water        | >     | 7000 G.P.M.        |
|----|--------------|--------------|-------|--------------------|
|    |              |              |       | (26500 l.per min)  |
| 2. | Salt cooling | water        | >     | 30000 G.P.M.       |
|    |              |              |       | (113600 l.per min) |
| 3. | Intermediate | salt cooling | water | 80000 G.P.M.       |
|    |              |              |       | (303000 1.per min) |
| 4. | Spent causti | c waste      |       | 4 G.P.M.           |
|    |              |              |       | (15 l.per min)     |
| 5. | Sanitary was | te           |       | 225 G.P.M.         |
|    |              |              |       | (850 l.per min)    |
|    |              |              |       |                    |

These effluents are discharged mixed in the sea after passing through segregation and effluent treatment system. This system has 9 sub-systems terminating into 2 final outlet channels which open in the Gulf. In these nine subsystems, treatment is given only in the sub-systems 3,4,5 and 8. In the rest, effluents being directly go to the outlet channels (Figure 3.4).

In the first sub-system, the sanitary waste of 200 G.P.M. directly goes into the open channel 1 (main stream) (Figure 3.5) which later joins outlet channel 1. In the second sub-system, the salt cooling water is also let out in the open channel 1 at the rate of 15000 G.P.M.

In the third sub-system, the intermediate salt cooling water goes to No.4 separator at the rate of  $\sim$  35,000 G.P.M. This separator has 7 cells.



Flume inlet channel.



FIGURE: 3.4 Simplified flow diagram of waste water segregation and effluent treating system. Symbols A, B and C indicate the positions of the outlets used in the toxicity tests.

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Salba Bay and outlet channel 1 (main stream). ( right: flume inlet channel ). These cells are made of concrete and arranged in a row . On either side of these cells are located two concrete channels. The channel of one side receives effluent (intermediate cooling water) containing some oil and flushes it into the separator cells. The latter have two rotating iron-pipes (Figure 3.6) of 10<sup>°</sup> diameter having a slit of  $4-5^{°}$  at the top so as to permit the entry of floating oil. These are called skimmer pipes. They are situated adjacent and parallel to the concrete channel. The floating oil constantly spills into these pipes from where it is directed to a storing tank for oil recovery. The waste water falling into the cemented channel on the other side flows out to open channel 1 (main stream) .

In the 4<sup>th</sup> sub-system, the oily process water comes into No.3 separator (Figure 3.6) at the rate of ~7000 G.P.M. The mechanical seperation of the major portion of floating oil here is similar to that in No.4 separator described above. The waste water containing residual oil from No.3 separator is let into an open earthern channel No.2 from where it goes into a skim pond through a sluice gate. The latter is a large earthern pond of the size 45' x 11' x 8'.

It has outlet weirs which remain closed normally but overflow when necessary. Effluent from the skim pond is pumped into the Induced Air Floatation (I.A.F.) unit (Figures 3.7 and 3.8) described later. The overflow goes into outlet channel 1.

The number 5 sub-system brings intermediate cooling water at the flow rate of 45,000 G.P.M. to No. 5 separator having 10 cells. The separation of oil here is mechanical as in No. 3 and 4 separators and the waste water is thrown





Schematic diagram of No. 3 separator (above). Separator No. 6 (below).

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Depurator machine float cell 'section view' (above). I.A.F. unit (below).



Induced Air Flotation (I.A.F.) unit, No. 4 separator outlet and open channel 1 .

ffluent

into an open channel 3 which joins outlet channel 1 (main stream) .

The sub-system 6 brings in salt cooling water at the rate of 15,000 G.P.M. This water is let out directly into open channel 3 for final discharge through outlet channel 1 (main stream).

The sub-system 7 brings spent caustic waste at the rate of 4 G.P.M. A part of this effluent is let out into the open channel 3 through the pipe of sub-system 6. Thus the spent caustic waste gets diluted in its travel to open channel 3 by the clean salt cooling water of the 6th sub-system. The remaining spent caustic waste is diverted to open channel 1.

The sub-system 8 carries process and salt cooling water at the rate of 13,000 G.P.M. to No. 6 separator (Figure 3.6) having 4 cells. The waste water after the mechanical recovery of oil goes to the sea through 2nd outlet channel (side stream).

The 9th sub-system bringing sanitary waste at the rate of 25 G.P.M. joins directly the second outlet channel without any treatment .

The IAF unit referred to above which was installed in 1981 receives waste water containing residual oil from the skim pond. In this unit, a polyelectrolyte is added to the effluent .

The I.A.F. unit is composed of four standard WEMCO floatation cells (Figure 3.7). Each cell is equipped

with a motor-driven self-aerating rotor mechanism. As the rotor spins, it acts as a pump, forcing water through a disperser and creating a vacuum in the standpipe. The vacuum pulls gas into the standpipe and thoroughly mixes it with the wastewater. As the gas/water mixture travels through the disperser at high velocity, a shearing force is created, causing the gas to form minute bubbles. Oil particles and suspended solids attach to the gas bubbles as they rise to the surface. The oil and suspended solids which gather in a dense froth on the surface, are removed from the cell by skimmer paddles and collected in external launders .

This foamy skimming is passed on to the separator 3 again for oil recovery through mechanical separation. The waste water from the I.A.F. chamber is let out in open channel 1 (Figure 3.8) for final discharge to the sea via outlet channel 1 (main stream).

The final discharge in the Gulf is 115,000 G.P.M. through outlet channel 1 (main stream) and 13,000 G.P.M. through outlet channel 2 (side stream)(Total: 128,000 G.P.M.). BAPCO treatment system composed of American Petroleum Institute (API) separtors, a skim pond and an induced air flotation unit (I.A.F) which was installed in 1981. The operating principle of the API separator is that as the oily water flows along the separator bay, insoluble oil rises to the surface and solids settle on the bottom. In a simple API separator an oil collecting trough is fitted at the exit end; one can also be fitted in the forebay for gross oil removal, with the oil being pumped to a recovered oil tank in both cases (CONCAWE, 1978). The disadvantage of this type of separator is that it can create vapour emission problems. If necessary, to overcome this, covers can be fitted to minimise emissions, but these covers can then create an explosion hazard. Another means of reducing vapour emissions is the use of floating plastic balls or rafts on the forebay of the API separators.

Oily sludges from the crude oil storage tanks amount to approximately 0.12% of the crude oil throughput(~17,500 t/year). Toxic sludges from the gasoline production are approximately 0.001% of the refinery stock (~146 t/year). This sludges are dumped in an open pits(oil sumps) situated south of the refinery grounds (Figure 3.9). As these oil sumps are very close to the sea shore, there is a potential danger for contamination of the marine environment . Underground water reservoirs could also be affected . Attempts are presently being made to decrease the volume of the sludge in the pits by enhancing its degradation .

The refined oil from the BAPCO refinery is pumped into storage tanks near the Sitra oil terminal. These tanks are periodically cleaned giving rise to another source of pollutions. Further, oily residues and slop - residues from vessels berthed at Sitra wharf are pumped ashore into holding tanks for oil recovery. The drainage from the tanks and the slop-residues goes to the Sitra separator . The discharge from this separator is approximately 20-30 G.P.M. and is discharged to the sea . The oil recovery separator at Sitra is without the Induced Air Floatation (I.A.F.) provision and hence the content of residual oil in the waste water is relatively high . 3.9 Materials and Methods :

3.9.1 Sampling :

3.9.1.1 Water samples :

Water samples during 1983 and 1984 were collected at monthly intervals from Sitra separator outlet and at weekly intervals from the other stages of BAPCO effluent treatment for the determination of oil, pH, ammonia, phenols, sulphides, chemical oxygen demand and biochemical oxygen demand .

In May 1980, surface water samples were collected from ten stations (Figure 3.9) in the vicinity of BAPCO refinery main stream outlet (final effluent) for the determination of temperature, salinity, pH, phosphate, nitrate, nitrite and ammonia.

In May 1984, surface water samples were collected from seventeen stations(Figure 3.10) in the vicinity of BAPCO refinery main and side streams outlets for the determination of temperature, dissolved oxygen, pH,salinity, phosphate, nitrate, nitrite, ammonia, oil, phenols, sulphides, suspended solids, chemical and biochemical oxygen demands.

In April 1986, 43 water sampling stations were selected to cover both the areas in the vicinity of the Sitra oil storage tanks outfalls, the main and side streams outfalls as shown in Figure 3.10. The parameters studied were temperature, salinity, pH, phosphate, nitrate, nitrite and ammonia.



Water sampling stations (May, 1980).



Location of water sampling stations

A : Main stream.
B : Flume inlet.
C : Side stream.
D : Sitra separator outlet.

The circles indicating May, 1984 samples. The triangles indicating April,1986 samples. Samples were obtained by Van Dorn water sampler (No. 135 WA - 141). The 1984 sampling stations were fixed in such a way that they reflected the mixing pattern in Salba Bay in relation to the surface effluent drift. The surface effluent drift is along the shore adjacent to the pump-house road and the stone-dyke extending from the pump-house for a distance of approximately 50 meters into the sea.

Beyond the end of the dyke, the drift is partially deflected southwards but retains its identity as a blackish surface stream. This stream is gradually mixed with the open waters. The station at the mouth of outlet channel 1 was designated as A and the other stations were fixed in the drift course at a distance of about 200 meters from one another (Figure 3.10). The depth at the sampling stations varied between 0.5 to 5.0 m, the shallow areas being within the Bay and deeper offshore. At the mouth of outlets, the depth was less than 0.5 m.

## 3.9.1.2 Sediment samples:

Seven stations were selected (May, 1984) for the collection of sediment samples. The stations were fixed at a distance of about 200 meters from one another (Figure 3.11). Samples were collected by a messenger operated Ekman grab having jaw size of 15.5cm.

## 3.9.2 Analysis of water samples:

#### 3.9.2.1 Temperature:

As in chapter 2 (2.2.1).

#### 3.9.2.2 Total dissolved solids:

As in chapter 2 (2.2.2).

## 3.9.2.3 pH value:

As in chapter 2 (2.2.3)



# FIGURE: 3.11

Location of sediment samples stations (1s - 7s)

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## 3.9.2.4 Dissolved oxygen:

As in chapter 2 (2.2.4)

3.9.2.5 Total ammonia - nitrogen:

As in chapter 2 (2.2.5)

#### 3.9.2.6 Nitrate - nitrogen:

As in chapter 2 (2.2.6)

## 3.9.2.7 Nitrite -nitrogen:

As in chapter 2 (2.2.7)

#### 3.9.2.8 Phosphate - Phosphorus:

As in chapter 2 (2.2.8)

#### 3.9.2.9 Oil content:

The sample was agitated after the addition of concentrated  $H_2SO_4$  and Freon 113. The water and Freon layers are allowed to separate, the Freon layer was filtered through phase separating paper and the absorbance of the Freon portion measured on a Miran 11 Infra Red Analyser.

#### 3.9.2.10 Phenols:

Phenol was determined by direct photometric method (APHA, 1980). Steam-distillable phenolic compounds reacted with 4 - aminoantipyrine at pH 7.9  $\pm$  0.1 in the presence of potassium ferricyanide to form a coloured antipyrince dye. This dye was kept in aqueous solution and the absorbance was measured at 500 nm.

## 3.9.2.11 Sulphide:

Sulphide was determined either by titrimetric (APHA, 1980) or methylene blue method (APHA, 1980) according to its concentration in the sample.

## 3.9.2.12 Total suspended matter :

#### 3.9.2.13 Chemical oxygen demand (COD) :

The chemical oxygen demand (COD) is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. For samples from a specific source, COD can be related empirically to BOD, organic carbon, or organic matter content.

Chemical oxygen demand was determined by dichromate reflux method (APHA, 1980), and the amount of oxidizable organic matter was calculated in terms of oxygen equivalent .

## 3.9.2.14 Biochemical oxygen demand (BOD) :

The biochemical oxygen demand (BOD) determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters. The test measures the oxygen required by microorganisms for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulphides and ferrous iron under aerobic conditions.

Dissolved oxygen (DO) was measured by the modified Winkler procedure (APHA, 1980) initially and after incubation. The BOD was computed from the difference between initial and final DO.

## 3.9.3 Analysis of sediment samples :

## 3.9.3.1 Organic carbon and organic matter :

The dried sediment sample was digested with a chromic acid-sulphuric acid mixture and the excess of chromic acid not reduced by the organic matter was titrated with a standard ferrous sulphate. This modification of Walkley's rapid method (Walkley and Black, 1934) for the determination of organic carbon in soilds has been found to give approximately 89 percent recovery of carbon, as compared to the dry-combustion method. The conversion factor 0.336 was abtained by dividing 0.003, the milliequivalent weight of carbon, by 89 and multiplying by 100 to convert to percent .

## 3.9.3.2 Particle size distribution :

Bottom sediment samples were analysed for particle size distribution by subjecting them to dry sieving in an electrically operated sieve shaker assembly (FRITCH GMBH Electromagnetic laboratory sieve shaker "analysette 3" ).

3.10 Results :

3.10.1 Water quality :

## 3.10.1.1 Water quality at different stages of BAPCO effluent treatment during 1983 :

Water quality data at different stages of effluent treatment during 1983 is given in Table 3.6. This

Table: 3.6

at different stages of treatment at BAPCO refinery and Sitra the Effluence analysis giving the contents of various polluting parameters

separator outlet during the period January - December 1983.

| ngq               |        | Hď      | Ň     | ALINITY   |        |               | H d    | ENOLS      | SUI   | PHIDES<br>H <sub>2</sub> S<br>PPm |               | CHLORIDES<br>as NaCl<br>ppm | so                                   | SPENDED<br>DLIDES<br>PPm           | 3994   | COD<br>PP= |   | 800<br>PPm |
|-------------------|--------|---------|-------|-----------|--------|---------------|--------|------------|-------|-----------------------------------|---------------|-----------------------------|--------------------------------------|------------------------------------|--|------------|---|------------|
| mean range        | 19 F F | range   | me an | range     |        | range         | ue au  | range      | nean  | range                             | mean          | range                       | Be a r                               | range                              | mean   | range      | mean  | rang       |
|                   |        |         |       |           |        |               |        | e de la    |       |                                   |               |                             |                                      |                                    | 99   |            |   |            |
| 1.5 0.09-4.00     | 8.1    | 7.9-8.5 | 40.8  | 11.5-45.1 | 0.3    | 8.1-JIN       | 0.02   | 111-0.20   | 10.0  | 1.0-11                            | 96.079        | 31,250-42,300               | 28.8                                 | 2.6-19.0                           | 9.5  | 0.86-11    |   |            |
| 16.0 19.00-282.0  | 00 8.2 | 7.5-8.8 |       |           |        |               |        |            |       |                                   |               |                             |                                      |                                    | 1.1.8  |            |   |            |
| 3.2 0.06-19.00    | 8.1    | 7.8-8.5 |       |           |        |               |        |            |       |                                   |               |                             |                                      |                                    |  |            |   |            |
| 1.5 0.07-4.00     | 8.1    | 7.8-8.5 |       |           |        |               |        |            |       |                                   |               |                             |                                      | 1.5.4                              |  |            |   |            |
| 26.3 9.30-104.00  | 8.3    | 1.5-9.0 | 29.5  | 17.4-33.4 | 10.1   | 1.5-28.3      | 1.19 0 | .11-5.602  | 2.60  | 1.1-57.1                          | 27,480        | 16,000-31,200               | 31.1                                 | 9.2-66.2                           |  |            |   |            |
| 104.0 19.50-892.0 | 0 8.2  | 6.9-8.7 |       |           |        |               |        |            |       |                                   |               |                             | 47.71                                | 5.6-173.6                          |  |            |   |            |
| 45.3 8.00-235.00  | 8.1    | 6.7-8.7 | 30.9  | 27.9-35.3 | 11.4   | 4.2-33.0      | 1.36 0 | .08-6.502  | 3.20  | 0.26-9.0                          | 28.177        | 25,900-11,000               | 1.26                                 | 5.4-17.5                           | i gan  |            |   |            |
| 3.8 0.70-16.80    | 8.2    | 7.8-8.5 | 39.4  | 25.9-44.3 | 1.0    | NIL-3.70      | 0.12 N | 11-0.95 0  | 16.   | 4.0C-11V                          | 36,808        | 24,000-41,300               | 28.6                                 | 1.8-56.0                           | 19.5 N   | 11-78.0    | 13.7  | . 5-32.0   |
| 1.6 0.10-4.50     | 8.1    | 7.2-8.5 |       |           |        | £ 1           |        | 10         |       |                                   | 1977<br>1977  | 10                          |                                      |                                    |  |            |   |            |
| 45.0 10.00-245.8  | 0 7.8  | 7.0-8.6 | 30.6  | 9.8-38.3  | 4.1    | 0.6-10.9      | 0      | .02-5.401  | 8.00  | (.8-48.3                          | 28,568        | 9,000-35,900                | 51.4                                 | 18.6-100.2                         | 254.3 3  | 6.5-581.0  |   |            |
|                   |        |         |       |           |        | 0.5           | t.h    | d'al       |       |                                   | , P           |                             |                                      | 00<br>5 1                          | 011.4  | cas        |   |            |
|                   |        |         |       |           |        | .0            | 2      |            |       |                                   | М.            |                             |                                      |                                    | •••  | 8.8        |   |            |
|                   |        |         |       | 100 00    | 12 908 | 10 -<br>135.0 | the    | 18 14 1 11 | dartn | erad<br>Sarta                     | erad<br>Sarta | una<br>L.P.M.               | the<br>but-<br>hroug<br>NR<br>1.P.M. | the<br>out-<br>hroug<br>of<br>P.M. | one<br>t vit<br>pet<br>des<br>te<br>te<br>te<br>te<br>te<br>te<br>te<br>te<br>te<br>te<br>te<br>te<br>te |            | cases<br>oreals<br>one<br>t with<br>nation<br>the<br>tout-<br>the<br>tout-<br>the<br>tout-<br>the<br>tout-<br>the<br>the<br>tout-<br>the<br>the<br>the<br>the<br>the<br>the<br>the<br>the<br>the<br>the |            |

(Data supplied by Bahrain Petroleum Company 'BAPCO')

data was collected at monthly intervals in the cases of the Sitra separator outlet and at weekly intervals in the case of the other stages for a period of one year from January to December 1983 to compare it with the quality of water at different locations in Bahrain coast which is conducted during January-December, 1983 and given in chapter 2. The discharge to the sea from the refinery is 115,000 G.P.M. through outlet channel 1 (main stream) and 13,000 G.P.M. through outlet channel 2 (side stream). The discharge from Sitra separator outlet is approximately 20-30 G.P.M.

## 3.10.1.1.1 <u>Oil</u> :

Figure 3.12 indicate that the higher encountered monthly mean oil concentration was 243.8 ppm during January at Sitra Separator outlet which has an oil level range of 10.0 - 243.8ppm followed by the main stream with a concentration range of 0.70 -16.80 ppm. I.A.F. outlet has a range of 8.0-235.0 ppm. Oil concentration at the flume inlet is higher than that of the side stream outlet during some periods reflecting the effect of the main stream outlet on the adjacent waters (e.g. flume inlet).

## 3.10.1.1.2 <u>pH</u>:

Monthly mean pH at the flume inlet, main stream, side stream and Sitra separator outlet during 1983 is shown in Figure 3.12. It is noticed that there is no big fluctuation in pH in the case of flume


Monthly mean oil(ppm) and pH at the flume inlet(------), main stream(-------), side stream(------) and Sitra separator outlet(------) during 1983.

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inlet (7.9 - 8.5), main stream (7.8 - 8.5) and side stream (7.2 - 8.5). The difference is higher in the case of Sitra separator outlet (7.0 - 8.6)and I.A.F. outlet (6.7 - 8.7).

# 3.10.1.1.3 <u>Salinity</u> :

Figure 3.13 indicate that the main stream outlet salinity was always lower than that of the flume inlet by an average of 1.4%.although the mean salinity at the flume inlet (40.8%.) is lower than the monthly average salinity of Bahrain coastal waters (Figure 2.19) (excluding Tubli station because it is near to the sewage treatment plant) which means that the main stream effluent had lowered the salinity of the adjacent waters .

Figure 3.13 indicate that the lowest observed salinity with abnormal reading (9.8%.) was at Sitra separator. It increased sharply from its minimum during February to its maximum (38.3%.) during December .

I.A.F. outlet has a range (27.9% - 35.55%) lower than the yearly average of salinity at Bahrain coastal water (Figure 2.19).

3.10.1.1.4 Ammonia :

Figure 3.13 shows that the flume inlet ammonia content is always lower than that of the main stream by an average of 0.7 ppm. It has a range of nil -1.3 ppm which means that it reached a concentration higher than that observed at the various



Monthly mean salinity(ppt) and ammonia(ppm) at the flume inlet(\_\_\_\_\_), main stream(\_\_\_\_\_) and Sitra separator outlet(\_\_\_\_\_) during 1983.

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Bahrain coastal waters (Table 2.6). It reached up to a concentration of 1.3 ppm which is even higher than that of Ras Tubli station (Table 2.6). which is located at an area close to Tubli sewage treatment plant and Asker station which is close to Ras Zuwayed sewage outfall . The flume inlet has a monthly mean of 0.3 ppm which is higher than that of the overall mean ammonia (0.08 ppm) at the various Bahrain coastal stations (Table 2.6). The probable cause of the high concentration of ammonia at the flume inlet is recirculation from the main stream outlet which has a range of nil - 3.7 ppm and a mean of 1.0 ppm. Sitra separator outlet has an abnormally high concentration of ammonia. It ranged from 0.6-10.9 ppm. I.A.F. outlet has higher concentration. It ranged from 4.2 - 33.0 ppm. Therefore, certain precautions should be taken to

lower ammonia concentration at the refinery effluents.

3.10.1.1.5 Phenol :

Phenol concentration of the flume inlet (Figure 3.14) is always lower than that of the main stream outlet by an average of 0.1 ppm (Table 3.6).Phenol concentration at Sitra separator outlet is high . It ranged from 0.02 - 5.40 ppm. Table 3.6 indicate that the overall mean concentration of phenol (1.38 ppm) of the I.A.F. outlet is higher than that of Sitra separator outlet (1.33 ppm). It ranged from 0.08 - 6.50 ppm .

3.10.1.1.6 <u>Sulphides</u> :

Monthly mean sulphides at the flume inlet is 0.01 ppm.



Monthly mean phenols(ppm) and sulphides(ppm) at the flume inlet(.........), main stream(...........) and Sitra separator outlet (.........) during 1983.

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It ranged from nil- 0.1 ppm while that of the main stream outlet is 0.910 ppm and ranged from nil-30.4ppm. Table 3.6 shows that sulphides content at Sitra separator outlet is very high (mean = 18.0 ppm) and that of the I.A.F. outlet is higher (23.2 ppm) (Figure 3.14).

#### 3.10.1.1.7 Suspended solids :

Table 3.6 shows that the flume inlet has slightly higher monthly mean concentration (28.8 ppm) of suspended solids than the main stream outlet (28.6 ppm). This could be probably due to the pumping of seawater through the pump house station which cause disturbance of the bottom sediment . The highest observed monthly mean suspended solids (Figure 3.15) was at Sitra separator outlet (51.4 ppm) I.A.F. outlet has a range of 5.40- 77.5 ppm .

# 3.10.1.1.8 Chemical oxygen demand :

Monthly mean COD for the flume inlet is always bwer than that of the main stream outlet and Sitra separator outlet (Figure 3.15). It ranged from nil -38.0 ppm while the main stream COD ranged from nil-78.0 ppm. Sitra separator outlet COD is very high . It fluctuates between 36.5 - 581.0 ppm .

#### 3.10.1.1.9 Biochemical oxygen demand :

BOD was estimated for the main stream outlet only. Its monthly mean ranged from 4.5 - 32.0 ppm (Figure 3.15) . - 207 -



Figure: 3.15

Monthly mean suspended solids(ppm) and COD(ppm) at the flume inlet(•----•), main stream(•---•) and Sitra separator outlet(------). and BOD(ppm) at the main stream during 1983.

# 3.10.1.2 Water quality at different stages of BAPCO effluent treatment during 1984 :

Water analysis data at different stages of treatment during 1984 is given in Table 3.7 . These data were collected at monthly intervals in the case of the Sitra separator outlet and at weekly intervals in the case of the other stages for a period of one year from January to December 1984 to compare it with the quality of water at an area adjacent to the refinery outfalls which was conducted during 1984. Mean values with the average oil content of the main stream is greater than that of the flume inlet. Ammonia, phenols, and sulphides were also higher in the main stream. In the side stream, the average level of oil was 1.6 ppm indicating that the water carried by this channel is relatively clean with respect to this parameter .

The skim pond, contains more oil residue along with all other pollutants (Table 3.7). Since February 1984, the skim pond has been closed. Comparison of the I.A.F. inlet and outlet water analysis data presented in Table 3.7, indicates a 46.8% recovery

treatment at BAPCO refinery and Sitra separator outlet during the period January - December 1984. titluents analysis giving the contents of variuos polluting parameters at different stages of

|                       |      |           |      |         |       |           |       |          |        |          |        | -             |        |            |          |          |         | 1    |
|-----------------------|------|-----------|------|---------|-------|-----------|-------|----------|--------|----------|--------|---------------|--------|------------|----------|----------|---------|------|
|                       |      | 011       |      | μd      | AM    | AINO      | PHE   | NOLS     | SU     | LPHIDES  | CHL    | ORIDES        | SUS    | SPENDED    | CO       | 9        | B       | QC   |
| SOURCE                |      | mqq       |      |         | Ľ.    | mqc       | PI    | ma       | Ŧ      | 2S ppm   | as     | Nacl ppm      | solic  | is ppm     | dd       | e        | d       | E.   |
|                       | mean | range     | mean | range   | mean  | range     | mean  | range    | mean   | range    | mean   | range         | mean   | range      | mean     | range    | mean    | rank |
|                       |      |           |      |         |       |           |       |          |        |          |        |               |        |            |          |          | enel.   |      |
| lume inlet            | 1.39 | 0.05-3.7  | 8.2  | 7.9-8.5 | 0.27  | Nil-0.98  | 0.011 | Ní 1-0.0 | 0.161  | Nil-1.00 | 40,020 | 38,000-41,500 | 31.2   | 8.2-90.0   |          |          |         |      |
| p.3 separator outlet  | 45.9 | 3.8-256.0 | 8.6  | 7.9-9.6 |       |           |       |          |        |          |        |               | ,      |            |          |          | <u></u> |      |
| o.4 separator outlet  | 1.97 | 0.05-5.8  | 8.1  | 7.6-8.5 |       |           |       |          |        |          |        |               |        |            |          |          |         |      |
| o.5 separator outlet  | 1.53 | 0.05-3.7  | 8.1  | 7.7-8.4 |       |           |       |          |        |          |        |               |        |            |          |          |         |      |
| kim pond outlet       | 24.1 | 21.0-30.0 | 8.3  | 7.6-8.9 | 27.5  | 1.4-57.7  | 1.71  | 0.6-4.9  | 18.9   | 9.9-38.8 | 23,900 | 15,600-32,700 | 36.8   | 34.0-44.0  | 31       | -        |         |      |
| .A.F. inlet           | 38.9 | 4.7-194.0 | 8.6  | 7.8-9.7 |       |           |       |          |        |          |        |               |        |            |          |          |         |      |
| .A.F. outlet          | 20.7 | 2.6-178.0 | 8.6  | 7.8-9.6 | 29.42 | 0.44-70.6 | 3.31  | 0.1-12.  | 5 29.6 | 6.8-90.1 | 23,109 | 15,800-40,300 | 1.04   | 4.0-120.2  | 0        | 9 53 53  | 26 1    |      |
| ain stream            | 2.35 | 0.09-10.0 | 8.2  | 7.6-8.5 | 6.93  | N11-3.7   | 0.04  | Ni1-0.5  | 10.71  | Ni1-3.3  | 39,406 | 36,600-41,200 | 21.8   | 1.0-81.0   | 13.0     | 0.10-11  |         |      |
| ide stream            | 1.61 | 0.05-5.0  | 8.1  | 1.6-8.4 |       |           |       |          |        |          |        |               |        |            | 1 1 1.60 | 1 1 0 00 |         |      |
| itra separator outlet | 24.5 | 4.5-89.5  | 7.8  | 6.7-9.0 | 1.71  | 0.24-8.4  | 1.64  | 0.15-4.7 | 5 16.7 | 2.7-43.5 | 30,220 | 16,200-40,80  | 0 53.6 | 23.0-100.4 | 10.7/7   |          | :       |      |
|                       |      |           |      |         |       |           |       |          |        |          |        |               |        |            |          |          |         |      |
|                       |      |           |      |         |       |           |       |          |        |          |        |               |        |            |          |          |         |      |
|                       |      |           |      |         |       |           |       |          |        |          |        |               |        |            | 1        |          |         | 1    |

(Data supplied by Baharin Petroleum Company 'BAPCO')

of oil in the I.A.F. unit and the final adjustment of pH to an average value of 8.6. In the I.A.F. outlet, the other contaminants are fairly high and these go directly to the open channel 1 and then to outlet channel 1. There is a considerable dilution of the 7000 G.P.M. of treated oily process water (I.A.F.outlet) to 115,000 G.P.M. by mixing it with cleaner water from subsystems 1,2,3,5,6, and 7 (Figure 3.4) thereby lowering of the concentrations of all the polluting ingredients in the final discharge of outlet channel 1 (main stream)as seen from the values of Table 3.7.

The pollutant composition and the polluting potential of the main and side streams described above is less than that of the Sitra separator outlet (Table 3.7).

Heavy metals and cyanide were estimated at the main stream effluent. Results are shown in Table 3.8 .

The discharge from BAPCO has been continuous for the last 45 years with varying quantities depending upon the volume of oil being processed . Table 3.7 reveals that the values of the flume inlet and main stream are fairly close except

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Heavy metals and cyanide concentrations in the main stream outlet during 1984.

| metal      | Concentration<br>ppm |
|------------|----------------------|
| Copper     | < 0.010              |
| Zinc       | < 0.025              |
| Lead       | < 0.050              |
| Iron       | 0.030                |
| Cadmium    | < 0.040              |
| Nickel     | 0.002                |
| Arsenic    | < 0.010              |
| Manganeese | < 0.025              |
| Mercury    | < 0.010              |
| Cyanide    | < 0.100              |
|            |                      |

for ammonia and sulphides. The Sitra separator outlet has, however, values closer to those of the skim-pond outlet indicating heavy pollution by the effluent discharge at Sitra .

Since Salba Bay is a shallow enclosed body of water, the mixing of Bay water with the open waters of the sea is low. This has enhanced the problem of pollution. The discharge from the main stream has accumulated the pollutants in the Bay for the last 45 years. The progressive decrease of all pollutants at the stations from outlet to offshore indicates this accumulation .

It is of interest to compare the effluent analysis data of some modern and old refineries and the limit values prescribed by selected countries with that of BAPCO refinery (main stream)(Table 3.9). It would be seen from this table that the values for oil, phenol, ammonia and sulphide are within the limits prescribed by the different industrialized countries and some of the modern refineries. However, the per day discharge of effluents is higher for BAPCO and as such the effluent load being received by the semi-stagnant enclosed Bay for the last 45 years is reflected in the pollutant accumulation and eutrophication of Salba Bay .

Table 3.10 shows the difference between the water quality data of the I.A.F. inlet and outlet. The table indicates that there is no significant difference between the concentrations of pollutants

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Example of concentration in effluent vater in two mudern refinerles (Germany and Britain), one old Swedish refinery and the BAPCO refinery and limit values, in mg/l for the EEC countries and USA and in kg/l ONO barrels of crude oil for Cauada (From Baker, 1979)

| Country                                | Discharged<br>amount | 8005 |            | COD    | 110   |        |                    | Phenols   |                       | Armonia |                         | Sulphide    |                    |
|--|----------------------|------|------------|--------|-------|--------|--------------------|-----------|-----------------------|---------|-------------------------|-------------|--------------------|
|  | ۲۴۵/۴m               | 1/bw | kg/day     | mg/1   | 1/b.  | kg/day | kg/1000<br>barrels | mg/l kg/d | ay kq/1000<br>barrels | mg/1 kg | /day ky/1000<br>barrels | Yeb/gy 1/gm | kg/1000<br>barrels |
| Germany                                |                      | 20   |            | 100    | 2     |        |                    | 0.2       |                       |         |                         |             |                    |
| One modern German<br>coastal refinery  | 10 400               |      | 260        |        |       | 73     |                    | v         |                       |         |                         | •           |                    |
| United Kingdom                         |                      | 8-25 |            | 20-400 | 20-50 |        |                    | F-1       |                       | 4-15    |                         | 1-5         |                    |
| One modern British<br>coastal refinery | 19 000               |      |            |        | 25    | 475    |                    | 15 E      |                       | 8       |                         |             |                    |
| Italy                                  |                      | 40   |            | 160    | s     |        |                    | 0.5       |                       | 12      |                         |             |                    |
| NSA                                    |                      | 15   |            | 80-115 | s     |        |                    | 0.1       |                       | :       |                         | - 0         |                    |
| Canada                                 |                      |      |            |        |       |        | 2.5                |           | 0.25                  |         | 36                      |             |                    |
| Old Svedish<br>refinery                | 45 000               |      | 500 (BOD,) |        |       | 100    | 133                | 10        |                       |         | 2                       |             | 41.0               |
| The BAPCO<br>refinery                  | 650 000              | 42   | 1 6,00     | (12    | 2.9   | 1 900  | 7.5                | 0.14 91   | 0.36                  | 1.1 70  | 2.7                     | 0 5 10      | -                  |
|  |                      |      |            |        |       |        |                    |           |                       |         |                         |             |                    |

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The difference between water quality data of I.A.F. inlet and outlet.

| Va<br>fe<br>Va | DATE           | OIL<br>ppm | рн  | AMMUNIA<br>as N. ppm | PHENOLS | SULPHIDES | CHLORIDES<br>as NaCl ppm | SUSPENDED<br>SOLIDS ppm | COO<br>ppm | 800<br>ppm |
|----------------|----------------|------------|-----|----------------------|---------|-----------|--------------------------|-------------------------|------------|------------|
| I.A.F. INLET   | 11.6.84        | 13.7       | 8.7 | 38.10                | 4.80    | 31.4      | 21,700                   | 122.0                   | 145        | 81         |
| 1.A.F. QUILET  | ospha<br>1 3.1 | 7.3        | 8.8 | 24.60                | 4.40    | 28.3      | 21,400                   | 26.0                    | 112        | 52         |
| I.A.F. INLET   | 16.7.84        | 8.9        | 8.2 | 1.10                 | 0.98    | 11.5      | 40,500                   | 31.7                    | 124        |            |
| I.A.F. OUTLET  | 7 0.075        | 5.3        | 8.2 | 0.74                 | 0.95    | 10.2      | 40,300                   | 16.8                    | 108        |            |
| re             | rines          |            |     |                      |         |           |                          | 144- 178 -              |            |            |

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of the I.A.F. inlet and outlet which means that the treatment process of the I.A.F. unit is fairly inefficient. The average oil content in the outlets of the No. 3 separator was 45.9 ppm (range : 3.8-256.0) and that of the Sitra separator was 24.5 ppm (range : 4.5 - 89.5) which indicate the inefficiency of these separators in the removal of oil.The Sitra separator outlet needs more attention as all the pollutants there are on the higher side creating a pollution hazard.

# 3.10.1.3 <u>Water quality in the vicinity of BAPCO refinery and</u> oil storage tanks outfalls :

Water quality data at areas adjacent to BAPCO outfalls during 1980 and 1986 is shown in Table 3.11 . Water sampling stations and distribution of water temperature, salinity, ammonia, nitrate, nitrite and phosphate during 1980 are shown in Figures 3.9 , 3.16 and 3.17.

Water quality data at surface and bottom of Salba Bay and adjacent waters in the vicinity of BAPCO refinery discharge system during 1984 are given in Tables 3.12, 3.13 and 3.14 , while Figures 3.10 and 3.18 to 3.23 show locations of water sampling stations, surface distribution of pH, salinity ammonia, nitrite, nitrate and phosphate during 1984 and 1986.

# 3.10.1.3.1 Temperature :

No temperature determination was done during 1980. Air temperature in the Bay fluctuated during 1984 between 32.5 and 36.5°C while the water temperature varied rather broadly between 26.0 to 40.0°C.Water

Water quality data at areas adjacent to BAPCO refinery discharges.

| DATE                                  | STATION        | ATHOSPHERIC                  | WATER | SALINITY | pH   | ug/1  |          |         |        |
|---------------------------------------|----------------|------------------------------|-------|----------|------|-------|----------|---------|--------|
|                                       | a construction | °c                           | °c    | 2        |      | PO4-P | NO3-N    | NO2-N   | NH4-N  |
| 1000                                  | 12.1           | 1000                         |       |          |      |       |          |         |        |
| May, 1900                             |                |                              | 38.0  | 39.3     | -    | 48.0  | 12.3     | 8.1     | 661.0  |
|                                       |                | -                            | 37.0  | 39.3     | -    | 23.3  | 11.2     | 7.6     | -      |
|                                       | G              | -                            | -     | 39.6     | -    | -     | 9.7      | -       | -      |
|                                       |                | -                            | 36.0  | 40.3     | -    | 20.9  | 7.3      | -       | 493.0  |
|                                       |                | -                            | 28.0  | 41.1     | -    | -     | 6.9      | 5.0     | 17.4   |
|                                       |                |                              | 28.0  | -        | -    | 10.2  | 6.2      | 4.0     | 5.0    |
|                                       | A States       | -                            | -     | 39.6     | -    | 18.2  | -        | -       | \$78.0 |
| **********                            |                | -                            | 25.0  | -        | -    | 5.3   | 6.3      | 3.9     | -      |
| 1 Garden                              |                | -                            | -     | 40.6     | -    | 23.3  | 8.6      | -       | 439.0  |
| Angl1 1986                            | 94             | -                            | 27.0  | 40.1     | -    | 5.3   | 5.2      | 3.9     | 29.0   |
| April, 1986                           | 104            |                              | -     | -        | 8.15 | -     | 60.6     | 1.6     | 43.5   |
|                                       | IUA            | -                            | -     | -        | -    | -     | -        | -       | -      |
| CENTRY AND                            | IIA            | 1                            | -     | 42.2     | -    | 10.2  | 71.7     | 2.4     | 216.0  |
|                                       | 12A            | 30.0                         | 31.5  | 42.2     | 8.30 | 4.0   | 66.5     | 6.4     | 122.   |
| and the second second                 | 1 JA           | 30.0                         | 31.5  | 44.7     | 8.30 | 5.3   | 51.4     | 5.6     | 81.    |
| Setting.                              | 14A            | 30.0                         | 31.5  | 45.0     | 8.29 | 4.0   | 40.1     | 4.9     | 69.1   |
| "Same Part                            | 154            | 30.0                         | 29.5  | 42.4     | 8.22 | 1.7   | 25.6     | 3.8     | 41.    |
| an Barrister and                      | 16A            | 31.0                         | 30.5  | 42.1     | 8.47 | 6.8   | 50.9     | 2.4     | 0.00   |
|                                       | 174            | -                            | -     | 42.1     | 8.11 | -     | -        | 2.5     | 114.   |
|                                       | 18A            | -                            | -     | 42.1     | -    | 7.9   | 66.8     | 1.2     | -      |
| ····································· | 19A            |                              | -     | -        | 8.20 | 6.8   | -        | 1.6     | -      |
| **********                            | 204            | -                            | -     | 42.8     | 8.15 | 8.5   | 52.1     | 1.2     | -      |
|                                       | 214            | -                            | •     | 42.4     | -    | -     | 68.2     | 1.2     | 33.    |
| 22242233333                           | 224            | and the second second second | -     | 42.2     | -    | -     | -        | 1.9     | -      |
|                                       | 6C             |                              | -     | 43.0     | -    | -     |          | 1.6     | -      |
| State of the second                   | 70             | -                            | -     | -        | 8.15 | -     | 1.000-00 | 100.000 | -      |
| AND ADDRESS OF TAXABLE PARTY.         | 80             | -                            | -     | -        | 8.13 | 6.8   | -        | 1.6     | -      |
|                                       | 90             | -                            | -     | 42.9     | -    | -     | 34.7     | -       | -      |
| Charles States                        | 100            | -                            | -     | -        | -    | -     | 59.9     | 1.9     | -      |
|                                       | 110            | -                            | •     | 42.9     | 8.13 | -     | -        | -       | 10.5   |
|                                       | 120            | -                            | -     | 42.4     | -    | 7.9   | -        | 1.6     | -      |
|                                       | 13C            | -                            | -     | •        | -    | -     | -        | -       | -      |
|                                       | 140            | -                            | •     | 43.2     | 8.15 | -     | 40.1     | 1.9     | -      |
| Flgure:                               | 150            | -                            | -     | -        | -    | 8.5   | -        | 1.6     | -      |
|                                       | D              | -                            | 32.0  | 42.2     | 7.86 | 12.0  | 95.5     | 5.6     | 53.4   |
|                                       | 10             | 29.5                         | 26.0  | 43.4     | 8.31 | 10.2  | 64.8     | 5.6     | -      |
|                                       | 20             | 32.0                         | 27.5  | 43.6     | 8.33 | 10.2  | 76.3     | 5.2     | 7.3    |
| DISCULT                               | 30             | 32.0                         | 27.5  | 43.3     | 8.33 | 8.5   | 63.8     | 4.9     | 7.3    |
| A Contraction                         | 40             | 28.0                         | 25.0  | 43.9     | 8.33 | 5.3   | \$7.9    | 4.9     | 7.3    |
| I way to a                            | 50             |                              | -     | -        | 8.28 | 4.0   | 42.0     | 1.9     | 5.5    |
|                                       | 20             | 28.0                         | 24.0  | 43.0     | 8.39 | 5.3   | 48.4     | 4.3     | 0.5    |
| and the second second                 | 80             | 32.0                         | 27.5  | 42.8     | 8.34 | 6.8   | 63.7     | 4.3     | 0.5    |
|                                       | 90             | 31.5                         | 27.0  | 42.8     | 8.37 | 4.0   | 62.4     | 4.3     | 0.004  |
|                                       | 100            | 31.5                         | 26.5  | 42.8     | 8.39 | 1.7   | 62.1     | 4.3     | 0.001  |
|                                       | 110            | 24.0                         | 24.0  | 42.1     | 86   | 4.0   | 57.5     | 2.8     | -      |
|                                       | 120            |                              | •     | 42.4     | 8.12 | 6.0   | 61.0     | 1.2     | 32.0   |
|                                       | 130            | -                            | •     | 42.2     | -    | 11.0  | 68.0     | 1.2     | 27.0   |
|                                       | 140            | -                            | •     | 42.4     | 8.08 | 6.8   | 59.1     | 1.2     | 15.3   |
|                                       | 150            | -                            | •     | •        | 8.12 | -     |          | 1.6     | 2.2    |
|                                       | 150            | -                            | •     | •        | 8.15 | -     | -        | -       | 7.3    |
|                                       | 160            | -                            | -     | -        | 8.16 | 12.0  | -        | 1.2     | 3.7    |
|                                       | 1/0            | -                            | •     | 41.0     | 8.14 | -     | -        | 1.6     | -      |
|                                       | 180            | -                            |       | -        | 8.16 | -     | 1 50 0   | 1 1 2   | 1 10 5 |



Distribution of water temperature and salinity (May, 1980).

Figures 3/17

May 1980



Distribution of ammonia, nitrate, nitrite and phosphate, May 1980.

Surface and bottom water quality data from Salba Bay and adjacent areas in the vicinity of BAPCO refinery discharge system. May, 1984

| (m)            | (°C) |      | ( mg    | /1)    |         |        | •;                                      |        |
|----------------|------|------|---------|--------|---------|--------|---|--------|
|                |      |      |         |        |         |        | , · · · · · · · · · · · · · · · · · · · | •      |
|                |      |      | SURFACE | BUTTUM | SURFACE | воттом | SURFACE                                 | BUTTOM |
|                | -    |      |         |        |         |        |   |        |
| A –            | -    | 40.0 | -       | -      | 8.64    | -      | 40.0                                    | -      |
| 1A 0.5         | 34.0 | 39.0 | 7.5     | -      | 8.50    | -      | 42.0                                    | -      |
| 2A 1.0         | 36.5 | 39.0 | 7.6     | 7.6    | 8.48    | 8.40   | 41.5                                    | 41.0   |
| <b>3A</b> 3.0  | 34.4 | 39.0 | 7.6     | 6.1    | 8.39    | 8.32   | 42.0                                    | 41.5   |
| 4 <b>A</b> 3.0 | 34.0 | 30.5 | 7.7     | 6.8    | 8.37    | 8.33   | 43.0                                    | 42.0   |
| 5A 1.5         | 34.5 | 36.0 | 7.8     | 6.8    | 8.40    | 8.38   | 42.5                                    | 42.0   |
| 6A 4.0         | 32.5 | 31.0 | 7.7     | 6.8    | 8.37    | 8.37   | 42.5                                    | 43.0   |
| 7A 4.5         | 34.0 | 30.0 | 8.0     | 7.9    | 8.33    | 8.34   | 41.5                                    | 42.0   |
| 8A 5.0         | 34.0 | 29.5 | 8.6     | -      | 8.30    | 8.32   | 40.5                                    | 41.8   |
| B -            | -    | 26.0 | -       | -      | 8.10    | -      | 41.0                                    | -      |
| C   -          | -    | 36.0 | -       | -      | 8.40    | -      | 41.0                                    | -      |
| 1C 2.0         | -    | -    | 7.1     | -      | 8.46    | 8.30   | 41.0                                    | 39.5   |
| 2C 1.0         | 35.0 | 28.0 | 7.1     | -      | 8.31    | 8.33   | 43.0                                    | 42.0   |
| 3C 3.5         | 36.5 | 30.0 | 8.0     | -      | 8.26    | 8.32   | 44.5                                    |        |
| 4C 1.3         | 36.0 | 30.0 | 7.2     | -      | 8.35    | 8.36   | 43.3                                    | 42.0   |
| 5C 3.0         | 36.0 | 27.0 | 7.4     | -      | 8.35    | 8.36   | 44.3                                    | 42.0   |
| D -            | -    | 34.0 | -       | -      | 7.84    | -      | 40.5                                    | -      |
|                |      |      |         |        |         |        |   |        |

Nitrogen and phosphorus salts (in  $\mu g/l$ ) at the surface and bottom in Salba Bay and adjacent waters in the vicinity of BAPCO refinery discharge system. May, 1984.

| STATION   | PHOSPHATE-<br>PO <sub>4</sub> -   | PHOSPHORUS<br>P  | NITRATE-<br>NO <sub>3</sub>  | NITROGEN<br>- N   | NITRITE-<br>NO  | -NITROGEN<br>2 <sup>-</sup> N                                       | AMMONIA-<br>NH2   | NITROGEN   |
|---|---|--|--|---|---|---|---|--|
|   | SURFACE   | BOTTOM   | SURFACE  | BOTTOM  | SURFACE   | BOTTOM  | SURFACE   | BOTTOM   |
| A<br>1A<br>2A<br>3A<br>4A<br>5A<br>6A<br>7A<br>8A<br>B<br>C<br>1C | 69.5<br>-<br>48.0<br>48.0<br>18.4<br>31.6<br>36.5<br>23.3<br>26.6<br>30.0<br>23.3<br>41.4 | -<br>59.6<br>50.0<br>36.5<br>34.8<br>28.2<br>43.1<br>50.0<br>-<br>50.0 | 119.3<br>-<br>69.4<br>78.6<br>69.0<br>85.7<br>80.9<br>100.6<br>59.0<br>57.6<br>264.6<br>24.3 | -<br>77.3<br>84.4<br>75.0<br>74.0<br>73.0<br>76.7<br>15.6<br>-<br>-<br>23.7 | 10.8<br>-<br>7.9<br>6.4<br>3.9<br>4.9<br>2.4<br>2.2<br>1.6<br>1.9<br>2.4<br>1.9 | -<br>-<br>7.7<br>2.2<br>1.9<br>4.6<br>2.2<br>1.9<br>2.4<br>-<br>2.2 | 740.0<br>-<br>526.0<br>415.0<br>194.0<br>342.0<br>80.0<br>37.0<br>43.5<br>140.0<br>55.2<br>40.5 | -<br>479.0<br>282.0<br>128.7<br>232.0<br>37.0<br>40.5<br>45.1<br>-<br>53.4 |
| 20  | 12.0  | 38.1   | -  | 28.3  | 1.9   | 2.2   | 46.6  | 45.1   |
| 40  | 6.8   | 4.0  | 17.6   | 30.9  | 2.8   | 2.2   | 37.0  | 40.5   |
| 5C  | 24.9  | 15.1   | 37.1   | 39.4  | 2.8   | 2.2   | 48.6  | 51.7   |
| D   | 234.8   | -  | 13.4   | -   | 50.2  | -   | 6120.0  | -  |

Oil, phenols, sulphides, suspended solids, COD and BOD concentrations at the surface and bottom in Salba Bay and adjacent waters in the vicinity of BAPCO refinery discharge system. May, 1984.

| STATION   | 011<br>ppr   | L.<br>N  | PHEN<br>PP   | OLS<br>m   | SULPH<br>AS H<br>ppm   | ides<br>2 <sup>S</sup>   | SUSPE:<br>SOLI<br>PPM  | NDED<br>DS<br>1  | CC<br>Pf  | )D<br>om                            | BO   | D   |
|---|--|--|--|--|--|--|--|--|---|-------------------------------------|--|---|
|   | <b>SURFACE</b>   | BOTTOM   | SURFACE  | BOTTOM   | SURFACE  | BOTTOM   | SURFACE  | BOTTOM   | SURFACE   | BOTTOM                              | SURFACE                                      | BOTTOM  |
| A<br>1A<br>2A<br>3A<br>4A<br>5A<br>6A<br>7A<br>8A<br>8<br>C | 1.6<br>1.1<br>-<br>1.0<br>0.5<br>0.5<br>0.4<br>0.3<br>0.3<br>1.1<br>1.2<br>1.1 | -<br>1.1<br>-<br>0.7<br>0.4<br>0.5<br>0.5<br>0.3<br>NIL<br>-<br>-<br>NIL | 0.01<br>-<br>0.01<br>0.01<br>0.01<br>0.01<br>0.01<br>NIL<br>0.01<br>NIL<br>NIL | -<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>- | 0.50<br>0.95<br>0.58<br>0.42<br>0.42<br>0.42<br>0.42<br>0.42<br>0.42<br>0.42<br>0.04<br>0.17<br>0.01 | -<br>0.88<br>0.58<br>0.42<br>0.42<br>0.42<br>0.83<br>0.58<br>0.09<br>-<br>-<br>- | -<br>38.2<br>24.9<br>18.2<br>17.8<br>19.0<br>18.2<br>9.2<br>-<br>45.6<br>5.0<br>26.8 | -<br>37.5<br>24.5<br>30.2<br>18.4<br>19.0<br>18.4<br>5.6<br>-<br>- | 10.0<br>-<br>10.0<br>10.8<br>-<br>-<br>2.1<br>6.0<br>-<br>118.8 | -<br>9.0<br>4.3<br>-<br>2.5<br>10.0 | 7.0<br>-<br>-<br>-<br>3.0<br>3.0<br>-<br>1.0 | -<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>- |
| 2C  | NIL  | NIL  | NIL  | NIL NIL  | 0.13   | 0.04   | 31.0   | 15.1   | 6.0   | 8.0                                 | 4.0  | 4.0   |
| 3C  | NIL  | NIL  | NIL  | NIL  | 0.13   | 0.09   | 33.0   | 20.0   | 9.0   | 9.0                                 | 3.0  | 3.0   |
| 4C  | 0.7  | NIL  | NIL  | NIL  | 0.13   | 0.13   | 23.2   | 33.3   | 8.0   | 11.0                                | 3.0  | 4.0   |
| SC  | NII  | 0.3  | NIL  | NIL  | 0.17   | 0.17   | 24.3   | 28.4   | 9.0   | 10.0                                | 4.0  | 4.0   |
| D   | 30.0   | -  | 0.20   | -  | 9.9  | -  | 51.5   | -  | 202.5   | -                                   | 25.0   | -   |



Surface distribution of pH.

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Surface distribution of salinity.

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Surface distribution of ammonia.

- 224 -



Surface distribution of nitrite.

- 225 -



Surface distribution of nitrate.



Surface distribution of phosphate.

temperatures at the mouth of the outlets were  $40.0^{\circ}$ C at the outlet of channel 1 (main stream) and  $36.0^{\circ}$ C at the outlet of channel 2(side stream). The temperatures gradually dropped at the subsequent stations seawards. Contrary to the normal temperature pattern, the water temperatures nearer the outlets were higher than the atmospheric temperature while at the seaward stations ( stations 4A , 8A , 2C , 3C , 4C and 5C ) the reverse was the case (Table 3.12) . The difference between water temperature at stations near the discharge and those away from it is approximately  $10 - 14^{\circ}C$ which indicates thermal pollution in the vicinity of the discharge .

In 1986, unlike the temperature of Salba Bay (near the main stream discharge), atmospheric temperature in an area near the Sitra separator outlet is always higher than water temperature, but again water temperature decrease as we go away from the discharge from  $32.0^{\circ}$ C at station D (Sitra separator outlet) to  $24.0^{\circ}$ C at station 10D (Table 3.11), a difference of  $8.0^{\circ}$ C which is not as big as that near the main stream outlet ( $14.0^{\circ}$ C) as shown in Table 3.12.

3.10.1.3.2 pH :

No pH data in 1980, for 1984 and 1986 the lowest pH was at station D situated at the Sitra separator outlet while the highest was at the main stream outlet. Opposite the main stream effluent (Salba Bay), pH decreases as we go away from the discharge from its highest concentration (8.64) at the discharge point to 8.11 and 8.13 at the distant stations (Figure 3.18). The reverse is true opposite the Sitra separator outlet, pH increase as we go away from the discharge from its minimum (7.86) to 8.46 at the distant stations. This means that the main stream outlet pH is higher than that of the sea while that of the Sitra separator outlet is lower than the pH of the sea.

#### 3.10.1.3.3 Dissolved oxygen :

Dissolved oxygen was measured during 1984 only . It was noticed that its concentration was less at the bottom samples in comparison to the surface except at station 2 A where the recorded values were the same . Probably because of the effect of the pump house station.

# 3.10.1.3.4 Salinity :

Figures 3.16 and 3.19 indicate that salinity increases in all years as we go away from the discharges reflecting the effect of the low salinity of the effluents . Although salinity at the offshore stations is lower than at the inshore ones, the salinity at the discharge point is even lower than at the offshore stations as could be seen from Figure 3.19 (e.g. station A '40.0%.' and station 8A '40.5%.'). It fluctuated between 39.3%. near the main stream discharge point (Figure 3.16) to 45.0% at the semienclosed area at station 14A (Figure 3.19). In Salba Bay, surface salinities were higher than those at the bottom in all the stations except stations 6A to 8A which were far from the discharge (Table 3.12).

#### 3.10.1.3.5 Ammonia :

For all the years, ammonia-nitrogen in Salba Bay

showed a gradual decline from station A (main stream) to station 7A (Table 3.13). Station 5A being situated within the Bay and nearer the station A(Figure 3.10), again showed a high ammonia content. Similarly, station B situated in the inlet flume but in the course of the deflected drift showed an elevated value for ammonia. Of the stations situated south of the pump house, station C (side stream) had a higher ammonia content. Bottom values for ammonia were lower than surface values at station A to 6A and 3C. For the remaining stations, they were only marginally higher .

Figure 3.17 and 3.20 indicate that ammonia concentrations at both the main stream and Sitra separator outlet areas decrease as we go away from the discharge points. The highest encountered concentration was at the main stream effluent (740.0  $\mu$ g/1). The ammonia concentration at the stations near the Sitra separator outlet is lower than those near the main stream outlet .

#### 3.10.1.3.6 Nitrite :

Nitrite concentration in all years showed the same declining trend from the outlet towards the offshore stations as was indicated by ammonia (Figures 3.17 and 3.21) with the highest observed concentration  $(10.8 \ \mu g/1)$  at the main stream effluent .

# 3.10.1.3.7 Nitrate :

Nitrate concentration in all years declined from higher concentrations at the main stream effluent

to lower concentrations at the distant stations (Figures 3.17 and 3.22), but the levels showed a variation from year to year with lower levels throughout 1980, while 1984 and 1986 were similar to each other.

#### 3.10.1.3.8 Phosphate :

Phosphate in all years (Figures 3.17 and 3.23) exhibits the same pattern as ammonia, nitrite and nitrate with  $48 - 69 \ \mu g/l$  near the effluent, and  $5 - 7 \ \mu g/l$  at distant stations which indicate that the concentration of phosphorus and nitrogen salts near the discharge points are higher than at the other stations .

Oil, phenols, sulphides, suspended solids, chemical and biochemical oxygen demand were determined at surface and bottom during 1984 only.

Oil content showed the same concentration trend as ammonia from the outlet to the subsequent stations (Table 3.14). The highest oil content was noticed at the Sitra separator outlet. The bottom values for oil were somewhat lower than the surface values. Phenols exhibited a stable distribution initially but fell subsequently. The Sitra separator outlet, however, had a higher value for phenols. The trends in sulphides and suspended solids were the same as in the earlier parameters for all stations with the Sitra separator oulet (station D) exhibiting the highest values. Surface hydrogen sulphide was low at the offshore stations 7A and 8A, but at other stations at Salba Bay it was high . The highest  $H_2S$  value of 9.9 ppm was noticed at the Sitra separator outlet. The bottom  $H_2S$  was mostly the same as or higher than that of the surface and among the bottom values, those of the stations within Salba Bay were higher (Table 3.14) .

The COD and BOD values were highest at the Sitra separator outlet . The side stream outlet (station C) showed a high value of COD .

It is felt that high levels of nitrogenous and phoshorous compounds in Salba Bay have induced the growth of bluegreen algae (Figure 3.24) which have then harbored the sulphur reducing bacteria which releases hydrogen sulphide and creating a black slimy bottom. The oil globules are invariably seen floating on the water surface and the entire see area looks black from a distance. The discharge from the main stream has created a black colored drift flowing along the shore adjacent to the road to the pumphouse. With low wind and wave action in this semienclosed Bay, this black drift is often clearly seen moving offshore to the north or south. The drift gradually mixes with the offshore waters somewhere near station 7S (Figure 3.11). No



The growth of bluegreen algae in the final effluent channel (main stream outlet).

schools of fishes were sighted in this area except the inlet enclosures and the fauna appears to be resticted to some species such as Grouper, Silversides, Haffara bream and Spotted halfbeak . Some shore crabs, isopods and amphipods were seen moving on exposed rocks of the dyke near the pump house (Figure 3.25).

#### 3.10.2 Sediment quality :

The bottom sediments, when analysed for their organic carbon and organic matter content, showed the same trend of higher values near the outlet and declining progressively at the other stations depending on their distance from the outlet (Table 3.15). The particle grading of these sediment samples (Table 3.16) indicate the existence of particles smaller than 0.090 mm in fair quantities especially at stations near the shore. Figure 3.26 show sediment samples collected from different stations (see Figure 3.11). Figure 3.27 show sediment particle size analysis: cumulative phi curves .

In light of the high organic matter at stations 1S to 5S, its anaerobic oxidation and the consequent creation of a black bottom containing hydrogen sulphide is understandable. Hydrogen sulphide is given off when organic matter decomposes in sediments. If oxygen is deficient, iron salts are converted to ferrous sulphide, which colours the sediment black. If the amount of hydrogen sulphide is in excess of the amount of iron available, then free hydrogen sulphide permeates the interstitial water and may extend into the water above. The permissible level

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The booms and dyke enclosing the pump house. (Salba bay on left).

% organic carbon and % organic matter at stations 1s to 7s.

| Station No. | % organic carbon | % organic matter |
|-------------|------------------|------------------|
| 15          | 8.69             | 15.65            |
| 2 S         | 8.16             | 14.95            |
| 3 S         | 8.13             | 14.49            |
| 4 S         | 4.27             | 8.04             |
| 5 S         | 3.08             | 5.86             |
| 6 S         | 2.42             | 4.76             |
| 7 S         | 1.28             | 2.86             |
|             |                  |                  |
**Table: 3.16** 

Cumulative medium sand 000.001 0.330mm 86.292 3.226 7.475 12.990 31.562 19.833 48.994 56.173 64.687 71.962 81.551 13.551 19.852 23.637 STATION 7 S +1.58 ~ Cumulative 2 ut. 7.179 8.514 9.589 13.707 3.226 4.249 5.515 2.561 3.785 7.925 9.161 7.275 4.741 sleve 4.301 8.271 uo 0.130mm muddy sand 100-001 STATION 6 S +3.00 0.732 2.234 6.336 0.30 1.326 1.901 3.541 13.968 24.685 38.901 50.213 60.157 67.071 2 0 X wt. Cumulative X wt. sleve 0.575 32.929 0.594 14.216 6.914 50 0.304 0.428 0.333 1.307 7.630 10.717 11.312 9.944 2.797 0 0.130mm STATION 5 S muddy sand 100.000 73.634 0.378 +3.00 0.162 0.550 0.729 1.147 2.217 6.043 16.424 34.826 49.641 62.691 0 0 ~ 10.943 26.366 0.216 0.179 0.418 14.815 13.050 0.162 0.172 1.070 3.826 18.402 sleve 10.381 **Б**0 0 0 7 wt. Cumulative < 0.063mm 100-000 STATION 4 S >+4.00 mud 19.017 0.174 0.188 0.172 0.172 0.172 0.385 0.739 1.793 3.915 5.429 6.213 0.172 0 2 sleve 12.804 80.982 0.002 0.014 1.514 0.172 0.197 0.354 1.054 2.122 0.784 5 000 0 **Sumulative** 0.088mm 100-001 S 41.270 65.062 3.483 50.713 0.199 1.200 5.043 13.333 16.102 muddy sand 0.126 0.348 0.704 162.83 +3.49 STATION 3 2 2 wt. sleve 14.349 12.679 0.126 0.03 0.149 0.356 0.496 2.283 1.560 8.290 2.769 12.489 9.443 766.46 8 0 **Cumulative** 0.088m 100.000 32.958 51.192 65.574 S 0.000 0.417 4.673 6.173 16.102 muddy sand 0.987 1.317 2.031 3.041 9.241 21.622 +3.49 STATION 2 2 " NE sieve 14.382 34.515 11.336 18.234 0.570 0.330 1.010 1.632 1.500 5.520 0.090 0.327 0.714 3.068 6.861 8 **Dumulative** 0.080mm 100-000 0.198 0.217 0.228 0.390 0.465 0.778 1.533 4.083 6.093 0.276 25.873 28.973 53.383 38.293 muddy sand +3.70 2 STATION 1 S 7 wt. sieve 0.019 0.114 0.198 0.048 0.313 2.550 2.010 0.011 0.075 0.755 19.780 46.620 3.100 9.320 15.090 50 m.p.d. 0.710 0.500 0.355 0.250 0.180 0.125 0.063 0.000 د 0.063 -uado Sieve > 5.6 4.0 2.8 2.0 4.1 1.0 g ing -2.0 -1.5 -1.0 -0.5 0.0 +0.5 +1.0 +1.5 +2.0 +2.5 +3.0 +3.5 4.0 Ø

Particle size distribution at stations 1 S to 7

Ś



# Figure: 3.26

Sediment samples collected from stations 1S tO 7S.



PHI Unit

# Figure: 3.27

Sediment particle size analysis: Cumulative Phi Curves.

of organic matter in a discharge is less than 15%. The constant accumulation of organic matter in Salba Bay, however, has brought it to its present state of high organic contamination .

Further, the particles less than 90 µm were found more in sediments at stations nearer to the outlet. This silt has blocked the aeration and interstitial spaces of the sediment thereby eliminating the epifauna and infauna. The black color of the sediments at stations 1S to 4S is due to an anoxic layer created by the fine silt and clay. The deposits at stations 5S to 7S have less silt and lesser organic load being away from the point of discharge of the effluent. As such, the color of the sediment here is turning from black to gray (Figure 3.26).

The relation between % organic matter and median particle diameter of the sediment samples is shown in Figure 3.28. When the regression is determined for the seven stations. A poor correlation is obtained with a regression of 0.54 as follows :

| Station | Median<br>particle<br>diameter | % organic<br>matter |
|---------|--------------------------------|---------------------|
|         | (x)                            | (y)                 |
| 15      | + 3.70                         | 15.65 🔺             |
| 25      | + 3.50                         | 14.98               |
| 3S      | + 3.50                         | 14.49               |
| 4S      | + 4.70                         | 8.04                |
| 5S      | + 3.00                         | 5.86                |
| 6S      | + 3.00                         | 4.76                |
| 7S      | +1.58                          | 2.86                |
|         |                                |                     |

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n = 7  

$$\bar{x} = 3.28$$
  
 $\bar{y} = 9.52$   
 $\bar{y} = 9.52$   
 $\bar{y} = 22.98$   
 $\bar{y} = 66.64$   
 $\bar{y} = 80.77$   
 $\bar{y}^2 = 809.10$   
 $\bar{y} = 235.21$   
 $1/n(\bar{y}x)^2 = 75.44$   
 $1/n(\bar{y}y)^2 = 634.41$   
 $1/n(\bar{y}x)(\bar{y}y) = 218.76$   
 $\bar{y}(\bar{y}-\bar{y})^2 = 174.69$   
 $\bar{y} = 9.52$ 

$$b = \frac{\Sigma(x-\bar{x}) (y-\bar{y})}{\Sigma(x-\bar{x})^2}$$

$$=$$
  $\frac{16.45}{5.33}$  = 3.08

$$a = \bar{y} - b\bar{x}$$
  
= 9.52 - 10.10 = 0.058

$$y = a + bx$$

y = -0.58 + 3.08 x

$$r = \frac{\sum (x - \bar{x}) (y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2 \sum (y - \bar{y})^2}} = \frac{16.45}{\sqrt{5.33 \times 174.69}} = \frac{16.45}{30.51} = 0.54$$

Hence, stations 1S, 2S and 3S which are close to the refinery main stream were omitted and a good correlation obtained with a regression of 0.97 as follows :

| Station | median<br>particle<br>diameter | %<br>organic<br>matter |  |  |
|---------|--------------------------------|------------------------|--|--|
|         | (x)                            | (y)                    |  |  |
| 4 S     | 4.70                           | 8.04                   |  |  |
| 5 S     | 3.00                           | 5.86                   |  |  |
| 6 S     | 3.00                           | 4.76                   |  |  |
| 7 S     | 1.58                           | 2.86                   |  |  |

n = 4 
$$\bar{x} = 3.07$$
  $\bar{y} = 5.38$   
 $\Sigma x = 12.28$   $\Sigma y = 21.52$   
 $\Sigma x^2 = 42.58$   $\Sigma y^2 = 129.82$   $\Sigma xy = 74.17$ 

 $\frac{1}{n(\Sigma x)^2} = 37.67 \quad \frac{1}{n(\Sigma y)^2} = 115.77 \quad \frac{1}{n(\Sigma x)(\Sigma y)} = 66.06$  $\sum (x-\bar{x})^2 = 4.88 \quad \sum (y-\bar{y})^2 = 14.04 \quad \sum (x-\bar{x})(y-\bar{y}) = 8.10$ 

$$b = \frac{\Sigma(x-\bar{x})(y-\bar{y})}{\Sigma(x-\bar{x})^2}$$

$$=\frac{8.10}{4.88}$$
 = 1.66

$$a = \bar{y} - bx$$
  
= 5.38 - 5.09 = 0.29  
 $y = a + bx$   
 $y = 0.29 + 1.66 x$ 

$$r = \frac{\sum (x - \bar{x}) (y - \bar{y})}{\sqrt{\sum (x - \bar{x}) \sum (y - \bar{y})^2}} = \frac{8.10}{\sqrt{4.88 \times 14.04}} = \frac{8.10}{8.27} = 0.97$$

This means that the concentration of the organic matter at stations 1S, 2S and 3S should lie in the range 6-7% and not over 14% (Figure 3.28).

#### 3.11 Discussion :

#### 3.11.1 Water quality :

The sea area opposite the enclosed Salba Bay lies on the western margins of Fasht Al-Adhum, the well-known live-coral of Bahrain (Figure 3.29). These western marginal flats of Fasht Al-Adhum serve as a nursery ground for shrimp post-larvae which apparently drifted to this area on the tidal current. The postlarvae and juveniles of the shrimps especially <u>Penaeus semisulcatus</u> occur in fair numbers in the weed-laden bottom of this sea. The juvenile shrimps appear to grow here and then move south towards Askar .

Price and Jones (1975) and Price (1979) recorded spawning peaks December - May and September - October for <u>Penaeus semisulcatus</u> in Saudi Gulf waters, and Farmer (1974) suggests the main spawning for this species commences in January in Bahrain waters. Spawning is delayed until March in the colder northern waters of Kuwait (Al-Attar, 1981).

Penaeid larvae hatch from newly spawned eggs in a matter of hours, so the presence of nauplier stages (the first



Figure: 3.28

The relation between % organic matter and median particle diameter of the sediment samples.



### Figure: 3.29

A map showing the close proximity of Sitra (10) and Ras Abu Jarjoor(1) desalination plants to Sitra separator outlet (8) and BAPCO refinery effluent (4). larvae) is usually a good indication of spawning activity and spawning grounds in the vicinity . Atkins and Partners  $(1985_a)$  noticed that the highest densities of nauplii were found in hauls taken at locations over the western end of Fasht Al-Adhum. The samples were collected at high water which therefore suggests that spawning was occurring to the north of the Fasht, the nauplii being carried over the reef on the incoming tide .

This ties in with what is already known about <u>P.semi-sulcatus</u> stocks in the region. This species is fished commercially to the north and to the south of the Fasht. Those individuals taken to the north (by the Manama / Muharreq fleet) are large adults, whilst those taken from the southern sea grassbeds by the Sitra fleet are smaller, and the fishery is based on individuals up to one year old (annuals). It is clear that these areas to the south of the Fasht are important nursery ground. This is evident not only from the small size of individual taken commercially, but also from the quantity of juveniles / sub-adults found in beach seine samples taken from the coastal margins of the area (Atkins and Partners, 1985<sub>a</sub>).

Seagrass beds, including those stretching southwards from Fasht Al-Adhum towards the Hawar Islands, are by far the most important, in economic terms, of Bahrain's marine habitats. They are the principal habitat supporting both the commercial species of shrimp, and the pearl oyster, <u>Pinctada radiata</u>. The shrimp are largely nocturnal, apparently burrowing among the seagrass blades by day, but emerging to feed by night when they are trawled for the fleet of Banoush based at Sitra. The larvae (spat) of the pearl oysters settle

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onto the seagrass blades and as they grow, drop down to the seabed from where the adults were traditionally harvested .

Even shrimp and oysters outside the seagrass beds may largely depend on the productivity of the seagrass Only a small proportion of the seagrass is consumed directly, by urchins such as E. mathaei, and to a small extent by a few fish such as Siganus javus. Most of the material of the dead seagrass blades decomposes and contributes to a detritus load that is also carried to surrounding areas and may be deposited in sheltered bays, such as the productive intertidal flats at Askar. The detritus and its associated microflora may be consumed directly by detritivores and filter feeders such as shrimp, oyster and other bivalves, or by some fish such as the mojarra, Gerres oyena, or may re-enter the food chain to provide food for numerous small commercial fish (Atkins,  $1985_{\rm h}$ ).

Al-Attar (1981) work indicate that <u>P. semisulcatus</u> postlarvae enter seagrass or seaweed beds as a transition from the planktonic to benthic stages in their life cycle. At the first benthic stage they are unable to burrow, and unless seagrass beds are available to supply protection, heavy predation will occur. Thus the availability of seagrass and weed beds in the east coast is of great importance .

Normally the whole water column in the area close to the refinery moved towards the south but on some occasions, during calm days, an opposite movement towards the north was noticed close to the channel (Mattson and Notini, 1981). This drift is not powerful enough to disperse the oily water containing pollutants over the wider sea-surface. All these have resulted in the conversion of more than half of the Salba Bay into a black area with flocculations at the bottom giving -a hydrogen - sulphide smell. Due to poor water exchange and subsequent bad oxygenation, the chemical and biological degradation of sedimenting organic material will turn to non-oxidative processes. In this oxygen free environment sulphur serves as an electron source instead of oxygen. Thus end products will be metal sulphides or H2S. H2S is toxic for macrofaunal organisms and makes survival impossible. However, anaerobic bacteria and other microorganisms adapted to these circumstances survive and thrive here (Fenchel and Riedl, 1970). The pollution in Salba Bay and its offshore drift present great hazards to this shrimp nursery ground . Some of the shrimp captured here gave oily taint (Personal observation). Stray fishes caught near the Sitra separator outlet and the flume inlet have also been reported by the amateur fishermen to give an oily smell .

A study of the marine environment off BAPCO oil refinery was carried out in 1986 by Linden, Larsson and Al-Alawi (1988). The study covers an area of some 100 km<sup>2</sup> and abundance and biomass of benthic fauna as well as oil content of sediments and bivalves were investigated. In addition some physio-chemical parameters of water and sediments were measured. The distribution of the fauma corresponds well with the concentrations of oil in the sediment , and an area of some 10 km<sup>2</sup> was considered severely contaminated (Figure 3.30). This is a considerably smaller area than that found to be contaminated in a similar study in 1981 by Mattsson and Notini (Figure 3.31) five years earlier. The reason

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### Figure: 3.30

The distribution of the aliphatic fraction of oil in sediments and bivalves. (From Linden <u>et al</u>, 1988).

Dark area: >1000 mg/kg dry weight in sediments Shaded area: >100 mg/kg dry weight in sediments Dotted area: >50 mg/kg wet weight in bivalves



or this is probably decreased quantities of petroleum generations released all the second released and the second se

#### Figure: 3.31

The distribution of the aliphatic fraction of oil in sediment and mussels. (From Mattsson and Notini, 1981)

Dark area: Shaded area: Dotted area: >1 000 mg/kg dry weight in sediments >100 mg/kg dry weight in sediments >50 mg/kg wet weight in mussels for this is probably decreased quantities of petroleum hydrocarbons released via the effluent .

The concentrations of oil found in the 1986 studygenerally ranged between 20 and 700 ppm. Previous results from the region show levels of 36 to 60 ppm from off Askar and 1-10 ppm from the Umm Nasan area in Bahrain (Fowler, 1985). Another study of the petroleum hydrocarbon (naphten-paraffin fraction) contamination at some 30 stations around eastern, northern and western Bahrain showed normally below 100 ppm (FA0,1982). Along the east coast, and particularly outside the refinery and south of the refinery outlet, however, concentrations were considerably higher, with a maximum value over 20,000 ppm. From Kuwait concentrations ranging from 5 to 310 ppm were found in surface sediments (Zabra et al, 1985) . Concentrations higher than 100 ppm were observed in areas close to a refinery and port area, and in areas where offshore drilling and production of oil took place .

The toxicity of oils varies according to the content of low boiling compounds and aromatics. The higher the concentration of these constituents, the more toxic the oil. Toxicity appears to increase along the series alkanes - alkenes-aromatics.Generally, aromatics with increased number of alkyl/substituent usually have higher toxicity (Crafts and Reiber, 1948; Havis, 1950; Van Overbeek and Blondeau, 1954).

Lethal effects on several marine organisms have been observed at comparatively low concentrations of the more toxic fractions of petroleum hydrocarbons. The effects occur in the 0.3 - 100 ppm range. Some evidence of lethal effects on larval and juvenile life stages of some species exists at even lower concentraions (down to 0.1 ppm). Sublethal responses have been observed at concentrations down to 0.02-0.03 ppm for fish(Lehtinen, 1981).

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Off the refinery the concentrations of lead in sediments were relatively high. It was 990 ppm, while mercury was 2.77 ppm, cadmium was 1.1 ppm. The background concentration of lead and mercury is 0.003 ppm. The concentration of lead in the refinery water discharge was 0.319 ppm (FAO, 1982).

The analysis of bivalves samples (FAO, 1982) showed that the petrogenic hydrocarbon fraction accumulated in the mussel tissue was relatively small. The concentrations were low or moderataly elevated compared to areas under influence of chronic pollution in other parts of the world .

#### 3.11.2 Sediment quality :

FAO (1982) has studied the concentration of heavy metals (mercury, zinc, copper, lead, cadmium, nickel and vanadium), certain chlorinated pesticides, polychlorinated biphenyls and petroleum hydrocarbons in sediments and biota at different areas along Bahrain coast (Figure 3.32).

All metals studied showed increased levels in sediments along the east coast from Sitra and southward , as compared to the concentrations found in other areas around Bahrain. Their concentrations found to be up to 600 times the background concentration to the south and west of Sitra (see Figure 3.33); however, with some exceptions, the total levels were low or moderate also there. Only off the refinery the concentrations of lead were relatively high. It seems likely that the lead here originates from the refinery where alkyl lead is used for gasoline production .



## Figure: 3.32

Location of sampling stations (From FAO, 1982).

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Summary of distribution of heavy metals in sediments. (From FAO, 1982).

The analysis of the naphten-paraffin fraction of petroleum hydrocarbons of sediment samples (Table 3.17) showed low or moderately elevated concentrations in most stations in the west and the north. Here concentrations were normally below 100 µg/g dw, which probably must be considered close to the background levels. Along the east coast, and particularly outside the refinery and south of the outlet, the concentrations were considerably higher. The highest value was over 20,000µg/g and such concentrations indicate severe chronic pollution conditions.

3.12 Conclusion :

### 3.12.1 <u>Water quality at different stages of BAPCO effluent</u> treatment :

It can be concluded from the results that the concentration of the various parameters are variable depending on the discharge. The inlet water to the refinery has a higher level of contaminants than other Bahraini coastal waters, due to recirculation of water from the outlet stream .

In general, the concentration of the pollutants are very high at the Sitra separator outlet and highest at the I.A.F. outlet .

### 3.12.2 <u>Water quality in the vicinity of BAPCO refinery</u> and oil storage tanks outfalls :

The 1986 results indicate that nitrogen and phosphorus contents of the Sitra separator outlet is lower than that of the main stream effluent. This is because subsequent to the 1984 study by the author, the company

#### Table: 3.17

Petroleum hydrocarbon (Paraffin-naphten) content in sediment and bivalve samples. Concentrations are in ppm dw for sediments and in ppm ww for bivalves (From FAO, 1982).

| SEDIMENTS   |   | BIVALVES         |                      |                       |  |  |  |
|---|---|------------------|----------------------|-----------------------|--|--|--|
| Station   | Concentration   | Station          | Sample No.           | Concentration         |  |  |  |
| 1<br>2<br>3<br>4<br>5<br>6<br>7<br>8<br>9<br>10<br>11<br>12<br>13<br>14<br>15 | 6<br>15<br>28<br>68<br>18<br>145<br>25<br>106<br>19<br>81<br>15<br>71<br>48<br>37<br>17 | 3<br>5<br>7<br>8 | 31<br>38<br>39<br>41 | 28<br>125<br>78<br>45 |  |  |  |
| 17<br>18<br>19<br>20  | 11<br>89<br>96<br>153   | 18               | 36                   | 40                    |  |  |  |
| 21<br>22<br>23<br>24<br>25<br>26<br>27<br>28<br>29                            | 20600<br>478<br>3950<br>139<br>11<br>214<br>-<br>13<br>7                                | 22               | 37                   | 220                   |  |  |  |

diluted the discharge to the sea from the Sitra separator effluents stream. Hence, the concentration of the pollutants in that effluent decreased.

Some pollutants are at levels much higher than background and show a marked dilution pattern, but other materials are discharged at levels only a little above background and therefore show less dilution effect. The figures include contour lines for the pollutants and show that most dilution is accomplished within 2Km from the main outlet stream for most pollutants. In the case of the Sitra separator, the contours reflect the different composition of that outfall.

#### 3.12.3 Water quality standards.

To control waste water discharges, standards for water quality need to be established. The determination of such standards is set out in the appendix to this chapter. APPENDIX TO CHAPTER THREE. Water Quality Standards.

#### Water Quality Standards :

When setting water-quality standards , other factors such as technological feasibility and cost should be considered in addition to the possible effects on human health or aquatic organisms. Such standards should, of course,minimize all the known environmental and health hazards and should be regularly reviewed in the light of new knowledge. Since water quality should always be considered in relation to the intended use of water, there is no unique set of standards for streams, lakes or ground water and the problem cannot be solved in a general way .

In Bahrain, no legal environmental standards have been submitted presently. The quality standards vary depending on the country concerned. In Saudi Arabia, which is located opposite to Bahrain the Meteorology and Environmental Protection Administration (MEPA) has submitted a performance standards for direct discharge (MEPA, 1981).

The following performance standards for Saudi apply to wastewaters at the end of the outfall and before discharge to coastal waters or to any channel of waste water (MEPA, 1981). Physio-chemical pollutants :

.

|                   | (Pollutant)                         | (Allowable  | Effluent Level)                                    |                    |  |  |  |
|-------------------|-------------------------------------|---|--|--------------------|--|--|--|
| (a)<br>(b)<br>(c) | Floatables<br>pH<br>Total suspended | None<br>6-9 pH un   | its  |                    |  |  |  |
|                   | solids (TSS)                        | 15 mg/1 (ma   | x.)  |                    |  |  |  |
| (d)               | Temperature                         | MEPA determines the thermal pro-<br>perties of discharged water to fit<br>the properties of receiving water<br>and such properties are determined |  |                    |  |  |  |
| (e)               | Turbidity                           | 75 NTU (max   | )  |                    |  |  |  |
| Org               | anic pollutants :                   |   |  |                    |  |  |  |
|                   | (Pollutants)                        | (   | Allowable Effluent                                 | Level)             |  |  |  |
| (a)               | Biochemical Oxyg                    | en Demand   | 25 mg/1  |                    |  |  |  |
| (Ъ)               | Chemical Oxygen                     | Demand  | 150 mg/l   |                    |  |  |  |
| (c)               | Total Organic Car<br>(TOC)          | rbon  | 50 mg/1  |                    |  |  |  |
| (d)               | Total Kjeldahl N<br>(TKN)           | itrogen   | 5 mg/l   |                    |  |  |  |
| (e)               | Total Chlorinated                   | d Hydro-  | 0.1 mg/1   |                    |  |  |  |
| (f)               | Oil and Grease                      |   | 8 mg/l (not to ex<br>mg/l in any ind<br>discharge) | ceed 15<br>ividual |  |  |  |
| (g)               | Phenols                             |   | 0.1 mg/1   |                    |  |  |  |

Non-organic pollutants :

|     | (Pollutant)                            | (Allowable Effluent Level<br>30 - day Average) |
|-----|--|--|
| (a) | Ammonia (as nitrogen)                  | 1.0 mg/l                                       |
| (Ъ) | Arsenic                                | 0.1 mg/1                                       |
| (c) | Cadmium                                | 0.02 mg/1                                      |
| (d) | Chlorine (residual)                    | 0.5 mg/1                                       |
| (e) | Chromium (total)                       | - 0.1 mg/1                                     |
| (f) | Copper                                 | 0.2 mg/1                                       |
| (g) | Cyanide                                | 0.05 mg/1                                      |
| (h) | Lead                                   | 0.1 mg/1                                       |
| (i) | Mercury                                | 0.001 mg/1                                     |
| (j) | Nickel                                 | 0.2 mg/1                                       |
| (k) | Phosphate (Total)<br>(as Phosphorous ) | 1.0 mg/1                                       |
| (1) | Zinc                                   | 1.0 mg/1                                       |

Biological Pollutants :

| (Pollutant)        | (Allowable Effluent Lev |  |  |  |  |  |
|--------------------|-------------------------|--|--|--|--|--|
|                    | 30 - day Average)       |  |  |  |  |  |
| (a) Total Coliform | 1000 MPN per 100 ml.    |  |  |  |  |  |

In Europe and U.S.A. the concentrations and limit values for waste-waters are shown in Table 7.1.

Table: 7.1 Concentrations and Limit Values for Waste-Waters in Europe and U.S.A. (from Huber, 1979) .

| a show a she had a show of the   |             |                 |           |                     | T   | T  | T             | mI   | 0           |                         |
|--|-------------|-----------------|-----------|---------------------|---|--|---------------|--|-------------|-------------------------|
| mg/l   | Belgium 1   | Denmark 2       | Germany 3 | United<br>Kingdom 4 | France 5  | Italy 6  | Ireland 7     | Luxembourg &   | Netherlands | USA 10                  |
| BODg   | 35-70       | 20              | 20        | 20-400              | 30-40   | 40   | -             |  | - 250       | 15<br>80-115            |
| COD<br>TOC   | 200-350     | -               | -         |                     | -   | -  | -             | -  | -           | 33                      |
| Of 1 hydrocarbon   | 20-30       | 5               | 2         | 20-50               | 5/20 <sup>8</sup>   | 5  | -             | -  | 20-30       | 5.                      |
| Phenol   | 0.5-1       | 0.2             | 0.2       | 1.3                 | 0.5-1   | 0.5  | -             | -  | 2.5         | 0.1                     |
| Mercaptan  |             | si <del>.</del> | n.d.      |                     | tinet i   | hron   | -             | -  | -           | -                       |
| Hydrogen sulphide  | ens for s   | 2               | nd-0.5    | 1.5                 | -   | 1  | -             | -  | 2.5         | 0.1                     |
| Total nitrogen   | 10-40       | -               | -         | -                   | -   | -  | -             | -  | -           | -                       |
| Ammonium   | -           | 2               | -         | 4.15                | -   | 15   | -             | -  | -           | (80%)10                 |
| Nitrite  | testops f   | 1.1             | 1002-00   | -                   | 104.00  | 0.6  | -             | -  | -           | -                       |
| Nitrate  | and walking | 1_              | co-gali   | 20 -03              | 100-0-0   | 20   | -             | -  | -           | -                       |
| Cvanide  | e el paga   | 0.1             | 0.13      | -                   | 100 (205)   | 0.5  | -             | -  | - 1         | -                       |
| Phosphorus   | n tha Re    | +               | 10000     | 1.20                | essi.   | 10   | -             | -  | -           | -                       |
| Lead   | 0.05        | 0.1             | and se    | 0.00 - 0            | 0.1   | 0.2  | -             | -  | 0.010       | -                       |
| Cadmium  | *******     | -               | 1000      | all and             | -   | 0.02   | -             | -  | -           | -                       |
| Chromium   | 0.05/0.5    | 0.2             | -         | -                   | 0.05  | 0.2/2  | 2 -           | -  | -           | 0.02/0.25               |
| Iron   | -           | -               | 33        | -                   | -   | 2  | -             | -  | -           | -                       |
| Copper   | the the     | 0.1             | ctos /    |                     | 19795   | 0.1  | -             | -  | -           | -                       |
| Nickel   | ici negeli  | 0.2             | 100       | -                   | Sec.  | 2  | -             | -  |             | -                       |
| Mercury  | ual cell    | see             | - 1       | -                   | an 11   | 0.00   | 5 -           |  |             | -                       |
| Zinc   | Cons Lites  | 0.5             | -         | -                   | 100-00  | 0.5  | -             |  |             | -                       |
| and the second sec |             |                 |           |                     | and the second se | and the subscription of the local division o | and the owned | and the second division of the second divisio |             | THE REPORT OF THE PARTY |

n.d. = not detectable

Numbers as superscripts refer to footnotes

Footnotes to Table 7.1 . The situation in 1974 was as follows:

#### 1. Belgium

Specific regulations for refineries with differentiation according to complexity (4 types).Hydrocarbons by carbon tetrachloride extraction; phenol as total phenol; lead as total lead. For chromium: separate determination for total chromium (limit 0.5 mg/l) and hexavalent chromium ( limit 0.05 mg/l).

#### 2. Denmark

Specific regulations for waste-waters in relation to the type of receiving water (e.g. fresh water, estuary, bay, sea) with division into 4 groups; only fresh water and estuary taken into account here. For COD, determination in relation to local conditions; oils and hydrocarbons are only determined as emulsions; chromium as total chromium; special regulations for mercury.

### 3. Germany

Specific recommendations for waste-waters from mineral oil processing (standard values), so-called minimum requirements with the character of regulations in preparation; at present, regulations vary in the Federal States. Phenols as steamvolatile phenols; mercaptan, cyanide and iron are employed as parameters and restricted in some Federal States.

#### 4. United Kingdom

The figures relate to the situation on 1.1.1974; these are exclusively regional regulations set by the Water Authorities for individual refineries; application of particular parameters varies considerably according to nature, extent and quality .

#### 5. France

Specific regulations for new refineries with differentiation for complexity (2 or 3 types according to quantity of wastewater). France moreover limits the output-related quantities of waste-water.Two different limits for hydrocabons in relation to the method of analysis. Chromium refers to hexavalent compounds .

#### 6. Italy

Specific regulations for industrial waste-waters, which are applied to new plants and, within a period of 9 years (from 1976) to existing plants .

Phenols as total phenol; ammonium as total ammonium  $(NH_4)$ , nitrite as  $NO_2-N$ ; nitrate as  $NO_3-N$ ; in the case of chromium separate determination for total chromium and hexavalent chromium .

#### 7. Ireland

Date are only known for the refinery in Whitegate, which has COD requirements .

#### 8. Luxembourg

No oil refinery in existence; data on possible limits therefore superfluous .

#### 9. Netherlands

According to the situation in 1974, with refineries mainly located on the coast or at ports, no nationally-uniform limits available .

Requirements generally only for oil content: COD only set at 1 out of 7 refineries, as also for lead; hydrogen sulphide as 5<sup>-</sup>.

#### 10. USA

Specific regulations of the EPA for refinery waste-waters taking into account size and complexity (size and process factor); further differentiation according to BPCTCA and BATEA; BPCTCA values (best practiable control technology currently available and converted to concentration . 1974 and 1975: Load values set in the EPA guidelines. For COD, differentiation according to complexity; chromium:separate determination for total and hexavalent chromium.Ammonium must be 80% removed with respect to raw water . In France, the analyses are standardized by the Association Francaise de Normalisation (AFNOR), whereas the methods of IRSA (National Institute for Water Research) are imperative in Italy. In the Federal Republic of Germany , the specific recommendations are based, according to the parameters, on the German Standard Methods (Deutsche Einheitsverfahren , DEV), the Standard Methods for the Examination of Water and Waste water, and the methods of the American Petroleum Institute (API). In the Netherlands, the API and ASTM analyses are often prescribed among others, though practice varies from one refinery to the next. In the United Kingdom and in Ireland, where the standard values for individual refineries are laid down by the area Water Authorities, there are no standard provisions concerning the analytical techniques to be employed. The majority of the recommended analysis originate from the provisions of the American Society for Testing and Materials (ASTM), the API, the society of analytical chemistry and the Standard Methods. The lower quoted limits for Chemical Oxygen Demand (8-25 mg/1) can be attributed to the fact that in the United Kingdom , this parameter is generally determined as KMnO, consumption, but the oxidising power of this method is inadequate , especially for hydrocarbons .

In the UK, most refinery effluents are discharged into tidal waters where the main problems are depletion of dissolved oxygen due to the oxygen demand, an effluent

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with a significant oil content or strong smell may lower amenity values, or finally, the tainting properties of the effluent may have a detrimental effect on local fisheries. Thus, the consent conditions for discharges set by Water Authorities have traditionally included stringent standards for biochemical oxygen demand, oil content and specific parameters, usually sulphide, which reflect the smell and tainting properties of the discharge. Treatment of the refinery waste is essential to achieve these stringent standards and in the process the lethality to aquatic organisms is normally reduced to acceptable levels so that, allowing for the high dilution and assimilative capacity of the receiving waters, there is little risk to indigenous marine life. This must be clearly demonstrated and it is accepted practice to measure the acutely lethal concentration of representative samples of such effluents to adult fish and shellfish in the laboratory .

There are no environmental legislation or an overall environmental Act. in Bahrain. The Public Health Act. of 1975 entrusts the Ministry of Health with several functions related to environmental protection such as buildings, sewage, water resources, sanitation, waste, public places and ports. Other Acts. include control of regulation of water Act. 1971 which prohibits drilling of new wells, unless prior permission is obtained . Another Act. which is relevant to land use and planning is the Act. of 1971 which prohibits the taking of sand, gravel, and stones for the purpose of land reclamation or construction . There are no water quality or air quality standards for Bahrain. Bahrain has actively participated in various ROPME (Regional Organisation for the Protection of the Marine Environment) meetings to discuss and establish various protocols, oil spill contingency plans, oil spill surveillance procedures, oceanographic monitoring, baseline studies, the signing of MARPOL 73/78 convention etc.. No Regional and International Conventions dealing with environment have been ratified as yet .

It is recommended that the Bahraini Government begin discussions with a view to implementing water quality standards legislation for Bahraini coastal waters .

### CHAPTER 4

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# TOXICITY OF THE REFINERY EFFLUENTS TO SAFEE ( SIGANUS CANALICULATUS )

Marine organisms get exposed to petroleum in a variety of ways such as through natural sub-marine petroleum seeps, oil spills from tankers, washouts from filling terminals and refinery effluents. Organisms living under chronic petroleum stress adapt to these conditions and become more tolerant of the toxic effects of oil. However, toxicity may manifest itself through several physiological stresses to the organisms before killing it or may not kill the organism at all. In the latter case, there is a phenomenon of bioaccumulation of hydrocarbons which could enter the aquatic food chain terminating in humans through the consumption of sea-food. The degree to which marine animals are exposed to petroleum depends on several factors, principal being the drift-course over the sea surface and the duration of exposure. The level of toxicity is different for different organisms and must be determined separately.

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It is becoming increasingly common for regulatory bodies concerned with water quality and the protection of living resources to attempt to evaluate the actual and potential polluting effects of effluents using various forms of toxicity test. There is a large scientific literature giving toxicity test procedure and results relating to industrial discharges. The number of approaches are great and in many cases the protocols advocated seem to be related more to research worker preferences than to logic. To the oil industry subject either to regulatory demands or simply wishing to evaluate environmental effect the position can be bewildering. The policy setters both within industry and the governmental groups that regulate them, need guidance or at least pointers to help them more rationally to define the issues raised.

Toxicity is the innate ability of any substance to cause harm to living organisms and it is important to realise that virtually all substances can be toxic to life at some level. The type of harm (effect) that is produced by a substance depends largely on its specific chemical properties but is also a function of the concentration of the substance and the exposure, that is, the length of time the biological system is exposed to it.

Aquatic toxicology tests and bioassays are a procedure in which the responses of aquatic organisms are used to measure the presence or effects of one or more substance, wastes, or environmental factors alone or in combination. These tests evaluate the toxicity of specific materials or effluents, to establish the relative sensitivity of different aquatic organisms, and to identify effects of physical and chemical variables such as temperature and pH on toxicity. Toxicity tests are necessary in water pollution evaluation because chemical and physical tests alone are not sufficient to assess potential effects on biota. The most common method of assessing the biological effects of a pollutant is to measure its short term lethality in an acute toxicity test.

Toxicity testing, despite its limitations can also be used for giving some predictive information on the possible effects of effluents before discharge is commenced. The data enables the risk of gross pollution to be significantly reduced and can be a first step in reducing discharges to less than toxic levels and amounts.

During the last two decades, numerous impact studies of refinery effluents have been carried out world-wide. Due to the varying experimental methods used and the different habitats studied, it is very difficult, to obtain a general consensus of these studies (Lehtinen, 1986).

Research studies so far have not identified the main toxic substances in refinery effluents-which may include sulphides, phenols and sometimes traces of cyanides in addition to hydrocarbons. Synergistic, additive, accumulative and antagonistic effects have also not been fully investigated (Baker, 1979).

In 1979, a major review work was published by Concawe in order to summarize the present knowledge of environmental impact of refinery effluents (Jenkins <u>et al</u>, 1979). The study focused on three parameters; toxicity, persistence, and bioaccumulation of pollutants in refinery effluents, and concluded that since these cannot be measured precisely and routinely at present, acute toxicity would be a more suitable parameter for monitoring purposes. In this work, Concawe furthermore show that the quality of effluents are adequate indicators of this impact on receiving waters and, therefore, are suitable for routine effluent quality measurements (CONCAWE, 1980).

Long term environmental impact studies cannot be carried out in a standardized way. It is always necessary to match the investigated parameters to the

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special characteristics of the recipient. A problem that the marine biologist has to tackle, however, is the number of uncontrolled variables present in every field study. A relevant example for the Baltic Sea is how to distinguish between observed effects and natural long-range ecological variations. Another very common problem is how to relate observed effects to a specific source if the area is a recipient for several sources of pollution (Rudling, 1976).

To avoid some of these problems, long-term impact studies can be carried out in model ecosystems. In these the ambient conditions can be controlled and the observed effects directly related to the dosed effluent. The remaining problem is how to relate the effects to the component(s) in the effluent that caused them. The proportions of this problem get even more pronounced when considering all the conversion processes that components initially present in the effluent undergo when released. These conversion processes are poorly understood, although attention has recently been paid to them (Rudling, 1976).

With this in mind, it is necessary to test the discharge biologically for the assessment of potential damage arising from it, and for subsequent monitoring and regulation. The first step is to obtain basic information on the acute toxicity of each pollutant such as the shortterm LC50, the shape of the graphical concentration/ response curve and the maximum concentration of the pollutant likely to occur in the environment, with all other relevant chemical, physical, and hydrographical data.
Chemical characterisation and monitoring can do much to indentify the source and nature of effluent quality problems. It is, however, impossible to analyse for all possible toxic components in effluents as complex as those produced in hydrocarbon refining. Simple toxicity test may be helpful to a regulatory agency to identify regulatory needs not picked up from wet chemistry.

The degree of risk to any organism from an effluent depends upon the method of its input, location and frequency, and also on the physical and chemical characteristics of the compounds involved, their toxicity and persistence. The complex interactions of effluents with the physical and chemical environment into which they are discharged, have yet to be defined (Jenkins <u>et al</u>, 1979).

There are many potential pollutants whose occurrence causes a reduction in the quality of the aquatic environment and about which a wealth of short-term toxicity test data has been accumulated. Results are commonly reported as a median lethal concentration (LC50) or median tolerance limit (TL50). Both indicate the concentration which kills 50% of the test species within a specified time span, usually 96 hours. On no account should LC50 or TL50 levels be viewed as safe levels. Safe levels must allow growth and other normal life processes such as reproduction to continue. Unfortunately, accurate data on safe levels are limited and in many cases the values are empirically derived by dividing the LC50 concentrations by a factor gained from experience.

Most chemicals exhibit a lethal threshold concentration to marine animals after four to five days. However, there are some substances such as DDT and mercury which, because they accumulate within the animal, build up to lethal levels only after several weeks or even months of exposure to low concentrations.

Some potential advantages can be cited for toxicology testing, including the facts that:

- (i) bioassays will give an integrated response reflecting all components of the effluent;
- (ii) bioassays will indicate whether there is likely to be a biological response in the environment.

Nevertheless, the following disadvantages must be recognised:

- (i) there are poor correlations between laboratory test results and field effects;
- (ii) the variability of biological systems makes the interpretation of results difficult.

Refinery effluents will be judged to be polluting if, directly or indirectly, they are a hazard to human health, harm living resources or aquatic ecosystems, damage amenities or interfere with other legitimate uses of receiving waters. Industry will therefore seek to identify the most economic method of disposing of refinery effluents without giving rise to any of these deleterious effects. The results of acute, chronic or sublethal toxicity tests may be used for assessing the likelihood of whole effluents or constituents of effluents harming living resources or aquatic ecosystems. However, because of the complexity and variability of both natural environment and refinery effluents, it is impossible to be sure that a discharge will be absolutely safe. More often than not a subjective judgement is made about the probability of harmful effects based largely on previous experience and a limited amount of relevant scientific data (Jenkins <u>et al</u>,1979).

Provided that it can be demonstrated that the treated effluent will be rapidly diluted in the receiving waters to give concentrations well below its 96 hour median lethal concentrations measured in the laboratory, then it is very unlikely that the Water Authorities will withold their consent to discharge.

Even though there are a number of published works on freshwater toxicity (Applegate <u>et al</u>, 1957; Mckee and Wolfe,1963) there is a limited amount of corresponding data regarding the marine environment (Jacob and Zarba, 1979). As it is unlikely that the toxicity of a given material would be the same to fresh water and marine fish, separate tests are needed for most toxicants.

The following chapter is aimed at studying the effects of refinery effluent in Bahrain on one of the most commonly consumed fish, safee (Siganus canaliculatus). The significance of selecting this fish as a test species depends on its wide popularity as food, small size for easy handling and abundance. Another important aspect is that it is not a long migrant and as such is more likely to be affected by any oil pollution or refinery effluents.

No studies on toxicity tests are previously available for safee or any other fish in Bahrain.

## 4.1.1 Terminology (Alabaster and Lloyd, 1982, EIFAC, 1975)

### Acclimation:

A physiological adaptation of fish to some selected experimental conditions, including any adverse stimulus which is involved (used by Sprague as equivalent to 'tolerance' as defined here).

### Acclimatization:

The genetic adaptation of a fish species to some change of natural or applied environmental condition.

## Acute toxicity:

The harmful properties of a substance which are demonstrated within a short period (hours to days) of exposure. Typically associated with a breakdown of tissues and physiological systems at rates which exceed rates of repair or adaptation. Commonly applied to lethal effects.

## Acute toxicity test:

A test made to determine the acute toxicity of a substance or waste.

## Additive toxicity:

The toxicity of a mixture of poisons which is equal to that expected from a simple summation of the known toxicities of the individual poisons involved (i.e., algebraic summation of effects).

## Antagonism :

Commonly used to define a mixture of poisons whose toxicity is less than that which would be expected from a knowledge of the toxicities of the individual poisons involved (i.e., algebraic substraction of effects). The term "less-than-additive" has been substituted for this response by Sprague, to the limit where one poison fails to exert any effect at all within the mixture. The term "antagonism" is restricted to any effect beyond this point, where an excess of one poison is required solely to exert the effects which it would have alone at a much lower level in the absence of the second substance.

## Application factor:

The factor by which a concentration observed as causing some harmful effect in a short-term experiment is converted to give what is frequently arbitrarily considered as an acceptable level in the environment. Thus, for example, the 96 hour LC50 is frequently multiplied by 0.1 or 0.01 to give this level; data obtained from chronic tests are, however, also used to derive such a factor.

#### Bioassay:

The use of living material to measure the concentration of a substance in water, by determining its potency in producing some specific effect. Frequently involves the use of standard reference compounds. Strictly speaking a fish toxicity test is not a bioassay.

## Chronic:

Of long duration; for example, chronic toxicity test is the same as a long-term toxicity test.

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Concentration-response curve:

The curve obtained when, after a given period of exposure, the different percentage responses of batches of fish exposed to different concentrations of poison are plotted against those concentrations.

## 95 percent confidence limits:

The upper and lower limits of the 95 percent confidence interval, effectively the limits within which, at a probability level of 0.95, the true EC50 for the population of fish under test lies. Thus, if tests were made on a large number of separate samples of fish taken from a single large population and the EC50 and its 95 percent confidence interval for each test sample was determined, then in about 95 tests in 100, the true value of the population EC50 would come within the sample confidence limits.

## Criteria (water quality):

The relation between the concentration of a pollutant and its measured effect on a target organism.

## Cumulative:

Increasing by successive additions.

#### Death time:

Survival time.

## Delayed:

Put off in time, delayed effects of a poison are those not exerted until some considerable time after first exposure to a poison or, when the period of exposure to poisoning is brief, not until after exposure has ceased.

## EC50:

Median effective concentration, the concentration of poison (or intensity of other stimulus) which produces some selected response in one half of a test population.

## Exposure period:

The interval of time during which a fish is exposed to a stimulus.

## Joint action:

The effects of two or more poisons exerting their effects simultaneously.

## LC50:

Median lethal concentration, the concentration of a poison lethal to one half of a test population of fish.

## LD50:

Median lethal dose, the dose (i.e., the quantity received by the body) which is lethal to one half of a test population of fish. A quantity not normally known for fish from typical toxicity tests, where LC50 is the correct term to use.

## Lethal:

Mortal, causing death.

#### Lethal threshold concentration:

(a) the threshold concentration producing death, for example, the median lethal threshold concentration is the concentration of poison lethal to one half of a test population; (b) the concentration at which a poison is first lethal to fish.

## Lethal time:

Survival time.

#### LT50:

Median lethal time, the survival time of one half of a population of fish in a given concentration of poison.

#### Mortality:

Death.

#### Overturning time:

The time interval between initial exposure of a fish to a poison (or other harmful stimulus) and its loss of equilibrium.

#### Probit:

Unit of probability or standard deviation.

#### Response:

The reaction of a fish (or some system thereof) to a stimulus. Both nature and time of onset of the response should be defined.

## Screening test:

A Test used to detect the ability of a chemical or waste to produce some selected effect.

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#### Short-term toxicity test:

A toxicity test of short duration, usually an acute toxicity test.

#### Static test:

A toxicity test in which either no replacement of test solution takes place, or in which all, or the greater part (95%) of the test solution is replaced batchwise only after relatively prolonged intervals (e.g., 12 or 24 h).

#### Stimulus:

The factor producing some response.

## Sub-acute:

Having effects less severe than those observed under conditions of acute poisoning and usually not demonstrated until after perhaps some weeks of exposure.

## Sub-lethal:

Not killing, usually applied to toxicity test with poison concentrations which are not lethal within the period of the experiment. Both period of exposure and observation, as well as the percentage of fish referred to, should be defined.

## Survival time:

The time interval between initial exposure of fish to -a harmful stimulus and death.

## Synergism:

Any joint action of poisons, but commonly used in fish studies to describe toxicity of a mixture of poisons which is greater than that which is to be expected from a knowledge of the toxicities of the individual poisons involved (i.e., greater than the algebraic summation of effects). The term "more-than-additive" has been substituted for this type of response.

## Threshold concentration:

(a) The minimum concentration of poison required to produce a selected response in a single test animal under controlled conditions. Can be used, if desired, to describe the threshold concentration for any particular percentage response in a test population of fish.

(b) That concentration allowing survival time equal to that of the control.

#### Time-response curve:

The curve obtained when the cumulative percentage response of a test batch of fish to a single concentration of poison is plotted against time.

## TL50:

TL<sub>m</sub>; LC50.

TL<sub>m</sub>: .

The median tolerance limit, the concentration of poison, or intensity of some harmful stimulus, lethal to one half of a test population of fish. ('Tolerance' here has the meaning' the intensity of stimulus required').

## Tolerance:

Acquired resistance of fish to a poison or other stimulus (e.g., high temperature, low dissolved oxygen) following continuous or repeated exposure.

Other definitions: (a) the ability to survive indefinitely under a given set of circumstances, (b) the oxygen pressure which just fails to bring about 50 per cent mortality in a sample of fish.

### Toxicity curve:

The curve produced when, for example, the median period of survival of test batches of fish exposed to different concentrations ære expressed in a graphical form. The curve obtained when, for example, the LC50 values of test population of fish after different periods of exposure are plotted. Resistance curve.

## Toxicity test:

The use of living material to define the nature and degree of harmful effects produced by a single poison or by a mixture of poisons.

## 4.1.2 Rabbitfish:

The rabbitfish (Siganidae) (Figure 4.2) is widely distributed in tropical and subtropical regions from the "Arabian Gulf" along the coasts of India to the Indo-Malayan Archipelago (Fischer and Bianchi, 1984). The Rabbitfish is a common species around Bahrain Island. The two species found in its waters are <u>Siganus canaliculatus (S.ormain) and Siganus javus</u> (Local name: safee).

They are moderate sized (maximum size 30 cm; common to 20 cm), they are primarily herbivorous) (Randall , 1983), feeding on a wide variety of benthic plants, but some may ingest sessile animals such as sponges or tunicates, and their most preferred food is the algae <u>Enteromorpha</u> (Al-Aradi <u>et al</u>, 1985), they scrape algae from rocks and corals and browse on seaweeds and sea grasses.

Some species live in pairs around coral, others in small schools around rocks and coral reefs, algal flats, seagrass beds, mangroves, estuaries and brackish lagoons (Masuda <u>et al</u>, 1975). They are very changeable in colouration and may rapidly assume a mottled pattern when they come to rest on the bottom. There are 26 species in the family, all in the Indo-Pacific region and all in the genus Siganus (Randall, 1983).

<u>S.canaliculatus</u> form about 95% of the rabbitfish catch of Bahrain. It is one of the most important species caught by the local fishermen. It forms about 15% of the total fish landed in Bahrain and claims high marketable value. The retail price per kilogram is fluctuated from 1.42 to 2.61 Bahraini Dinars (1984).



Figure: 4.2

Family: Species: Local name: English name:

Siganidae <u>Siganus</u> <u>canaliculatus</u> Safee Pearl - spotted rabbitfish During 1985, the rabbitfish catch was 1702.0 metric tons valued at 2.1 million Dinars (Anon., 1986.).

The industrial sector use fish trawls which operate in relatively deeper areas which generally characterized by soft bottoms. In contrast, the artisanal sector operates mainly in relatively shallow areas associated with coral reefs (Abdul-Qader, 1986) and sea grassbeds.

The wire traps (gargoors), barrier traps and seine nets are the main gears for this species and hence the artisanal sector is the main contributor in the rabbitfish landing with a catch of 1590.3 mt.(92.81%) in 1985. While the industrial sector catch was only 121.7 mt. (7.2%).

Rabbitfishes have a spawning peak in April, consequently, the fresh recruits appear in the stock a few months later, usually in September. Examination of the catch and effort data shows that rabbitfish season begins in July and ends in June of the next year (Anon., 1984). Table 4.1 shows monthly rabbitfish catch (in kg), effort (No. of wire traps) and catch per unit effort for the artisanal wire trap fishery in Sitra landing site for the seasons 1979-1980/ 1980-1981/ 1981-1982/ 1982-1983/ 1983-1984.

## 4.2 Materials and Methods:

## 4.2.1 Fish sampling:

Safee (Figure 4.2). were collected for the toxicity tests during the night, at low tide from a sea-grassbed of Ras-Romman (in Manama)using a 50 meter beach seine of 15mm mesh size. Fish samples from selected toxicity

Table: 4.1

artisanal wire trap fishery in Sitra landing site for the seasons 1979-1980/1980-1981/1981-1982/ Nonthly Rabbitfish catch (in Kg), effort (No. of wire traps) and catch per unit effort for the 1982-1983/1983-1984. (From Anon., 1984).

| Year       |         | 1979 - 19 | 80                             | -       | 980 - 198  | 6 1<br>6 1                     | vat<br>n ( | 161 - 1961 | 32                             |         | 1982 - 196 | 13                             | 81)<br>V | 1-6961   | 184                           |
|------------|---------|-----------|--------------------------------|---------|--|--------------------------------|------------|------------|--------------------------------|---------|------------|--------------------------------|----------|----------|-------------------------------|
| Month      | catch   | effort    | catch per<br>unit of<br>effort | catch   | effort   | catch per<br>unit of<br>effort | cetch      | effort     | catch per<br>umit of<br>effort | catch   | effort     | catch per<br>unit of<br>effort | cetch    | effort   | catch pe<br>unit of<br>effort |
| ylul       | 27,501  | 160,62    | 0.5                            | 7,094   | 24,687   | 6.0                            | 7,583      | 30,249     | 0.3                            | 12,501  | 40,582     | 0.3                            | 19,708   | 51,275   | 0.4                           |
| August     | 21,755  | 50.050    | 4.0                            | 12,527  | 29,422   | . 0.4                          | 11,033     | 36,514     | 0.3                            | 21,106  | 52,979     | 9.0                            | 22,809   | 166,931  | 0.4                           |
| Sept ember | 31,562  | 58,629    | 0.5                            | 20,350  | 34,140   | 0.6                            | 16,246     | 41,065     | 0.4                            | 17,065  | 49,316     | 0.3                            | 23,217   | 46,731   | 0.5                           |
| October    | 18,915  | 45,950    | 9.6                            | 18,350  | 34,561   | 0.5                            | 20,289     | 41,333     | 0.5                            | 14,936  | 40,359     | 9.0                            | 16,659   | 43,619   | 0.4                           |
| November   | 15,879  | 40,490    | .0.4                           | 10,503  | 24,755   | 0.4                            | 9,170      | 25,418     | 0.4                            | 19,235  | 40,906     | 0.5                            | 18,122   | 47,691   | 0.4                           |
| Decmber    | 7,693   | 27,818    | 0.3                            | 8,404   | 20,595   | 0.4                            | 8,483      | 33,235     | 0.3                            | 14,788  | 39,449     | 0.4                            | 10,350   | 36,815   | 0.3                           |
| January .  | 4,502   | 27,994    | 0.2                            | 12,115  | 26,693   | 0.5                            | 7,463      | 25,080     | 0.3                            | 9,278   | 32,765     | 0.3                            | 10,422   | 38,394   | 0.3                           |
| Februery   | 3,832   | 28,593    | 0.1                            | 7.446   | 24,661   | 0.3                            | 6,706      | 13,228     | 0.5                            | 11,405  | 33,713     | 0.3                            | 3,574    | 31,840   | 0.1                           |
| March      | 15,928  | 31,352    | 0.5                            | 13,704  | 43,049   | 0.3                            | 10,288     | 169,10     | 0.3                            | 11,046  | 36,555     | 0.3                            | 16.987   | 56,870   | 0.3                           |
| April      | 7,571   | 29,973    | 0.3                            | 9,062   | 33,860   | 0.3                            | 21.570     | 40,241     | 0.5                            | 13,726  | 48,659     | 0.3                            | 5,939    | 52,513   | 0.1                           |
| Kay        | 6,210   | 35,433    | 0.2                            | 9, 533  | 39.410   | 0.2                            | 11,138     | 31,516     | 7.0                            | 7.347   | 40,773     | 0.2                            | 8,769    | \$1, 398 | 0.2                           |
| June       | 2,423   | 24,089    | 0.1                            | 9,342   | 34,868   | 0.3                            | 12,128     | 21,080     | 0.6                            | 10,576  | 33,936     | 0.3                            | 11,976   | 399,998  | 0.2                           |
| Total      | 166,866 | 368,185   | 0.5                            | 136,430 | 370, 701   | 0.4                            | 142,097    | 370,850    | 7.0                            | 162,927 | 485,992    | 0.3                            | 168,532  | 585,075  | 0.3                           |
|            |         |           |                                |         | ALL DATE AND |                                |            |            |                                |         |            |                                |          |          |                               |

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test tanks and from different locations in Bahrain waters (Figure 4.3) were collected for the determination of polynuclear aromatic hydrocarbons and trace metals concentration.

# 4.2.2 Measurement of toxicity of treated effluents to safee:

The fish were initially maintained in well aerated, gently flowing sea water for more than 10 days before the start of the range finding test in order to acclimate them to laboratory conditions. They were fed daily with a mixture of chicken starter, minced trash fish and starch.

Subsequently, five toxicity tests were conducted on safee with wastewaters from the main stream (channel 1 outlet), side stream (separator No.6 outlet), Sitra separator outlet and the I.A.F. outlet (Figure 3.4). Starvation trials were conducted to determine the maximum starvation period for safee and it was noticed that safee can survive without food and change of water for more than 45 days under well aerated water condition. Accordingly, 96 h range finding or exploratory tests were conducted with each wastewater to determine the approximate concentration range to be covered in the main tests for the different wastewaters stated above.

Four experiments with different concentrations of the main stream effluent (channel 1 outlet) were set up, with a control using clean sea water. The concentrations chosen were 0.33, 1.0, 10 and 100% (i.e., at approximate logarithmic intervals). The test containers were filled with 10 1 solution. Three fish



# Figure: 4.3

Fish sampling stations.

there were no more allow were there are an and 30% rations chosen is the were test work there all and 30% concentrations (20,21,23,25 and 30%) along with a control of class sea water. The tests terms derived out . in 100 1 capacity perspect tanks contacting to these solutions. During experimentation, the temperature. of 6.0-8.5 cm total length and 4.0-6.5 g weight were used in each container. No fish died in the experimental tanks.

A long term exposure for 15 days was then planned and four 100 1 capacity perspex tanks (two as experimental and the other two as controls) were set up with 50 1 of main stream outlet (100% concentration) in the experimental tanks and 50 1 of clean seawater in the control tanks. Ten safee of 7.0-8.5 cm total length and 4.0-6.5 g wt. were randomly selected for each tank. The fish were not fed during the test and for 24 h before the start of the experiment. The tanks were kept covered with perspex lids to prevent the fish from escaping. The test solutions were renewed every 24 h to reduce errors introduced through loss of toxins by uptake, evaporation, etc., and to discard metabolites. The experiment was conducted at a temperature between 25.5-26.0°C with a photoperid of about 12 h light: 12 h dark. The solutions were aerated (7.5-7.8 mg/l dissolved oxygen concentrations) and the tanks were inspected frequently.

A similar experiment was conducted for the wastewater of the side stream (separater No.6 outlet).

In the case of the I.A.F. outlet, the 24 h range finding test was conducted with 5 different concentrations (10,20,30,40 and 100%) with 3 fish in each, gave 100% mortality within 24 h of exposure in the 30,40 and 100% concentrations. In the 10 and 20% concentrations there were no mortality. In view of this, the concentrations chosen in the main test were between 20 and 30% concentrations (20,21,23,25 and 30%) along with a control of clean sea water. The tests were carried out in 100 1 capacity perspex tanks containing 50 1 test solutions. During experimentation, the temperature remained between  $26.8-27.1^{\circ}$ C. The normal 24 h photoperiod was allowed. The test medium was aerated to maintain the dissolved oxygen level between 7.1-7.6 mg/l. Ten safee of 6.5-8.5 cm total length and 5.0-7.5 g weight were randomly selected for each tank. The tanks were covered with lids as in the earlier case. The experiment was run for 96 h and the solutions were renewed every 24 h. The tanks were inspected frequently and dead fish removed.

Similar experiments but with medium size safee (12.5-14.5 cm total length and 18.0-25.0 g weight) were conducted with I.A.F. outlet waste. In this case, the main purpose was to see the weight dependent toxicity and to make comparison between the toxicity of the I.A.F. outlets collected on different days. Based on the range finding test, the concentrations selected in the main test were 15,21.5,23,25 and 30% along with a control of clean sea water. The tests were carried out in perspex tanks containing 100 1 test solutions.

In the case of effluent from Sitra separator, the concentrations chosen were 15, 20, 23, 25 and 30% along with a control of clean sea water. Each tank was filled with 50 1 test solution. Ten safee of 6.0-8.5 cm total length and 5.0-7.5 g weight were employed for these experiments.

From the data obtained, the cumulative percentage mortality at the time of each observation, and for each tank was calculated using the following

Formula:

$$\frac{2m-1}{2p} \times 100$$

Thus where 10 fishes were used in each tank, the response of the first was regarded as 5%, that of the second as 15% and the tenth as 95%. This was because the median response time relates not to the response time of the fifth fish out of total of 10, but to a response time between the fifth and sixth fish (Lloyd, 1979).

At each concentration the percentage mortality was plotted against time of exposure on logarithm/ probability paper and the time for 50% mortality LT50) was read off from the eye-fitted line. Estimates of the response of the test populations (95% confidence limits) were made from the slope of the time-mortality line (Litchfield, 1949).

The cumulative percentage mortalities were plotted on a probit scale against concentration on logarithmic scale and the concentrations lethal to 50% of the test fish (LC50) at fixed observation times were calculated from the eye fitted line. A concentration/response relationship is then obtained by plotting the values of the LT50 against concentration and the estimated values of the LC50 against the corresponding time, using log-log graph paper.

## 4.2.3 Chemical analysis of fish samples:

## 4.2.3.1 Heavy metals:

The sample solutions of the digested fish tissues (8 to 10 fish in each sample) were analyzed for cadmium.

chromium, copper, lead, vanadium and zinc by an Inductively Coupled Argon Plasma-Atomic Emission Spectrometer (Jarrell-Ash Plasma Atomcomp Series 800) using optimized condition.

Mercury was analyzed by a cold vapour atomic absorption spectrometry using acidic stannous chloride as the reducing solution for Hg vapour production from a sample.

## 4.2.3.2 Polynuclear aromatic hydrocarbons:

Concentrated hexane extracts from fish tissues (8 to 10 fish in each sample) were analyzed with a High Pressure Liquid Chromatography (HPLC) equipped with reversed-phase C18 column and fluorescence detector.

## 4.3 Results:

#### 4.3.1 Toxicity test:

### 4.3.1.1 Main stream effluent:

Water quality data of the main stream effluent sample used as an experimental medium in the toxicity test tanks is shown in Table 4.2. After 15 days of exposing the fish to the main stream effluent, no fish died in the experimental tanks. That is because the 7000 GPM oily process water (I.A.F. outlet) was diluted to 115,000 GPM (i.e., 94 times less than its original concentration) by mixing with cleaner water from the subsystems one, two, three, five, six and seven (Figure 3.4) and thereby lowering the concentrations of all polluting ingredients in the final discharge of outlet channel one.

**Table:4.2** 

Water quality data of the main and side streams samples used as an experimental medium in the toxicity test tanks.

|          | Temperature | Total                 | Dissolved      |     | PO4 - P | NO3- N | NO2- N  | N - 17 | 110           | phenols | Sulphides            | Suspended | COD   | BOD  |
|----------|-------------|-----------------------|----------------|-----|---------|--------|---------|--------|---------------|---------|----------------------|-----------|-------|------|
| iffluent | °c          | dissaved<br>solids 7. | oxygen<br>mg/l | Hq  | 1/34    | 1/81   | 1/8/1   | 1/34   | т <u>в</u> /1 | ng/1    | H <sub>2</sub> Smg/l | ng/1      | mg/1  | ng/1 |
|          |             |                       |                |     |         |        |         |        |               |         |                      |           |       |      |
| stream   | 26.0        | 42.0                  | 7.5            | 7.9 | 23.3    | 48.3   | 12.3    | 300.0  | 2.4           | 0.01    | 0.3                  | 18.4      | 104.2 | 2.0  |
| Side     | 0 90        | 0.52                  | 7 6            | 4-8 | 10.2    | 46.8   | <br>8.0 | 158.0  | 1.2           | NIL     | 0.1                  | 5.0       | 118.8 | 1.0  |
|          |             |                       |                | ;   |         |        |         | _      |               |         |                      |           |       |      |

Baker (1979) reports that "in several cases, toxic effects have not been observed in discharge areas (coastal areas) because the effluent (receiving primary treatment only) is rapidly diluted to below toxic levels by the receiving water.

## 4.3.1.2 Side stream effluent:

Table 4.2 shows the water quality data of the side stream effluent used as an experimental medium in the toxicity test tanks. It was noticed that most pollutants were higher in the main stream effluent than in the side stream.

After 15 days of exposing the fish to the side stream effluent, no fish died in the experimental tanks. However, the long term sub-lethal effects and bioaccumulation of the pollutants from the effluents are not ruled out as could be seen from the results of the analysis of fish samples collected from the main and side streams toxicity tests tanks (Table 4.9).

## 4.3.1.3 I.A.F. outlet effluents (small and medium size safee):

Tables 4.3 and 4.4 indicate the water quality of the I.A.F. effluents samples used in the toxicity tests and the experimental medium (diluted I.A.F. outlet samples) at the beginning and end of the tests.The total dissolved solids content of the control and the experimental medium were higher than that of the original I.A.F. effluent. The variations of total dissolved solids affect the osmotic regulations of fish and determine the buoyancy of pelagic eggs, and very often indicate the change in water masses or in their stability conditions. Freshwater is a pollutant when introduced into marine environment in excess.

Table: 4.3

Water quality data of the control, I.A.F. effluent and the diluted experimental media at the beginning and end of the toxicity test (small safee).

| led COD 60D |                 | mg/l mg/l    | 0 1 8 971                        | 0.001  |             |         |                     |                                 |   |   |  |  |  |  |  |   |  |   |  |   |
|-------------|-----------------|--------------|----------------------------------|--|-------------|---------|---------------------|---------------------------------|---|---|--|--|--|--|--|---|--|---|--|---|
| Suspend     | solids          | mg/1         | 27.9                             |  |             |         | 2                   | 2                               | 2   | 1   | 3  | 1  | 3  | 3  | 3  | 1   | 3  | 3   | 3  | 3   |
| Sul chide   | ond the         | 1/8m         | 2.4                              |  |             | 0.7     |                     |                                 |   |   |  |  |  |  |  |   |  |   |  |   |
| Phenole     |                 | 1 mg/1       | 6 0.3                            |  |             | 328     | 1                   |                                 | 1   |   | 1  | 1 2 3 3  | 2393   | 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2  | 1 2 2 2 2 2 2  | 1 2 3 3 2 2<br>   | 23834 4  |   | 23922 283  |   |
| H - W 011   | 4               | Hg/I mg/I    | 23920.0 13.6                     | Contraction of the local division of the loc |             | 6.12    | 41.0<br>11622.0     | 41.0<br>11622.0<br>9685.0       | 41.0<br>11622.0<br>9685.0<br>7920.0   | 41.0<br>41.0<br>9685.0<br>7920.0  | 41.0<br>41.0<br>9685.0<br>7923.0<br>7680.0<br>7576.0   | 41.0<br>41.0<br>9685.0<br>7920.0<br>7680.0                         | 41.0<br>11622.0<br>9685.0<br>7920.0<br>7680.0<br>7576.0      | 41.0<br>11622.0<br>9685.0<br>7920.0<br>7576.0                                    | 41.0<br>11622.0<br>9685.0<br>7920.0<br>7680.0<br>7576.0                  | 41.0<br>11622.0<br>9685.0<br>7620.0<br>7576.0<br>7576.0                             | 41.0<br>11622.0<br>9685.0<br>7923.0<br>7923.0<br>7576.0<br>7576.0<br>7576.0  | 41.0<br>11622.0<br>9685.0<br>7923.0<br>7680.0<br>7576.0<br>7576.0<br>7576.0<br>14088.0  | 41.0<br>11622.0<br>9685.0<br>7680.0<br>7680.0<br>7576.0<br>7576.0<br>7576.0<br>7576.0<br>7576.0<br>7576.0  | 41.0<br>11622.0<br>9685.0<br>7680.0<br>7680.0<br>7576.0<br>7576.0<br>7576.0<br>7576.0<br>7576.0<br>7576.0<br>7576.0                                   |
| N - CN      |                 | 1/8/         | 5.2                              | and the second se  |             | 4.3     | ¢.3<br>6.13         | 6.4<br>13.6                     | 4.3<br>13.6<br>11.2<br>11.1   | 4.3<br>13.6<br>11.2<br>11.1<br>2.9  | 4.3<br>13.6<br>11.2<br>11.2<br>5.9<br>5.9  | 4.3<br>13.6<br>11.2<br>11.1<br>5.9<br>5.9<br>5.6                   | 4.3<br>11.2<br>11.1<br>5.9<br>5.9<br>5.6                     | 4.3<br>11.2<br>11.2<br>5.9<br>5.6  | 6.3<br>11.2<br>5.9<br>5.6<br>5.6<br>5.6                                  | 4.3<br>11.2<br>11.2<br>5.6<br>5.6<br>3.8  | 4.3<br>11.2<br>5.9<br>5.6<br>3.8<br>3.8<br>40.7  | 4.3<br>11.6<br>11.1<br>5.9<br>5.9<br>5.6<br>5.6<br>5.6<br>7.0<br>2.8<br>2.8<br>11.3   | 4.3<br>11.6<br>11.1<br>5.9<br>5.9<br>5.6<br>5.6<br>3.8<br>40.7<br>11.3<br>10.8   | 4.3<br>13.6<br>11.2<br>5.9<br>5.9<br>5.6<br>5.6<br>3.8<br>40.7<br>11.3<br>10.8<br>11.3<br>10.8  |
| P ND N      | г               | 1/8/         | 0 1.5                            | and the state of the second seco   |             | 2 65.1  | 2 65.1<br>1 6.5     | 2 65.1<br>1 6.5<br>0 6.1        | 2 65.1<br>3 6.5<br>9 6.3<br>2.8   | 2 65.1<br>3 65.1<br>6.3<br>6.3<br>2.8   | 65.1<br>6.5<br>6.3<br>6.3<br>6.3<br>2.8<br>2.8<br>2.8<br>2.7   | 65.1<br>6.5<br>6.3<br>6.3<br>2.8<br>2.8<br>2.8                     | 65.1<br>6.5<br>6.3<br>6.3<br>2.8<br>2.8<br>2.8<br>2.8<br>2.7 | 65.1<br>6.5<br>6.3<br>6.3<br>2.8<br>2.8<br>2.8<br>2.7<br>1.9                     | 65.1<br>6.5<br>6.3<br>6.3<br>2.8<br>2.8<br>2.8<br>2.8<br>2.7<br>1.9      | 61<br>63<br>28<br>28<br>28<br>27<br>19  | 2 65.1<br>6.5<br>6.3<br>6.3<br>6.3<br>2.8<br>2.8<br>2.8<br>2.8<br>2.7<br>1.9<br>1.9<br>1.9   | 2 65.1<br>6.5<br>6.3<br>6.3<br>6.3<br>2.8<br>2.8<br>2.8<br>2.7<br>1.9<br>1.4<br>31.4<br>53.8  | 2 65.1<br>6.5<br>6.3<br>6.3<br>5.8<br>2.8<br>2.8<br>2.8<br>2.8<br>2.7<br>1.9<br>1.4<br>53.6<br>53.6  | 2 65.1<br>6.5<br>6.3<br>6.3<br>5.8<br>5.8<br>6.3<br>6.3<br>6.3<br>7.9<br>1.9<br>1.4<br>53.6<br>53.6<br>53.6   |
| - 02        | 4 H             | 1/8/         | 10 400.0                         |  | <u>te  </u> | 92 28.2 | 92 28.2<br>83 117.3 | 92 28.2<br>83 117.3<br>80 105.0 | 32     28.2       92     28.2       83     117.3       80     105.0       78     91.9 | 92     28.2       83     117.3       80     105.0       78     91.9       78     94.3 | 32     28.2       83     117.3       83     117.3       80     105.0       77     84.3       75     81.2 | 92 28.2   83 117.3   80 105.0   78 91.9   77 84.3   75 81.2        | 92 28.2   83 117.3   80 105.0   77 84.3   77 84.3   75 81.2  | 92 28.2   83 117.3   80 105.0   78 91.9   77 84.3   75 81.2                      | 92 28.2   83 117.3   80 105.0   77 84.3   77 84.3   75 81.2              | 92 28.2   83 117.3   80 105.0   78 91.9   75 81.2   75 81.2   13 5.3                | 92 28.2   83 117.3   80 105.0   70 91.9   77 84.3   75 81.2   75 81.2   73 81.2   73 81.2   75 81.2   75 81.2   75 81.2   76 81.2   77 81.2   78 5.3   107.6 107.6 | 92 28.2   83 117.3   80 105.0   71 84.3   77 84.3   75 81.2   75 81.2   75 81.2   76 91.9   77 84.3   75 81.2   75 81.2   76 91.2   77 84.3   78 8.1.2   79 91.2   79 91.2   79 91.2   70 107.6   29 99.8 | 92 28.2   83 117.3   80 105.0   78 91.9   77 84.3   75 81.2   75 81.2   75 81.2   76 91.9   75 81.2   75 81.2   75 81.2   75 81.2   76 99.8   77 50.3   78 50.3   79 99.8   70 107.6   25 66.1 | 92 28.2   83 117.3   80 91.9   78 91.9   78 84.3   79 84.3   75 81.2   75 81.2   75 81.2   75 81.2   80 107.6   29 99.8   26 99.8   26 66.1   26 66.1 |
| Dissolved   |                 | ng/l         | 1                                |  |             | 7.4     | 7.4 7.              | 7.4<br>7.1<br>7.1<br>7.1        | 7.4<br>7.1<br>7.1<br>7.1<br>7.1<br>7.5<br>7.5   | 7.4<br>7.3<br>7.1<br>7.1<br>7.1<br>7.1<br>7.1<br>7.1<br>7.1<br>7.1                    | 4 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1  | 4.7<br>7.1<br>7.1<br>7.1<br>7.5<br>7.5<br>7.7<br>7.7<br>7.7<br>7.7 | 4 C C C C C C C C C C C C C C C C C C C                      | 4.7<br>1.7<br>1.7<br>1.7<br>1.7<br>1.7<br>2.7<br>7.7<br>7.7<br>7.7<br>7.7<br>7.7 | 4 C C C C C C C C C C C C C C C C C C C                                  | 4.7<br>1.7<br>1.7<br>1.7<br>1.7<br>1.7<br>1.7<br>2.5<br>2.7<br>8.7<br>8             | 7.4<br>7.1<br>7.1<br>7.1<br>7.5<br>7.5<br>7.5<br>7.5<br>7.5<br>7.5<br>7.5<br>8.7<br>8.7<br>8.7<br>8.7  | 7.4<br>7.1<br>7.1<br>7.1<br>7.5<br>7.5<br>7.5<br>7.5<br>7.5<br>7.5<br>7.5<br>7.5<br>7.5<br>7.5  | 4  | 4   |
| IOCAL       | Dissolved       | Solids<br>2. | 25.5                             |  |             | 0.94    | 46.0                | 46.0<br>41.9<br>42.2            | 46.0<br>41.9<br>42.2<br>42.4  | 46.0<br>41.9<br>42.2<br>42.4<br>43.6  | 46.0<br>41.9<br>42.2<br>43.6<br>43.8   | 46.0<br>41.9<br>42.2<br>42.4<br>43.6<br>43.8                       | 46.0<br>41.9<br>42.4<br>43.6<br>43.8                         | 46.0<br>41.9<br>42.2<br>42.4<br>43.8<br>43.8                                     | 46.0<br>41.9<br>42.4<br>43.6<br>43.8                                     | 46.0<br>41.9<br>42.2<br>42.4<br>43.8<br>43.8<br>43.8                                | 46.0<br>41.9<br>42.2<br>43.6<br>43.6<br>43.8<br>43.8<br>43.8<br>43.8<br>43.0   | 46.0<br>41.9<br>42.4<br>42.4<br>43.6<br>43.8<br>43.8<br>43.8<br>43.0<br>42.2  | 46.0<br>41.9<br>42.4<br>42.4<br>43.6<br>43.8<br>43.8<br>43.8<br>45.0<br>42.3   | 46.0<br>41.9<br>42.2<br>42.4<br>43.6<br>43.8<br>43.8<br>43.8<br>42.0<br>42.3<br>42.8  |
| Temperature |                 | 2            | 0.04                             |  |             | 27.1    | 27.1                | 27.1<br>27.0<br>26.9            | 27.1<br>27.0<br>26.9<br>27.0  | 27.1<br>27.0<br>26.9<br>27.0<br>27.1  | 27.1<br>27.0<br>26.9<br>27.0<br>27.1<br>26.9   | 27.1<br>27.0<br>26.9<br>27.0<br>27.1<br>26.9                       | 27.1<br>27.0<br>26.9<br>27.0<br>27.1<br>26.9                 | 27.1<br>27.0<br>26.9<br>27.0<br>27.1<br>26.9                                     | 27.1<br>27.0<br>26.9<br>27.0<br>27.1<br>26.9                             | 27.1<br>27.0<br>26.9<br>27.1<br>26.9<br>25.9  | 27.1<br>27.0<br>26.9<br>27.0<br>27.1<br>26.9<br>26.9<br>26.8   | 27.1<br>27.0<br>26.9<br>27.0<br>27.1<br>26.9<br>26.9<br>26.8<br>26.8  | 27.1<br>27.0<br>26.9<br>27.1<br>26.9<br>26.9<br>26.8<br>26.8<br>26.9   | 27.1<br>27.0<br>26.9<br>27.1<br>26.9<br>26.9<br>26.8<br>26.8<br>26.9<br>26.9<br>26.9  |
| ar arpau    | 1.A.F. effluent |              | Original concentration<br>(100%) | At the beglaming<br>of the test:   |             | Control | Control<br>301,     | Control<br>30,<br>25,           | Control<br>30",<br>23",   | Control<br>30°.<br>23°.<br>21°.   | Control<br>30°.<br>23°.<br>21°.<br>20°.  | Control<br>30°.<br>23°.<br>21°.<br>20°.                            | Control<br>30°.<br>23%<br>21°.<br>20°.<br>At the end of the  | Control<br>30%,<br>23%,<br>21%,<br>21%,<br>20%,<br>Af the end of the<br>test:    | Control<br>30%<br>23%<br>21%<br>21%<br>20%<br>Af the end of the<br>test: | Control<br>30%<br>23%<br>21%<br>21%<br>20%<br>At the end of the<br>test:<br>control | Control<br>30%<br>21%<br>21%<br>21%<br>20%<br>At the end of the<br>test:<br>control<br>30%   | Control<br>30°.<br>23°.<br>21°.<br>21°.<br>20°.<br>Af the end of the<br>test:<br>30°.<br>30°.   | Control<br>30°,<br>23%<br>21°,<br>20°,<br>20°,<br>20°,<br>20°,<br>23°,<br>23°,<br>23°,<br>23°,   | Control<br>30°,<br>23°,<br>21°,<br>20°,<br>20°,<br>20°,<br>20°,<br>23°,<br>23°,<br>23°,<br>23°,<br>23°,<br>23°,<br>23°,                               |

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| I.A.F. effluent               | Temperature<br><sup>o</sup> C | Total<br>Dissoved<br>Solids<br>7. | Dissolved<br>oxygen | £              | 1/8(        | N - EON        | N - 20N | NH4 - N<br>JB/1 | 011<br>mg/1 | Phenols<br>mg/l | Sulphides<br>H <sub>2</sub> S<br>mg/1 | Suspended<br>Solids<br>mg/l |
|-------------------------------|-------------------------------|-----------------------------------|---------------------|----------------|-------------|----------------|---------|-----------------|-------------|-----------------|---------------------------------------|-----------------------------|
| Original concentration (100%) |                               | 25.5                              | 100<br>198          | 9.7            | 236.5       | 12.8           | 7.7     | 27590.0         | 1.11        | 9.5             | 37.4                                  | 10.2                        |
| At the begiming of the        |                               | 1                                 | irain<br>air        | 6 1 3<br>P 6 6 |             | 510)<br>118    | 87.3    | ni e<br>ter     | l sh        |                 | va l<br>we                            |                             |
| test :                        |                               | id P                              |                     |                |             |                | 10.1    |                 | 101         | wi              | ui<br>Ti                              |                             |
| control 0%                    | 29.2                          | 45.0                              | 7.3                 | 8.30           | 23.2        | 32.7           | 5.9     | 38.0            |             | 15              |                                       |                             |
| 301.                          | 29.0                          | 39.5                              | 6.9                 | 9.24           | 71.0        | 22.6           | 7.3     | 71540.0         |             | it:             |                                       |                             |
| 252                           | 29.1                          | 40.0                              | 7.0                 | 9.22           | 61.8        | 12.8           | 1.1     | 5160.0          | 14.         |                 |                                       |                             |
| 237.                          | 29.1                          | 41.0                              | 7.0                 | 9.16           | 64.5        | 12.6           | 6.9     | 4332.0          | 1.8<br>1.8  | 10              |                                       |                             |
| 21.5%                         | 29.0                          | 41.5                              | 7.2                 | 9.15           | 54.5        | 12.6           | 6.5     | 3508.0          | 6<br>1      | e               |                                       |                             |
| 151                           | 29.3                          | 43.3                              | 6.7                 | 8.94           | 23.3        | 9.4            | 5.8     | 2820.0          | 6 1<br>5 E  | Chie<br>1       | 9.81<br>9.81 9<br>9.81 9              |                             |
| At the end of the test:       | 00                            | iow<br>th                         | be<br>al            | ion<br>Aug     | с. р<br>109 | (2.0)<br>(2.0) | ratio   | 10              | 213.<br>    | n               | it D<br>Rui                           |                             |
| 301                           | 29.2                          | 36.9                              | 7.3                 | 9.25           | 44.7        | 38.1           | 9.2     | 7890.0          |             | che<br>eve      |                                       |                             |
| 257                           | 28.9                          | 40.2                              | 7.5                 | 9.24           | 30.0        | 1.44           | 14.5    | 6580.0          |             |                 | ¥<br>(, .                             |                             |
| 237                           | 28.9                          | 41.1                              | 7.6                 | 9.15           | 21.6        | 15.1           | 41.6    | 6559.0          |             |                 |                                       |                             |
| 21.5%                         | 28.8                          | 41.7                              | 7.4                 | 6.13           | 21.8        | 15.0           | 42.8    | 5588.0          | R.C.        |                 | 0                                     |                             |
| 15 %                          | 28.6                          | 43.3                              | 4.1                 | 11.78          | ī           | 1              | 1       | 80<br>1<br>00   | n.<br>ten   | he<br>n         | sa<br>pli                             |                             |
|                               | シアトロー                         | 1                                 | h                   |                |             | 10             |         |                 | 0           | _               |                                       |                             |

Water quality data of the control, I.A.F. effluent and the diluted experimental media at the beginning and end of the toxicity test (medium size safee). \_

The dissolved oxygen values were essentially the same in all experiments as were the temperatures. The pH of the test solutions shifted to the lower side because pH of the I.A.F. outlet was higher than that of the control. The values of nitrate have, however, been elevated due to the higher levels of this nutrient in the sea water. The very high level of ammonia in the experimental medium which must have affected the survival rate of the fish is attributable to the ammonia content of the I.A.F. effluent.

The before and after experimentation water quality tests do not exhibit any marked shifts in any parameter except nitrates, ammonia and, to a lesser extent, nitrites. It is felt that the higher levels of nitrates and nitrites in relation to the values prior to experementation were the result of the conversion of ammonia to these constituents in the constantly aerated water of the fish tanks. The higher levels of post experimentation ammonia may have been due to the metabolic activities of the experimental fish.

Mortality data at the end of different time intervals within the experimental periods are shown in Tables 4.5 and 4.6. Figures 4.4 and 4.5 show the time/ mortality curves. The concentration/mortality curves are shown in Figures 4.6 and 4.7. The concentration/ response curve in Figure 4.8 indicates that the 96 h LC50 of the I.A.F. effluent to small size safee was 24.4%, the response reached a threshold after about nine hours, so this concentration can also be described as the threshold LC50. The concentration/ response curve in Figure 4.9 indicates that the 96h LC50 of the I. A. F. effluent to medium size safee was 20.0%. The steepness of the

## Table:4.5

Mortality data for small safee (I.A.F. outlet).

| Concentration   | No. of test |     |     |     | Num | ber | of   | Ces | t   | f    | ish  | dead | at   |      |
|-----------------|-------------|-----|-----|-----|-----|-----|------|-----|-----|------|------|------|------|------|
| of I.A.F.outlet | fish        |     |     |     | the | ene | d of | :   |     |      |      |      |      |      |
| % by volume     |             | lhr | 2hr | 3hr | 4hr | Shr | 6hr  | 8hr | 9hr | 12hr | 24hr | 48hr | 72hr | 96hr |
|                 |             |     |     |     |     |     |      |     |     |      |      |      |      |      |
| 30              | 10          | 1   | 5   | 7   | 7   | 9   | 10   | 10  | 10  | 10   | 10   | 10   | 10   | 10   |
| 25              | 10          | 1   | 1   | 2   | 3   | 4   | <    | 5   | ς   | 5    | . د  | ς    | 5    | 5    |
|                 |             | -   | •   | -   |     | -   | 2    |     | 2   | ,    | ,    | ,    |      | ,    |
| 23              | 10          | 0   | 0   | 1   | 1   | 3   | 3    | 3   | 4   | 4    | 4    | 4    | 4    | 5    |
|                 |             |     | •   | •   | •   | •   | -    |     |     |      |      |      |      |      |
| 21              | 10          | 0   | 0   | 0   | U   | 0   | 0    | 0   | 1   | 1    | 1    | 1    | 1    | 1    |
| 20              | 10          | 0   | 0   | 0   | 0   | 0   | 0    | 0   | 0   | 0    | 0    | 0    | 0    | 0    |
|                 |             |     |     |     |     |     |      |     |     |      |      |      |      |      |

Mortality data for medium size safee (I.A.F. outlet).

| Concentration                  | No. of test |     | Numb       | er (      | of t | est         |     | fi   | sh           | dead  | j at          | -    |               |      |      |
|--------------------------------|-------------|-----|------------|-----------|------|-------------|-----|------|--------------|-------|---------------|------|---------------|------|------|
| of I.A.F.outlet<br>2 by volume | fish        | 1h  | the<br>2b- | end<br>7- | of   | :<br>5h     | 6h- | 7    | 8 <b>5</b> ~ | Qih.e | 1 <b>0</b> b~ | 116- | 1 <b>2</b> hr | 135- | 96b- |
|                                |             | 701 | <u> </u>   | 3116      | 411  | <i>A</i> 11 |     | /111 |              | 7111  | 1011          |      |               |      | 7011 |
| 30.0                           | 10          | 6   | 9          | 10        | 10   | 10          | 10  | 10   | 10           | 10    | 10            | 10   | 10            | 10   | 10   |
| 25.0                           | 10          | 2   | 9          | 9         | 10   | 10          | 10  | 10   | 10           | 10    | 10            | 10   | 10            | 10   | 10   |
| 23.0                           | 10          | 1   | 9          | 9         | 9    | 10          | 10  | 10   | 10           | 10    | 10            | 10   | 10            | 10   | 10   |
| 21.5                           | 10          | 0   | 3          | 6         | 6    | 7           | 8   | 8    | 8            | 8     | 9             | 9    | 9             | 10   | 10   |
| 15.0                           | 10          | 0   | 0          | 0         | 0    | 0           | 0   | 0    | 0            | i 0   | 0             | 0    | 0             | 0    | 0    |
|                                |             |     |            |           |      |             |     |      |              |       |               |      |               |      |      |













concentration/response curves (Figures 4.8 and 4.9) indicates that the toxic components of the waste were rapidly lost from solution or excreted or detoxified by the fish. This type of response is typical of materials with cyanide or ammonia which are detoxified at low concentrations. The truncated time/mortality curves in Figure 4.4 for 25% and 23% effluents (small safee) are an indication of such loss of toxicity.

The effluents coming from the I.A.F. has been found to be lethal to safee at the discharge point. In the final discharge, the I.A.F. effluent was diluted with cleaner sea water. The LT50 value for the medium size fish treated with a 30% I.A.F. effluent (Figure 4.5) was lower than that of the small size fish tested at the same concentration (Figure 4.4). The LC50 values (Figure 4.8 and 4.9) also showed lower levels at all exposure durations in the case of medium size fish indicating their sensitivity even to the lower concentration levels. These results indicate that the I.A.F. effluent used for the experiment with medium size fish was more dense and black in color with a higher concentration of pollutants (Table 4.3 and 4.4).

# 4.3.1.4 Sitra separator effluent:

Water quality data of the Sitra separator effluent sample used in the toxicity test and the experimental medium at the beginning and end of the test is shown in Table 4.7. Mortality data at the end of different time intervals within the experimental period is given in Table 4.8. Figure 4.10 shows the time/mortality curve while the concentration/mortality curve is shown in Figure 4.11.

| media at the                      | e beginning a     | ind end of                        | the toxicit                 | y test | : (small | safee)  | outlet<br>se                |                   | elicy d     | LLLL            |                                       |                             |
|-----------------------------------|-------------------|-----------------------------------|-----------------------------|--------|----------|---------|-----------------------------|-------------------|-------------|-----------------|---------------------------------------|-----------------------------|
| Sitra separator<br>effluent       | Tamperature<br>°C | Total<br>Dissoved<br>Solids<br>7. | Dissolved<br>oxygen<br>mg/l | Æ      | PO4 - P  | N - EON | NO <sub>2</sub> - N<br>JB/L | л44 – н<br>н – лы | 011<br>mg/1 | Phenols<br>mg/l | Sulphides<br>H <sub>2</sub> S<br>mg/l | Suspended<br>Solids<br>mg/l |
| Original concentration<br>(1007,) | 34.0              | 40.5                              | 1                           | 6.9    | 236.5    | 13.4    | 50.3                        | 3660.0            | 30.0        | 0.2             | 6.9                                   | 51.5                        |
| At the begimning of the           |                   |                                   |                             |        |          |         |                             | and and           |             |                 |                                       |                             |
| test :                            |                   |                                   |                             |        |          |         |                             |                   |             |                 |                                       |                             |
| control (01)                      | 25.0              | 46.2                              | 6.9                         | 8.49   | 18.4     | 45.8    | 3.1                         | 27.0              | 1           |                 |                                       |                             |
| 30%                               | 25.0              | 42.9                              | 1.7                         | 8.26   | 85.8     | 46.0    | 4.6                         | 920.0             | 01          |                 | •                                     |                             |
| 25%                               | 24.5              | 43.8                              | 6.9                         | 8.40   | 73.9     | 30.8    | 4.6                         | 633.0             | in a        |                 |                                       |                             |
| 237.                              | 24.5              | 44.1                              | 7.0                         | 8.43   | 66.9     | 27.4    | 3.1                         | 573.0             |             |                 |                                       |                             |
| 20%                               | 25.0              | 45.0                              | 7.0                         | 8.45   | 46.2     | 24.6    | 2.8                         | 560.0             | 194<br>1    |                 |                                       |                             |
| 15%                               | 25.0              | 45.5                              | 7.0                         | 8.47   | 41.5     | 24.5    | 2.4                         | 126.6             | 1000        |                 |                                       |                             |
| At the end of the test:           |                   |                                   |                             |        |          |         |                             |                   | E E A       |                 |                                       |                             |

Water quality data of the control. Sitra separator effluent and the diluted experimental Table: 4.7

202.5 25.0

1

1/Bu

COD

- 296 -

713.0 701.0 657.0

5.6 4.9 4.7

38.7 38.4 37.9

40.1

8.44 8.63 8.70

44.5

24.5

36.5

7.2 7.1 7.2

45.5

24.9

23% 20% - 297 -

## Table: 4.4

Mortality data for small safee (Sitra separator outlet).

| Concents    | ation              | No. of test |    |     |     | Num        | ber        | of  | tes      | t   | £i   | sh   | dead | at   |      |
|-------------|--------------------|-------------|----|-----|-----|------------|------------|-----|----------|-----|------|------|------|------|------|
| of Sitra se | ep. outlet<br>lume | fish        | hr | 1hr | 2hr | the<br>3hr | end<br>4hr | Shr | :<br>6hr | 7hr | 12hr | 24hr | 48hr | 72hr | 96hr |
|             |                    | Aler is     |    |     |     |            |            |     |          |     |      |      |      |      |      |
| 30          |                    | 10          | 4  | 10  | 10  | 10         | 10         | 10  | 10       | 10  | 10   | 10   | 10   | 10   | 10   |
| 25          |                    | 10          | 1  | 10  | 10  | 10         | 10         | 10  | 10       | 10  | 10   | 10   | 10   | 10   | 10   |
| - 23        | 64                 | 10          | 0  | 0   | 1   | 6          | 6          | 6   | 8        | 9   | 9    | 9    | 9    | 9    | 9    |
| 20          |                    | 10          | 0  | 0   | 0   | 1          | 2          | 2   | 3        | 3   | 3    | 3    | 5    | 5    | 5    |
| 15          |                    | 10          | 0  | 0   | 0   | 0          | 0          | 0   | 0        | 0   | 0    | 0    | 0    | 0    | 0    |




The concentration/response curve in Figure 4.12 indicates that the 96 h LC50 of the Sitra separator effluent to small safee was 20.3%.

### 4.3.2 Fish analysis:

Polynuclear aromatic hydrocarbons and trace metals concentrations in fish samples from selected toxicity test tanks and from different location in Bahrain waters are shown in Tables 4.9 and 4.10 respectively. Figures 4.13, 4.14 and 4.15 show the analysed fish, leather jacket (lehlah), haffara bream (gorgofan) and spotted halfbeak (sils). Out of the polynuclear aromatic hydrocarbons determined, Benzo (a) pyrene was not detected in any fish samples. Flouranthene was detected only in fishes exposed to the main and side streams, the fish in the latter show elevated Unknown substances values (Table 4.9). were. however, present in all the fish collected from the toxicity test tanks. Slightly elevated values of these unknown substances were obtained in small safee exposed to 21% I.A.F. effluent. Table 4.10 shows that these substances were detected only in the fish samples collected from the south and east of the pump house. The concentration of zinc was also high there.

Fish from the experimental medium of the main and side streams showed a higher accumulation of cadmium (Table 4.9). Lead which is a normal ingredient in oil pollution, showed elevated values in the experimental fish tested in all the effluents except those from 15% I.A.F. effluent (Table 4.9). Vanadium and zinc also exhibited higher values in all the experimental fish except those tested in 15%





Table:4.9

Polynuclear aromatic hydrocarbons and trace metals concentration  $\overset{f a}{}$  in fish samples from selected toxicity test tanks.

| Fish samples from the toxicity test tanks              | Exposure | Polynuclear a<br>(on wet weigh | romatic hydr<br>t basis) | ocarbons JB/Kg                            | Trace<br>weig | metal<br>sht basi | concen<br>is ) | t ration | mg/kg | uo ) | wer               |
|--|----------|--------------------------------|--------------------------|---|---------------|-------------------|----------------|----------|-------|------|-------------------|
| containing effluents<br>from:                          |          | Benzo(a) pyrene                | Fluoranthene             | Unknown (Ret.tin                          | e Cd          | Cr                | C              | P P      | >     | 2n   | Нg                |
| 1. the main stream                                     | 15 days  | Not Detected                   | 1.46                     | 0.49 (4.58)                               | 0.06          | < 0.2             | 0.7            | 1.0      | 1.0   | 21.3 | <b>&lt;</b> 0.002 |
| 2. the side stream                                     | 15 days  | Not Detected                   | 6.44                     | 0.11 (5.52)                               | 0.07          | ح 0.2             | 0.5            | 1.0      | 1.0   | 16.8 | 0.041             |
| 3. Sitra separator                                     | 7 days   | Not Detected                   | Not Detected             | I   | <0.05         | < 0.2             | < 0.2          | 1.0      | 1.0   | 16.1 | <0.002            |
| <pre>(\$mall safee) (\$mall safee) (Small safee)</pre> | 7 days   | Not Detected                   | Not Detected             | 0.66 (2.79)<br>4.83 (4.62)<br>0.50 (7.72) | <0.05         | 0.4               | 0.4            | 1.0      | 1.6   | 28.0 | 0.015             |
| 5. I.A.F. outlet (15%)<br>(medium size safee)          | 12 hours | Not Detected                   | Not Detected             | 2.31 (5.45)                               | <0.05         | < 0.2             | 0.5            | <0.5     | < 0.2 | 4.7  | <b>&lt;</b> 0.002 |
|  |          |                                |                          |   |               |                   |                |          |       |      |                   |

\* Analysed by KISR

**Table: 4.10** 

Polynuclear aromatic hydrocarbons and trace metals concentration  $\dagger$  in fish samples from different locations.

|  |                                       | Polynuclear a fon wet weigh | romatic hydr<br>c basis) | ocarbons JB/Kg     | Trace I<br>weigh | netal (<br>t basi | concent<br>s) | ration | m8 / K8 | uo 1 | Ae L    |
|--|---------------------------------------|-----------------------------|--------------------------|--------------------|------------------|-------------------|---------------|--------|---------|------|---------|
| LOCALION                               |                                       | Benzo(a) pyrene             | Fluoranthène             | Unknown (Ret.time) | pp               | Cr                | ŋ             | ٩٩     | >       | Zn   | Чĸ      |
| 1. Karzakan                            | Safee <sup>*</sup>                    | Not Detected                | Not Detected             | i                  | د0.05            | د ٥.2             | <0.2          | 0.5    | د0.2    | 4.7  | 0.012   |
| 2. Muharreq                            | Safee                                 | Not Detected                | Not Detected             | i                  | ¢ 0.05           | د0.2              | 1             | 1      | 1       | 1    | < 0.002 |
| 3. Sufalah                             | Safee                                 | Not Detected                | Not Detected             | 1                  | <0.05            | < 0.2             | ٤.0 ۷         | 0.5    | <0.2    | 3.2  | < 0.002 |
| 4. Pump house<br>enclosure             | Lehlah*<br>and Corgof <del>a</del> n* | Not Detected                | Not Detected             | ı                  | <0.05            | < 0.2             | ۲0.2          | 0.5    | ۲0.2    | 3.9  | <0.002  |
| 5. South and east<br>of the pump house | Sils* and<br>Corgofan                 | Not Detected                | Not Detected             | 6.38 (7.33)        | د0.05            | د0.2              | ۲0.2          | 0.5    | د0.2    | 10.3 | 0.012   |
|  |                                       |                             |                          |                    |                  |                   |               |        |         |      |         |

| * LOCAL NAME | ENGLISH NAME             | SCIENTIFIC NAME             |
|--------------|--------------------------|-----------------------------|
| Saffee       | Pearl spotted rabbitfish | Siganus canaliculatus       |
| Lehlah       | Leather jacket           | Scomberoides commersonianus |
| Gorgofan     | Bream                    | Rabdosargus sarba           |
| Sils         | Spotted halfbeak         | Hemiramphus far             |

Analysd by KISR

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## Figure: 4.13

Family: Species: Local name: English name: Carangidae <u>Scomberoides</u> <u>commersonianus</u> Lehlah Leather jacket



## Figure: 4.14

| Family:       | Sparidae             |
|---------------|----------------------|
| Species:      | Rhabdosargus haffara |
| Local name:   | Gorgofan             |
| English name: | Haffara bream        |



a static toxicity test with Maily replacement of th test solution during a 96 h exposure period. The toxicities of a number of detergents, pesticides, polychlorinated biphenyls (PCBs) and pure chemicals to a number of species have been determined using t

#### Figure: 4.15

Family: Species: Local name: English name: Hemiramphidae <u>Hemiramphus</u> <u>far</u> Sils Spotted halfbeak I.A.F. effluent. This might be because those fish were exposed to the outlet for only 12 hours. The fish in the experimental medium of 21% I.A.F. outlet discharge showed the highest concentration of zinc (28.0 mg/kg). Except for the fish exposed to the side stream and 21% I.A.F. effluent the values for mercury were low (Table 4.9 and 4.10).

#### 4.4 Discussion:

### 4.4.1 Toxicity tests:

Since the early 1960s the acute toxicity of various pollutants to marine organisms has been evaluated at the Ministry of Agriculture, Fisheries and Food (MAFF), Fisheries Laboratory, Burnham-on-Crouch (U.K.) using a static toxicity test with daily replacement of the test solution during a 96 h exposure period. The toxicities of a number of detergents, pesticides, polychlorinated biphenyls (PCBs) and pure chemicals to a number of species have been determined using this method (Portmann 1972, Portmann and Wilson 1971). The static test was also used for the evaluation of oil dispersants under the voluntary approval scheme which existed prior to 1974 (Portmann and Connor 1968; Wilson 1974). Dispersants with a satisfactory performance in efficiency tests carried out at the Warren Spring Laboratory of the Department of Trade and Industry and with a low toxicity in the static test were approved for use in the U.K. (Franklin, 1980).

According to Jenkins (1964), the most toxic constituents of the waste waters from oil refinery were found to be ammonia, phenol, and sulphide. The toxicity of Table 4.11 shows a comparison between the LC50 of the I.A.F. and Sitra separator effluents, The Table indicates that the I.A.F. effluent applied to the medium size safee was of higher toxicity. The results in Tables 4.3, 4.4 and 4.7 also indicate that the concentration of pollutants (oil, phenols, sulphides, ammonia, nitrite and pH) in that I.A.F. effluent was higher than that in the I.A.F. and Sitra separator effluents applied to the small safee.

The toxicity curves for the I.A.F outlet and small and medium safee (Figures 4.8 and 4.9), and for the Sitra separator (Figure 4.12), are very steep and indicate that a threshold LC50 is reached in a very short period of time. Such curves are typical of HCN and ammonia, where there is little evidence for chronic toxicity at concentrations considerably lower (say, greater than 10x) than the 96 h LC50.

The time/mortality curves also show a shallower slope with decreasing concentration and this reinforces the existence of a sharply defined threshold concentration. Therefore, this type of result indicates that chronic effects of these effluents on fish are unlikely at concentrations lower than 2% effluent; that no significant bioaccumulation will occur which could exert a chronic effect on fish, although taint may still be a problem for the human consumer of such fish; and that the fish are probably able to detoxify or metabolise the harmful substances in the effluent which are absorbed into their tissues.

# TABLE :4-11

Comparison between the LC50s of the I.A.F. and Sitra Sepatator Effluents.

| with<br>predi               | aris<br>t 1e   | 8 (4)<br>1913 |      | atin<br>Typ |    | LCSO | 13  |      | 848<br>245 |      |     | NCC Y | 50<br>171        | the C |
|-----------------------------|----------------|---------------|------|-------------|----|------|-----|------|------------|------|-----|-------|------------------|-------|
| EFFLUENT                    | 1h L(          | cso :         | 3h l | LCSO        | 6h | LC50 | 12h | LCSO | 24h        | LCSO | 48h | 1050  | 96h              | LCSO  |
| 1st<br>Experiment:          | 16285<br>16.80 | Lon<br>Clai   |      |             |    |      |     |      |            |      |     |       |                  |       |
| I.A.F. outlet               |                |               |      |             |    |      |     |      |            |      |     |       |                  |       |
| (small size<br>safee )      | > 3            | 0.0           |      | 28.5        |    | 25.1 |     | 24.5 |            | 24.5 |     | 24.6  |                  | 24.4  |
| 2nd<br>Experiment:          |                |               |      |             |    |      |     |      |            |      |     |       |                  |       |
| I.A.F. outlet               |                |               |      |             |    |      |     |      |            |      |     |       |                  |       |
| (medium size<br>safee )     | 2              | 9.9           |      | 21.0        |    | 20.2 |     | 20.2 |            | 20.0 |     | 20.0  |                  | 20.0  |
| <u>3rd</u><br>Experiment:   |                |               |      |             |    |      |     |      |            |      |     |       |                  |       |
| Sitra sepa-<br>rator cutlet |                |               |      |             |    |      |     |      |            |      |     |       |                  |       |
| (small size<br>safee )      | 2              | 2.3           |      | 22.8        |    | 21.5 |     | 21.1 |            | 21.1 |     | 20.3  | 4.508<br>1910-19 | 20.3  |

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Therefore, so far as the safety of fish is concerned, an application of 100 on the 96 h LC50 may be too stringent in practice. However, there may be other reasons for requiring a greater dilution on discharge, or an improvement of the quality of the discharge.

An important objective of toxicity tests of pollutant with marine organisms is to develop the ability to predict levels of pollutants in sea water that are safe to the survival, growth, reproduction, and the general well-being of the species. The 'safe level', the concentration of a pollutant which does not have an adverse sublethal or chronic effect on fish is a measure empirically determined from the median lethal concentration.

The LC50 is multiplied by an application factor, such as 0.1, to obtain a concentration which presumably has no sublethal or chronic effects. The value of the application factor is assigned on the basis of the judgement of scientists. Safe concentrations are generally expressed as fractions of the acute lethal level called the toxic unit. Most estimates of safe levels are between the limits of 0.1 to 0.4 toxic units  $(0.1-0.4 \times LC50)$ . Estimates for some pollutants, especially cumulative and persistent poisons with important chronic or sublethal effects, are as low as 0.01 toxic units (IMCO <u>et al</u>, 1977). Sprague (1971, 1971<sub>a</sub>) feels that the higher values approaching 0.4 come rather close to harmful levels.

In the absence of detailed toxicity data, other than the 96 h LC50, an arbitrary application factor of 0.01 shall be used as the criterion of permissible levels, according to Perkins (1976). Lloyd (1979) identified three types of pollutants, types A, B and C each with a distinctive concentration-response curve (Figure 4.16).

An appropriate estimation of the application factor required to predict the "safe" concentration can be obtained from an inspection of the concentrationresponse curve together with the LC50 (Lloyd, 1979).

Curve A becomes rapidly parallel with the time axis and the 96 h LC50 can be confidently termed a lethal threshold concentration, below which 50% of the test population would be expected to survive for a long time. Lloyd states that chemicals which produce this type of response curve include those which are readily detoxified, or excreted by the test animal, for example ammonia against fish.

Curve B is similar to curve A, except that the lethal threshold concentration can be defined only after a longer exposure period. For fish, Lloyd claims that this is probably the most common type of concentrationresponse curve, and indicates an ability to slowly detoxify the pollutant, for example phenol or zinc against fish.

Curve C is a straight line, which indicates that the test organism has no method of detoxification for their pollutant. Bryant et al (1984, 1985 and 1985<sub>a</sub>) noted such a response for chromium, arsenic, nickel and zinc against several species of invertebrates. For such a response there is no lethal threshold concentration, and prolonged exposure to concentrations below the 96 h LC50 will be lethal. Such a response is typical of bioaccumulative toxins.



## Figure: 4.16

Three types of possible log concentration - log response curves (From Lloyd, 1979).

wastes may or may but the related on the essimilative ispacities of the receiving waters, or the amounts of filution of the westes after simplers. In either case, restrictions should be streed to include of toxic substances discharged ver tokic of the eathy discharge of a small volume of a bighter there estimate can be less harmful to equatic life show the discharge into the same body of a much larger values if a less toxic effluent Lloyd recommend that for pollutants with type A, an application factor of 10(=0.1) is appropriate, for type B a factor of 20(=0.05) is appropriate, and no application factor is relevant to type C, since even a small concentration may be lethal beyond 96 h.

IMCO <u>et al</u>, 1977 suggest that safe levels can be determined by multiplying the LC50 by 0.1 to 0.4, or for persistant poisons by 0.01. Sprague (1971, 1971<sub>a</sub>) feels that the higher values of 0.4 are too close to harmful levels.

Thus the 'safe' level is the concentration of a pollutant which does not have an adverse sublethal or chronic effect on fish, and may be calculated empirically from the median lethal concentration.

In the present study the results appear to be in the form of a type A curve of Lloyd, and a factor of 0.1 is appropriate. In the case of the I.A.F. and Sitra separator effluents of BAPCO, the safe level may be suggested to be 2.4% and 2.0% respectively.

Requirements or standards regulating the discharge of wastes may or may not be related to the assimilative capacities of the receiving waters, or the amounts of dilution of the wastes after discharge. In either case, restrictions should be placed on amounts of toxic substances discharged per unit of time, and not only their concentrations in effluents. The daily discharge of a small volume of a highly toxic effluent can be less harmful to aquatic life than the discharge into the same body of a much larger volume of a less toxic effluent. The "toxicity concentration" in an effluent, expressed in "toxicity units" (t.u.) is taken to be the reciprocal of the median lethal concentration (LC50) expressed as a decimal fraction by volume.

The "toxicity emission rate" (TER) for each waste outfall is taken to be the effluents' toxicity concentration in t.u. multiplied by its flow rate (volume discharged per unit of time), expressed in any suitable discharge rate units.

The computation of TER values facilitates comparison of the environmental impacts of large and small discharges of waste waters having widely different toxicities.

It can be seen from Table 4.12 that the I.A.F. outlet which is applied to the medium size safee is number one in toxicity and first in order of TER, while number two (Sitra separator outlet) in toxicity is third in order of TER. This means that although the toxicity of Sitra separator outlet is higher than the toxicity of I.A.F. outlet to small safee. The TER of I.A.F. outlet to the same fish is higher than that of Sitra separator outlet. Such an assessment can be especially helpful when comparisons are made of different industrial plants whose products and wastes are similar (e.g. different petrochemical plants, or different pulp and paper mills using essentially the same process but different equipment, amounts of water, etc.).

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There are numerous encodes of organisms accumulating petroleum hydrocarites from the marine and estuarine environments, and of addresses release. Release times are different for different independent independent and organisms There is so far as considering estuance of food chain biomarnificaries of a solution of food chain

# Table : 4.12

Toxicity Emission Rate (TER) of the I.A.F. and Sitra separator outlets .

|  | 96h   | LC 50   | Toxicity         | Effluent                                 | Toxicity                                       |
|--|-------|---------|------------------|--|--|
| Type of effluent                                     | 7.    | Decimal | (1/decimal LC50) | discharge                                | rate (TER)                                     |
| I.A.F. outlet (small safee )                         | 24.30 | 0.2430  | 4.12             | 7000 USG/min<br>(26 m <sup>3</sup> /min) | 28840.0 USG/min<br>(107.0 m <sup>3</sup> /min) |
| I.A.F. outlet (big safee )                           | 18.93 | 0.1893  | 5.28             | 7000 USC/min<br>(26 m <sup>3</sup> /min) | 36960.0 USG/min<br>(137.0 m <sup>3</sup> /min) |
| Sitra separator outlet (small<br>safe <del>e</del> ) | 20.28 | 0.2028  | 4.93             | 25 USG/min<br>(0.1 m <sup>3</sup> /min)  | 123.3 USG/min<br>(0.5 m <sup>3</sup> /min)     |

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0.72.74.75

### 4.4.2 Fish analysis :

There are numerous examples of organisms accumulating petroleum hydrocarbons from the marine and estuarine environments, and of subsequent release. Release times are different for different hydrocarbons and organisms. There is so far no convincing evidence of food chain biomagnification of petroleum hydrocarbons (Baker, 1979).

Heavy metals from industrial and natural sources may accumulate in marine organisms, but the limited evidence examined suggests that heavy metal concentrations of refinery effluents are low. For example, shellfish near refinery effluents in Milford Haven did not appear to be significantly contaminated with zinc, cadmium, copper, lead or mercury (Baker, 1979).

Jenkins <u>et al</u> (1979) reported that a few detailed investigations have been undertaken into the bioaccumulation and biomagnification of hydrocarbons in freshwater systems.As a rule such studies are confined to problems of odour and taste in fish contaminated with hydrocarbons and phenols. There are no indications that bioaccumulation and depuration processes of hydrocarbons from mineral oils in fresh water differ from those in the marine environment .

Further studies have been made of the bioaccumulation of mercury, cadmium and lead in fresh water organisms, especially animals, and concentration factors of several thousands are known for some metals (Jenkins et al, 1979). Release times are different for different hydrocarbons and organisms, but from the limited data available it appears that polynuclear components are released relatively slowly (Jenkins et al, 1979).

Linden, Larsson and Al-Alawi (1988) found that the concentrations of petroleum hydrocarbons (Aliphatic fraction) in bivalves in an area off BAPCO oil refinery ranged between 14 and 56 ppm on a wet weight basis. The highest level measured in mussels of the same area by Mattsson and Notini (1981) was 180 mg/kg wet weight, which is equivalent to approximately 1,200 - 1,300 mg/kg dry weight. In comparison to values obtained in the temperate regions in connection with oil spills or refinery effluents this is a low figure (Linden et al, 1979; Mattsson, 1981). In oysters from UAE and Oman concentrations between 7 and 75 ppm (wet weight, expressed as Kuwait crude) have been reported (Fowler 1985). The highest concentration, 75 ppm, were found in rock oysters from Musandam (Jazairat Kun). From Kuwait levels of 39.2 - 348 ppm (dry weight) have been reported (Anderlini et al, 1981). From other regions of the World's oceans levels up to several thousand ppm have been reported in areas exposed to chronic oil pollution: up to 3220 ppm (dry weight) in Mytilus edulis from Westernport Bay, Australia (Burns and Smith 1977), up to 8000 ppm (dry weight) in M.edulis from the vicinity of an oil refinery outlet on the Swedish east coast

(Mattsson and Lehtinen, 1981). It should be kept in mind that these concentrations were recorded in different species of bivalves. This might explain some of the differences, as there may be differences in the metabolism and depuration of the hydrocarbons in different species. However, it seems likely that there is also an effect of the ambient temperature here. In warmer waters, the processes that eliminates the hydrocarbons from the water as well as from tissues are much faster than in cool water.

FAO (1982) has measured the concentrations of heavy metals (mercury, zinc, copper, lead, cadmium, nickel and vanadium) and petroleum hydrocarbons in sediment and biota of different areas along Bahrain coast. In finfish, only the levels of mercury appear to be slightly increased. No metals showed elevated levels in shrimp. Except for cadmium, which showed slightly elevated levels in certain bivalves, no indication of harmful levels of any of the metals could be detected in clams and oysters.

The analysis of naphten-paraffin fraction of the bivalves samples (Table 3.17) showed that the petrogenic hydrocarbon fraction, accumulated in the mussel tissue, was relatively small. The concentrations were low or moderately elevated compared to areas under influence of chronic pollution in other parts of the world.

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## CHAPTER 5

## EFFECT OF SITRA OIL STORAGE TANKS EFFLUENT ON THE INTERTIDAL FAUNA OF THE ADJACENT AREA

#### 5.1 Introduction:

The refined oil from BAPCO refinery is pumped into storage tanks near the Sitra oil terminal. These tanks are periodically cleaned giving rise to another source of pollution. Further, oily residues and slop-residues from vessels berthed at Sitra Wharf are pumped ashore into holding tanks for oil recovery. The drainage from the tanks and the slop-residue goes to Sitra separator. The discharge from this separator (Figure 5.1) is approximately 20 - 30 G.P.M. and is discharged into about 10m wide effluent channel in the sea (Figure 5.2). The oil recovery separator is without the Induced Air Flotation (I.A.F.) provision and hence the content of residual oil in the waste water is relatively high.

The intertidal area receiving the effluent from the oil storage tanks (Figure 5.3) is shallow with a depth from O to about 5 m. The area is exposed during the low tide, and then covered by the tide. The effluent discharge point is located at the top of the beach.

The present study is the first study of the intertidal area opposite to the oil storage tanks effluent discharge. Samples were collected from 22 stations along transect lines shown in Figure 5.2. The study aims to examine the fauna at the discharge area and to record its abundance, biomass, diversity and eveness. Biomass is defined as the amount of living substances constituting the organisms which are being studied. Alternative terms found in the literature are "standing crop" or "standing stock" (Holme and McIntyre, 1971).



Figure: 5.1

The intertidal area adjacent to Sitra oil storage tanks.



## Figure: 5.2 Location of the sampling stations.



# Figure: 5.3

Sitra oil storage tanks treated effluent (Sitra separator outlet).

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5.2 Materials and Muthoda:

The sediment samples were collected during January 1968, along a series of parallel transacts. The transacts are about 150m apart. The location and humbaring of each The results of this study will be related to the sediment composition throughout the study area, as well as to distance from the effluent, and tidal height.

Animals were identified using the key of Jones (1986) which is the only comprehensive text available for the Arabian Gulf region. In some cases, it was not possible to assign full specific names, but identification to generic level has always been attained. As in most intertidal studies, the commonest fauna found were annelids, crustacea and molluscs.

The polychaetae are arguably the most prominent infaunal benthic taxon, so knowledge of them is essential in surveys and ecological monitoring. Although polychaetae are probably less important to man than some other invertebrates, they can directly affect us. <u>Eunice spp</u>. (palolo worms) are eaten, Nereis, <u>Arenicola</u> and others are used as fish bait, serpulids and spirorbids foul ships and piers, amphinomids can sting and sabellids are decorative to the diver and aquarist (Jones, 1986).

On the other hand, crustaceans are often of commercial importance to man. This is specially true in the Arabian Gulf where penaeid shrimp form the basis of important fisheries and use intertidal areas. Barnacles are important fouling organisms especially on ships and many of the smaller crustaceans form essential food chain links for commercial fin fisheries (Jones, 1986).

### 5.2 Materials and Methods:

The sediment samples were collected during January 1988, along a series of parallel transects. The transects are about 250m apart. The location and numbering of each sample station is shown in Figure 5.2. The samples were collected with No.217WA060 Kahlsico hand operated, shore-line coring tube having a diameter of 35mm. Six samples were collected from each station, five for animals and one for the particle size analysis.

The sediment was sampled to a depth of 20cm. Each sample collected was retained in a bag, and labelled in the field. In the laboratory the samples were sieved through a 500 micron sieve. The material retained by the sieve was preserved in 70% alcohol coloured with Rose Bengal stain, and subsequently carefully examined under a binocular microscope. All animals found were removed, identified and counted. The dry weight of the animals of the five samples together at 100°C, weighed and then ignited at 400°C to determine ash-content.

The results are presented in Tables 5.1 to 5.7, and the species are plotted graphically in Figures 5.4 to 5.31.

The diversity was calculated with the Shannon - Wiener index (Shannon and Weaver, 1963).

This index (H) was calculated as:

$$H = - \sum_{i=1}^{s-} P_i \log_2 P_i$$

and evenness (J) as:

$$J = \frac{H}{H_{max}} \qquad (H_{max} = \log_2 s)$$

Where  $P_i$  is the proportion of the abundance of species i, and s the number of species.

Table: 5.1 Mean abundance (mean No. of individuals  $\overline{n}/m^2$ ), standard deviation ( $\sigma$ ), No. of species (s), biomass (g dry weight/m<sup>2</sup>), diversity(H) and evenness (J).

| COSCIES  | STATIO                  | ON B                 | STATIO                              | N C                                | STATIC                     | N E                          |
|--|-------------------------|----------------------|-------------------------------------|------------------------------------|----------------------------|------------------------------|
| SPECIES  | n/m2                    | 5                    | n/m <sup>2</sup>                    | 8                                  | n/m <sup>2</sup>           | 9                            |
| <ol> <li>Oligochaete spp.</li> <li>Syllis gracilis</li> <li>Neanthes spp.</li> <li>Ceratonereis spp.</li> <li>Ceratonereis cultifera</li> <li>Eunice spp.</li> <li>Spionid spp.</li> <li>Scololepis spp.</li> <li>Polydora ciliata</li> <li>Prionospio pinnata</li> <li>Magelona spp.</li> <li>Phyllochaetopterus spp.</li> <li>Scoloplos spp.</li> <li>Scoloplos armiger</li> <li>Capitella spp.</li> <li>Arenicola spp.</li> <li>Orbelia spp.</li> </ol> | 416                     | 509                  | 17663<br>416<br>8520<br>416<br>1247 | 7435<br>509<br>4757<br>509<br>2494 | 5818<br>416<br>2909<br>416 | 2238<br>509<br>1212<br>509   |
| 20.0phelia spp.B<br>21.Maldane spp.<br>22.Owenia spp.<br>23.Sabella spp.<br>24.Megalomma spp.<br>25.Echiuroid spp.<br>26.Cerithidea cingulata<br>27.Pirinella conica<br>28.Cerithium scabridum<br>29.Clypeomorus bifasciata<br>30.Mitrella blanda<br>31.Ancilla castanea<br>32.Diplodonta globosa<br>33.Dosina caelata   | 11429<br>3533           | 7994<br>1409         | 208<br>38235<br>2909                | 416<br>19197<br>2579               | 38235<br>623<br>416        | 42451<br>509<br>509          |
| <ul> <li>34.Donax spp.</li> <li>35.Angulus adenesis</li> <li>36.Gonadactylus demani</li> <li>37.Cyclaspis picta</li> <li>38.Eocuma affine</li> <li>39.Penaeus semisulcatus</li> <li>40.Urothõe grimaldi</li> <li>41.Grandidierella exilis</li> <li>42.Ocypode spp.</li> <li>43.Cleistostoma dotilliforme</li> <li>44.Macrophthalmus spp.</li> </ul>  | 7485                    | 1863                 | 415                                 | 831                                | 208<br>208<br>208          | 416 416 416                  |
| Total No. of individuals(N)<br>No. of species (s)<br>Biomass (g dry weight/m <sup>2</sup> )<br>Shannon-wiener diversity(H)<br>evenness (J)   | 1537<br>3<br>300<br>0.9 | 8<br>. 5<br>96<br>51 | 70<br>1<br>1<br>0                   | 030<br>9<br>.4.3<br>.92<br>.61     | 49<br>1<br>91<br>1.        | 457<br>10<br>9<br>.27<br>.38 |

Table: 5.2

Mean abundance (mean No. of individuals  $\bar{n}/m^2$ ), standard deviation ( $\sigma$ ), No. of species (s), biomass (g dry weight/m<sup>2</sup>), diversity(H) and evenness (J).

| SDECTES   | STATIC                | N F                        | STATIO           | N G                            | STATIO           | N H                        |
|---|-----------------------|----------------------------|------------------|--------------------------------|------------------|----------------------------|
| SPECIES   | ñ/m <sup>2</sup>      | o                          | n/m <sup>2</sup> | Ь                              | n/m <sup>2</sup> | 6                          |
| 1. Oligochaete spp.<br>2. Syllis gracilis<br>3. Neanthes spp.   | 9143                  | 3623                       | 2701             | 831                            | 12676            | 5022                       |
| 2. Ceratomereis spp.<br>5. Perimereis cultifera<br>6. Eunice spp.<br>7. Spionid spp.  | 1662                  | 509                        | 208              | 416                            | 1247<br>1039     | 416<br>929                 |
| <ol> <li>Scololepis spp.</li> <li>Polydora ciliata</li> <li>Prionospio pinnata</li> <li>Magalona spp.</li> </ol>  | .2014                 | -                          | -                | 105                            | 208              | 416                        |
| 12.Magelona heteropoda<br>13.Phyllochaetopterus spp.<br>14.Mesochaetopterus minutus   |                       | 234<br>2456                |                  |                                |                  |                            |
| 15.Scoloplos spp.<br>16.Scoloplos armiger<br>17.Capitella spp.<br>18.Arenicola spp.<br>19.Ophelia spp.A<br>20.Ophelia sop.B   | 208                   | 416                        |                  |                                | 2078             | 1859                       |
| 21.Maldane spp.<br>22.Owenia spp.<br>23.Sabella spp.<br>24.Megalomma spp.   | 7689                  | 5900                       | 62548            | 92115                          | 208<br>17247     | 416<br>8831                |
| 25.Echluroid spp.<br>26.Cerithidea cingulata<br>27.Pirinella conica<br>28.Cerithium scabridum<br>29.Clypeomorus bifasciata<br>30.Mitrella blanda<br>31.Ancilla castanea   | 694.                  |                            | 2701             | 2139                           | 4572             | 3054                       |
| 32.Diplodonta globosa<br>33.Dosina caelata<br>34.Donax spp.<br>35.Angulus adenesis<br>36.Gonadactylus demani<br>37.Cyclaspis picta  | 1455                  | 1555                       |                  |                                | 2009<br>2009     | 657<br>436                 |
| <ul> <li>38.Eocuma affine</li> <li>39.Penaeus semisulcatus</li> <li>40.Urothõe grimaldi</li> <li>41.Grandidierella exilis</li> <li>42.Ocypode spp.</li> <li>43.Cleistostoma dotilliforme</li> <li>44.Macrophthalmus spp.</li> </ul> |                       | 674<br>674                 |                  |                                | 208              | 416                        |
| Total No. of individuals(N)<br>No. of species (s)<br>Biomass (g dry weight/m <sup>2</sup> )<br>Shannon-wiener diversity(H)<br>evenness (J)  | 201<br>2.<br>1.<br>0. | 157<br>5<br>.1<br>68<br>72 | 68<br>19<br>0    | 158<br>4<br>95.1<br>.72<br>.36 | 39<br>27<br>2.   | 483<br>9<br>.4<br>14<br>68 |

<u>Table: 5.3</u> Mean abundance (mean No. of individuals  $\overline{n/m^2}$ ), standard deviation ( $\sigma$ ), No. of species (s), biomass (g dry weight/m<sup>2</sup>), diversity(H) and evenness (J).

|  | STATIO           | I IM       | STATIO           | L N  | STATIO           | NK        |
|--|------------------|------------|------------------|------|------------------|-----------|
| SPECIES                                | n/m <sup>2</sup> | o          | n/m <sup>2</sup> | ď    | n/m <sup>2</sup> | 9         |
| 1. Oligochaete spp.                    | 9351             | 8455       | 11429            | 8128 | 31586            | 16024     |
| 2. Syllis gracills                     | 6.7.7            | 12/7       |                  |      | 208              | 416       |
| / Caratonereis SDD.                    | 023              | 1241       |                  |      | 416              | 831       |
| 5. Perinereis cultifera                | 1039             | 929        | 1455             | 1060 | 2286             | 778       |
| 6. Eunice spp.                         |                  |            |                  |      |                  |           |
| 7. Spionid spp.                        |                  |            |                  |      |                  |           |
| 8. Scololepis spp.                     | 208              | 416        | 208              | 416  | 416              | 509       |
| 9. Polydora ciliata                    | S. S. Barrow     |            | Sec. 1           |      | 1.100            | 94.9      |
| 10.Prionospio pinnata                  | 607              | 071        | 10.25            |      |                  |           |
| 12 Magelona betaropoda                 | 023              | 0.31       |                  |      |                  |           |
| 13. Phyllochaetopterus spp.            | 208              | 416        |                  |      |                  |           |
| 14. Mesochaetopterus minutus           | . 1870           | 3246       | 1039             | 1610 |                  |           |
| 15.Scoloplos spp.                      |                  |            |                  |      | 1247             | 1212      |
| 16.Scoloplos armiger                   |                  |            | 623              | 831  | 1024             | 557       |
| 17.Capitella spp.                      |                  |            | 2701             | 2757 |                  |           |
| 18.Arenicola spp.                      |                  |            | · 208            | 416  |                  |           |
| 19.Ophelia spp.A                       | 208              | 410.       | 1 4 1 2 1        |      |                  | 1.35.0.53 |
| 20. Opnella spp. B                     |                  |            |                  |      |                  |           |
| 21. Maldane spp.                       |                  |            | /16              | 871  | 831              | 1018      |
| 23. Sabella spp.                       |                  |            | -10              | 001  | 208              | 416       |
| 24. Megalomma spp.                     | 8312             | 5537       | 12052            | 5158 | 92679            | 33426     |
| 25.Echiuroid spp.                      |                  |            |                  |      |                  | 1         |
| 26.Cerithidea cingulata                | 208              | .416       | 1039             | 1314 | 416              | 831       |
| 27.Pirinella conica                    | 1000             | and a set  |                  |      | 1                |           |
| 28.Cerithium scabridum                 |                  |            | 416              | 509  |                  |           |
| 29.Clypeomorus birasciata              | 1. States        | The second |                  |      | A CONTRACT       |           |
| J Ancilla castanea                     |                  |            | 116              | 800  | General States   | 12323     |
| 32. Diplodonta globosa                 | 1 martines       | P. Lazz    | 2701             | 1060 | 1030             | 657       |
| 33.Dosina caelata                      | 623              | 831        |                  | 1000 | 1055             | 0.57      |
| 34. Donax spp.                         | 831              | 1212       | 623              | 509  | 208              | 416       |
| 35.Angulus adenesis                    |                  |            |                  |      |                  |           |
| 36.Gonadactylus demani                 | 208              | 416        | 208              | 416  | 1.000            | 1 Same    |
| 37.Cyclaspis picta                     | 1870             | 1662       | 416              | 509  |                  |           |
| 30 Perseus semisulatur                 | 208              | 410        |                  |      |                  |           |
| 40. Urothõe grimaldi                   |                  |            |                  |      |                  | 1 dam     |
| 41.Grandidierella exilia               | 623              | 509        |                  |      |                  | 1 States  |
| 42. Ocypode spp.                       |                  | 1          |                  |      |                  |           |
| 43.Cleistostoma dotilliform            |                  |            |                  |      |                  |           |
| 44.Macrophthalmus spp.                 |                  |            |                  |      | 208              | 416       |
|  |                  |            |                  |      |                  |           |
| Total No. of individuals(N)            | 27               | 013        | 35               | 950  | 13               | 1748      |
| No. of species (s) 2.                  | 1 10             | .6         | 1 1              | 16   |                  | 13        |
| Blomass (g dry weight/m <sup>-</sup> ) | 10               | 0.)        | 26               | 9.9  | 6                | .1        |
| Shannon-wiener diversity(H             | 2.               | 79         | 2.               | .54  | 1                | . 34      |
| evenness (J                            | 1 0.             | /0         | 0                | .64  | 0                | . 30      |

Table: 5.4

Mean abundance (mean No. of individuals  $\overline{n}/m^2$ ), standard deviation ( $\sigma$ ), No. of species (s), biomass (g dry weight/m<sup>2</sup>), diversity(H) and evenness (J).

| SPECIES   | STATIO                 | NL                              | STATIO           | I M                            | STATIO            | N N                             |
|---|------------------------|---------------------------------|------------------|--------------------------------|-------------------|---------------------------------|
| SPECIES   | n/m <sup>2</sup>       | •                               | ñ/m <sup>2</sup> | 6                              | n/m <sup>2</sup>  | o                               |
| 1. Oligochaete spp.<br>2. Syllis gracilis   | 23482                  | 4812                            | 3948             | 4847                           | 10806             | 6323                            |
| <ol> <li>Neanthes spp.</li> <li>Ceratonereis spp.</li> <li>Perinereis cultifera</li> <li>Eunice spp.</li> </ol>   | 1247<br>5195           | 1212<br>1469                    |                  | a series                       | 623               | 509                             |
| 7. Spionid spp.<br>8. Scololepis spp.<br>9. Polydora ciliata<br>10. Prionespio pinnata  | -                      |                                 | ales.            | 258                            | 208               | 416                             |
| 11. Magelona spp.<br>12. Magelona heteropoda<br>13. Phyllochaetopterus spp.<br>14. Mesochaetopterus minutus   | 67933                  | 1                               |                  |                                |                   |                                 |
| 16.Scolopios armiger<br>17.Capitella spp.<br>18.Arenicola spp.  | 423                    |                                 | 856.<br>- (.16.1 | -79<br>000                     | 1039              | 657                             |
| 19.0phelia spp.A<br>20.0phelia spp.B<br>21.Maldane spp.<br>22.0wenia spp.   | 208                    | 416                             |                  |                                | 975               | 1013                            |
| 23.Sabella spp.<br>24.Megalomma spp.  | 208<br>55275           | 39816                           | 7273             | 14032                          | 6650              | 2238                            |
| 25.Echiuroid spp.<br>26.Cerithidea cingulata<br>27.Pirinella conica<br>28.Cerithium scabridum<br>29.Clypeomorus bifasciata<br>30.Mitrella blanda<br>31.Aprilla castanea | 208                    | 416                             | 416              | 831                            | 3740              | 1688                            |
| 32.Diplodonta globosa<br>33.Dosina caelata<br>34.Donax spp.   | 1039                   | 929                             | 208              | 416                            | 208<br>416<br>623 | 416<br>509<br>831               |
| 35.Angulus adenesis<br>36.Gonadactylus demani<br>37.Cyclaspis picta<br>38.Eocuma affine   | 623                    | 1247                            |                  | 100                            | 203               | 100                             |
| 39.Penaeus semisulcatus<br>40.Urothöe grimaldi<br>41.Grandidierella exilis<br>42.Ocypode spp.<br>43.Cleistostoma dotilliform<br>44.Macrophthalmus spp.                  | 208<br>208             | 416<br>416                      | SIM              | 5755 F                         | 208               | 416                             |
| Total No. of individuals(N)<br>No. of species (s)<br>Biomass (g dry weight/m <sup>2</sup> )<br>Shannon-wiener diversity(H<br>evenness (J                                | 87<br>2<br>1<br>1<br>0 | 7901<br>11<br>0.4<br>.48<br>.43 | 1                | 1845<br>4<br>7.4<br>26<br>0.63 | 24<br>1<br>2<br>0 | 4521<br>10<br>5.4<br>.25<br>.68 |

<u>Table: 5.5</u> Mean abundance (mean No. of individuals  $\bar{n}/m^2$ ), standard deviation ( $\sigma$ ), No. of species (s), biomass (g dry weight/m<sup>2</sup>), diversity(H) and evenness (J).

|   | STATIO                                   | • •         | STATION                               | Р              | STATION                                    | Q           |
|---|--|-------------|---------------------------------------|----------------|--|-------------|
| SPECIES   | n/m <sup>2</sup>                         | œ           | n/m <sup>2</sup>                      | 6              | n/m <sup>2</sup>                           | 8           |
| 1. Oligochaete spp.   | 7481                                     | 7786        | 9559                                  | 6385           | 15793                                      | 7759        |
| 2. Syllis gracilis  | 208                                      | 416         | 10 1 2 2                              | 981194         | 1978 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 | 10 1 200    |
| 3. Neanthes spp.  | 623                                      | 831         |                                       |                | 1.1.1.1                                    |             |
| 4. Ceratonereis spp.  | 1. |             | 2078                                  | 2709           |  |             |
| 5. Perinereis cultifera   | 2701                                     | 1927        | 6                                     |                | 7481                                       | 1212        |
| 6. Eunice spp.  | 1.1.1.1.1                                |             | 100 100                               |                |  |             |
| 7. Spionid spp.   |  |             |                                       |                |  |             |
| 8. Scololepis spp.  |  |             | 1000                                  |                |  |             |
| 9. Polydora ciliata   |  |             |                                       |                |  | 100         |
| 10.Prionospio pinnata   | 416                                      | 509         | 208                                   | 416            |  |             |
| 11.Magelona spp.  |  |             |                                       |                |  |             |
| 12.Magelona heteropoda  |  |             |                                       |                |  |             |
| 13.Phyllochaetopterus spp.  | 2701                                     | 2595        |                                       |                |  |             |
| 14. Mesochaetopterus minutus  | •  |             |                                       |                |  |             |
| 15.Scoloplos spp.   |  |             |                                       |                |  |             |
| 16.Scoloplos armiger  |  |             |                                       |                |  |             |
| 17.Capitella spp.   | 831                                      | 778         | 831                                   | 778            |  |             |
| 18.Arenicola spp.   |  |             |                                       |                |  |             |
| 19.0phelia spp.A  |  | •           | 1247                                  | 1018           |  |             |
| 20.Ophelia spp.8  |  |             | 623                                   | 831            |  |             |
| 21.Maldane spp.   |  |             |                                       |                | 071  | 1010        |
| 22. Owenia spp.   | 623                                      | 831         |                                       |                | 0.51                                       | 1010        |
| 23.Sabella spp.   |  |             |                                       |                | 100/10                                     | 5963        |
| 24.Megalomma spp.   | 15169                                    | 6425        | 4364                                  | 3563           | 22442                                      | 2002        |
| 25.Echlurold spp.   |  |             |                                       |                | 6.77                                       | 500         |
| 26.Ceritnidea cingulata   |  |             |                                       |                | 043  | 20.3        |
| 27. Pirinella conica  | 1.1.1                                    |             |                                       |                | 208  | 116         |
| 28.Cerithium scabridum  |  |             | The Ballet                            | A Statistics   | 200  | 410         |
| 29.Clypeomorus birasciata   |  |             |                                       |                | 12.4                                       |             |
| 31 Angilla Castange   | 1 2                                      |             | 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 |                |  |             |
| 32 Diplodonta globosa   | 208                                      | 416         | 208                                   | 416            | 623  | 1247        |
| 33 Dosina caelata   |  |             | 1 200                                 |                | 0.0  |             |
| 34 Donax SDD.   | 623                                      | 831         | 416                                   | 831            | 1662                                       | 1409        |
| 35. Angulus adenesis  |  |             |                                       |                | 1  | 16 6 61     |
| 36.Gonadactylus demani  | 208                                      | 416         | 416                                   | 509            | 11845                                      | 3054        |
| 37. Cyclaspis picta   | 1662                                     | 1247        | 416                                   | 831            | 208  | 416         |
| 38. Eocuma affine   |  |             | 1                                     |                |  | 1.1         |
| 39.Penaeus semisulcatus   |  | 1. 16       |                                       |                |  |             |
| 40. Urothõe grimaldi  | 1 2 36                                   |             |                                       |                |  | 1.1.1.1.1.1 |
| 41.Grandidierella exilis  | 1. |             | 2286                                  | 1527           | 416  | 509         |
| 42. Ocypode spp.  |  | 1.1         |                                       |                |  |             |
| 43.Cleistostoma dotilliform   |  |             |                                       |                | A Contraction                              | 1.1.1.1.1.1 |
| 44.Macrophthalmus spp.  |  |             |                                       |                |  |             |
| The second se | - Constant                               | Service Ser | and a stand a strength                | And the second | -  |             |
| Total No. of individuals(N)   | 33.                                      | 454         | 22                                    | 652            | 62   | 132         |
| No. of species (s)  | 1  | 3           |                                       | 12             |  | 11          |
| Biomass (g dry weight/m <sup>2</sup> )  | 45                                       | .1          | 3                                     | 1.4            | 20   | 5.6         |
| diversity(H   | ) 2.                                     | 59          | 2                                     | . 68           | 2  | . 35        |
| Snannon-wiener evenness (J  | ) 0.                                     | 70          | 0                                     | .75            | 0  | .68         |

Table: 5.6

Mean abundance (mean No. of individuals  $\bar{n}/m^2$ ), standard deviation ( $\sigma$ ). No. of species (s). biomass (g dry weight/m<sup>2</sup>), diversity(H) and evenness (J).

| SPECIES                      | STATIO           | N R              | STATIO                  | N S       | STATIO                                   | T        |
|------------------------------|------------------|------------------|-------------------------|-----------|--|----------|
| SPECIES                      | n/m <sup>2</sup> | œ                | n/m <sup>2</sup>        | Ь         | n/m <sup>2</sup>                         | 6        |
| 1. Oligochaete spp.          | 7065             | 3179             | 13299                   | 16499     | 9559                                     | 3040     |
| 2. Syllis gracilis           | 208              | 416              |                         |           |  |          |
| 3 Neanthes SDD.              | 416              | 509              | 1.18.18                 |           |  |          |
| / Caratonerais spp.          | 208              | 416              | 728 3 3                 | 124 10    |  |          |
| 5 Parimereis cultifera       | 11429            | 2788             | S. S. A.                |           | 831                                      | 778      |
| 6 Punice ann.                |                  |                  | 1.1.1                   |           |  |          |
| 7 Spionid enn                |                  |                  | 1                       |           |  |          |
| Scololenia spp.              |                  |                  | 1399                    | 6.816.61  |  |          |
| 0. Bolydora ciliata          |                  |                  | 1                       |           |  |          |
| 9. Polydora ciliada          |                  |                  |                         |           |  |          |
| 10.Prionospio pinnaca        | 2018             |                  | Los Martin              |           |  |          |
| 11.Magelona spp.             |                  |                  | 1-22-22                 |           |  |          |
| 12. Magelona heteropoda      |                  |                  | area 19                 | 0.80      |  |          |
| 13.Phyllochaetopterus spp.   |                  |                  | And and a second second | 1.0       |  |          |
| 14. Mesochaetopterus minutus | • 1247           | 1212             | 122.00                  |           |  |          |
| 15.Scoloplos spp.            |                  |                  |                         |           | 208                                      | 410      |
| 16.Scoloplos armiger         |                  |                  |                         | 1.1.1.1.1 |  |          |
| 17.Capitella spp.            | and the          | Section 1        | Lane I.                 | Law St.   | Constant in                              |          |
| 18.Arenicola spp.            | 1000             | 10000            | 1                       |           |  |          |
| 19.Ophelia spp.A             |                  | •                |                         |           | 208                                      | 416      |
| 20.Ophelia spp.B             | 1455             | 509              | A State of the          |           | 1.00                                     |          |
| 21.Maldane spp.              |                  |                  | A State of the          | 10 1      | 1. |          |
| 22. Owenia spp.              |                  |                  |                         |           | Section 1                                | an a Sid |
| 23.Sabella spp.              | 1428.4           | 10000-11         |                         | DEST 1    |  |          |
| 24.Megalomma spp.            | 6442             | 3682             | 623                     | 1247      | 10598                                    | 865      |
| 25. Echiuroid spp.           | ¥16 [            | 399              | a start and a start     |           | No. State                                |          |
| 26.Cerithides cingulata      | and the second   | Same in          |                         |           | 416                                      | 509      |
| 27.Pirinella conica          | 208              | 416              |                         |           | A State of the                           |          |
| 28.Cerithium scabridum       |                  |                  | 2011                    | 103.8     | A State State                            |          |
| 29.Clypeomorus bifasciata    |                  |                  |                         |           |  |          |
| 30.Mitrella blanda           | 208              | 416              |                         | and the   |  |          |
| 31.Ancilla castanea          |                  |                  | ALC: NO                 | The state |  |          |
| 32 Diplodonta globosa        | 208              | 416              | Sec. St.                | Att 1     |  |          |
| 33 Dosina caelata            | 1 -00            |                  | BASE ST                 | Letter 1  | 416                                      | 83       |
| 34. Donax spp.               | 831              | 1212             |                         |           | 208                                      | 410      |
| 35. Angulus adenesis         | 416              | 831              | 1236                    | 227 3     |  |          |
| 36 Consdactvlus demani       | 623              | ATI              | 1.5 15                  | No. I     | 623                                      | 83       |
| 37 Cuclaente picta           | 025              | 0.01             |                         |           | 1  |          |
| 38 Focume affine             |                  |                  |                         |           |  |          |
| 30. Bocoma alline            | 1 200            | 110              | 1.5.6                   | and 1     |  |          |
| 59.Penaeus semisulcatus      | 208              | 410              |                         |           |  |          |
| 40.0rothoe grimaidi          |                  | 1                | 1000                    |           |  | 1.00     |
| 41.Grandidierella exilis     | 208              | 410              |                         | 1 2 2 2 2 | 1 2 2 2 4 2                              |          |
| 42. Ocypode spp.             |                  | 1                |                         |           |  | 1111     |
| 43.Cleistostoma dotililiorm  | a section in the | - and the second | in an and               |           | and the second second                    |          |
| 44.Macrophthaimus spp.       |                  | L                |                         |           |  |          |
| Total No. of individual=(N)  | 1 77             | 380              |                         | 1022      | 23                                       | 275      |
| No of species (a)            | 1 .              | 6                | 1                       | 322       |  | 10       |
| NO. OI Species (S) 2,        |                  | 0                | 1                       | 2         |  |          |
| Blomass (g dry weight/m)     | 3                | .9               | 0                       | -4        | 27                                       | .0       |
| Shannon-wiener diversity(H   | 1 2.             | .79              | 0                       | .25       | 1  | .03      |
| evenness (J                  | ) 0.             | .70              | 0                       | .25       | 0  | .5/      |

Table: 5.7 Mean abundance (mean No. of individuals  $\overline{n/m}^2$ ), standard deviation ( $\sigma$ ). No. of species (s), biomass (g dry weight/m<sup>2</sup>), diversity(H) and evenness (J).

| SPECIES  | STATION U  |                                      | STATION V         |                                     | STATION          |                 |
|--|--|--------------------------------------|-------------------|-------------------------------------|------------------|-----------------|
|  | ñ/m <sup>2</sup>   | 4                                    | ñ/# <sup>2</sup>  | ø                                   | n/m <sup>2</sup> | •               |
| 1. Oligochaete spp.<br>2. Syllis gracilis  | 10598<br>208   | <b>3</b> 314<br>417                  | 24105             | 12596                               |                  | 17              |
| <ol> <li>Neantnes spp.</li> <li>Ceratonereis spp.</li> <li>Perinereis cultifera</li> <li>Eunice spp.</li> <li>Spionid spp.</li> <li>Scololepis spp.</li> </ol>   | 416<br>3117  | 509<br>1739                          | 8728              | 3124                                | 102              | 1               |
| 9. Polydora ciliata<br>10.Prionospio pinnata<br>11.Magelona spp.   | 8  |                                      |                   | 6300                                |                  | 1               |
| 12.Magelona heteropoda<br>13.Phyllochaetopterus spp.<br>14.Mesochaetopterus minutus<br>15.Scoloplos spp.   | 208  | 416                                  | 2494<br>208       | 1060<br>416                         |                  |                 |
| 16.Scoloplos armiger<br>17.Capitella spp.<br>18.Arenicola spp.<br>19.Ophelia spp.A   | 831  | 1212                                 | 1039              | 657                                 |                  |                 |
| 20.0phelia spp.B<br>21.Maldane spp.<br>22.Owenia spp.  |  |                                      | 623<br>416<br>208 | 509<br>831<br>416                   | k                | 12              |
| 24.Megalomma spp.<br>25.Echiuroid spp.<br>25.Cerithidea cingulata  | 1455<br>416<br>416   | 1060<br>831<br>509                   | 13299             | 13377                               | .8.              | 2.00            |
| 28.Cerithium scabridum<br>29.Clypeomorus bifasciata<br>30.Mitrella blanda  |  |                                      | 208               | 416                                 | 1 0/01 -1 0      | . 506 -         |
| 32.Diplodonta globosa<br>33.Dosina caelata<br>34.Donax spp.  | and the second sec |                                      | 623<br>208<br>208 | 831<br>416<br>416                   | 1.001-3          | 0,000<br>194000 |
| 35.Angulus adenesis<br>36.Gonadactylus demani<br>37.Cyclaspis picta<br>38.Eocuma affine  | 623<br>1455  | 831<br>2036                          | 1662<br>416       | 1247<br>831                         |                  |                 |
| <ul> <li>39.Penaeus semisulcatus</li> <li>40.Urothõe grimaldi</li> <li>41.Grandidierella exilis</li> <li>42.Ocypode spp.</li> <li>43.Cleistostoma dotilliform</li> <li>44.Macrophthalmus spp.</li> </ul> | 1662   | 2323                                 | 416               | 831                                 |                  |                 |
| Total No. of individuals(N)<br>No. of species (s)<br>Biomass (g dry weight/m <sup>2</sup> )<br>Shannon-wiener diversity(H<br>evenness (J   | 21<br>16<br>2<br>) 0   | 21405<br>12<br>161.7<br>2.55<br>0.71 |                   | 54861<br>16<br>20.4<br>2.41<br>0.60 |                  |                 |



## Figure: 5.4 Oligochaete spp.



## Figure: 5.5 Perinereis cultifera



# Figure: 5.6 Ceratonereis spp.




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Eunice spp.



# Figure: 5.9 Mesochaetopterus minutus



## Figure: 5.10 Phyllochaetopterus spp.



## Figure: 5.11 Scoloplos armiger

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# Figure: 5.12 Scoloplos spp.

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# Figure: 5.18 Scololepis spp.



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## Figure: 5.21 Cerithidea cingulata



# Figure: 5.22 Cerithium scabridum





•



## Figure: 5.24 Dosina caelata



Donax spp.

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### Figure: 5.26 Gonadactylus demani



# Figure: 5.27 Cyclaspis picta





Eocuma affine







### Figure: 5.30 Grandidierella exilis

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Figure: 5.31

- 0 N.R.
  - $(1-1,000 m^{-2})$ Penaeus semisulcatus, Mitrella blanda, Pirinella conica, Angulus adenesis  $(1-1,000 m^{-2})$
- Arenicola spp. , Ancilla castana
- $(1-1,000 \text{ m}^{-2})$ Meldane spp., Clypeomorus bifasciata
- $(1-1.000 \text{ m}^{-2})$ Magelona heteropoda, Echiuroid spp.
- $(1-1,000 \text{ m}^{-2})$ Ocypode spp., Cleistostoma dotilliforme
- $(1-1.000 \text{ m}^{-2})$ Mageluna spp.,
- $(1-1,000 \text{ m}^{-2})$ Spionid spp.,
- $(1-1.000 \text{ m}^{-2})$ Macrophthalmus spp.,
- $(1-1.000 \text{ m}^{-2})$ Prionspio pinnata
- $(1-1,000 \text{ m}^{-2})$ Polydora ciliata

The data was subjected to computer analysis, using Pearson correlation matrix, and regression analysis on a microcomputer.

### 5.3 Results:

#### 5.3.1 Faunal analysis:

The abundance of each species (the number of individuals per  $m^2$ ) is presented in Figures 5.4 to 5.31. Mean abundance, standard deviation, number of species, biomass, diversity and eveness are shown in Tables 5.1 to 5.7 and Figures 5.32 - 5.36.

Considering each major species in turn:-

#### 5.3.1.1 Oligochaete:

The oligochaete (or, sludge) worms were found at almost all stations except station A and D which are near the effluent discharge. It reached a peak of abundance of  $31,586 \text{ m}^{-2}$  at station K, with a mean of  $10,749 \text{ m}^{-2}$  recorded at the 22 stations and a standard deviation of 8057.7.

Lowest numbers were recorded close to the oil storage tanks effluent discharge.

#### 5.3.1.2 Nereis species:

Three Nereis species were found in the study area:

5.3.1.2 (i) <u>Perinereis cultifera</u> (Figure 5.5) was abundant at many stations except those at the western coast with a mean of  $2,314m^{-2}$  recorded at the 22 stations and a standard deviation of 3171,9.





Total number of individuals.



### Figure: 5.33

Number of species (s).





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- 364 -

. •



Eveness (J).

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It reached a peak of abundance at station R of  $11,429m^{-2}$ , and was absent from stations near the effluent, or at the top of the beach.

- (ii) <u>Ceratonereis spp</u>. (Figure 5.6) was found in lower abundance than <u>Perinereis cultifera</u> with a mean of 217m<sup>-2</sup> recorded at the 22 stations and a standard deviation of 506.9. It reached a peak of abundance of 2,078m<sup>-2</sup> at station P.
- (iii) <u>Neanthes</u> <u>spp</u>. (Figure 5.7) was found in lowest percentage and at a fewer station with a mean of  $95m^{-2}$  recorded at the 22 stations and a standard deviation of 210.

### 5.3.1.3 Eunice spp.:

Although Eunice spp. was found at only stations C and H (Figure 5.8). It was abundant at a relatively high percentage at these stations with a mean of  $435m^{-2}$  recorded at the 22 stations and a standard deviation of 1819.4. It reached a peak of abundance of  $8,520m^{-5}$  at station C.

5.3.1.4 Chaetopterus spp.

Two Chaetopterus species were found in the survey area:

- 5.3.1.4 (i) <u>Mesochaetopterus minutus</u> (Figure 5.9) with a mean of  $302m^{-2}$  recorded at the 22 stations and a standard deviation of 701.7. It reached a peak of abundance of  $1,870m^{-2}$  at station I.
  - (ii) <u>Phyllochaetopterus spp</u>. (Figure 5.10) had a lower abundance with a mean of  $132m^{-2}$  recorded at the 22 stations and a standard deviation of 575.5. It reached a peak of abundance of 2,701m<sup>-2</sup> at station 0.

Two Scoloplos species were found in the survey area:

<u>Scolopos</u> armiger (Figure 5.11) with a mean of  $227m^{-2}$  recorded at the 22 stations and a standard deviation of 543.8. It reached a peak of abundance of 1,039m<sup>-2</sup> at station N.

The other <u>Scoloplos</u> <u>spp</u>. (Figure 5.12) were found at more stations but with lower abundance with a mean of  $104m^{-2}$  recorded at the 22 stations and a standard deviation of 277.8. It reached a peak of abundance of  $1,247m^{-2}$  at station K.

### 5.3.1.6 Ophelia spp.:

Ophelia <u>spp</u>. was found only at stations well away from the effluent.

Two species were found in the study area, <u>Ophelia spp.A</u> (Figure 5.13) reached a peak of abundance of  $1,247m^{-2}$  at station P with a mean of  $160m^{-2}$  recorded at the 22 stations and a standard deviation of 368.

While <u>Ophelia spp.B</u> (Figure 5.14) reached a peak of abundance of  $1,455m^{-2}$  at station R with a mean of  $123m^{-2}$  recorded at the 22 stations and a standard deviation of 349.3.

### 5.3.1.7 Owenia spp.:

<u>Owenia</u> <u>spp</u>. (Figure 5.15) was found at different stations most of them away from the effluent discharge with a mean of  $151m^{-2}$  recorded at the 22 stations and a standard deviation of 273.4. It reached a peak of abundance of  $831m^{-2}$  at stations K and Q. <u>Owenia</u> habitat is intertidal downwards in a membranous tube with grains of sand or shell debris attached; generally on muddy sand from lower shore downward; part of the tube usually apparent.

#### 5.3.1.8 Megalomma spp.:

<u>Megalomma</u> spp. (Figure 5.16) was the most abundant species in the study area with a mean of  $19,637m^{-2}$ recorded at the 22 stations and a standard deviation of 23786.7. It was found at all the stations except stations A and D. It may be considered pollution tolerant species. Again, like the Oligochaetes, <u>Megalomma</u> reached a peak of abundance at station K of  $92,679m^{-2}$ . It inhabits intertidal shallow water.

#### 5.3.1.9 Other polychaete species:

The following species (<u>Syllis gracilis</u>, <u>Spionid spp.</u>, <u>Scololepis spp.</u>, <u>Polydora ciliata</u>, <u>Prionspio pinnata</u>, <u>Magelona spp.</u>, <u>Magelona heteropoda</u>, <u>Capitella spp.</u>, <u>Arenicola spp.</u>, <u>Maldane spp.</u>, <u>Sabella spp</u>. and <u>Echiuroid</u> <u>spp.</u>) (Figures 5.17 to 5.20 and Figure 5.31) were found at only a few stations, predominantly in the areas away from the effluent.

#### 5.3.1.10 Gastropods:

Six gastropod species were found in the survey area, <u>Cerithidea cingulata</u>, <u>Pirinella conica</u>, <u>Cerithium</u> <u>scabridum</u>, <u>Clypeomorus bifasciata</u>, <u>Mitrella blanda</u> and <u>Ancilla castanea</u> (Figures 5.21, 5.22 and 5.31). The most abundant of them was <u>Cerithidea cingulata</u>. It was found in abundance at the stations near the effluent discharge. Jones (1986) reports that it is common in polluted areas. It reached a peak of abundance of  $4572m^{-2}$  at station H with a mean of  $963m^{-2}$ recorded at the 22 stations and a standard deviation of 1463.1.

<u>Cerithium scabridum</u> was found only at station J and Q. Jones (1986) reports that it is common on sheltered rocky shores, often on patches of mud or weed between high-and mid-tide levels.

The other gastropod species were found at only a few stations, predominantly in the areas away from the effluent.

### 5.3.1.11 Bivalves:

Four bivalves species were found in the study area, <u>Diplodonta globosa</u>, <u>Dosina caelata</u>, <u>Donax spp</u>. and <u>Angulus adenesis</u> (Figures 5.23, 5.24, 5.25 and 5.31).

The most abundant species being <u>Donax</u> <u>spp</u>. with a mean of  $378m^{-2}$  recorded at the 22 stations and a standard deviation of 189.8. It reached a peak of abundance of  $1455m^{-2}$  at station F.

The second most abundant species being <u>Diplodonta globosa</u> with a mean of  $340m^{-2}$  recorded at the 22 stations and a standard deviation of 626.7. It reached a peak of abundance of  $2701m^{-2}$  at station J.

Dosina caelata found in less abundant with a mean of  $104m^{-2}$  recorded at the 22 stations.

<u>Angulus</u> <u>adenesis</u> found only at station R which is away from the effluent discharge.

#### 5.3.1.12 Crustaceans:

Mantis shrimp, <u>Gonodactylus</u> <u>demani</u> (Figure 5.26) was found only at stations away from the effluent especially at the lower areas. Jones (1986) reports that it inhabits the sublittoral and on lower shore. A mean of  $775m^{-2}$  was recorded at the 22 stations and a standard deviation of 2504.5. It reached a peak of abundance of 11,845m<sup>-2</sup> at station Q.

Two cumacea species were found in the survey area, <u>Cyclaspis</u> <u>picta</u> (Figure 5.27) and <u>Eocuma</u> <u>affine</u> (Figure 5.28). The former is more abundant with a mean of  $302m^{-2}$  recorded at the 22 stations and a standard deviation of 576.2. It reached a peak of abundance at staion I of 1,870m<sup>-2</sup>.

Eocuma affine was found at only three adjacent stations (E, H and I) with a mean of  $28m^{-2}$  recorded at the 22 stations.

Two amphipod species were found in the survey area, <u>Urothöe grimaldi</u> (Figure 5.29) with a mean of  $28m^{-2}$ recorded at the 22 stations and <u>Grandidierella exilis</u> (Figure 5.30) with a mean of  $236m^{-2}$  recorded at the 22 stations.

The shrimp <u>Penaeus</u> <u>semisulcatus</u> (Figure 5.31) was found in low abundance at only station R which is away from
the effluent with a mean of  $10m^{-2}$  recorded at the 22 stations and a standard deviation of 44.4.

### 5.3.1.13 Crabs:

Three crab species were found in the study area, <u>Ocypode</u> <u>spp.</u>, <u>Cleistosoma</u> <u>dotilliforme</u> and <u>Macrophthalmus</u> <u>spp</u>. (Figure 5.31), all present in low abundance.

Each at one station only with a similar mean of  $10m^{-2}$  recorded at the 22 stations and a standard deviation of 44.4.

### 5.3.2 Particle size:

Particle size distribution, median particle diameter, sorting coefficient and skewness are shown in Tables 5.8 to 5.10. Sediment particle size analysis: Cumulative phi curves are shown in Figures 5.37 to 5.39.

In order to classify the sediments according to their median particle diameters (m.p.d.) the following notation was used (after Wolff 1973 with modifications).

#### m.p.d. between

| <u>phi units</u> | mı         | name        |  |  |
|------------------|------------|-------------|--|--|
| 0 - 1            | 500 - 1000 | coarse sand |  |  |
| 1 - 2            | 250 - 500  | medium sand |  |  |
| 2 - 3            | 125 - 250  | fine sand   |  |  |
| 3 - 4            | 63 - 125   | muddy sand  |  |  |
| > 4              | < 63       | mud         |  |  |

It is found that particle sizes of 250 µm were present in high percentage at the most stations.

Particle size distribution, median particle diameter (m.p.d.), sorting coefficient  $(QD_{g})$  and skewness  $(SK_{q_g})$ .

| SIEVE        |       | STATION A |             | STAT          | ION B   | STAT   | NON C     | STATION D |         |  |
|--------------|-------|-----------|-------------|---------------|---------|--------|-----------|-----------|---------|--|
|              |       | % wt.     | Cumula-     | % wt.         | Cumula- | % wt.  | Cumula-   | % wt.     | Cumula- |  |
| ø            | ۳щ    | sieve     | *           | sieve         | ×       | sieve  | ×         | sieve     | ×       |  |
| >-1.0        | >2000 | 7.704     | 7.704       | 20.818        | 20.818  | 15.562 | 15.562    | 29.928    | 29.928  |  |
| 0.0          | 1000  | 14.966    | 22.670      | 15.918        | 36.736  | 2.086  | 17.648    | 22.540    | 52.468  |  |
| +1.0         | 500   | 18.860    | 41.530      | 17.812        | 54.548  | 8.746  | 26.394    | 14.338    | 66.806  |  |
| +2.0         | 230   | 19.446    | 60.976      | 23.231        | 77.779  | 33.928 | 60.322    | 12.756    | 79.562  |  |
| +3.0         | 125   | 16.360    | 77.336      | 13.899        | 91.678  | 28.704 | 89.026    | 9.706     | 89.268  |  |
| +4.0         | 63    | 9.344     | 86.680      | 3.663         | 95.341  | 6.704  | 95.730    | 4.832     | 94.100  |  |
| ≤+4.0        | €63   | 13.320    | 000.000     | 4.659         | 100.000 | 4.270  | 100.000   | 5.900     | 100.000 |  |
| m.p          | .d.ø  | +1        | 1.41<br>400 | +0            | .73     | +1.3   | .69<br>25 | -0        | .12     |  |
| QD g<br>SK g |       | 0.41      |             | 2.91<br>0.093 |         | -3.39  |           | 0.32      |         |  |

| SIEVE<br>OPENING |             | STATION E                    |         | STATION F                     |         | STATION G                      |         | STATION H                     |         |
|------------------|-------------|------------------------------|---------|-------------------------------|---------|--------------------------------|---------|-------------------------------|---------|
|                  |             | % wt.                        | Cumula- | % wt.                         | Cumula- | % wt.                          | Cumula- | % wt.                         | Cumula- |
| ø                | m           | sieve                        | *       | sieve                         | *       | sieve                          | *       | sieve                         | *       |
| >-1.0            | >2000       | 5.862                        | 5.862   | 9.658                         | 9.658   | 28.334                         | 28.334  | 7.722                         | 7.722   |
| 0.0              | 1000        | 5.838                        | 11.700  | 3.400                         | 13.058  | 2.650                          | 30.984  | 2.052                         | 9.774   |
| +1.0             | 500         | 15.160                       | 26.860  | 10.854                        | 23.912  | 9.084                          | 40.068  | 9.100                         | 18.874  |
| +2.0             | 250         | 42.626                       | 69.486  | 46.386                        | 70.298  | 24.668                         | 64.736  | 42.144                        | 61.018  |
| +3.0             | 125         | 23.720                       | 93.206  | 25.418                        | 95.716  | 27.436                         | 92.172  | 32.578                        | 93.596  |
| +4.0             | 63          | 4.776                        | 97.982  | 2.480                         | 98.196  | 5.564                          | 97.736  | 4.940                         | 98.536  |
| ≤+4.0            | <b>\$63</b> | 2.018                        | 100.000 | 1.804                         | 100.000 | 2.264                          | 100.000 | 1.464                         | 100.000 |
| QDg<br>SK        |             | +1.55<br>350<br>1.17<br>1.21 |         | +1.55<br>350<br>1.26<br>-0.02 |         | + 1.41<br>400<br>3.29<br>-0.60 |         | +1.73<br>325<br>1.00<br>-0.03 |         |

Particle size distribution, median particle diameter (m.p.d.), sorting coefficient  $(QD_g)$  and skewness  $(SK_{Q_g})$ .

| SIEVE |       | STATION I |         | STAT   | STATION J |        | STATION K |             | STATION L       |  |
|-------|-------|-----------|---------|--------|-----------|--------|-----------|-------------|-----------------|--|
|       |       | % wt.     | Cumula- | % wt.  | Cumula-   | % wt.  | Cumula-   | % wt.<br>on | Cumula-<br>tive |  |
| ø     | m     | sieve     | ×       | sieve  | *         | sieve  | *         | sieve       | *               |  |
| 2-1.0 | >2000 | 11.093    | 11.093  | 10.350 | 10.350    | 5.570  | 5.570     | 3.362       | 3.362           |  |
| 0.0   | 1000  | 3.629     | 14.722  | 2.900  | 13.250    | 7.292  | 12.862    | 3.182       | 6.544           |  |
| +1.0  | 500   | 10.906    | 25.628  | 11.592 | 24.842    | 11.065 | 23.927    | 14.630      | 21.174          |  |
| +2.0  | 250   | 41.521    | 67.149  | 45.762 | 70.604    | 36.097 | 60.024    | 46.972      | 68.146          |  |
| +3.0  | 125   | 25.335    | 92.484  | 27.550 | 98.154    | 26.767 | 86.791    | 25.088      | 93.234          |  |
| +4.0  | 63    | 4.411     | 96.895  | 1.502  | 99.656    | 9.694  | 96.485    | 3.658       | 96.892          |  |
| €+4.0 | ≤63   | 3.105     | 100.000 | 0.344  | 100.000   | 3.515  | 100.000   | 3.108       | 100.00          |  |
| ø     |       | +:        | +1.58   |        | +1.56     |        | +1.75     |             | .61             |  |
| m.p   | mit   | 3         | 50      | 3      | 150       | 3      | 00        |             | 350             |  |
| QD    | ø     | 1         | .27     | 1.     | . 12      | 1 1.   | 20        | 0           |                 |  |
| SK    |       | -(        | 0.15    | -0     | -0.17     |        | -0.03     |             | 0.03            |  |

| SIEVE    |       | STATION M |         | STAT   | STATION N |        | STATION O |        | STATION P       |  |
|----------|-------|-----------|---------|--------|-----------|--------|-----------|--------|-----------------|--|
|          |       | % wt.     | Cumula- | % wt.  | Cumula-   | % wt.  | Cumula-   | % wt.  | Cumula-<br>tive |  |
| ø        | μm    | sieve     | *       | sieve  | *         | sieve  | *         | sieve  | ×               |  |
| 2-1.0    | >2000 | 3.215     | 3.215   | 4.104  | 4.104     | 21.063 | 21.063    | 7.479  | 7.479           |  |
| 0.0      | 1000  | 3.154     | 6.369   | 1.362  | 5.466     | 1.966  | 23.029    | 3.908  | 11.387          |  |
| +1.0     | 500   | 8.344     | 14.713  | 5.566  | 11.032    | 9.157  | 32.186    | 18.633 | 30.020          |  |
| +2.0     | 250   | 26.882    | 41.595  | 37.968 | 49.000    | 39.716 | 71.902    | 49.856 | 79.876          |  |
| +3.0     | 125   | 46.388    | 87.983  | 41.686 | 90.686    | 23.366 | 95.268    | 17.499 | 97.375          |  |
| +4.0     | 63    | 5.231     | 93.214  | 6.916  | 97.602    | 3.801  | 99.069    | 2.158  | 99.533          |  |
| ≤+4.0    | €63   | 6.786     | 100.000 | 2.398  | 100.000   | 0.931  | 100.000   | 0.467  | 100.00          |  |
| ø.p.     | . 15  | +2,18     |         | +2.01  |           | +1.45  |           | +1.40  |                 |  |
| m.p.d.um |       |           | 325     | 2      | 50        |        | 375       |        | 00              |  |
| QD       | ø     | 0         | .93     | 0      | .86       | 2      | . 54      | 1      | .00             |  |
| SK       | 9     | -         | 0.20    |        | 0.03      |        | -0.58     |        | -0.16           |  |

Particle size distribution, median particle diameter (m.p.d.), sorting coefficient  $(QD_p)$  and skewness  $(SK_{q_0})$ .

| SIEVE   |       | STAT         | ION Q   | STAT         | ION R     | STATION S    |         |  |
|---------|-------|--------------|---------|--------------|-----------|--------------|---------|--|
| OPEN    | ING   | % wt.        | Cumula- | % wt.        | Cumula-   | % wt.        | Cumula- |  |
| ø       | mسر   | on<br>sieve  | tive %  | on<br>sieve  | tive<br>% | sieve        | tive %  |  |
| 2-1.0   | >2000 | 3.040        | 3.040   | 14.500       | 14.500    | 1.336        | 1.336   |  |
| 0.0     | 1000  | 2.598        | 5.638   | 10.798       | 25.298    | 2.314        | 3.650   |  |
| +1.0    | 500   | 13.540       | 19.178  | 19.462       | 44.760    | 6.652        | 10.302  |  |
| +2.0    | 250   | 46.314       | 65.492  | 30.700       | 75.460    | 34.940       | 45.242  |  |
| +3.0    | 125   | 31.392       | 96.884  | 17.922       | 93.382    | 50.015       | 95.257  |  |
| +4.0    | 63    | 2.402        | 99.286  | 4.960        | 98.342    | 4.224        | 99.481  |  |
| ≤+4.0   | ≤63   | 0.714        | 100.000 | 1.658        | 100.000   | 0.510        | 100.000 |  |
| m.p.d.ø |       | +1.66<br>325 |         | +1.18<br>450 |           | +2.08<br>238 |         |  |
| QD,     | ð     | 0.           | .92     | 1.           | . 67      | 0.81         |         |  |
| SKqø    |       | 0.           | .02     | -0           | . 24      | -0.15        |         |  |

| procession of the local division of the loca | and the second division of the second divisio | and the second se | and the second se |             |           |             |           |  |
|--|--|---|---|-------------|-----------|-------------|-----------|--|
| SIEVE  |  | STAT  | ION T   | STAT        | TION U    | STATION V   |           |  |
| OPEN   | ING  | % wt.   | Cumula-   | % wt.       | Cumula-   | % wt.       | Cumula-   |  |
| ø  | ۳۳   | on<br>sieve   | tive<br>%   | on<br>sieve | tive<br>% | on<br>sieve | tive<br>% |  |
| ≥-1.0  | >2000  | 6.200   | 6.200   | 3.569       | 3.569     | 18.768      | 18.768    |  |
| 0.0  | 1000   | 2.446   | 8.646   | 2.801       | 6.370     | 4.704       | 23.472    |  |
| +1.0   | 500  | 11.286  | 19.932  | 23.623      | 29.993    | 12.820      | 36.292    |  |
| +2.0   | 250  | 48.814  | 68.746  | 45.914      | 75.907    | 36.146      | 72.438    |  |
| +3.0   | 125  | 25.308  | 94.054  | 19.770      | 95.677    | 23.632      | 96.070    |  |
| +4.0   | 63   | 3.656   | 97.710  | 3.225       | 98.902    | 3.404       | 99.474    |  |
| <+4.0  | €63  | 2.290   | 100.000   | 1.098       | 100.000   | 0.526       | 100.000   |  |
|  |  |   |   |             |           |             |           |  |
|  | ø  | +1  | .61   | +1          | . 42      | +1.37       |           |  |
| m.p.d.um   |  | 3   | 20  | 4           | 00        | 4           | .00       |  |
| QDa  |  | 0   | .98   | 1.          | 00        | 1.99        |           |  |
| SK   |  | 0   | .04   | 0.          | 01        | -0.43       |           |  |



Cumulative percent %



Cumulative percent %



% trapage evitelumu

The sediments of almost all the stations were medium sand except station B with coarse sand, station D with very coarse sand, stations M.N and S with fine sand as follows:

- STATION A is well sorted, negatively skewed, medium sand with median diameter 400 سير.
- STATION B is very poorly sorted, positively skewed, coarse sand with median diameter 650 µm.
- STATION C is moderately well sorted, negatively skewed, medium sand with median diameter 325 Jum.
- STATION D is very poorly sorted, positively skewed, very coarse sand with median diameter 1100 سیر.
- STATION E is very poorly sorted, positively skewed, medium sand with median diameter 350 µm.
- STATION F is poorly sorted, negatively skewed, medium sand with median diameter 350 µm.
- STATION G is very poorly sorted, negatively skewed. medium sand with median diameter 400 µm.
- STATION H is moderately sorted, negatively skewed, medium sand with median diameter 325 um.
- STATION I is poorly sorted, negatively skewed, medium sand with median diameter 350 µm.
- STATION J is poorly sorted, negatively skewed, medium sand with median diameter, 350 µm.
- STATION K is poorly sorted, negatively skewed, medium sand with median diameter 300 um.
- STATION L is moderately sorted, positively skewed, medium sand with median diameter 350 um.
- STATION M is moderately sorted, negatively skewed, fine sand with median diameter 225 µm.

- STATION N is poorly sorted, negatively skewed, fine sand with median diameter 250 µm.
- STATION O is very poorly sorted, negatively skewed, medium sand with median diameter 375 ......
- STATION P is moderately sorted, negatively skewed, medium sand with median diameter 400 um.
- STATION Q is moderately sorted, positively skewed, medium sand with median diameter 325 بس.
- STATION R is poorly sorted, negatively skewed, medium sand with median diameter 450 µm.
- STATION S is moderately sorted, negatively skewed, fine sand with median diameter 238 um.
- STATION T is moderately sorted, positively skewed, medium sand with median diameter 350 µm.
- station U is moderately sorted, positively skewed, medium sand with median diameter 400 µm.
- STATION V is poorly sorted, negatively skewed, medium sand with median diameter 400 um.

### 5.4 Discussion:

At stations A and D (Figure 5.2) located just outside the effluent outlet, no fauna was found. The sediment of station A was black, slimy, heavily oiled with a bad smell and contains dead shells and turrets.

The number of individuals was relatively high at station B although it is near to the outfall is due to the mass occurrence of one polychaete species (<u>Megalomma spp</u>.). Whereas a large gastropod (<u>Cerithidea cingulata</u>) which is common in polluted areas contributed to the high biomass in this station. Station K had the highest number of individuals due to mass occurrence of <u>Megalomma spp</u>.  $(92,679m^{-2})$  and <u>Oligochaete spp</u>.  $(31,548m^{-2})$ .

Low number of species at stations G, M and S may be due to being at the top of the beach and therefore more prone to drying-out. The water there is very shallow with a maximum depth of less than 0.5m during the high tide especially at station S, which may explain why it had low biomass, diversity and eveness although it is well away from the effluent discharge.

Oligochaetes and <u>Megalomma</u> were found at almost all stations - and may be considered pollution-tolerant species in this area. Whereas <u>Perinereis</u> was absent from stations near the effluent, or at the top of the beach, and <u>Ophelia</u> was found only at stations well away from the effluent.

Medium sand classified according to Wolff(1973) is common in the sediment of the most stations.

Computer analysis using a Pearson correlation matrix showed that there was no correlations between individual species and sediment parameters. Oligochaetes, <u>Perinereis spp</u>. and <u>Ophelia spp.A</u> however correlate with distance from the effluent as shown in Figures 5.40, 5.41 and 5.42.

There was very little correlation between the number of individuals, or species number, or biomass, or diversity or eveness. Except biomass with quartile deviation of sediment, and particle size um with J. But there were good correlations of species number with diversity and

- 380 -



The correlation between the oligochaete and distance from the outfall.



The correlation between <u>Perinereis</u> <u>Spp</u>. and distance from the outfall.



The correlation between Ophelia spp. A and distance from the outfall.

eveness, and of diversity and eveness. This shows that these factors are inter-related with diversity consequent upon species number, and eveness too is dependant upon diversity, which is dependant upon species number. But basically there was little or no correlation of the benthic community parameters with any of the sediment characteristics.

It is found that species number, diversity and eveness all correlate with distance from the effluent. Therefore distance from the effluent appeared important, whereas the sediment parameters were not.

Since species number, diversity and eveness correlate with distance from effluent, this indicates an increase in species diversity as one moves away from the effluent. Biomass shows a negative correlation with distance, showing some enrichment near to the effluent which might be due to mass occurrence of <u>Cerithidea cingulata</u> at the stations near the effluent since it is common in polluted areas.

This indicates that the influence of Sitra oil storage tanks effluent on the fauna of the adjacent intertidal area (Figure 5.43) presented a similar picture to that noted by Pearson and Rosenberg (1978) for the influence of organic enrichment and by McLusky (1982) for the influence of petrochemical effluent on the fauna of the Kinneil intertidal estuarine mudflat.

Leppakoski (1975) has classified the benthic fauna of brackish-water areas into five groups of species with reference to their response to environmental changes due to organic pollution. These groups are:-



Figure 5.43

A: Species number, B: Abundance of animals (number  $m^{-2}$ ), C: Biomass (g flesh dry weight  $m^{-2}$ ), in Sitra oil storage tanks intertidal area, in relation to distance from Sitra oil storage tanks effluent. 1. Progressive species of the 1st order:

Scarce in unpolluted areas, but occur in great numbers in polluted areas. Their numbers increase as the degree of pollution increases, until inhibitory effects are noticed in the most polluted areas. e.g. Oligochaeta-Limnodrilus hoffmeisteri, Peloscolex heterochaetus. Polychaeta-Polydora ciliata, Capitella capitata.

2. Progressive species of the 2nd order:

Tolerate only slight pollution, but increase in number as the degree of pollution increases. e.g. Polychaeta -<u>Nereis diversicolor</u>, <u>Manayunkia</u> <u>aestuarina</u>.Mollusca-<u>Macoma balthica</u>, <u>Thyasira spp</u>., <u>Montacuta spp</u>.

3. Regressive species of the 1st order:

Tolerate only slight pollution, but decrease in number as the degree of pollution increases. e.g. Crustacea-<u>Corophium volutator</u>, <u>Gammarus spp</u>.. Mollusca-<u>Hydrobia spp</u>., <u>Cardium spp</u>.. The majority of benthic species.

4. Regressive species of the 2nd order:

Clean water species, totally absent from polluted areas. e.g. Crustacea-<u>Pontoporeia</u> <u>affinis</u>, Ostracoda.

5. Indifferent species:

Distribution unaffected by pollution. e.g. Oligochaeta-<u>Tubifex</u> <u>costatus</u> Polychaeta-<u>Nephthys</u> <u>incisa</u>, <u>Glycera</u> <u>alba</u>. Applying Leppakoski system to the Bahrain intertidal area we may suggest that <u>Megalomma</u> and <u>Cerithidea</u> as progressive spp., <u>Perinereis</u> and <u>Ophelia</u> as regressive spp., and Oligochaeta as indifferent spp..

It is noticed that close to the effluent (less than 500m) there is a reduction in species number and diversity, but a high biomass at 200m due to only three opportunistic species (<u>Megalomma spp., Oligochaete spp</u>. and <u>Cerithidea cingulata</u>). Beyond 500m there are fluctuations in species, biomass etc., which reflect the varying fauna at each station. These fluctuations may be due to a variety of reasons, including sediments, feeding, tides, biological interactions etc.

It may thus be suggested that the Sitra effluent effect is mainly confined to the area up to 500m from the outfall.

Mattsson and Notini (1981) noted that at the end of BAPCO oil refinery outfall all benthic fauna was totally absent and the bottom covered in blue-green algae. Nearby, the fauna was severely disturbed with only scattered individuals of a few species. Elsewhere there was little or no disturbance and seagrass was abundant. Coral reefs towards the refinery outlet were dead and covered with algae, bryozoans and hydroids.

The results of a studies carried out by Linden, Larsson and Al-Alawi during 1986 of the diversity, abundance and biomass of benthic fauna in an area adjacent to BAPCO refinery outfall (Figure 5.44) are shown in Table 5.11. This table also show the corresponding figures from Mattson and Notini study which was carried out during 1981. A general trend in most stations (Figure 5.44) is that the number of species as well as the number of individuals per m<sup>2</sup> (abundance), the biomass and the diversity have increased or are at approximately the





The investigated area with different main habitats and sampling stations indicated. (From Linden et al, 1988).

The results of the studies of the benthic fauna in 1986, and the corresponding figures for 1981. (From Linden <u>et al</u>, 1988).

|         |        |         |       |        | Bion    | lass         |       |      |
|---------|--------|---------|-------|--------|---------|--------------|-------|------|
|         | No. of | species | In    | id./m2 | g wet v | eight/m2     | Diver | sity |
| Station | 1981   | 1986    | 1981  | 1986   | 1981    | 198 <b>6</b> | 1981  | 1986 |
|         |        |         |       |        |         |              |       |      |
| 7       | 45     | 10      | 8065  | 1160   | 35.0    | 89.2         | 3.75  | 1.73 |
| 16      | 29     | 35      | 2946  | 6175   | 21.4    | 128.4        | 4.05  | 4.32 |
| 28      | 5      | 4       | 421   | 2500   | 0.9     | 52.2         | -     | -    |
| 27      | 27     | 40      | 2735  | 7575   | 28.6    | 39.2         | 4.25  | 3.53 |
| 26      | 26     | 33      | 2420  | 8525   | 12.7    | 136.3        | 4.38  | 3.92 |
| 24      | 23     | 49      | 2630  | 12550  | 32.1    | 119.1        | 3.40  | 4.23 |
| 20      | 26     | 27      | 3261  | 3025   | 27.6    | 240.1        | 3.80  | 3.86 |
| 12      | 0      | 2       | 0     | 200    | 0       | 2.7          | -     | -    |
| 23      | 28     | 24      | 6347  | 1925   | 34.6    | 15.3         | 3.80  | 3.13 |
| 18      | 2      | 7       | 40180 | 41100  | 125     | 19.2         | 0.37  | 0.74 |
| 13      | 0      | 5       | 0     | 150    | 0       | 2.6          | 0     | 0.66 |
|         |        |         |       |        |         |              |       |      |

same level as in 1981. The only stations where a drastic decrease in the fauna have occurred are in stations 7 and 2. The decrease in station 7 could most probably be related to the high concentrations of oil found in the sediment (higher than in 1981). The reason for this higher oil concentration may be related to the newly constructed marina, which is located at the southern part of Sitra Island. This had concentrated much of the boating activities to an area which previously was not much affected by such activities. The decrease in benthic fauna found in station 2 should be treated carefully since this station was moved to a new location in 1986 due to land reclamation activities. The substrate (sand etc.) in the new location appeared to be different from the normal material in the area and had probably recently been transported to the area and dumped there.

The results of the observations made during the sampling at each station are given below. However, in order to avoid repetition, the description is summarized to review the different habitats observed with principal species of groups only. Thus, the results from the individual stations are not given here.

The reef and algal rock area north of the refinery outlet (see Figure 5.44): Depth between 1 and 2 meters. The sea bed was covered by dead and some living corals, coral debris, rock and firm sand. Sea urchins (<u>Echniometra mathaei</u>) appeared in abundance. Benthic macroalgae covered some 15-20% of the seabed. Dominating algal species were <u>Sargassum binderi</u>, <u>S. latifolium</u>, and <u>Padina sp</u>. Some colonial sea anemonies were observed. Brain corals (<u>Platygra sp</u>.) were noted occasionally. Few fishes (gobies, sea bream) were noted. Crabs were abundant in cavities, under coral rubble etc..No bivalves were found. The water was relatively turbid with a visibility of approximately 4 m.

The northern edge of the coral rubble area east of the outlet (marked "mainly living coral" in Figure 5.44): Depth between 1 and 3 meters. Living corals covered 95-100% of the sea bed. About 10 coral species were noted although Acropora (two species) dominated over large areas. Other abundant corals were Porites sp., Platygyra sp. (two species), Goniastrea sp. and Stylophora sp., Leptastrea sp. were noted occasionally. The coralline algae Lithothamnium sp. was abundant. Two types of brown algae, Pocochiella variegata and Hydroclathrus clathratus, occurred sometimes in large quantities, covering corals and other organisms. Sea urchins (E.mathaei) were abundant and starfishes occasional. About 10 fish species were abundant; damselfish (Pomacentrus aquilus, P.albicaudatus, Ρ. sulfureus), angelfish (Pomacanthus maculosus), doublebar bream (Acanthropagrus bifasciatus), emperor (Lethrinus sp.), snapper (Lutjanus sp.) and gobies.

The western edge of the coral rubble area east of the outlet (marked "90-100% dead coral" and "80-90% dead coral" in Figure 5.44): Depth between 1 and 2 m. A reef dominated by dead corals. Only three living coral species (<u>Platigyra sp., Acropora sp., Stylophora</u> <u>sp.</u>) were found occasionally. Dead coral and coral rubble were often covered with the brown algae <u>Pocochiella</u> <u>variegata</u>. Areas of coralline sand were to 75% covered with brown algae (<u>Sargassum</u>). The green algae <u>Auranvillea</u> was common. Crabs and a few different gastropods were observed occasionally. Bivalves found occasionally were jewel-box (<u>Chama sp.</u>), scallops (<u>Chlamys sp.</u>), rock oyster (<u>Spondylus sp.</u>) and pen shells (<u>Pinna</u> <u>sp.</u>). A few fish species were observed such as <u>Therapon puta</u>, <u>Diplodus noct</u>, <u>Pomacentrus sp.</u> and gobies . Poor visibility of the water and large amount of sediment covered algae, corals etc.

The northern part of the soft bottom area surrounding the outlet from the refinery (basically the area where stations 7 to 14 are located in Figure 5.44): Depth between 4 and 5 meters. Light grey to yellowish-brown very fine sediment. The sediment were covered with a carpet of filamentous bacteria and algae. A few leaves of <u>Halodule uninervis</u> was noted per  $m^2$ . <u>Padina sp</u>. was noted occasionally. Burrows of polychaete worms were frequent. The gastropod <u>Cerithidea</u> were also quite common (several per  $m^2$ ).

The sea bed of the southern part of the soft bottom area (basically the area where stations 19,20, 24 to 28 are located in Figure 5.44): Depth 5 to 6 meters consisted of light yellow-brown well oxygenated sediment with sand and shell debris. The vegetation of <u>Halophila</u> <u>ovalis</u> and <u>Halodule uninervis</u> was gradually becoming denser towards the south. Venus shells (<u>Circe sp.</u>), brittle stars, tunicates (<u>Botryllus sp.</u>), colonial anemonies and sponges were noted with increasing abundance towards the south. Several species of fish were frequent, including gobies, snappers and <u>Therapon sp.</u>.

## CHAPTER 6

# GENERAL DISCUSSION

.

#### 6.1 Introduction:

The results obtained during the course of this study have led to some very interesting conclusions and recommendations which are relevant not only to BAPCO but to any and all sources of pollution that may have an effect on the marine environment of Bahrain and the surrounding areas of the Arabian Gulf.

The Arabian Gulf is a shallow semi-enclosed sea. Its marine environment has very special geographical and meteorological conditions, and therefore is not comparable to any other sea areas, except perhaps the Red Sea and the Gulf of Aden (FAO, 1981).

Rapid industrialization and urbanization in the last couple of decades had subjected the Gulf to stressful environmental extremes. The Gulf, being the receiver of sewage, industrial, oil extraction and transportation discharges appears to be becoming increasingly polluted.

Bahrain is located in the Arabian Gulf, and is an archipelago of more than 33 islands. Traditional fishery was the major economic activity in Bahrain prior to the discovery of oil in 1930s. Bahrain coastal ecosystems are not only diverse but are also very productive. Seagrass beds, coral reefs and tidal marshes are the most productive marine ecosystems, and their productivity can approach or exceed that of agricultural land (McLusky, 1981). As might be expected, therefore, fish is an important component in the Bahraini diet.

The fishing villages of Bahrain are restricted to the northern half of the island. Fishing in the west coast is relatively unproductive and provides less than 5% of total landings by weight. This is attributed to the low effort and also probably to the bottom type and comparatively poor water circulation off the more productive northern and eastern grounds.

Since 1930, the coastal waters have been exposed to man-made pollution. The marine environment receives wastes from different sources such as the refinery, dredging and land reclamation activities, sewage outfalls, aluminium industry, power stations, desalination plants, petrochemcial industry, iron and steel company, ship building yards, asphalt and cement factories, agro industry (lamb feedlots , dairy farms, layer houses), food manufacturing (slaughter houses, flour mill, soft drinks), plastic industries and photolaboratories. In the car service stations, no used oil collection and recycling is practiced. Therefore, it may be assumed that most of the spent car lubricant oil finds its way into the sea.

The above activities indicate the current need for controlling waste disposal into the sea.

In Bahrain monitoring of pollution is inadequate. Regulations and standards for waste disposal have not yet been enacted. Most industrial wastes are carelessly dumped into the sea creating a potential marine pollution problem.

The status of Bahrain as an oil producing country and as an oil refining centre, in addition to its proximity to major tanker routes, exposes it to a continuous risk of oil pollution. The Arabian Gulf had 142 major coastal plants in existence or planned during 1976 (Jacob and Zarba, 1979). In addition to oil refineries, cement plants and desalination-power plants, these included about 8 fertiliser plants (Walgate, 1978). All these industries are adding to the pollution load of an almost enclosed sea which averages only 34 m deep with shore water less than 10 m deep. The rapid coastal urbanization, untreated sewage effluents, industrial wastes, the hot waste water discharge from different plants into this shallow sea may create many ecological problems beyond recovery.

## 6.1.1 Water quality:

The physical and chemical properties of sea waters, are of primary importance in determining the occurrence of marine plants and animals. The fluctuations in the environmental conditions have a profound influence on the aperiodic and seasonal migrations and occurrence of fish. Furthermore, the conditions in the aquatic environment and their changes influence the recruitment, survival and growth of the fish. The environment also interferes with such biological activities as spawning and growth (Hela and Laevastu, 1961).

The transport, distribution and ultimate fate of pollutants in marine waters is controlled by physical, chemical and biological oceanography. Therefore, in order to understand the capacity of the marine environment to support pollutants without adverse effects, one must first understand the oceanography affecting them. Physical, chemical and biological oceanographic data can be used to determine and predict circulation and water residence time. This is most important because upon these two factors is based the ability of the sea area to flush itself clean of polluting substances.

Considering the importance of oceanographic conditions, and because of the lack of such information about Bahrain waters, the study was carried out during the period January-December 1983 to determine the distributions of temperature, salinity, pH, phosphate, ammonia nitrate and nitrite at different locations in Bahrain waters and their fluctuations at different seasons.

From the study conducted, it could be said that in general the water quality of the western and northern regions of Bahrain is better than the water quality of the eastern region. The east has in general higher pH, higher ammonia, higher nitrite, lower nitrate, and higher phosphate levels than the other regions. The higher concentrations of all these substances reflects the urbanisation and industrialisation of this part of Bahrain and the consequent discharges of waste material.

The concentration of ammonia seems to be inversely related to the concentration of nitrate reflecting the known chemical changes in nitrogen cycle in the sea.

The results of the present study could be used to study the relationships between the various measured parameters, and the presence and absence of different fish species in certain areas and in various seasons. For example, in Bahrain, the diversity of fish has been shown to be seasonly variable with a greater diversity in September to December (Abdul Qader, 1986). Fish landings in the adjacent state of U.A.E. was studied by Ali and Cherian (1983) in relation to water temperature. A temperature oriented landing was observed in some of the common species. Queen fish, Snapper and Scad recorded the maximum percentage of landing (>70%) during May to October (warm water period) whereas major percentage (>70%) of landing of Sardines, Mackerel and King fish was during low temperature period (December - March). A more elaborate study is required to draw authentic conclusions regarding the relationships between the catch composition and prevailing water temperature of the region.

The abundance of shrimps appears to be related to salinity with more juvenile shrimps found in low salinity area. (Personal observation).

#### 6.1.2 <u>Refinery discharges:</u>

Before considering the specific effects of the BAPCO refinery, we should consider the general effects of oil refinery discharges in the world. Oil refineries produce complex polluting discharges, although recently, increasing emphasis on means for improving effluent quality and reducing effluent flows has led to a general reduction in total pollutant loads (and particularly oil losses) from refineries in Europe, and elsewhere.

The effluents of the modern refineries are usually of low total volume compared with those of pre-1960 refineries, and are presumably rapidly diluted in the receiving water. Dilution cannot necessarily, however, be regarded as "the solution to pollution" because unless the discharge area is capable of adequately degrading, metabolising and assimilating the compounds discharged, there may be a gradual build-up to toxic levels.

A typical older established refinery can be

shown to have pollutant loads five to thirty times as high as those of a modern refinery, even before treatment, while the waste water production of the former, per ton of crude processed, is 70 times as high. (The flow of waste water produced varies widely, depending on the types of cooling applied and on the degree of segregation maintained between the oily sewer and the cooling water system) (CONCAWE 1979; UNEP 1980<sub>b</sub>).

It appears to be impossible to generalise about why refinery effluents are toxic. Available toxicity test data for coastal refinery effluents show little obvious correlation between toxicity and parameters such as pH, biological oxygen demand and concentration of ammonia, sulphide, or 'oil'. The large number of hydrocarbons and other chemical compounds contained in oils and in refinery effluents yield such a high number of possible combinations, synergistic and antagonistic effects, that it appears very difficult for laboratory experiments to produce reliable information on the probable ecological effects of refinery effluents on the receiving bodies of water.

Some examples of interactions are the effects of pH on sulphide and ammonia toxicity and the formation of metal complexes, synergistic toxic effects with cyanide/ ammonia and cyanide/zinc mixtures, and mutual reduction of toxicity with cyanide/nickel mixtures (Côté, 1976). Free chlorine reacts with components such as ammonia and phenol, forming chloramines and chlorophenols which are as toxic or even more toxic and longer-lived than the original unchlorinated compounds (Murphy et al., 1975). In the case of low salinity effluents entering normal seawater condition, there is evidence that the lower salinity contributes to biological responses observed in marine organisms (Dicks, 1976). Conversely, some well-known bioassay organisms such as Daphnia may rapidly succumb in tests with coastal refinery effluents because the salinity is too high (Rambaud et al., 1975).

The degradation of organic constituents in refinery effluents depends not only upon the nature of the compound but also upon temperature, oxygen, nutrients and microbial species present. Given optimum conditions, many petroleum hydrocarbons and phenols will degrade easily but higher molecular weight polynuclear aromatics and trihydric phenols degrade slowly, and it is not clear how long they are likely to remain in different types of marine environment. Incorporation into anaerobic bottom sediments may greatly increase degradation times of all organic compounds, both those occurring naturally as well as those derived from effluents.

The solubility of the hydrocarbon in water is also an important factor which determines its rate of degradation. The degradation of hydrocarbons is very slow under anaerobic conditions.

In general, the aerobic degradation of aliphatic compounds by the microflora takes place most readily. However, individual substances display appreciable differences in their rates with medium to long chain and saturated hydrocarbons being generally less resistant to microbial attack than the lower molecular weight compounds, especially those molecules that exhibit unsaturated character (viz, ethylene). Chain branching also influences the rate of hydrocarbon oxidation, degradation often proceeding only up to the branching points. Degradation of aromatic hydrocarbons takes place primarily in accordance with three different types of reactions. A number of bacteria. are involved, together with yeasts and fungi. Polycyclic aromatics, such as naphthalene, anthracene and phenanthrene are also degraded by bacteria, and some of the higher condensed polycyclic aromatics with more than three rings persist for appreciable times, perhaps in part because of their low solubility in water.

Phenols, ammonium salts, sulphides and cyanides are all known to be subject to rapid biochemical conversion processes.

Sulphides and ammonia may be oxidised chemically or by bacteria and are not likely to accumulate in well-aerated discharge areas. High sulphide levels may be found in anaerobic mud both in effluent discharge areas and in naturally anaerobic areas distant from industry.

It can be concluded from the study of the water quality of the BAPCO effluent, that the concentrations of the various parameters are variable depending on the discharge. The flume inlet of the refinery has a higher level of contaminant than other Bahraini coastal waters, due to recirculation of water from the outlet stream. In general, it was noticed that the concentration of the pollutants are very high at the Sitra separator outlet but the accumulation of pollutants was greatest at the main stream discharge as it went into Salba Bay as well as in the sediments of the Bay itself.

The water temperature and chemical results, and the concentration of pollutants in the sediments near the discharge points indicate that the treatments units were inefficient in treating contaminants introduced into the water. With the dumping of waste water and its pollutants in the semi-confined Salba Bay, there is a noted concentration gradient of pollutants that has its highest concentration near the outfalls of the refinery treatment system and its lowest concentration far out to sea. This same concentration gradient exists in the same pattern in terms of toxicity, aerobic conditions of the sediments, and the abundance of certain types of algae which indicates the eutrophication of the immediate marine environment. The distribution of the pollutants into the areas of the grassbeds and Fasht Al-Adhum has the immediate potential of destroying the breeding area of economically important species of shrimps of Bahrain.

The sediments of Salba Bay exhibit the effects of forty-five years of contamination by showing a distinct color gradient from the areas near the treated waste water outfall to those areas that are further out to sea. The sediments of the inshore region are distinctly black in color which slowly changes to the normal gray color as one proceeds to the offshore area where there is less pollution. The black color indicates an anaerobic condition where sulphur reducing bacteria are active in the production of hydrogen sulphide.

With the conditions in Salba Bay as bad as they are, there has been a noted migration of the mobile fauna from the Bay and the destruction of the sessile fauna due to the accumulation of toxic materials from the refinery. An ultimate research objective could be the identification of those constituents of refinery effluents which are responsible for observed environmental effects.

It is clear that further improvement in refinery effluent quality will involve major capital investment. The ability for the industry to examine better quality data which explores the relationship between effluent quality and environmental impact must be a necessary prerequisite to decisions on such capital investment. The examination of the data will need clearly to show the need for further improvement in quality, over and above that currently generally achieved, and that further control on the refinery discharge will have a significant impact in relation to all other sources of the pollutants.

Because some oil sumps are very close to the sea, an extremely dangerous potential exists for polluting the marine environment as well as contaminating underground fresh water reservoirs. This is particularly true because the oil that might beireleased from the sumps goes into the marine and soil environment in an untreated and therefore more dangerous state.

### 6.1.3 Biological effects:

Marine surveys show that effluents from some coastal refineries which carry out primary treatment only, can decrease the number of species (or individuals) or plants or animals living in water close to the discharge point. It is not known whether occasional peak concentrations or continuous low levels of substances cause these effects, which are normally observable only where large, complex and relatively old refineries discharge large volumes of effluent into enclosed waters that are unaffected by other discharges. Various techniques can be successfully employed to reduce such effects and some case histories are given. Other primary treated effluents show no observable effects, particularly where they arise from less complex, modern, air-cooled refineries with lower effluent flows, or where the effluent is well-dispersed in a large body of water. Secondary treatment of refinery effluents can eliminate any detectable toxic effects, (Jenkins et al, 1979).

Alexander et al (1982) examined the hydrocarbons in mullet captured near a petroleum refinery outfall at Cockburn Sound in Western Australia and adjudged by a tasting panel to be tainted with petroleum and compared with those from untainted mullet captured in a comparatively pristing area. The tainted mullet contained approximately 15 mg/kg of aromatics, principally substituted naphthalenes, strongly suggesting that is the source of the tainting.

Knap and Williams (1982) undertook laboratory experiments to investigate the biological and physical fates of refinery effluent once discharged to Southampton Water estuary. The most important removal mechanism within the time scale of the estuarine system appears to be adsorption of petroleum hydrocarbons to estuarine sediments. In the experimental systems, 70% of the hydrocarbons originally in the water column were found in the sediments after 1 h. The rate-determining factor appears to be initial concentration of the starting material.

Within the last 25 years there have been considerable advances in the techniques of measuring the effect of pollution on fish, in the understanding of the effect of chemical and physical variables both on the toxicity of poisons and on the susceptibility of fish to them, and also in the statistical treatment of the results. Concomitant with this has been the development of various standard test techniques, some of which, such as the U.S. and U.K. methods, became nationally adopted. However, although these tests were satisfactory for a limited purpose, they tended to become used for providing information beyond their original purpose and capability, for example, 'safe concentrations' were assumed to be 10 per cent of a 1-or 3-day LC50, and although this may be valid for some poisons it cannot be taken as a general rule. It is not intended to review these tests in detail, nor indeed to set out fully the requirements for fish bioassays since this had already been carried out by Sprague in some detail (1969, 1970, 1971) as well as in a simplified version (Sprague, 1973). Instead, the types of pollutional situations which may cause hazards to fish and fisheries will be considered so as to indicate the type or types of bioassay procedure which would give the type of data appropriate for the control of pollution in each case.

Pollutional situations may be separated into five main groups (Sprague, 1973):-

(1) Theoretically, most chemicals could find their way into the aquatic environment as a result of accidental discharges, either from storage depots or while being transported by air, land, or water or from irresponsible or illinformed disposal of unwanted surplus material. Such discharges are likely to be isolated occurrences, in which the initial concentration of chemicals will decrease due to their subsequent dispersal, dilution and degradation. Information is required on the degree of risk attending such accidents so that the necessary steps can be taken to minimize their possible occurrence.

Some chemicals may find their way into the aquatic ecosystem as a result of normal usage or misusage and again, assessment

is required of the degree of risk involved for fisheries. If the likely maximum concentration of a particular chemical in the environment is very much smaller (say by a factor of  $10^{-4}$ )\* than the acutely lethal level for a particular species of fish, then it might be safe to assume that such a chemical poses no pollutional problems for fisheries. The type of test procedure required to give a measure of the acute lethal concentration for fish can be termed a preliminary screening test. Such a screening test could also be used to determine the potentially least toxic of a group of chemicals or products which may find their way into the aquatic ecosystem from normal usage, so that the use of the least hazardous substance can be investigated further.

(2) However, there are many poisons which appear in the environment at levels greater than 10<sup>-4</sup> times the acute lethal level, as a result of industrial, agricultural, and domestic effluent discharges, or from direct application to water (as with aquatic herbicides). Such chemicals may remain in the aquatic ecosystem for long periods of time, perhaps permanently, and for these substances much more information is required to assess the hazard, formulate water quality criteria and impose water quality standards. The nature and extent of the additional tests depend upon the nature of the substance and the degree of risk which its use entails. The test procedures necessary to provide such information can be described as tests to establish water quality criteria.

\* The value of 10<sup>-4</sup> is only an approximate guide. The factor for persistent or accumulating toxic substances may be less than this value.
- (3) Normally, the quality standards set for an effluent are described in chemical terms and the subsequent monitoring of the effluent is carried out by chemical. analysis. However, where effluents contain substances or complex mixtures which are hazardous to fisheries and which are difficult to analyse, fish toxicity test have to be carried out to estimate the extent of the risk and a simple test used for subsequent monitoring of the effluent. Such a test can be called an effluent monitoring test.
- (4) Where the quality standards set for those effluents described above need to be legally binding, a closely defined, reproducible test procedure is necessary to establish evidence in a court of law of a failure to comply with a fish toxicity standard. Such a test can be described as legal test.
- (5) As mentioned above, an aquatic ecosystem can be suddenly polluted from a variety of sources, giving rise to hazards for water-users downstream. In cases, a monitoring system can be of some value whereby a continuous surveillance of a few test fish for signs of stress can provide an early warning of unfavourable conditions, and allow the water supply to, say, water treatment works or fish farms to be temporarily shut off. Such tests can be described as aquatic ecosystem monitoring tests.

During the last three decades several techniques have been tried to assess the toxicity of pollutants to fish and other organisms (Doudoroff <u>et al.</u>, 1951; Alabaster and Abram, 1965; Sprague, 1971, 1973; Nishiuchi, 1974; APHA, 1980; EIFAC, 1975; EPA, 1975; etc.). The toxicity of pollutants is commonly determined using some sort of test in which organisms respond, or fail to respond, to given conditions, The LC50 test, identifying the concentration of a test substance lethal to 50% of test organisms within a specified period of time (e.g. 2 days) has been widely adopted. Sub-lethal tests, determining concentrations which are deleterious to a variety of physiological processes, behaviour , growth or reproduction, are being increasingly used, particularly for research purposes.

A variety of test types are available, and their advantages and disadvantages have been summarised by Davis (1976) as in Table 6.1.

Davis stresses the importance of defining the objective of any particular test and of selecting a method appropriate for that objective. For example, a short term static test may be suitable for a crude comparison of the toxicity of two waste streams, but some toxicants may not act immediately and require long-term continuous flow procedures for the accurate definition of toxicity thresholds. It also has to be borne in mind that many factors such as salinity, temperature, light, natural activity rhythms of test organisms, species sensitivity and effluent collection and handling procedures, may affect bioassay results. Results are not necessarily independent of the type of organism used, for example Hiscock (1976), using a variety of organisms to rank waste streams within a refinery in order of toxicity, found significant differences in rank according to the test organism used (see Table 6.2). This table also demonstrates the variability of any one effluent stream with time and the difficulty of predicting environmental effects from infrequent toxicity test.

## Table: 6.1

Types of toxicity tests (From Davis, 1976).

| Static Test                | Advantages<br>Simple, inexpensive;<br>economical of toxicant<br>and manpower;<br>well-documented | Disadvantages<br>Detoxicification<br>Possible;<br>wastes accumulate;<br>volatiles easily<br>lost                                      | Optimum Use<br>Tests 12<br>hrs.<br>Comparative<br>tests  |
|----------------------------|--|---|--|
| Static with<br>Replacement | Simple, fairly<br>accurate;<br>fairly economical<br>of toxicant                                  | Requires regular<br>attention;<br>organisms stressed<br>during replacement  | Routine<br>LC <sub>50</sub> s;<br>Tests<br>96 hrs.   |
| Continuous<br>Flow         | Often most accurate;<br>no detoxification or<br>waste build-up;<br>good methods available        | Complex apparatus<br>high toxicant use<br>space required  | Rigorous<br>LC <sub>50</sub> s;<br>Tests 96<br>hrs; for<br>max. accuracy                       |
| In situ                    | Includes natural<br>conditions; can use<br>local species; no<br>effluent collection<br>required  | Difficult to<br>observe and<br>monitor;<br>organisms<br>stressed during<br>observations?<br>Difficult to<br>control and<br>interpret. | Receiving water<br>screening tests;<br>testing<br>interactions<br>under natural<br>conditions. |

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#### Table: 6.2

Toxicity ranking of different waste streams within a refinery, using a variety of test species (From Baker, 1979).

A,B,C,D,E,F and G are the waste streams from 7 different process units. The number 1-8 indicate the ranking from most toxic, through decreasing toxicity, to the non-toxic control. Samples 1 and 2 were taken from the waste streams on different dates. Brackets indicate no difference in toxicity between the samples bracketed.

|   |   | Sample 1                                   |   |  |  |
|---|---|--|---|--|--|
| Rank Order  | <u>Littorina</u><br>nigrolineata                | <u>Mytilus</u><br><u>edulis</u>            | <u>Gobius</u><br><u>sp</u> .                    | <u>Gammarus</u><br>chevreuxi               | <u>Ostracoda</u>                           |
| 1 (most toxic)<br>2<br>3<br>4<br>5 .<br>6<br>7<br>8 (non-toxic) | A<br>D<br>C<br>B<br>E<br>F<br>G<br>Control      | C<br>D<br>B<br>F<br>A<br>G<br>E<br>Control | A<br>B<br>G<br>C<br>E<br>F<br>D<br>Control      | B<br>F<br>G<br>D<br>C<br>E<br>A<br>Control | A<br>E<br>F<br>B<br>D<br>G<br>C<br>Control |
|   |   | Sample 2                                   |   |  |  |
| Rank Order  | <u>Littorina</u><br>nigrolineata                | <u>Mytilus</u><br>edulis                   | <u>Gobius</u><br><u>sp</u> .                    | <u>Gammarus</u><br><u>chevreuxi</u>        | Ostracoda                                  |
| 1 (most toxic)<br>2<br>3<br>4<br>5<br>6<br>7<br>8 (non-toxic)   | B<br>D<br>F<br>G<br>A<br>E<br>C<br>C<br>Control | C<br>D<br>E<br>F<br>B<br>A<br>G<br>Control | B<br>A<br>D<br>C<br>E<br>E<br>G<br>F<br>Control | D<br>B<br>F<br>C<br>E<br>G<br>A<br>Control | B<br>D<br>C<br>F<br>A<br>E<br>G<br>Control |

It is thus difficult to make ecological predictions from laboratory toxicity test data alone.

The toxicity of oils should be distinguished from their hazard. For example, a low-boiling toxic oil may under natural conditions evaporate quickly and have relatively little effect on a marine community. Other factors which may influence toxicity are water solubility and degree of dispersion.

Early research on the toxicity of various oils was carried out with a view to developing herbicides or pesticides for agricultural use. This work showed that oils vary in their toxicity according to the content of low-boiling compounds, unsaturated compounds and aromatics. The higher the concentration of these constituents the more toxic the oil. Toxicity appears to increase along the series alkanes - alkenes - aromatics. In addition as a general rule, aromatics with increased numbers of alkyl substituents have higher toxicities (Crafts and Reiber, 1948; Havis, 1950; Van Overbeek and Blondeau, 1954). These conclusions are in general supported by later work concerning the toxicity of hydrocarbons to estuarine and marine organisms (Anderson et al., 1974; Neff et al., 1976; Ottway, 1976; Rossi and Neff, 1978).

Available data on the toxicity of cycloalkanes and cycloalkenes suggests that these compounds are more toxic than alkanes and that in some cases they are more toxic than aromatics. Currier and Peoples (1954) tested barley and carrot with hydrocarbon vapours and found that toxicity increases along the series haxanehexene-cyclohexane-cyclohexene-benzene. Crisp <u>et al</u> 1967), quoted by LeGore (1974), testd the narcotic effect of several hydrocarbons to barnacle larvae and ranked the compounds in order of increasing effect: decane, octane, heptane, hexane, pentane, cyclooctane, naphthalene, p-xylene, cyclohexane, toluene, cyclopentane, benzene and cyclohexene. LeGore (1974) found that cyclooctane was more toxic to larvae of the oyster <u>Crassostrea gigas</u> than isopropyl benzene, o-, m- or p-xylene, benzene, ethyl benzene or toluene. Some workers have reported that mononuclear aromatics with increased numbers of alkyl substituents have higher toxicities (Crafts and Reiber, 1948; Havis, 1950; Van Overbeek and Blondeau, 1954), but other work (e.g. LeGore, 1974) has shown no clear relationship between structures of these compounds and their toxicity.

Lethal effects on several marine species or groups have been noted for the more toxic fractions of petroleum and petroleum products and pure hydrocarbons, in the 0.3-100 ppm range with some evidence of lower concentrations (down to 0.1 ppm) being lethal to larval and juvenile life stages of some species. Sub-lethal responses have been commonly observed over this range of concentrations, and in some cases below 0.1 ppm. Extensive data supporting these generalisations are tabulated by Nelson-Smith (1972); Rice <u>et al</u> (1976); Neff <u>et al</u> (1976); Hyland and Schneider (1976) and Craddock (1977).

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From the limited information available on bulk properties of recovered oils from effluents systems, it seems likely that the hydrocarbons present in effluent after primary gravity separation will resemble those found by contacting a very light crude oil with water, except that one might expect higher proportions of light materials and especially aromatics up to  $C_{o}$  in the water. This applies particularly to modern low effluent volume refineries, where the major hydrocarbons inputs to effluent apart from ballast water will be from crude oil desalting and tank drainings. These light hydrocarbons would be relatively toxic but also relatively easily degraded. Secondary treatment, particularly biological oxidation, will greatly alter the remaining hydrocarbon composition in the effluent as well as reducing the total amounts present (CONCAWE, 1979).

Organisms are exposed to the pollutant partly directly via the water, partly via solid particles, that is food, sediments and suspended material. Because of the low oxygen level in water as compared to the atmosphere, water as a carrier medium can be much more important than air. Organisms living in the aquatic environment have to consume large amounts of water in order to appease their oxygen demands, thus exposing them to larger volumes of carrier medium compared to terrestrial animals. Theoretically this indicates that pollutants in an aquatic environment can be a more severe risk than air born pollutants. This counts especially for sessile, filtering organisms, for instance molluscs (CONCAWE, 1982).

When the uptake of the pollutant has taken place, the fate of the substance depends on the capability of the organism to metabolise it. The metabolising ability of aquatic organisms also depends on the physical and chemical characteristics of their environment, and of course on the type of pollutant. If the metabolism is incomplete the pollutant as such or as a metabolite can remain in the organism and gradually accumulate. The concept of bioaccumulation is therefore very complex since it includes all the biological transfer processes: uptake, storage and discharge of both parent pollutants and their metabolites. Furthermore, several authors have reported both selective uptake and accumulation of toxic substances (CONCAWE, 1982).

Hydrocarbons display short life under normal environmental conditions. Only high molecular weight polynuclear aromatics (PNA) persist for some time, but:

- a. They constitute only a minute fraction of the oil discharged.
- b. They can be reduced if justified to prevailing background level by deep de-oiling or biotreatment.

- Biotreatment can also remove phenols, ammonia, sulphides and cyanides that may be present.
- Metals such as cadmium and mercury are only present at prevailing background levels in refinery effluents.

Neff (1979) has exposed an estuarine clam to four polyaromatic hydrocarbons (Table 6.3). Phenanthrene was taken up most rapidly and released most slowly. The rapid release of naphthalene masked а similarly rapid uptake during exposure, since both influx and efflux of this compound undoubtedly occurred simultaneously. These results can be explained in terms of relative aqueous solubilities and lipid/water partition coefficients of the four PAH's. Naphthalene is the most water soluble of the PAH tested, and thus more readily bioavailable. Although it has a high affinity for lipids, its lipid/water partition coefficient favours rapid release to water when naphthalene concentrations in the medium are reduced. Benzo - (a) pyrene on the other hand, has a very low aqueous solubility so that most of it will be in colloidal or particulate forms, thus, decreasing its bioavailability.

. In conclusion, basing oneself on this information, it

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# Table: 6.3

Accumulation from seawater and release of PAH by the estuarine clam Rangia cuneata (From Neff, 1979).

| Aromatic Hydrocarbon                                     | Naphthalene            | Phenanthrene | Chrysene  | Benz(a)pyrene |
|--|------------------------|--------------|-----------|---------------|
| Exposure<br>concentration (ppm)                          | 0.071                  | 0.089        | 0.066     | 0.052         |
| Tissue concentration after<br>24 hr. exposure (ppm)      | 0.43±0.1               | 2.85±1.1     | 0.54±0.3  | 0.45±0.1      |
| Bioaccumulation factor<br>(Tissue/Water)                 | 6.1                    | 32.0         | 8.2       | 8.7           |
| Tissue concentration<br>after 24 hr. depuration<br>(ppm) | 0.1 <del>5±</del> 0.02 | 2.47±1.2     | 0.40±0.15 | 0.38*         |
| %Released in 24 hours                                    | 66                     | 13           | 26        | 16            |

\* Only one sample analysed. Other figures are based on five samples.

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information about the bioaccumulation factors of certain

is easy to see how complex the biological transfer of hydrocarbons in organisms is. Even if we have some information about the bioaccumulation factors of certain components of the oil, little is known about the relationship between the amount of this component in animal tissue and the total amount of hydrocarbons in the surrounding water. Unfortunately this counts especially for refinery effluents, since very few studies have been carried out with weathered oils over long periods (CONCAWE, 1982).

It is necessary to test BAPCO discharge biologically for the assessment of potential damage arising from it, and for subsequent monitoring and regulation. The first step is to obtain basic information on the acute toxicity of each pollutant such as the short-term LC50, the shape of the graphical concentration/response curve and the maximum concentration of the pollutant likely to occur in the evironment, with all other relevant chemical, physical, and hydrographical data.

Part of the present research aims at studying the effects of refinery effluent in Bahrain on one of the most commonly consumed fish, safee (<u>Siganus canaliculatus</u>). The significance of selecting this fish as a test species depends on its wide popularity as food, small size for easy handling and abundance. Another important aspect is that it is not a long migrant and as such is more likely to be affected by any oil pollution or refinery effluents.

No studies on toxicity tests are available on <u>Siganus</u> <u>canaliculatus</u> or any other fish in Bahrain.

Concentrations in water should be correlated not only with responses of the organisms, but also with measurements of the accumulated pollutants in the tissues. This is because it is easier to monitor subsequently the levels in a specific organism than those in the aqueous medium which may vary with season, tide, wind, etc., as well as with variation in effluent discharge (IMCO, 1977).

The results of this study have shown that safee can survive in a well aerated aquarium without food or change of water for at least forty-five days indicating a high degree of tolerence to abnormal conditions by this fish.

When tested with the full concentrations of I.A.F. and Sitra separator effluents of BAPCO, all of the test fish (safee) died within fifteen minutes of being placed into the test medium. The lethal concentration of I.A.F. and Sitra separator effluents which brought death to fifty percent of the test population of fish (safee) within 96 hours was approximately twenty percent.

Although certain dilutions of the effluents did not kill the fish, there was an increased concentration of some contaminants such as hydrocarbons and heavy metals in the tissues of the fish which could be passed on up the food chain and eventually be consumed by man with severe deleterious results.

FAO (1977<sub>a</sub>) suggest that safe levels can be determined by multiplying the LC50 by 0.1 to 0.4, or for persistant poisons by 0.01. Sprague (1971, 1971<sub>a</sub>) feels that the higher values of 0.4 are too close to harmful levels.

Thus the 'safe' level is the concentration of a pollutant which does not have an adverse sublethal or chronic effect on fish, and may be calculated empirically from the median lethal concentration.

In the case of the I.A.F. and Sitra separator effluents of BAPCO, the safe level may be suggested to be 2.4% and 2.0% respectively.

Rowe <u>et al</u> (1983) found that continuous exposure to 30% treated refinery effluent had severe effects on growth of rainbow trout, <u>Salmo gairdneri</u> during 44 days; their size at the end of the experiment was not significantly

greater than at the beginning. Effluent at 10% concentration also resulted in a significant reduction in specific growth rate compared to the control and lower

concentrations.

Rowe <u>et al</u> (1978) performed laboratory tests using samples of treated effluent from a petroleum refinery, to determine the effect of various dilutions on rainbow trout, small tropical flagfish and <u>Daphnia pulex</u>. Threshold concentrations were determined for adverse effects on growth, reproduction and behavioural symptoms. Two- day tests with <u>Daphnia pulex</u> are suggested as a possible bioassay procedure for monitoring effluent quality.

Westlake <u>et al</u> (1983) found that the 48-h LC50 of treated refinery effluent for 2-day-old <u>Daphnia pulex</u> was 76% effluent. The 14-day LC50 was 6.4% effluent and this was a threshold value for mortality. For reproductive failure, the 14-day was 3.1% effluent, and the EC50 of 0.52% effluent was considered to approximate the threshold of sublethal effect.

The authors found that Daphnia reproduction was the most sensitive response in a series of studies that included fish growth, reproduction, locomotion, and respiration. Results are considered representative for a well-treated effluent from a petroleum refinery. The 48-h lethal test with <u>D.pulex</u> would be a useful tool for monitoring or assessing such effluents, since it is simple small-scale, quick, and about 2.6 times as sensitive as a lethal test with trout.

Buikema <u>et al</u> (1980) have carried out 48 hour toxicity tests on Daphnia and 96-hour tests on goldfish, in a refinery effluent before and after secondary treatment, and inhabition tests with glucose-6-phosphate dehydrogenase (G6PDH). The tests were also carried out on an artificial refinery mixture (ARM) and were used to show that in vitro inhabition of G6PDH can be used to predict toxicity of actual refinery effluents.

The Estuarine Forth is subject to the introduction of many domestic and industrial wastes, ranging from domestic sewage, and distilling waste discharged from the Alloa area, to chemical and refinery effluent discharged from the petro-chemical complex at Grangemouth.

Smith (1987) has found that in examining the lethal effects of the chemical and refinery effluent to  $\underline{P}$ . <u>flexuosus</u>, <u>C.volutator</u> and <u>H.ulvae</u>, the resultant median lethal times indicated that the animals could only survive exposure to the effluents for short periods of time.

All LT50 values decreased with increasing effluent concentrations, with <u>Praunus</u> the most sensitive, surviving in the chemical and refinery effluent for 38.8 h to 0.5 h and 170 h to 6.8 h respectively, when exposed to a concentration range 1.25% to 7.5%.

The median lethal concentrations (LC50) of the effluent decreased with increasing exposure periods (24h to 96h). The 96h LC50 values indicated a rank order of sensitivity of <u>P. flexuosus</u>(most sensitive)><u>C.volutator</u>><u>M.</u> <u>balthica> H. ulvae</u> (least sensitive) under all test conditions.

The LC50 values produced by each species on exposure to each effluent resulted in the formation of a linear log concentration - log response curve. Lloyd (1979) and Franklin (1980) stated that such a linear relationship indicated that the test organisms had no means by which they could de-toxify the toxic components of an effluent. The linearity of the response showed that there was no lethal threshold concentration so that exposure to a range of concentrations lower than the 96h LC50 values would be lethal on exposure

The LC50 values obtained from these linear relationships indicated that in spite of variations in the toxicity of the individual samples, the chemical effluent was always the more toxic of the two effluents tested.

at longer time periods.

Kupchanko and Krishnaswami (1969) carried out laboratory studies on tainting of rainbow trout by oil refinery waste waters discharged to the Bow river, Alberta, confirmed that the oily taste of the fish could be related to the concentration of waste waters present, expressed as the threshold odour number (as defined in the American standard methods for the examination of water and waste waters "APHA", 1980). Test fish were exposed for periods of 6-72 hours to effluents diluted with unchlorinated water to give odour levels ranging from 0.015 to 2.0, then examined for flavour by panels of judges. It was found that, in the laboratory tanks, tainting occurred within 24 hours at odour levels of 0.25. Fish held in cages in the river, about 15 miles below the effluent outfall, developed an oily taste when the threshold odour number of the river water was 1.0 or higher.

In connexion with studies on the effect of oil refineries waste waters on aquatic life and the effectiveness of waste-treatment methods. Graham (1963) carried out

bioassays, both short-term (up to 96 hours) and longterm (16 to 32 days) with fathead minnows to compare the effects of waste waters from 4 oil refineries, two of which provided extensive treatment for waste waters and two only partial treatment. For the longterm tests, a constant-flow apparatus was constructed, capable of renewing 10 litres of test solution every 51/2 hours. The waste waters were also analysed chemically. With the partially-treated waste waters of relatively high initial toxicity, the 96 hours TLm value was 6.5-16.5 per cent. When these effluents were stored for 16-32 days, the concentrations of ammonia, phenol, and sulphide, and usually the pH value, decreased, but there was no appreciable change in toxicity. These effluents required a dilution of 90 per cent or more to give sub-acute concentrations and the resulting solutions had no adverse effects on fish during prolonged exposure (for 32 days). In contrast, effluents of relatively low initial toxicity, which had received various degrees of treatment in lagoons, required little or no dilution to give sub-acute concentrations and the resulting solutions had chronic toxic effects on fish after prolonged exposure. Although the lagoons reduced the concentration of substances causing acute toxicity they probably did not remove certain constituents such as cyanides and metal salts which could cause chronic toxicity, and since little dilution was needed to prepare solutions of sub-acute concentration relatively large amounts of trace materials were still present. At least 60 per cent dilution of the lagoon effluents would be necessary to prevent chronic toxicity. The components responsible for the chronic toxic effects are not known. When compared with the more toxic effluents, effluents from lagoons contained more planktonic organisms and caused more slime growths.

Reddy <u>et al</u> (1983) has observed the toxic effects of Hindustan Petroleum (Caltex) Ltd., Gnanapuram, oil refinery effluent on green alga <u>Scenedesmus incassatulus</u> and the blue-green alga <u>S. aeruginosus</u>. The growth decreased with the increasing concentrations of effluent in both the algae but blue-green alga <u>Synechoccocus aeruginosus</u> showed a higher tolerance. The effluent inhibits the growth and also reduces the synthesis of biochemical products like proteins, pigments and activity of acid phosphate.Photosynthesis and respiration processes were also inhibited in both algae.

Rowe et al  $(1983_{\rm h})$  found that the treated petroleum refinery effluent had average values for ammonia, pH and oil plus grease. Continuous life-cycle exposure of the flagfish, Jordanella floridae, to a sublethal concentration of treated effluent (28 per cent) resulted in reduced size of both first generation males (after 47 days) and second generation fry. Marked abnormalities haemorrhaging in first generation fish and spinal deformities in the second generation. Spawning was delayed and less frequent with fewer eggs per attempt. None of these effects were noted at lower concentrations (0.13 and 0.92 per cent). In the group exposed to 9.1 per cent effluent, first generation males were smaller than controls but, as the corresponding females were larger than controls, this observation is of questionable significance.

Saha and Konar (1984) found that sublethal concentrations of petroleum refinery effluent (2.10%) decreased the yield and fecundity of fish <u>Tilapia mossambica</u>. The fish at this concentration showed respiratory distress. Exposed fish became lethargic. Continuous exposure of effluents may be more hazardous. Heming <u>et al</u> (1983) exposed Rainbow trout for 44 days to sublethal concentrations (1, 3.1, 10 and 30 per cent) of treated petroleum refinery effluent whose chemical characteristics were within Canadian government limits. In term of fork length and wet weight, growth in the 30 per cent group was virtually zero and mortality approximately 16 per cent. A significant but less marked reduction in growth rate was apparent at 10 per cent effluent but there was no significant difference between controls and fish exposed to concentrations of 1 and 3.1 per cent. The threshold for growth inhibition is probably in the vicinity of 6 per cent treated effluent.

Initial experiments involving intraperitoneal administration of Beta-naphtholflavone to estuarine sculpin (Leptocottus armatus) carried out by Boese et al (1982) demonstrated the presence and inducibility of the mixed-function oxidase (MFO) system. Subsequently sculpin were exposed to various concentrations of class B petroleum refinery effluent from two west coast refineries. After 10 days, hepatic aldrin epoxidase activity and cytochrome content was determined. Tabulated results reveal that differences in the extent of MFO induction by the two refinery effluents may be correlated with differences in the concentration and compostion of organic compounds in the wastewaters.

Kaufman and Horne (1964) have used large analogue tanks continuously flushed with estuarine water to study the effects of treated and diluted petrochemical waste waters on biota from San Francisco bay. The treated petroleum refinery effluent had no apparent effect on fish, in contrast to results obtained with untreated waste water, but it had marked effects on the growth and metabolism of indigenous aufwuchs and phytoplankton, the degree of stimulation depending on the period of contact between the full-strength effluent and the diluting sea water. The experiments indicated that the refinery effluent, at the dilutions to be expected, will have a moderate overall stimulatory effect on phytoplankton and aufwuchs communities in the vicinity of the outfall.

Although many different fish have been used in toxicity tests, few studies have been made to compare the reactions of different species to a particular toxic agent, Douglas and Irwin (1962) have therefore carried out experiments on the resistance of 16 different species of fish to an oil refinery waste water. The fish used were goldfish (Carassius auratus), carp (Cyprinus carpio), orange-throat darter (Etheostoma spectabile), brook stickleback (Eucalia inconstans), mosquito fish (Gambusia affinis), plains minnow (Hybognathus placitus), brook silverside (Labidesthes sicculus), guppy (Lebistes reticulatus), bluegill (Lepomis macrochirus), smallmouth bass (Micropterus dolomieni), white sucker (Castostomus commersoni), plains shiner (Notropis percobromus), bleeding shiner (Notropis zonatus), fathead minnow (Pimephales promelas), rainbow trout (Salmo gairdneri), and creek chub (Semiotilus atromaculatus). Statistical analysis of the 24 hours TLm showed that the most resistant species was Lebistes reticulatus, followed, in decreasing order of resistance, by C. auratus, G.affinis, C.carpio, P.promelas, E.inconstans, N. percobromus, L. sicculus, M. dolomieni, L. macrochirus,

<u>H.placitus</u>, <u>S.atromaculatus</u>, <u>C.commersoni</u>, <u>S.gairdnerif</u>, <u>N.zonatus</u>, and <u>E.spectabile</u>. These results are considered to be more applicable and significant than the 96 hour TLm, where the order of resistance of some species differed slightly, as most of the deaths occurred within the first 24 hours of testing and little change occurred during the following 72 hours. <u>Lebistes reticulatus</u> is considered to be the most convenient species used, as it accepts testing conditions calmly, eats readily, is small and of uniform size, matures quickly, is free of common diseases, is easily raised in the laboratory, and is similar to native American fish in resistance to refinery effluent.

#### 6.1.4 Field studies:

The study of the effect of Sitra oil storage tanks effluent on intertidal fauna of the adjacent area is the first of its kind in this area. The study aims to examine the fauna at the discharge area and to record its abundance, biomass, diversity and eveness.

It is found that at stations located just outside the effluent outlet, no fauna was found. The sediment of station A (Figure 5.2) was black, slimy, heavily oiled with a bad smell and contains dead shells and turrets.

From the conducted study it may be suggested that the Sitra effluent effect is mainly confined to the area up to 500 m from the outfall.

McLusky, (1982) has described the influence of petrochemical industrial effluent on the fauna of the Kinneil intertidal area of the Forth estuary, over a 6-year period. The fauna has a restricted species richness and is often abundant with a high biomass. Zones of pollution around the effluent are delimited and associated changes in species composition, abundance, biomass and redox potential are documented. Closing one discharge during the study period led to the rapid recovery of a previously polluted area.

Ecological surveys in the discharge areas of coastal refineries (mainly with primary treatment) have shown that in some cases numbers of species and/or numbers of individuals decrease near the discharge point and in other cases no such effect has been observed. The overall impression is that effects of primary-treated effluents vary tremendously with factor which include age, size, complexity and organisation of the refinery; and physical, chemical and biological characteristics of the receiving area.

The greatest changes are associated with high volumes of effluent from complex large old water-cooled refineries, discharged into enclosed waters. There is some evidence that such changes can be at least partly reversed following effluent improvement. Changes have not been observed in the case of welldispersed primary-treated effluents from some of the more modern aircooled refineries. These effluents are usually of low total volume compared with those of pre-1960 refineries, and are presumably rapidly diluted to below toxic levels. Dilution cannot necessarily however be regarded as 'the solution to pollution' because unless the discharge area is adequately degrading, metabolising and assimilating the compounds discharged, there may be a gradual build-up to toxic levels.

It is not known if changes, where present, result from above specification peaks of effluent components, or continuous low-level discharge (Baker, 1979).

Heitkamp and Johnson (1984) have examined the survival, functions, and physiological diversity of autochthonous sediments microbiota in situ at five stations along the Little Popo Agie River, WY, one station above, one at, and three below a discharge point for oil wastewater from Union Oil Company's Dallas Field. Microorganisms appeared to maintain physiological diversity and increased in numbers and activity in a riverine environment that contained petroleum hydrocarbon concentrations known to be deleterious to freshwater fish and macrobenthic communities.

Refinery effluents may conceivably cause changes in discharge areas through:

- a) direct toxic effects on flora and fauna leading to reduction in numbers, lower growth rates, or changes in other variables,
- b) avoidance behaviour of some species, which may include fish of commercial importance.

- c) tainting of some species, which may include fish and shellfish of commercial importance,
- d) other factors such as reduction in dissolved oxygen or eutrophication.

A variety of approaches may be used to find out if changes have taken place (Baker, 1979).

Factors determining effects include:

- Volume of discharge (which in turn depends upon size and cooling system of the refinery);
- quality of discharge (which depends upon effluent treatment methods and the efficiency with which they are operated.type of crude oil used by the refinery, and complexity of processing);
- salinity of discharge (which depends upon relative volumes of fresh and salt water used for cooling and processing, nature of ballast water handled by the system, and volumes of rainwater draining off the refinery area);
- variability of discharge (i.e. size of fluctuations of volume, salinity, and concentrations of oil, sulphide, ammonia and other constituents);
- siting of outfall (shore, headland, jetty, offshore, subtidal);
- physical conditions of discharge area (tidal range, currents, turbidity and temperature of receiving water, and intertidal and subtidal substrate type);
- chemical conditions of discharge area (salinity, oxygen concentration, and nutrients concentration of receiving water);
- proximity of other effluents (e.g. sewage);

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- presence of other pollutants (e.g. oil spills or dispersants used for cleaning);
- biological conditions of discharge area (saltmarsh plants, shellfish beds, etc.).

This list of factors is not necessarily in order of importance (Baker, 1979).

It should be borne in mind that well-dispersed primary treated effluents could become a problem if a number of them were discharged to the same area. Some badly-dispersed primary treated effluent in estuaries have produced easily observed localised effects such as death of salt marsh vegetation, reduction of shore mollusc population, increase of some species of algae, and visible oil residues in mud (Jenkins <u>et al</u>, 1979).

In Europe it is suggested that a set of agreed minimum specifications could be used throughout Europe as a guideline or as a statutory control, and that additional restrictive regulations could be imposed by states, provinces or regional water authorities to protect sensitive areas (such as sheltered estuaries, or previously unindustrialised coasts rich in wildlife or fisheries resources). The minimum specifications should be achievable with efficient primary treatment but the more restrictive specifications for sensitive areas would require some form of further treatment (Baker, 1979).

## CHAPTER 7

## CONCLUSIONS AND RECOMMENDATIONS

The abatement of water pollution in established refineries cannot start at the end of the sewer pipe, but must begin in the plant. It involves the segregation of the diluting streams and, where possible, the treatment of the highly contaminated streams at sources. The implementation of "in-plant control measures" in established and often complex refineries requires considerable effort and capital expenditure (Pauluis, 1979).

Locations which are sensitive, because of fishery, wildlife, amenity or water quality interests, or conversely due to a high total load of pollution, may require stricter local standards; secondary treatment may be necessary to achieve these specifications.

A significant contribution to future work, in marine pollution, would be the development of quantitative methods to describe the ability of an ecosystem to recover from external stress when that is removed. This could be a decisive influence in evaluating the human influence on ecosystems and particularly in the prediction of its ultimate recovery potential.

The idea that "the solution to pollution is dilution" does not hold for all types of waste. Lloyd (1979) noted that no dilution factor could be applied to wastes which were bioaccumulative. Hence in order for dilution to alter the long term survival of species exposed to the effluent discharged by the oil refinery, it would be essential for the effluent's treatment to be improved. Only by improving the quality of effluents, to prevent the build up of toxic components within the animals exposed to it, would the dilution of the effluents directly affect the long term survival of the species.

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In view of the above study, it is suggested that treatment measures should be undertaken for BAPCO effluents, especially the I.A.F. and Sitra separator effluents, to strip them of the H<sub>2</sub>S and remove the residual oil, hydrocarbons, phenols etc.

From the above study a series of general recommendations can be made as follows:

1. Studies similar to the one reported here should be conducted on the wastes of the other industries of Bahrain that are released to the marine environment.

2. Standards should be established for the State of Bahrain for the discharge of waste water effluents to the marine environment. Such standards should take account of international conventions, such as the "black, grey and red" lists of prohibited substances. The standards should be chosen to protect the population of Bahrain, with regard to both fishery interests and the intake of water for the desalination plants. It is recommended that standards similar to those recommended by other Gulf states, such as Saudi Arabia and Kuwait, be adopted to ensure equality of treatment within the Gulf area. (Information on standards is presented as an appendix to Chapter 3.)

3. It is suggested that a testing laboratory needs to be established in Bahrain. Such a laboratory should determine the toxicity levels of waste waters to the natural inhabitants of the marine environment. It should also monitor the levels of contaminants in fish and shrimp species, and water produced by desalination plants, to ensure their safe consumption by the inhabitants of Bahrain.

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4. With the benefit of information from the above recommendations, it is recommended that "consents" be issued to existing or new industries, or other waste discharges, to ensure that all discharges comply with the appropriate requirements. Such consents should conform to international standards, and should be chosen to protect the life of Bahraini waters, for the benefit of the State of Bahrain. Pages 436 - 443 have been omitted. Replaced by appendix to Chapter 3 (page 257)

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