

**MARINE MONITORING PROGRAM**

**STUDY OF PHYSICAL, AND CHEMICAL  
OCEANOGRAPHY IN BAHRAIN TERRITORIAL WATERS**

**1993**

**ENVIRONMENTAL PROTECTION COMMITTEE**

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**BAHRAIN**

**With the Co-operation of  
Directorate of Fisheries  
Ministry of Commerce & agriculture.**

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## 1. INTRODUCTION

A program to evaluate changes in the marine environment at a number of sites around Bahrain was started in 1988. Biological, oceanographic and chemical studies were undertaken during 3 cruises at 7 sites around the island. Analyses had shown no severe pollution at any site. Temporal and seasonal changes could not be evaluated due to insufficient data.

The Marine Monitoring Program (formerly Marine Ecosystem Survey) was initiated in January 1988. The first circum-Bahrain cruise was made in March of that year aboard the Danat Al-Bahrain. Since then 2 additional cruises have been made, Oct. 88 and Apr. 89. During these cruises a large volume of data concerning physical and chemical oceanography and the ecology of each site was collected.

To continue some of the marine water quality monitoring program, we decided to monitor physical, and chemical changes within Bahrain's territorial waters during 1993. The main objectives were :

1. To measure physical and chemical properties of sea water and sediments in the east coast of Bahrain.
2. To check whether the water is free from major contamination, to affect the overall productivity of the ecosystem.
3. To enable us to report to ROPME, the status of the marine environment, on an yearly basis.
4. To help the national authorities to formulate guidelines and standards or criteria for the quality of sea water.
5. To meet the provisions of the ROPME Protocol for the protection of the marine environment against pollution from land-based sources (article-VII- to assess systematically the levels of pollution within territorial waters, in particular with regard to the substances that may have potential significant impact on the marine environment).

East coast was selected as it was near the discharge of major industries and in an area that has been characterized as the most polluted area in Bahrain . .

## **SITE SELECTION**

Four sampling sites were selected in the East coast. Only the offshore sites were studied due to manpower shortages. Figure 1 shows the location of each site. . All samples were collected and analyzed in accordance with the Regional Organization for Protection of the Marine Environment (ROPME) Manual of oceanographic Observations and Pollutant Analysis Methods (MOOPAM). These methods are summarized in relevant sections.

## **2. PHYSICAL AND CHEMICAL OCEANOGRAPHY**

### **2.1 METHODS**

#### Physical

Temperature, pH, DO, conductivity, and salinity were profiled in-situ at the surface (below 25cm) utilizing a Hydrolab Surveyor II. Turbidity was measured by use of a H.F. Instruments DRT 100 D Turbidimeter.

The sediment sample was collected for each site using Van Veen Grab. The samples were then washed through a 63 micron sieve to get rid of the clay fraction so the samples could be sieved. After drying the samples were then placed in a sieve shaker for 10 minutes for fractioning the samples into particle sizes. Each fraction was then weighed.

#### Chemical:

Water sampled using Niskin bottles from the surface for nutrient analysis were filtered through 0.45 um filters using an Antlia pump set, then transferred into plastic bottles and frozen immediately. Samples for phosphate determination were collected in 100ml glass bottles and refrigerated. Samples for chlorophyll-a were filtered through GF/C 4.2cm filters and kept in the dark.

**Ammonia nitrogen:** The filtered sample was treated in an alkaline citrate medium with sodium hypochlorite and phenol in the presence of sodium nitroprusside as a catalyst. The reaction is for ammonia nitrogen which includes  $\text{NH}_4$  ions and the unionized  $\text{NH}_3$ . The absorbance was measured at 640nm using a Bausch and Lomb Spectronic 21 Spectrophotometer, with 5cm cells. Concentrations were calculated using a calibration factor derived from calibration curves.

**Nitrite nitrogen:** was determined by diazotizing with sulfanilamide and coupling with N (-1-Naphthyl)-ethylenediamine to form a highly colored azo dye which was measured with a spectrophotometer at 543nm using 1 cm cells.

**Nitrate nitrogen:** Nitrate was reduced to nitrite by passing the sample through a column containing cadmium filings coated with metallic copper. The nitrite produced was analyzed as above. Any nitrite initially present was corrected.

**Nitrite nitrogen:** Nitrite was determined as in Nitrate nitrogen.

**Phosphate phosphorus:**

Sea water was reacted with a composite reagent containing ammonium molybdate and potassium antimonyl tartrate to form a heteropoly acid (phosphomolybdic acid) which was reduced to the intensely colored molybdenum blue by ascorbic acid. Absorbance was measured at 885nm using 5 cm cells.

**Silicate silicon:**

This method involved the reaction of molybdate-reactive silica with ammonium molybdate in an acid solution to form yellow silicomolybdic acid. Oxalic acid was added to destroy phosphomolybdic acid and to minimize interference from tannin. Silicomolybdic acid was reduced to heteropoly blue by using ascorbic acid as the reductant. Absorbance was measured at 810nm using 1cm cells.

**Chlorophyll-a:**

One liter of water from the surface was filtered through 4.2 mm diameter Whatman GF/C filters and adding few drops of (MgCO<sub>3</sub>) to it. After filtration the residual water content of the filter was reduced by pulling air through the water for a period of time. The filter was removed, rolled up, and placed in a glass centrifuge tube. Ninety percent acetone in water was added to cover the filter. Extraction was brought about slowly overnight by keeping the tubes at 4 C. The extract was clarified by centrifugation. A suitable volume of clear supernatant was removed by pipette and transferred to a 1cm cell. Absorbance was measured at 750nm, 665nm, 645nm and 630nm. Calculations were done in accordance with Strickland and Parsons as outlined in MOOPAM.

**Total Coliform Bacteria:**

Were analyzed by Millipore filter technique.

### **Alkalinity:**

Titration of 100ml of sea water using 0.02 N-sulfuric acid to a pH 4.5 was used to calculate alkalinity.

## **2.2 RESULTS AND DISCUSSION.**

### **Physical Data.**

The physical data shown in Appendix-A, Table-1-10 did not reflect any anomalies from expected values and no data indicated severe problems. The pH was slightly alkaline and ranged from 7.03 to 8.83. Dissolved oxygen showed higher values in colder water in March. The highest D.O. reading was 8.84 at station 3 with a water temperature of 19.4 degrees C. and the lowest 3.43 mg/l. even in very warm water, 34.46 degrees C. Salinity values ranged from 40.4 to 43.5 parts per thousand. Based on previous knowledge of these waters, salinity values tend to vary with tidal fluctuations but generally increase towards the south.

It should be noted, these data do not reflect the full annual ranges of temperature and salinity, and that some of the flora and fauna are surviving in highly stressed conditions. Coral reef communities are generally not found in waters with salinities exceeding 46 ppt however some individual colonies do exist in areas of 50 ppt. The low temperatures, 12-14 C, exhibited in the winter time impose a major constraint on coral reef development.

Appendix-A, Table-1-10 shows the percentage of the sediment fractions that were retained on the sieves, in the sand, silt and clay categories. It can be seen from this table that the majority of the samples contained higher percentages of sand fraction. Note that the data are highly variable which can be attributed to the inconsistency in site location.

### **Chemical Data:**

Nutrients and other chemical data are shown in Appendix-A, Table 1-10. Ammonia nitrogen levels ranged from 3.97 to 801.0 ug/l with an average of 108.1 ug/l, while nitrate ranged from 0.37 to 91.2 ug/l and averaged 19.56 ug/l. Phosphate concentrations averaged 1.96 ug/l and with a range of 0.68 to 5.4 ug/l. These levels are in general quite low when compared to other coastal areas outside the gulf due to very limited surface runoff.

The highest values for NH<sub>3</sub>-N was observed at the Ras Abujarjur desalination plant site (site-3). This is due to the proximity of the Ras Abu Jarjur desalination plant, the effluent of which contained about 2 mg/l ammonia.-N. The Silicate-Si

varied from 31.60 to 7871.80 ug/l with an average of 695.55 ug/l. The highest reported was near the Ras Abu Jarjur desalination plant. This is because of the silicates contained in fresh ground water.

The low nutrient levels resulted in very low chlorophyll-a concentrations which ranged from 0.80-9.1 ug/l and averaged 1. ug/l. This would indicate low levels of primary productivity in the surface waters of the area. According to W.S. Atkins (1985) in their study of Fasht Al Adm, and others have found generally higher concentrations of chlorophyll-a in benthic samples and this tends to indicate more primary productivity from benthic communities such as sea grass and algae beds rather than from free floating cells or colonies.

#### **4. POLLUTION STUDIES**

##### **4.1 INTRODUCTION:**

The sources of petroleum hydrocarbons and trace metals are well-known and well defined, examples of which are tanker accidents and ballast discharges, industrial effluent, dumping activities and atmospheric deposition.

The fate of these pollutants or their residence time in the aquatic system is affected by different variable and processes including evaporation, oxidation, emulsification, uptake by living organisms, absorption in bottom sediments, weathering, remobilisation processes, etc.

Other factors do affect the nature and behaviour of these pollutants: the sediment grain size whether they are silt, sand or clay differ in binding metals. The physical, chemical and biological characteristics influence the level of these pollutants.

The study of petroleum hydrocarbons and trace metals in the marine environment has gained a high concern in the last few decades. This stems from the fact that they affect the biological resources and marine organisms beside their toxicity nature.

##### **4.2 MATERIALS AND METHOD**

Sampling and analysis of petroleum hydrocarbons and trace metals in sediments and sea water were carried out according to the standard method specified in the Regional Organization for the protection of the marine environment

(ROPME) Manual of oceanographic Observations and Pollutants Analysis Methods (MOOPAM, 1988).

## **A. PETROLEUM HYDROCARBONS**

Sea water was sampled using Niskin bottles at 1m depth from the four stations. 50 ml hexane were added to each sampling bottles at the time of collection.

Surface sediments were collected from Askar (site-4) and Jaw , using stainless steel Van Veen grab sampler, placed in precleaned aluminum containers and frozen until the time of analysis.

The sediment samples were air dried and then sieved by sieve shaker in order to separate the smallest possible fraction (< 63  $\mu\text{m}$ ).

### **Reagents:-**

1. Hexane
2. Dichloromethane
3. Hexane - Dichloromethane mixture; 7:3 v/v.
4. Anhydrous Sodium Sulphate.
5. ROPME crude oil standard.
6. Alumina.

### **Extraction of Petroleum Hydrocarbons from Sea Water**

Petroleum hydrocarbons were extracted from the sea water with 50 ml of 7:3 hexane - dichloromethane solvent mixture. The sample - solvent mixture was shaken vigorously to facilitate extraction and few grams of anhydrous  $\text{Na}_2\text{SO}_4$  were added to break any emulsion and to remove excess water. The dry extract was made up to 100 ml in a clean, solvent-rinsed volumetric flask.

### **“Extraction of Petroleum Hydrocarbons from Sediment**

Approximately 15g of the air dried sediment sample were weighed in a pre-extracted thimble and extracted in a Soxhlet extractor with dichloromethane (Ca. 130 ml) for about 8 hr.

Using a rotary evaporator, the dichloromethane was evaporated to a volume of 20 ml and the extract was made up to 25 ml with dichloromethane.

## Sediment Extract Clean-up

3 ml of the extract was quantitatively transferred to a 10 ml tube and made up exactly to 10 ml with hexane. 0.1-0.5 ml of the extract was added, with a micro-pipette, on the top of a Pasteur pipette plugged with preheated glass wool and filled with activated alumina. Two fractions were eluted, the first with 5 ml hexane and the second with 15 ml of the solvent mixture. The second fraction contained the aromatics.

### **Calibration:**

Crude oil calibration standards were prepared from the ROPME crude oil standard. From this stock solution a series of standard solutions were prepared.

### **Measurement:**

The fluorescence intensity of the standards and samples were measured on the Spectro Fluorophotometer-meter which was set to the following conditions:

Abscissa Scale x 4	Ordinate Scale	x8
Scan Speed fast	Sensitivity	high
Excitation Slit	(nm)	5
Emission Slit	(nm)	5
Excitation wavelength	(nm)	310
Excitation start wavelength	(nm)	250
Emission start wavelength	(nm)	250
Emission wavelength	(nm)	360
Excitation and wavelength	(nm)	550
Emission and wavelength	(nm)	550

The intensities verses concentrations were plotted and the sample concentration was calculated as ROPME crude oil equivalent.

## **B. TRACE METALS**

### **i. Sediments**

A few grams of freeze-dried sediment samples were digested in Teflon beakers by the addition of 5.0 ml of HNO<sub>3</sub>, HClO<sub>4</sub>, HF and HNO<sub>3</sub> sequentially and then made up to 25 ml with 1% HNO<sub>3</sub>. Philips - Pye Unicam SP9 Graphite furnace Atomic Absorption Spectrophotometer (GFAAS) with an autosampler, video furnace programmer was used for measuring Cd, whereas flame AAS was used for Cu, Pb and Zn.



## ii. Sea Water

Trace metals were analysed using Metrohm 401 Anodic Stripping Voltameter.. Calibration graph for each metal was prepared using 1000 ppm standard solution obtained from Fisher Scientific Inc.

### 4.3 RESULTS AND DISCUSSION

#### A. Petroleum Hydrocarbons:

Table 4.1 shows the concentration of petroleum hydrocarbons in sea water (ugl ) collected for the Marine Monitoring Programmes ..

**Table - 4.1**

Stations

Date	1	2	3	4
1-3-93	1.7	1.2	1.2	1.3
7-4-93	2.6	1.8	2.5	2.1.
4-5-93	3.1	3.9	1.6	3.1
5-6-93	3.5	1.4	2.5	2.6
7-7-93	1.9	2.1	1.1	1.4
7-8-93	1.2	0.9	0.7	1.7
6-9-93	3.4	3.9	1.4	2.6
6-10-93	5.0	4.2	2.3	4.0
1-11-93	2.5	3.1	5.0	3.6
6-12-93	6.3	3.7	3.9	3.3

Table 4.2 shows the concentrations of petroleum hydrocarbons in sediment (ugg) collected for the three cruises.

**Table - 4.2**

Station	Askar	Jaw
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1-3-93	266.0	NS
7-4-93	232.0	NS
4-5-93	172.0	NS
5-6-93	NS	19.0
7-7-93	242.4	111.3
7-8-93	41.0	222.9
6-9-93	158.5	NS
6-10-93	243.3	106.1
1-11-93	171.6	106.1
6-12-93	113.0	NS

The results were presented as ROPME crude oil equivalent.

The concentration of the dissolved petroleum hydrocarbons in sea water ranged from 0.7 to 6.3 ug/l for all the stations with an average of 2.63 ug/l.

Although Bahrain waters are frequently impacted with frequent oil spills the dissolved petroleum hydrocarbon levels are relatively low if compared with values reported elsewhere. For examples levels reported in the Mediterranean ranges from 1-123 ug /l, (Fowler, 1983).

For sediments, the values of petroleum hydrocarbons were not exceptionally high based on ROPME crude as a reference oil. Very wide ranges of concentration were observed, 19-266 ug/g with an average of 157.5 ug/g. .

Fowler, 1983 reported 43.20 ug/g at Askar (st.4) and 60.2 ug/g in 1984. The highest levels were always found in sediment at Askar.

Linden, O. et al reported a range of 6-3950 ug/g .

The possible reasons that sediments possess higher concentration than sea water is due to the ability of sediments to accumulate oil especially at the situation of chronic input into the area and that reflect the actual state of the this environment.

## **B. Trace Metals**

Table-1-10 shows the concentration (ug/g ) of trace metals in sediments and in sea water, (ug/l) .

The results did not show much variation between and within stations. The concentration of trace metals in the marine life is influenced by several mechanisms. The physical and chemical nature of the marine environment is

one of the important factor that determine the level of the elements. Sediment type is another factor. Trace metal distribution in surfacial sediment are affected by clay, organic matter and metal oxides as enrichment factor. The sediments grain size at the sampling stations range from coarse to medium sand.

However, in spite of the role of the sediment and the importance of their chemical characterisation in monitoring programme, the problem related to spatial and temporal variation caused by physical and biological reworking of the bottom deposits made it difficult to obtain representative data.

The ranges of trace metals in sediment and sea water are shown in Table - 4.5.

Table - 4.3

TM	Cd	Cu	Pb	Zn
Sediment (ugg )				
Range	<0.2	16.56-76.95	31.17-76.95	29.22-110.07
Average	0.1	35.9	55.59	51.00
Sea Water (ugl )				
Range	<0.2	0.1-17.6	5.3-32.0	0.1-57.20
Average	0.1	3.63	13.68	12.32

Linden et“ al, 1982 had reported the following ranges in sediments.

TM	Cd	Cu	Pb	Zn	V
ugg	0.09-0.22	1.3-53	1-627	1-51	0.1-5.3

Therefore the ranges of trace metals reported in this study are not significantly different from the values reported earlier.

## **5. CONCLUSIONS AND RECOMMENDATIONS**

Bahrain's marine environment can be described as a fairly productive environment that seems to get most of its primary productivity from benthic flora and fauna. The coastal marine environment exhibits number of diverse and different habitats, mainly sea grass beds, algal beds, rocky, sandy and muddy bottoms and the occassional coral reef. These in turn support a wide

variety of fish, crustaceans and bivalves that are commercially important to Bahrain. In addition there is a large population of seacows (*Dugong dugong*) as well as dolphin and sea turtle.

Due to the complicated situation related to the marine monitoring programme's design, it is rather difficult to draw a definite conclusion. The geographical location for the station was not fixed; the sediments differ in their grain size. Therefore these spatial and temporal variation make it difficult to have a trend for the pollution as well as to have a direct comparison. The observation suggests that these sort of incomparable levels of petroleum hydrocarbons and trace metals may be due to incident input of pollution; time; physical, chemical or biological processes or change in pollution budget. However the level of the pollution is not exceptionally high and they are within the range reported earlier by different workers.

The data presented within this report are in many ways too fragmented to be able to draw any conclusions about trends in the marine environment. We cannot possibly show any increase or decrease in pollution levels or population dynamics.

In order for this program to be completely effective it needs to continue.

A number of factors need to be evaluated before the program can continue:

1. The number of stations can be up to five  
Three on the east coast , One on the west coast (Zallaq)  
and One at Fasht Al Jarim .
2. Equipped boat should be available.
3. Qualified divers and biologists should be onboard while sampling.

## **REFERENCES**

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