DISTRIBUTION OF SOME SELECTED TOXIC METALS IN THE COCHIN HARBOUR REGION

THESIS SUBMITTED TO
THE COCHIN UNIVERSITY OF SCIENCE & TECHNOLOGY
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

ENVIRONMENTAL STUDIES

By

P. P. OUSEPH

CHEMICAL DIVISION
CENTRE FOR EARTH SCIENCE STUDIES
TRIVANDRUM - 695 031

DECEMBER, 1992

CERTIFICATE

This is to certify that this thesis is an authentic record of research work carried out by Sri P.P. Ouseph, M.Sc. under my supervision and guidance in the Centre for Earth Science Studies for the Ph.D. degree under the faculty of Environmental Studies of the Cochin University of Science and Technology and no part of it has previously formed the basis for the award of any other degree, diploma or associateship in any university.

(PROF.K.P. BALAKRISHNAN)
Supervising Guide,
Former Professor & Head,
School of Environmental Studies,
Cochin University of Science & Technology.

CONTENTS

PREFACE

Estuaries are the interface between fresh water and salt water systems, the biological productivity of which are normally very high consequently the population density is also very high resulting many biotic and abiotic problems including pollution aspects. With the increasing concern over the environmental consequences of waste discharges into the aquatic environment it has become necessary if not mandatory to determine the toxic load reaching the aquatic system all over the world. The present study is an attempt to identify and estimate metal pollutants in the sediments and over lying water column in the Cochin harbour area.

The first chapter introduces a comprehensive account on the historical background of the Cochin harbour, significance of metals in aquatic environment, review of pertinent literature and identification of the study area.

The second chapter describes the methodology in detail, and a review of the state of the art of extraction technique.

The third chapter contains the results on the concentration of the dissolved and particulate metals in the water column. Efforts have been made to understand the relation of these metals with salinity during estuarine mixing.

The fourth chapter describes the concentration of metals in sediments and core samples. The quantum of metals to which the biotic constituents are likely to interact have been estimated to assess their bioavailability and toxicity in the system.

The fifth chapter summarises the results and conclusions emanating from the study.

The papers published/presented in the relevant field in National and International journals/seminars have been appended.

LIST OF FIGURES

LIST OF TABLES

4.3. Concentration of metals in sediments in Cochin estuary and river Periyar April, 1986 (Pre-monsoon).

4.4. Size fraction and major element concentration in sediments in Cochin estuary and river Periyar July, 1985 (Monsoon).

4.5. Size fraction and major element concentration in sediments in Cochin estuary and river Periyar November, 1985 (Post-monsoon).

4.6. Size fraction and major element concentration in sediments in Cochin estuary and river Periyar April, 1986 (Pre-monsoon).

4.7. Distribution of metals in ppm (minimum and maximum) at surface and at 90 cm depth of a core sample from Cochin harbour area.

4.8. Correlation-regression relationship of metals with major elements and silt fraction in sediments in Cochin estuary, Nov. 1985.

4.9. Concentrations of metals in sediments (ppm) and organic carbon (in %) (minimum and maximum values during monsoon, post-monsoon 1985 and pre-monsoon 1986).

CHAPTER - 1

INTRODUCTION

1.1. History of Cochin Harbour in Brief

Cochin, 'the queen of the Arabian sea', has her majesty and tranquility being a protected natural harbour on the south-west cost of India. The study area lies between 9^{o} 49' and 10^{o} 14' north latitudes and 76^{o} 10' and 76^{o} 31' east longitudes (Fig. 1).

It is presumed that the Cochin inlet was formed somewhere in 1341 (Robert Bristow, 1959) and since then the capital of the ancient rulers was shifted from Muziris to Cochin. From the sixteenth century Cochin faced rapid changes through trading and colonizing attempts of European powers, the Portuguese, the Dutch and in 1875 the British.

The presence of 'mud banks' along the Kerala coast and the extensive backwater systems prompted charting of the Cochin port as early as 1836, followed by revisions in 1858, 1879 and 1882. Suitability of Cochin port as a stop over in the long ocean route to far east countries was recognized as an alternative to Bombay and in 1870 J.H. Aspinwall, a British merchant and the president of

the Cochin Chamber of Commerce, conceived the idea of developing a safe deep water harbour in the Cochin backwaters. In 1880, the Cochin Chamber of Commerce submitted a memorandum concerning the establishment of a new port at Cochin to the Duke Buckingham and further in 1900 to Lord Curzon, Viceroy and Governor General of India. Considering various aspects the Madras government in 1919 requested the British Government for the services of an Harbour Engineer to study the feasibility of establishing a new port at Cochin and Sir Robert Bristow was appointed for this purpose. He reached Madras on 4th April, 1920 and the Governor of Madras directed him to Cochin with the task of developing the Cochin Harbour. The sagacity and hard work of Sir Robert Bristow and his colleagues was monumental in declaring Cochin Harbour as an all time port by about 1940.

Kerala has a coast line of 560 km long, extending from Manjeswar in the north to Poovar in the south, having 14 km of coastal stretch against 100 sq.km of its area. Parallel to the coast, there is a chain of backwater lagoons, or estuarine systems, interconnected with natural or artificial canals. There are 41 west

flowing rivers, which reach Laccadive sea through estuaries or backwaters. Most of the rivers are fast flowing consequent on the prevailing terrain nature, discharging their contents including toxicants into the estuary/backwater/coastal zone at a faster rate than in many other river systems. Since rivers, backwaters and sea are inter-connected, there is a fair amount of mixing and flow of energy from one system to the other.

1.2. Industrial Pollution and Importance of Metal Studies.

There are over 200 medium and large scale industries and about 2000 small scale industries, handling diverse organic and inorganic formulations, discharging their effluents either directly or indirectly into the water bodies besides municipal wastes. Apart from this, indiscriminate use of fertilizers insecticides/fungicides and other consumables causes considerable damage to the water quality of both riverine and marine systems posing a serious threat to biotic community including man.

It is known for the past several years that some of the rivers of Kerala, viz. Chaliyar, Periyar,

Chitrapuzha, Kallada etc. are polluted. It has been recognised that a greater potential hazard exists in estuarine and near shore areas because of their proximity to sites of industrial and domestic activity, resulting in high concentration of specific pollutants. In recent years, several man-made changes in the Cochin backwater have introduced marked changes in its ecology.

Cochin has been identified as the industrial capital of Kerala and a lion share of chemical industries are situated on the banks of river Periyar. The effluents are mainly generated from chemical and engineering industries, food and drug manufacturing as well as from paper, rayon, rubber, textiles and plywood industries. Tables 1.1 and 1.2 provide the quantity and nature of effluents discharged into the river Periyar.

The route of entry of metals to man may be direct, by way of drinking water, or indirect often involving food chain. Out-breaks of mercury and cadmium poisoning in Japan (Nitta, 1972) triggered serious concern among scientists about heavy metal pollution.

It is estimated that more than 90% of the elemental mercury is transformed to highly toxic methyl mercury by marine organisms. The instances of mercury pollution known as "Minamatta disease" caused by the consumption of mercury contaminated fin and shell fish meat from the Minamatta Bay, maimed and multilated the life of many people. The cadmium poisoning causing the "ita ita" disease has affected the residents of Jintsu river area in Japan. Estuaries are one of the most productive and biologically active areas in the aquatic system where many of the fin and shell fishes get congenial environment for their breeding and early growth. Nonbiodegradable heavy metals tend to accumulate in the aquatic community through a food chain and ultimately reach men. A knowledge on the metal concentrations in this estuarine environment is, therefore, of extreme importance in order to understand the bioavailability and the extent of toxicity and provide data for the planners and decision makers.

1.3. Previous Studies in and around the Cochin Harbour

The ever increasing loads of industrial waste and sewage in the Cochin estuary have created conditions which are extremely destructive to plants and animals

(Qasim and Madhupratap, 1981). Benthos of the backwaters have been studied by Kurian (1972) and by Ansari (1977). The studies, indicate that the density of bivalves, gastropods and isopods in the backwaters have been considerably reduced with time. These have been attributed to the increasing pollution (Qasim and Madhupratap, 1981). Study by Remani (1979) indicates that in some of the polluted areas, the BOD values reach 513.76 mg/litre, sulphide 4.97 mg/litre and oxygen content less than 0.05 ml/litre. The effects of industrial pollution are seen in the form of depletion of biota, especially, benthic organisms, fish mortality and presence of high concentrations of ammonia in water. Hydrobiological conditions of Cochin estuary are greatly influenced by sea water intrusion and influx of river water as shown by the distribution of salinity and temperature (Lakshman et al., 1982). It has been shown that the organic carbon in the sediments is higher during monsoon due to the contribution from land run off (Remani et al., 1980). The study with reference to the indicator bacteria reveals that the principal source of fecal pollution is non-human type, originating from land drainage, sewage and organic discharge (Gore

et al., 1979). The higher C.O.D. values observed are probably due to domestic sewage and the wastes discharged into the harbour area (Sarala Devi et al., 1979). Studies have further shown that there is appreciable degree of organic pollution in the Harbour area (Unnithan et al., 1975; Vijayan et al., 1976).

The hydrographical conditions, especially, salinity undergo wide fluctuations in the Cochin Harbour area with season. During the south-west monsoon period (June - September) it is fresh water dominated and therefore, the salinity is very low, whereas during pre-monsoon period just the reverse happens as a result of evaporation and decreased freshwater in flow. The overall change in salinity at the harbour region is in the range of 34.31 ppt in April, to 1.11 ppt in July (Vijayan et al., 1976). The change in salinity has been found to have a profound effect on the sequences of fluctuation in the abundance and ecological succession of the fauna and flora in the estuary (Madhupratap et al., 1977).

Seasonal changes in the surface temperature are well marked in the harbour area. The temperature shows

seasonal change from 4° to 5.4°C in the surface water and from 3.7° to 5.7°C in the bottom. The lowest value recorded was 25.8°C and the highest 32.6°C in the surface water whereas, the bottom water recorded 25.2°C and 32.0°C as the lowest and highest temperatures, respectively (Vijayan et al., 1976).

Significant seasonal fluctuations in the values of dissolved oxygen both at surface and bottom are seen in the estuary with the lowest oxygen content usually found during pre-monsoon periods. It is seen that the oxygen content is always low at the bottom, which is attributed to the oxygen consumption during decomposition of organic matter in the deeper strata of the water body. The BOD is also increased gradually with the commencement of pre-monsoon and shows a decreasing trend with the onset of monsoon periods, but is always found lower at the harbour as compared with any other part of the estuary (Haridas et al., 1975).

The faunal and floral composition, their succession and pattern of distribution in the harbour area are essentially controlled by the hydrographic changes. The primary producers ie, the phytoplankton, in the region

show their maximum numbers in November and minimum in September with an average concentration varying from 22,200 to 2,99,700 cells/litre (Devassy and Bhattathiri, 1974).

The Chlorophyceae and Cyanophyceae are observed with a concentration ranging from 2 to 44% of the total phytoplankton population (Devassy and Bhattathiri, 1974).

Several phytoplankton blooms are observed in the Cochin Harbour area, which are directly correlated with the water characteristics, particularly the nutrients and salinity (Qasim, 1980).

Zooplankton population in the Cochin Harbour fluctuates with seasons and they can be correlated with the hydrographical conditions as well as the phytoplankton concentration. Zooplanktons are recorded in advance during the low saline pre-monsoon period and are very poor during the low saline period, from May to November. The average zooplankton production is estimated as 31.8 mg dry wt. per cubic meter per day (11.6 g/m^3/year) (Madhupratap et al., 1975) Organic

detritus derived from the various sources such as land drainage, wastes dumping, fecal pellets of the inhabitants and the decay of large quantities of the weed Salvinia auriculata brought during monsoons, also plays an important role in the secondary production of the estuary (Gopalan and Sreekumaran Nair, 1975).

Hydromedusae are abundant in the pre-monsoon period, disappear when the salinity becomes low during monsoon, except for an influx, presumably, from outside the mouth, in June. Four common species occurring in abundance are Phialidium brunescens, Eutima commensalis, Eirene ceylonersis and Blackfordia virginica. Several studies so far made indicate that all the endemic species that are metagenetical ie. that have a benthic stage of hydroid in their life cycle probably survive the adverse low salinity period by developing endurance stages. Stolonar resistance 'capsules' are known for a few species (Santhakumari and Vannucci, 1977).

Pleurobrachia sp. is the dominant form of the Ctenophora group and their distribution is more or less similar to that of hydromedusae. The dominant Chaetognath species found in the harbour is Sagitta

bedoti. The other species include Sagitta robusta, and Sagitta oceanica, which is an oceanic form. The Sagitta enflata is seen during pre-monsoon season. During the monsoon period, chaetognaths are totally absent from the area (Vijayalakshmi Nair, 1975).

Copepods are the most cosmopolitan group in the harbour and are present in all seasons. High numbers are recorded during the high saline period, which decline with the onset of monsoon, begin to increase again during post-monsoon periods. The family Acartidae constitutes majority of the copepods in the area and include species such as Acartia centrura and Acartia bilobata present during pre-monsoon period. The Acrocalanus similis, Paracalanus aculeatus, Centropages alcoki and Centropages trispinosus are present during January and February. Pseudodiaptomus erricandatus is observed during the peak salinity month of April. (Gopalan and Sreekumaran Nair, 1975).

Amphipods are present in small numbers in all seasons in the harbour area; it higher abundance being noticed during pre-monsoon period. The Cladocera group is also present during monsoon and post-monsoon periods.

The prominent members of the group are Evadna tergestina and Penilia avirostris.

Several species of food fishes like Arius, Scatophagus, Apogon, Hemiramphus and Mullets are often found along with many other benthic forms like the flat fish Cynoglossus sp. (Ansari , 1977).

Study of particulate matter of water from Cochin backwater for trace metals indicates high concentrations of Zn, Cr. attributed to industrial pollution (Sankaranarayanan and Rosamma Stephen, 1978). High concentration of Zn. Cu, Fe, Mn, Sn and Hg has been observed in the oyster - Crassostrea madrasensis (Preston) of the Cochin Harbour. High metal load in tissues is observed during the breeding period and also when the estuary maintains high salinities during October to April. The suitability of the oyster as an indicator organism for metal pollution in Cochin backwater has been discussed by Rajendran and Kurian (1986). Some of the benthic organisms, such as mussels and oysters, have accumulation of zinc higher than the permissible limit (Remani, 1979). The concentrations of dissolved particulate and sedimentary metals are well

documented (Venugopal, 1982; Ouseph, 1986, 1987, 1989, and 1992). Mass mortality of fish and cattle have been reported from Chitrapuzha area (Silas and Pillai, 1976).

1.4. Details of Station Location

The sampling has been made from 18 stations in the Cochin Harbour, the stations 19 to 23 from the effluent discharge point, stations 24 to 27 from the upstream of the effluent discharge point (Fig.1.2). Investigations were carried out in July (monsoon) and November (post-monsoon) 1985 and March (pre-monsoon) 1986. An attempt has been made to study the semi diurnal variations of abiotic factors in Cochin Harbour area during the maximum storm water flushing period - 31st July, 1987 (Fig. 1.3).

Table-1.1. Quantity of wastes and nature of pollutants discharged into the river Periyar (Joysingh, 1979)

Factories discharging wastes	Quantity of wastes lakh litres per day	Pollutants
M/S. Travancore Rayons, India Aluminium Co., F.A.C.T., T.C.C., Hindustan Insecticides, Indian Rare Earths, Periyar Chemicals, T.C.M. Co. Ltd.	1722.00	Suspended solids, Mercury, Zinc, Copper, Cadmium, Lead, Hexa-valent Chromium, Radioactive material, etc.

Table-1.2. Quantity of waste and nature of pollutants discharged into the river Periyar.

Company	Volume KL/day	Type of pollutants
Hindustan Insecticides Ltd., Elur, Alwaye.	100	Phenolic, compounds, insecticides etc.
Periyar Chemicals, Elur, Alwaye.	3.3	Sulphate, chloride, etc.
Travancore Cochin Chemicals Ltd., Elur, Alwaye.	980	Mercury, Sulphate, chloride, etc.
Indian Rare Earth Ltd., Elur, Alwaye.	3000	Lead, zinc, fluoride, etc.
Indian Aluminium Co. Ltd., Elur, Alwaye.	3662	Fluoride, oil, grease, etc.
Travancore Chemical Manufacturing Co. Ltd., Elur, Alwaye.	900	Copper, chloride, zinc, etc.
FACT, Elur, Alwaye	88	Chloride, sulphate, fluoride, ammonia, etc.
Kerala Acids & Chemicals Ltd., Alwaye.	87	Oil & grease, phosphate, etc.

MAJOR INDUSTRIES CAUSING AQUATIC POLLUTION IN KERALA

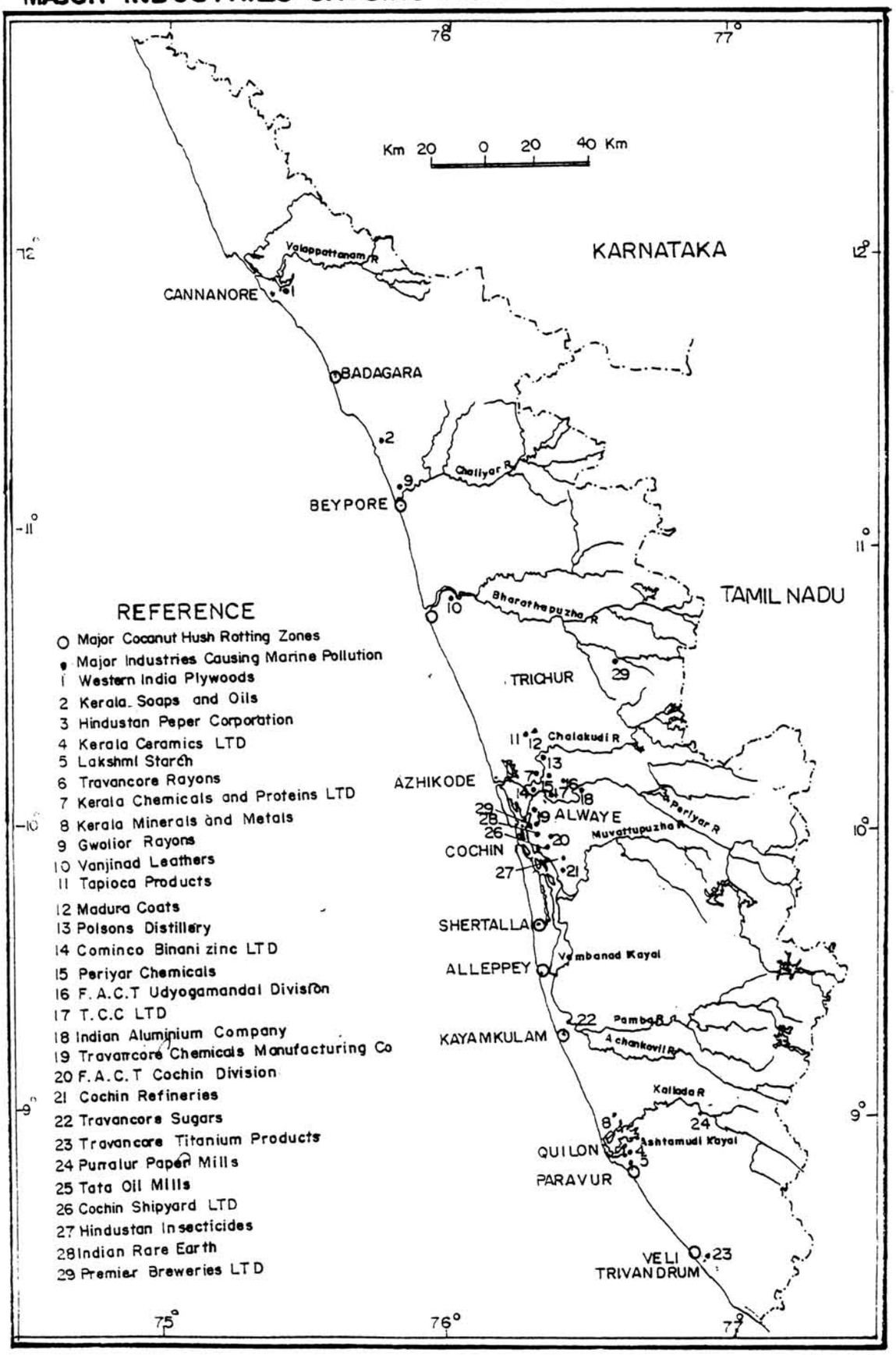
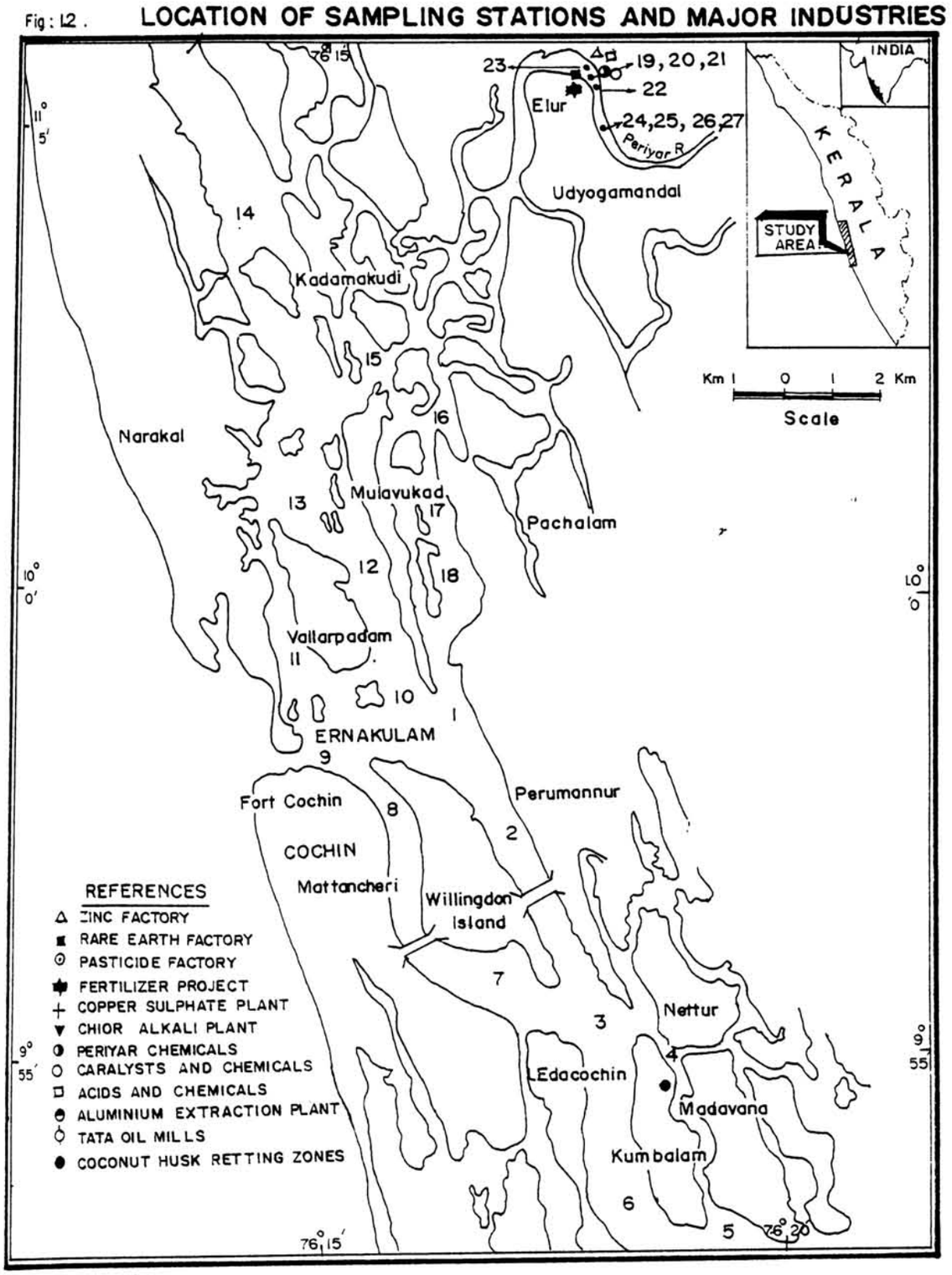


Fig: 1.1

Fig : 12 . **LOCATION OF SAMPLING STATIONS AND MAJOR INDUSTRIES**



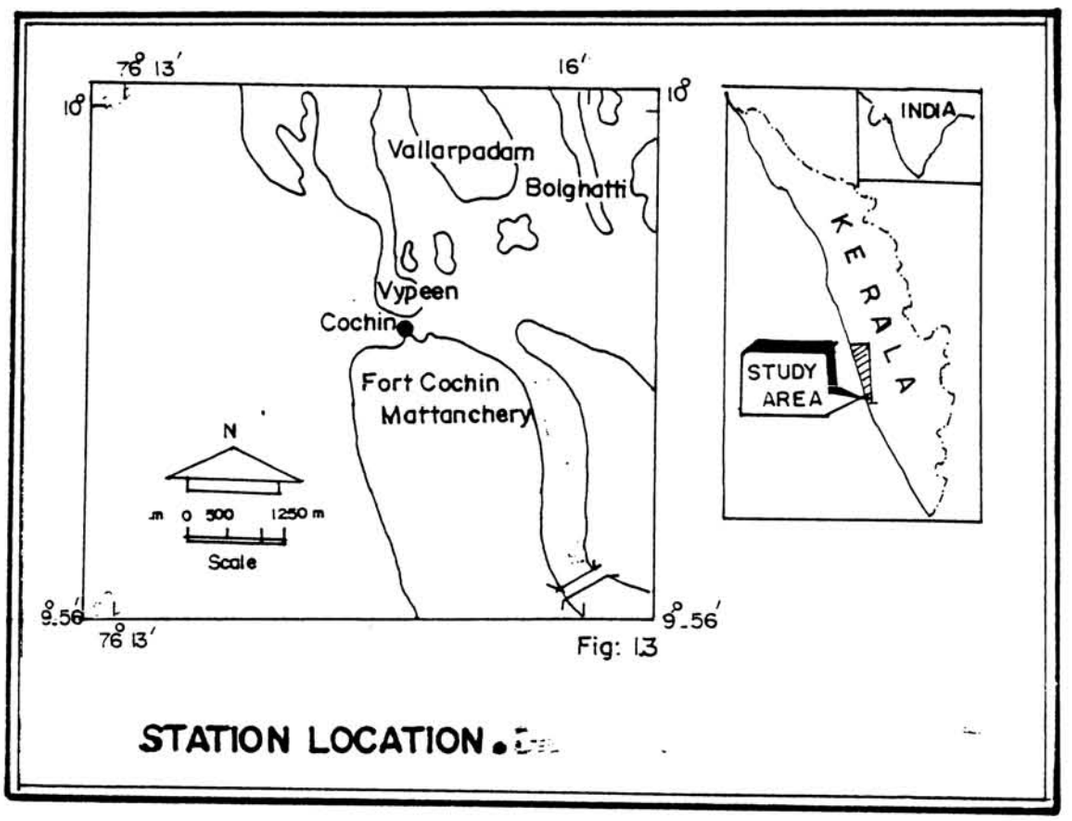


Fig: 13

STATION LOCATION •

CHAPTER - 2

MATERIALS AND METHODS

2.1. Sample Collection

Water samples from surface and bottom were collected from all the stations 1 - 18 located in the Cochin Harbour area. Surface samples were collected using a clean plastic bucket and bottom samples by a Van Dorn sampler, during monsoon, post-monsoon (1985) and pre-monsoon (1986) seasons. Since stations 19 - 27 were shallow regions only surface samples were preferred. Sediment samples were taken from all stations using a Van Veen Grab and core samples with a gravity corer. The stations 1, 2, 8 and 9 located in the channel were disturbed areas due to the periodical dredging activities for navigational purposes. The core samples taken from such stations were disturbed. An intact core sample was collected at station 13 during post-monsoon season. To avoid contamination PVC core liners were used in all cases. After collection the PVC liners containing the core samples were capped at both ends to minimise disturbance and compaction. The core samples were brought to the laboratory in vertical position and cut into 10 cm columns. Surface and bottom

samples were collected over a tidal cycle during the maximum storm water flushing period from a point in the Cochin Harbour (July, 1987). All wares wherever possible were cleaned by soaking in 6N Hcl and subsequently washed in double distilled water. The chemicals used were of a high purity Excellar and GR grade only.

2.2. Analytical techniques - Brief review

Standard extraction techniques were employed for the estimation of dissolved metals from sea water. The reported procedures for the extraction of trace elements in water involves either by a simple extraction at $p^H 4$ (Sengupta et al., 1978) or by two extractions at $p^H 3$-4, and other at p^H 5-6 with different complexing agents (Sujatha and Moraces, 1979). Other extraction procedures employed consisted of Ammonium Pyrollidine, Dithiocarbomate (APDC), chloroform by Spencer and Bewer (1969) by Preston et al. (1972) for Cu, Fe, Zn, Co, Ni for Cu, Zn, Ni, by Bewers et al. (1974) for Pb, Cu, Zn, Cd, Ni, Co, Fe, by Scmidt (1976) for Pb, Cu, Cd, Fe, by Duinker and Kramir, (1977) for Pb, Cu, Zn, Cd, by Kremling and Peterson (1977) for Cu, Zn, Cd, Fe, by Duinker and Nolting (1977) for Cu, Zn,

Cd, from sea water. Sujatha and Moraces, 1979 extracted Fe, Cu, Zn, Co, Ni, Mn using APDC/Methyl Isobutyl Ketone,(MIBK), Diethyl Dithio Carbomate (DDC)/MIBK. Brulant and Franks 1970 estimated Cu, Cd, Zn, Ni by APDC/DDC chloroform extraction and back extraction with nitric acid, Armansson, 1979 used dithizone chloroform in two different basic p^H conditions for the estimation of Zn, Cd, Pb, Ni, Co, Ag and Grassoff et al., 1983 used APDC/DDC and extracted by Freon for the determination of Cd, Cu, Fe, Ni, Co, from sea water.

The organic extracts when directly fed into the AAS for the estimation of elemental concentrations, due tothe volatile nature of the organic extracts, it may evaporate and cause error in the estimation and also produce smell in AAS room. In order to avoid such difficulties the complexed metal ions were back extracted from the organic layer using Hcl or HNo_3 and the aqueous extracts thus obtained were used for the estimation of elements and discarded the organic layer. Very few reports are available regarding the quantum of metals available in the organic layer after back extraction. Armansson (1979) found that certain metals such as Cu, Ni, Co and Ag remained in the organic layer

after back extraction. In the present study, all suitable procedures were incorporated to estimate the dissolved metals in sea water, the details of which are appended elsewhere.

2.2.1. Estimation of Total Mercury in Sea Water

2.2.1.1. Principle: Preconcentration of mercury in sea water was done by complexing it with dithizone at low p^H. The complex was extracted with carbon tetrachloride and back extracted into 5 M hydrochloric acid. The acid extract was shaken with sodium nitrite to decompose the dithizone and reverted mercury to aqueous phase. Excess of nitrite was reduced with hydroxylamine hydrochloride. Inorganic mercury compounds in the final solution were reduced to elemental mercury with stannous chloride and estimated by cold vapour atomic absorption spectrophotometer (AAS) Perkin Elmer 4000.

2.2.1.2. Sampling and storage of samples: Immediately after collection, the samples were transferred to acid washed 2.5 litre glass bottles and acidified to a p^H below 2 by adding 9 N sulphuric acid (18 ml per litre of sample) which has been purified by extraction with a 0.05% solution of dithizone in carbon tetrachloride.

2.2.1.3. Reagents: Double distilled water (DDW) was used for all dilutions.

Dithizone solution (0.005%): Dithizone (25 mg) was dissolved in double-distilled carbon tetrachloride (CCl_4) (500 ml). The solution was stored in a dark glass bottle in a refrigerator.

Sodium nitrite solution (10%): Dissolved Na NO_2. A.R. (10 g) in water (100 ml).

Hydroxylamine hydrochloride solution (20): Dissolved hydroxylamine hydrochloride (20 g) in water (100 ml).

Hydrochloric acid (5 M): The concentrated hydrochloric acid (208 ml) was diluted with distilled water (500 ml). Usually, hydrochloric acid contains traces of mercury. It was therefore, tested for mercury content prior to use. For this purpose prepared 1 N Hcl by diluting concentrated Hcl (8.3 ml) to 100 ml with water. Added stannous chloride solution and determined its mercury content by cold vapour atomic absorption spectrophotometry.

Stannous chloride reagent (30%) : Dissolved Sn Cl_2 $2H_2O$ (15 g) in 30 ml of 5 N hydrochloric acid and

diluted to 50 ml with water. A piece of tin metal was added to this reagent.

Mercury standard stock solution: Dissolved mercuric chloride ($HgCl_2$) A.R., (0.1353 g) in water (25 ml) and diluted to 100 ml with water containing 0.5 ml of H_2SO_4. This solution contained 1000 µg Hg/ml.

Secondary standard solution: Diluted 1.0 ml of the standard stock solution to 100 ml with water containing 0.3 ml of H_2SO_4. This solution contained 10 µg Hg/ml.

2.2.1.4. Apparatus: Borosil glass wares like separating funnels, conical flasks (2 litre), graduated cylinders with stoppers, volumetric flasks, magnetic stirrer, Atomic absorption Spectrophotometer Perkin Elmer 4000.

2.2.1.5. Procedure: Calibration and determination of blank: Extracted ten aliquots (1 litre each) of sea water with dithizone solution (15 ml). Discarded the organic layer and extracted again with dithizone solution (10 ml). Discarded the organic layer again and retained the mercury-free sea water for blank determination and calibration.

For blank determination extracted two aliquots (1 litre each) of the mercury-free sea water twice with dithizone solution (15 ml and 10 ml, respectively) retaining the organic extracts in a 60 ml separating funnels. Treated the combined extract with 5 M hydrochloric acid (15 ml). Added sodium nitrite solution (0.5 ml) to each and shaken for 5 min to revert the Hg to aqueous phase. Separated the aqueous phase in another separating funnel. Washed the CCl_4 layer with distilled water (5 ml). Combined the aqueous phase and the washings in a 25 ml stoppered measuring cylinder. Added hydroxylamine hydrochloride (1 ml) to reduce the nitrite and made the volume upto 25 ml with water.

For calibration, prepared working standard solutions so as to contain 100 ng Hg/ml. Using the working standards spiked the mercury-free sea water with 50, 100, 150, and 200 ng of mercury. Carried out the extractions exactly as in the case of blanks and retained the final aqueous phases.

Within 30 minutes after the extraction taken aqueous phases of blanks and standards sequentially in

Dreshel bottle. Added freshly prepared stannous chloride solution (2 ml) and closed the bottle immediately. Switched on the aerator to sweep the vapours of elemental mercury into the quartz cell of the instrument. Noted the maximum absorbance of blanks (A_b) and standards (A_{st}) at 251 nm. Prepared a calibration curve by plotting the absorbance of standards against the concentration.

Found the slope and calibration factor (F) from:

$$\text{Slope} = \frac{\text{Absorbance}}{\text{Concentration}}$$

$$F = \frac{1}{\text{Slope}}$$

2.2.1.6. Sample analysis: Taken aliquote of a sample 800 ml in duplicate (pre-adjusted by acidifying to a p^H below 2) in a separating funnel. Extracted with dithizone and analysed as described above and noted the absorbance (A_s) on the atomic absorption spectrophotometer.

2.2.1.7. Calculations: Calculated mercury concentration in the sample from:

$$ng\ Hg/litre = F \times (A_s - A_b)$$

2.2.2. Estimation of dissolved mercury in sea water.

A duplicate set of sea water samples (2.2.1.5.) were filtered using a millipore filtration unit and suspended particulate matter was estimated. The filtrate was acidified to a p^H below 2 and processed similar to the estimation of total mercury (2.2.5.2.). The above values were computed to get the concentration of particulate mercury.

2.2.3. Estimation of Dissolved and Particulate Metals

2.2.3.1. Principle: Preconcentration of dissolved metals from sea water was achieved by chelating them with ammonium pyrolidine dithiocarbomate (APDC) at an optimum p^H followed by extraction of the metal chelates into a suitable organic solvent (methyl isobutyl ketone (MIBK). The organic extract was unstable which was, therefore, back extracted into inorganic form using a suitable concentrated acid nitric acid (A). The metals present in the organic layer after back extraction was also estimated by digesting with perchloric acid (B). The final extract (A+B) was diluted to a suitable volume of 8 ml and analysed by flame atomic absorption

spectrophotometry (AAS) Perkin Elmer 4000.

2.2.3.2. Sampling and storage of samples: Samples were collected in acid washed pre-cleaned polyethylene bottles using plastic gloves while handling the samples. Care was taken to minimise the exposure of samples to the atmosphere.

Extensive cleaning of polyethylene and glass wares were done prior to the collection. For this purpose, the bottles were immersed in concentrated nitric acid for a few days and then transferred to a trough filled with dilute nitric acid and allowed to remain there until the collection of samples. Bottles were washed thoroughly with double distilled water before collecting the sample.

For the analysis of trace metals in sea water, the samples were filtered using a millipore R filters with pore size of 0.45 micron size. Polyethylene bottles pre-cleaned with acid were used for the storage of samples. The bottles were rinsed with the sample prior to the sample storage. Samples were acidified with Supra-Pure grade nitric acid or hydrochloric acid (5ml of 1 M acid per litre of sample) and stored preferably

at constant low temperature to avoid evaporation.

2.2.3.3. Reagents: All dilutions in the preparation of reagents and standards were made using double distilled water(DDW).

Methyl isobutyl ketone (MIBK): Distilled MIBK solvent in an all glass still apparatus.

Ammonium pyrolidine dithiocarbomate (APDC) solution 2%): Dissolved APDC (Fluka cat. No. 09935) (5 gm) in water (500 ml).

The solution was made metal-free as follows: Transferred the filtrate through a separating funnel added MIBK (15 ml) shaken for 2 min and allowed it to stand. After 20 min collected the aqueous layer into a receiving flask and discarded the organic layer.

Hydrochloric acid (1 M): Added concentrated hydrochloric acid (8.3ml) to water and diluted to 100ml.

Concentrated nitric acid AR grade

Metal standard stock solutions: AR/GR chemicals were used for the preparation of standard stock solutions containing 1000 µg/ml of Cu, Zn, Cd, Pb, Ni, Cr and Fe.

2.2.3.4. Apparatus: Separating funnels, wooden or plexi glass stands volumetric flasks, beakers, funnels, polyethylene bottles (50 ml), Eppendorf^{R} pipettes, atomic absorption spectrophotometer (AAS Pekin Elmer 4000).

2.2.3.5. Procedure: Calibration and determination of blank: Prepared metal-free sea water as follows: Measured out eight aliquots (800 ml each) of sea water in pre-cleaned separating funnels. Adjusted the p^{H} of each solution to 4.0 by adding 1 M Hcl (2 ml). Added APDC solution (10 ml) and shaken. After 30 sec. added the MIBK solvent (15 ml) and shaken vigorously for 2 min discarded the MIBK layer and extracted again with APDC solution (5 ml) and MIBK solvent (10 ml). Discarded the MIBK layer and retained the metal free sea water for blank determination and calibration.

Diluted the metal standard stock solutions of metals (1 ml each) to 100 ml with water containing 1 ml of concentrated HNO_3. Diluted again 10 ml of this solution to 100 ml with water containing 0.6 ml of concentrated HNO_3. Again diluted 10 ml of this solution

to 100 ml containing 0.5 ml of concentrated nitric acid. This working standard solutions contained 0.1 µg metal per ml.

Measured out eight aliquots of metal-free sea water (800 ml each) in pre-cleaned separating funnels. Spiked them (in duplicate) with different concentrations of working standard. Added to each funnel APDC solution (10 ml). Shaken the funnels for 3 minutes. Added MIBK solvent (15 ml) to each funnel and shaken vigorously for 2 min. Allowed the solutions to stand for 20 min for phases to separate. Collected the aqueous layer in a clean polyethylene bottle of 1000 ml capacity. Taken the MIBK extract in a smaller separating funnel of 60 ml capacity. Extracted the aqueous layer once again with APDC (5 ml) and MIBK solvent (10 ml). Discarded the aqueous layer and added the MIBK extract into the separating funnel containing the first extract. Washed the combined extract with DDW and discarded the aqueous layer, carefully.

For back extraction added concentrated nitric acid (0.2 ml) into the combined MIBK extract and shaken vigorously. Allowed to stand for 20 min. Added water

(19.8 ml) with the help of an Eppendorf^{R} pipette/ shaken and allowed the phases to separate. Collected the aqueous layer and stored it in 50 ml polyethylene bottle (A). The organic layer after back extraction was treated with perchloric acid 1.0 ml and evaporated to dryness and redissolved in 0.1 N Hcl (B). Both extracts (A+B) were taken in a beaker and evaporated to dryness and made upto a volume of 8 ml using 0.1 N Hcl.

Measured the absorbance of the aqueous solutions of blanks and standards on flame atomic absorption spectrophotometer at wave length 324.8 nm for Cu, 213.9 nm for Zn, 228.9 nm for Cd, 283.3 nm for Pb, 232.0 nm for Ni, 357.9 nm for Cr and 248.3 nm for Fe.

Prepared calibration curves for Cu, Zn, Cd, Pb, Ni, Cr and Fe by plotting respective absorbance against the concentration. Found out the slope and factor (F) from:

$$\text{Slope} = \frac{\text{Absorbance}}{\text{Concentration}}$$

$$F = \frac{1}{\text{Slope}}$$

2.2.3.6. Sample analysis: The samples were filtered

using a millipore filtration unit and the particulate matter is estimated and the filter paper was transferred into a 25 ml beaker added 1 ml perchloric acid when digestion was completed and treated with two aliquote of concentrated nitric acid (2 ml each at a time). When all nitric acid was expelled, added a drop of concentrated Hcl and evaporated. The residue was redissolved in 0.1 N Hcl heated to boil and the volume was made upto 10 ml with DDW. The metals were estimated by AAS techniques.

Measured out duplicate aliquots of filtered sample (800 ml) (previously adjusted the p^H to 4.0 with 1 M Hcl) in separating funnels and followed the extraction procedure as mentioned above for blanks and standards. Measured the absorbance of the final aqueous solution (As) on atomic absorption spectrophotometer.

2.2.3.7. Calculations: Calculated the concentration of metal from:

µg metal (Cu, Zn, Cd, Pb, Ni, Cr and Fe)/L.

= F x As x 1.25.

A duplicate filtration of the water samples was undertaken and the particulate matter was digested

with 0.1 Hcl for the estimation of leachable metals (Duinker et al. 1974).

2.2.4. Estimation of Salinity by Argentometric Titration Method.

2.2.4.1. **Definition:** Salinity is defined as 'the amount of dissolved inorganic matter contained in 1 kg of sea water after all bromides and iodides were replaced by an equivalent amount of chloride and all carbonates were replaced by an equivalent amount of oxides'. The relationship between salinity and chlorinity was given as:

S (Salinity) = 1.80655 x Cl (Chlorinity)

2.2.4.2. **Principle:** The halogen ions of chloride, bromide and iodide form a precipitate with a low solubility product with silver nitrate.

2.2.4.3. **Reagents:** Standard Sea Water (SSW): SSW prepared by Institute of Oceanographic Sciences, U.K and supplied in sealed glass ampoules was used for standardizing silver nitrate solution.

Silver nitrate solution: Ag No_3, A.R. (60.0 g)

was dissolved in 1 litre of distilled water and stored in a glass bottle painted black on the outside.

Potassium chromate indicator sol: K_2CrO_4, AR (8.0 g) was dissolved in 100 ml of distilled water and stored in stoppered glass bottle.

2.2.4.4. Apparatus: Burette with a measuring accuracy of 0.05 ml, Knudsen pipette or 10 ml bulb pipette, conical flask (150 ml) and magnetic stirrer.

2.2.4.5. Procedure:

Standardisation of Ag NO_3 solution: Pipetted out the SSW (10.0 ml) into a conical flask. Added distilled water (about 25 ml) and indicator (6 drops). Added Ag NO_3 solution from burette while stirring the titrant vigorously on the magnetic stirrer. Continued the titration till first sign of constant colour change was observed. Rinsed the inner walls of conical flask with distilled water and continued the titration adding the titrant drop wise till the colour changes from yellow to dirty orange. Recorded the burette reading (C ml). Repeated the standardisation at least thrice and obtained the mean burette reading (Cm ml). Found the standardisation factor (F) as follows:

$$F = N/Cm$$

where N was the nominal chlorinity of SSW marked on the ampoule.

2.2.4.6. Analysis of samples: Pipetted out the sample (10.0 ml) into a conical flask. Added distilled water (about 25 ml) and indicator (6 drops). Titrated against $AgNO_3$ in the same manner as described above. Recorded the mean reading (Vc) of three titrations from the above salinity of the sample was calculated S = 1.80655 x chlorinity.

2.2.5. Estimation of total alkalinity

2.2.5.1. Outline of the method: The sample was titrated against standard acid using methyl orange indicator.

2.2.5.2. Reagents: Standard Hydrochloric acid - 0.02 N Methyl orange indicator - dissolved 0.1 gm of methyl orange in distilled water and diluted to one litre.

2.2.5.3. Procedure: Titrated over a white background 100 ml of sample contained in a 250 ml conical flask against standard hydrochloric acid using two or three drops of methyl orange indicator.

2.2.5.4. Calculation: Total alkalinity (as $CaCO_3$),

mg/litre = 10V where 0V where

V = Volume in ml of standard hydrochloric acid used in the titration.

2.2.6. Estimation of mercury in sediment

2.2.6.1. Outline of the method

Mercuric ions were reduced to ground state mercury atoms in acidic solution by a reducing agent such as sodium borohydride. The mercury atoms were then swept by an inert gas stream into a quartz absorption cell placed in optical path of an atomic absorption spectrophotometer adjusted for estimation of mercury.

2.2.6.2. Reagents: Acid mixture prepared just before use by carefully adding one volume of concentrated sulphuric acid to two volumes of concentrated nitric acid. Stored in a glass reagent bottle.

Hydroxylamine hydrochloride: Dissolved 12 g of hydroxylamine hydrochloride and diluted to 100 ml with DDW stored in a glass reagent bottle.

Potassium permanganate (5%): Dissolved 5 g of potassium permanganate (AR) in 100 ml of DDW and stored in a glass reagent bottle.

Sodium borohydride (0.3%): Dissolved 0.75 g of sodium borohydride in 250 ml of 0.5% sodium hydroxide. Transferred to the 'Reductant container' supplied with the instrument.

Hydrochloric acid (5 M): Carefully diluted 104 ml of concentrated acid to 250 ml with DDW. Transferred to an 'Acid container' supplied with the instrument.

Stock mercury solution: Dissolved 0.1354 g of mercuric chloride (AR) in 75 ml of DDW. Added 10 ml of concentrated nitric acid adjusted the volume to 100 ml. This solution contains 1 mg Hg/ml.

Working mercury solution: Pipetted out 0.1 ml of above stock solution into 100 ml volumetric flask containing 1.5 ml of concentrated nitric acid and diluted to the mark with DDW. This solution contains 0.1 µg Hg/ml.

2.2.6.3. Apparatus

1. Atomic absorption spectrophotometer with attachment of vapour generation accessories for mercury

determination.

2. Volumetric flasks (100 ml)

3. Reagent bottles (250 ml)

4. Conical funnels.

5. Water bath with temperature regulator, etc.

2.2.6.4. Procedure

Calibrations and blanks:

Pipetted 0, 0.5, 1.0, 1.5 and 2.0 ml of working standard into 250 ml clean reagent bottles in duplicate to obtain concentrations of 0, 0.05, 0.1, o.15 and 0.2 ug Hg. Cover the bottles with funnels. Added DDW so that the total volume in each bottle was 10 ml. Added 5 ml of Acid mixture and heated for 2 min in a water bath adjusted for 95^{o}C. Allowed the samples to cool and added 50 ml of DDW and 15 ml of potassium permanganate solution to each bottle and kept again in the water bath for 30 min. Cooled and added 6 ml of hydroxylamine hydrochloride solution to reduce excess permanganate. Added 50 ml DDW, mixed well and analysed for mercury by the cold vapour technique. Measured the absorbance of each standard and blanks. Plotted the standard curve and calculated the slope and the factor F (Hg).

2.2.6.5. Analysis of samples

Weighed 1.0 gm of the wet sediment in triplicate and placed at the bottom of 250 ml reagent bottles covered with funnels. Another three reagent bottles were kept for blanks. Added 5 ml of DDW and 5 ml of Acid mixture to each bottle. Heated for 2 min in a water bath at 95°C. Cooled, added 50 ml of DDW and 15 ml of potassium permanganate solution to each bottle. Mixed thoroughly and kept in the water bath for 30 min at 95°C. Cooled and added 6 ml of hydroxylamine hydrochloride to reduce excess permanganate. Analysed the samples as described above. Measured the absorbance of samples A(s) and blanks A(b).

2.2.6.6. Calculations

Calculated the mercury concentration in the sample by the relation

$$\text{Hg } \mu g/g = \frac{F(Hg) \times A\ (s) - A\ (b) \times F}{\text{wt of sample taken in g}}$$

where f(Hg) = Factor obtained from standard curve (µg/g).

A(s)= mean absorbance of sample

A(b)= mean absorbance of blank

F= correction factor for moisture

Moisture of sample was estimated and a correction factor F was incorporated in order to obtain the concentration on dry basis.

2.2.7. Estimation of Metals in Sediments

2.2.7.1. Outline of the method: Sediment was gently heated and digested with hydrofluoric acid in teflon beaker whereby silica volatalizes as silicon tetrafluoride. This was followed by treatment with nitric acid and perchloric acid to destroy the organic matter. The residue after evaporation of acids was dissolved in 0.1 M hydrochloric acid and metals were determined by atomic absorption spectrophotometry.

2.2.7.2. Reagents: Double distilled water was used for preparing reagents blanks and standards.

Hydrofluoric acid (AR)

Perchloric acid (AR)

Nitric acid (AR)

Hydrochloric acid (AR)

Acetone (AR)

Hydrochloric acid (0.1M): Diluted 8.3 ml concentrated hydrochloric acid to 1000 ml with DDW.

Cu, Zn, Cd, Pb and Cr stock solution 1000 ppm were

prepared from Ar/GR grade reagents.

2.2.7.3. Apparatus.

Atomic absorption spectrophotometer.

Teflon beakers (100 ml) and teflon rods.

Funnels (small)

Volumetric flasks (100 ml)

Agate mortar.

Aspirated the blanks DDW and the standards in the range 2 to 20 µg/ml and noted down the absorbance. Plotted the calibration graph and obtained the factor.

2.2.7.4. Preparation of sample for aspiration by Acid-digestion method:

- Dry sediment was powdered in a agate mortar and kept in a plastic bottle
- Accurately weighed about 0.5 g of powdered sediment in a teflon beaker containing little DDW (in triplicate).
- Similarly weighed about 0.5 g of standard rock in teflon beaker (in triplicate)
- Another three beakers were taken for blanks.
- Transferred all the nine beakers to the fuming chamber.
- Added concentrated acids (10 ml each) in all the beakers in the following order concentrated

hydrofluoric acid, perchloric acid, nitric acid and hydrochloric acid.

- Added the next acid only after allowing the contents to complete dryness by evaporating on a sand bath kept on a hot plate. The volume of acid addition, was kept constant in all the beakers (5 to 10 ml), except perchloric acid (2 ml).
- Finally added 0.1 M hydrochloric acid to dissolve the contents and transferred quantitatively to a volumetric flask (100 ml). Centrifuged the solution when not clear.
- Aspirated the clear solution in the flame and determined the absorption of the sample, standard rock and blanks, noted the absorbance A(s), A(st) & A(b), respectively.

2.2.7.5. Calculations

Plotted the calibration graph and calculated the factor F for respective metal

$$F = \frac{\text{Concentration of standard}}{\text{Absorption of standard}}$$

$$C\ (PPM) = \frac{F \times A\ (s) - A\ (b) \times \text{final volume made}}{\text{Weight of the sample taken}}$$

where A(s) = mean absorbance of sample.

A(b) = mean absorbance of blanks.

2.2.8. Estimation of total iron

Pipetted out 25 ml of the solution (2.2.7.4.) to a 250 ml beaker, diluted to 40 ml added 10 ml concentrated Hcl to oxidise all iron to Fe^{3+} state. Boiled the solution and added stannous chloride solution till it becomes colourless. The solution was then rapidly cooled to about $20^{\circ}C$ with protection from air. Added 10 ml saturated Mercuric chloride solution to remove the excess stannous chloride. The solution was allowed to stand for five minutes. Added 20 ml 1:1 H_2SO_4, 5 ml orthophosphoric acid and a few drops of Barium diphenylamine indicator. Titrated with standard 0.01 N potassium dichromate solution until the pure green colour changes to grey-green. Then added dichromate drop wise until the first tinge of blue-violet, which remains permanent on shaking, appears. The volume was noted.

Fe_2O_3 (Total) = vol. of $K_2 Cr_2O_7$ x Factor

F = 0.63764

2.2.9. Estimation of total aluminum

Pipetted out 25 ml solution (2.2.7.4) to a 250 ml beaker added a few drops of phenolphthalein indicator and added 20% NaoH till just alkaline added 5 ml more and boiled for a few minutes. Cooled and filtered the solution through a Whatman No.40 filter paper and washed the filtrate with hot water. collected the filtrate and washing in a 400 ml beaker.

Neutralised the filtrate by adding 1:1 Hcl till the solution becomes colourless. Added very dilute NaoH in drops to the solution to change it just alkaline. Added 15 ml Ammonium acetate and 10ml 0.1 M EDTA cover the beaker and boil in a low flame for 30 minutes. Cooled in ice and added 1 ml acetic acid and 2 drops of xylenol orange indicator and titrated with 0.1 M zn solution until the colour changes from Lemon-yellow to red colour.

$Al_2O_3\%$ = (B-V) x Factor

(B-V) = volume of EDTA consumed

F = 4.07852.

2.2.10. Estimation of organic carbon in marine muds

2.2.10.1. Principle: The principle of the method was that under suitable conditions organic carbon in muds can be oxidised with chromic acid and the excess of

chromic acid was back titrated with ferrous ammonium sulphate.

2.2.10.2. Reagents

Chromic acid: Dissolved 13 gm of chromium trioxide A.r. in a minimum amount of water. Added about 900 ml of concentrated sulphuric acid and diluted to 1 litre with concentrated H_2SO_4.

Ferrous ammonium sulphate (0.2N): Dissolved 39.3 gm of reagent grade salt in 400 ml of distilled water containing 10 ml of concentration H_2SO_4. Diluted to 500 ml with distilled water.

Ferrous Phenanthrolline indicator: Dissolved 0.337 gm of phenanthrolline mono hydrate in 25 ml of water.

2.2.10.3.Preparation of samples

In order to remove salts from marine muds it was carefully washed with distilled water on a sintered glass funnel (porosity 4) or on a Buchner funnel fitted with a fine texture, hardened filter paper. After drying at 105^{o}C the samples were ground to pass a 100 - mesh sieve.

2.2.10.4. Method: Weighed out 0.3 - 1.5 gm of the prepared sample into a boiling tube (15 x 2.5 cm). Added 10 ml of chromic acid from a wide tipped pipette. Gently shaken the tube and fitted it with a loosely fitting bulb stopper. Heated in a bath of boiling water for 15 min cooled and poured the contents of the tube into 200 ml of water. Added 1 drop of ferrous - phenanthrolline indicator and titrated with 0.2 N ferrous ammonium sulphate solution until a pink colour just persists. Carried out a blank determination in the same manner.

2.2.10.5.Calculation: 1 ml of 0.2N ferrous ammonium sulphate was taken as equivalent to 6.0 mg of carbon. If the blank titre = X and the sample titre = Y, then % of organic carbon in mud = $\frac{6 (X - Y) 100}{W}$

where W = weight of the sample.

2.2.11. Estimation of size fraction analysis: Immediately after collection a known weight of the wet sediment sample was sieved through a 230 mesh and the sand was collected and weighed on dry basis. A known weight of the wet sediment sample was dried and the moisture was calculated. The above values were computed

to get the percentage of sand and silt. The silt is defined as the fraction less than 0.0625 mm.

2.2.12. Enumeration of Tables and Figures, and Abbreviations:

2.2.12.1. Enumeration of Tables and Figures. Enumeration of Tables and Figures were numbered in accordance with the chapter numbers.

2.2.12.2. Abbreviations: ng = nanogram, ppm = parts per million, µg = micro gram, ppt = parts per thousand, T/Fe = Total iron, T/Al = Total Aluminium, T/Org.c = Total Organic Carbon.

CHAPTER - 3

RESULTS AND DISCUSSION - PART A

3.1. Metals Present in the Water Column

The geochemistry of metals in aquatic medium was dominated by complexation, particulate association, dissociation, precipitation and mobilization processes. Floculation, sorption, desorption and disintegration process control the interaction between suspended matter and the liquid phase. The effective management and control of discharge of contaminants to estuaries demands a proper understanding of dissolved and particulate phases of heavy metals and its seasonal variation. The fate of contaminants in water is related to the fate of suspended matter (Michaelis, 1989). This chapter reports the concentrations of metals in water both dissolved and associated with particulate during monsoon, post-monsoon 1985 and pre-monsoon 1986 seasons. The relation of metals with salinity, alkalinity and p^H were presented in Tables 3.1 - 3.19.

Five replicate determinations done for one sample from each set of samples collected seasonally, gave a coefficient of variation, for dissolved metals, 3.8 to

4.2% for mercury, 4.2 to 7.8% for copper, 6.4 to 8.2% for zinc, 5.2 to 6.8% for cadmium, 2.3 to 4.4% for lead, 6.4 to 9.3% for nickel and 3.1 to 5.2% for iron and for metals in sediments, 5.2 to 6.8% for mercury, 4.8 to 5.2% for copper, 6.5 to 6.7% for zinc, 7.5 to 7.7% for cadmium, 4.8 to 5.1% for lead and 3.5 to 3.8% for chromium.

3.1.1. Mercury

The seasonal distribution of dissolved mercury in the Cochin estuary ranged from 40 to 180 ng/L. during monsoon, 50 to 240 ng/L. during post-monsoon 1985 and 80 to 280 ng/L. during pre-monsoon 1986 seasons. The dissolved concentration of mercury in the Cochin estuary were 40 - 150 ng/L., 50 - 210 ng/L. during monsoon, post-monsoon season of 1985 and 60 - 260 ng/L. during pre-monsoon 1986 season at surface and the values were higher at bottom being 50 - 180 ng/L., 60 - 240 ng/L. and 80 - 280 ng/L. during the respective seasons (Tables 3.1 - 3.3, stations 1 - 18). The dissolved concentrations in the upstream zone was found to be 15 ng/L. during monsoon, post-monsoon 1985 and 25 ng/L. during pre-monsoon 1986 seasons. Hence, the observed concentrations were 2.6 - 6 times higher during monsoon,

3.3 - 14 times higher during post-monsoon 1985 and 2.4 - 10.4 times higher during pre-monsoon 1986 seasons, at surface and at bottom the values were 3.3 - 12.0 times higher during monsoon, 4 - 16 times higher during post-monsoon and 2.4 - 11 times higher during pre-monsoon seasons, in comparison with the upstream values.

The dissolved concentrations near the effluent discharge point showed high values ranging from 85 - 95 ng/L. 115 - 120 ng/L. during monsoon and post-monsoon 1985, and 120 - 135 ng/L. during pre-monsoon 1986 seasons (Tables 3.1 - 3.3, Stations 19 - 23). Hence, the observed concentrations were 5.6 - 6.3 times higher during monsoon 7.6 - 8 times higher during post-monsoon 1985 and 4.8 - 5.4 times higher during pre-monsoon 1986 seasons in comparison with upstream values.

The mercury concentrations in particulate matter in the Cochin estuary ranged from 2 - 8 ppm during monsoon and post-monsoon 1985 and 8 - 34 ppm during pre-monsoon 1986 at surface and the values at the bottom being 2 - 20 ppm and 8 - 36 ppm during the respective seasons (Tables 3.1 -3.3, Stations 1 - 18). The particulate

concentrations observed in the upstream zone were found to be 2 ppm during monsoon, 2.5 ppm during post-monsoon 1985 and pre-monsoon 1986 seasons. Hence, the reported concentrations were 1 - 4 times higher during monsoon and post-monsoon 1985 and 3.2 - 13.6 times higher during pre-monsoon 1986 at surface and at bottom the values were 1 - 10 times higher during monsoon, 0.8 - 8 times higher during post-monsoon 1985 and 13.2 - 14.4 times higher during pre-monsoon 1986 in comparison with the upstream levels. Surface particulate mercury values were higher at the effluent discharge point 24.5 ppm during monsoon, 32 ppm during post-monsoon 1985 and 36.8 ppm during pre-monsoon 1986 seasons (Tables 1.3 - 3.3, Stations 19 - 23). Hence, the reported concentrations were 12.25 times higher during monsoon 12.8 times higher during post-monsoon 1985 and 14.72 times higher during pre-monsoon 1986 seasons in comparison with the upstream levels.

3.1.2. Copper

The values for dissolved copper in the Cochin estuary range from 2.22 to 2.8 µg/L. during monsoon and 10.4 - 18.8 µg/L., during post-monsoon 1985 and 14.8 - 22.2 µg/L. during pre-monsoon 1986 seasons. Its

concentration in particulates ranged from 44 to 190 ppm during monsoon, 65 - 230 ppm during post-monsoon 1985 and 76 - 298 ppm during pre-monsoon 1986 seasons. The dissolved concentration of Copper in the Cochin estuary ranged from 2.20 to 2.80 µg/L., 10.6 - 18.8 µg/L. during monsoon, post-monsoon 1985 respectively and 15.8 - 22.2 µg/L. during pre-monsoon 1986 at surface and the values at bottom being 2.2 - 2.7 µg/L., 10.4 - 18.4 µg/L., 14.8 - 21.8 µg/L., during the respective seasons. (Tables 3.4 - 3.6, Stations 1 - 18). The dissolved concentrations of copper in the upstream zone were 0. 8 µg/L., 10 µg/L., and 8 µg/L., during monsoon, post-monsoon 1985 and pre-monsoon 1986 seasons, respectively (Tables 3.4 - 3.6, Stations 24 - 27). Hence, reported concentrations in the Cochin estuary were 2.75 -3.50 times higher during monsoon, 1.06 - 1.88 times higher during post-monsoon 1985 and 1.97 - 2.77 times higher during pre-monsoon 1986 at surface and at bottom the values were 2.70 - 3.48 times higher during monsoon, 1.04 - 1.84 times higher during post-monsoon 1985 and 1.85 - 2.27 times higher during pre-monsoon 1986 seasons in comparison with the upstream levels.

The particulate concentrations of copper in the

Cochin estuary were 44 - 111 ppm, 65 - 179 ppm during monsoon, post-monsoon 1985 respectively and 76 - 280 ppm during pre-monsoon 1986 seasons at surface and at bottom the values were 46 - 197 ppm, 65 - 230 ppm and 122 - 298 ppm during the respective seasons (Tables 3.4 - 3.6, Stations 1 - 18). The particulate concentrations in the upstream zone were 48 ppm, 85 ppm and 140 ppm during monsoon, post-monsoon 1985 and pre-monsoon 1986 seasons respectively. Hence, the reported particulate concentrations in the Cochin estuary were 1 - 23 times higher during monsoon, 0.76 - 2.70 times higher during post-monsoon 1985 and 0.87 - 2.17 times higher during pre-monsoon 1986 season at surface and at bottom the values were 0.95 - 4.1 times higher during monsoon, 0.76 - 2.7 times higher during post-monsoon 1985 and 0.87 - 2.1 times higher during pre-monsoon 1986 seasons in comparison with the upstream levels. The dissolved concentrations of copper at the effluent discharge point were almost constant during monsoon and post-monsoon 1985 in comparison with the upstream levels. The values of dissolved concentrations during pre-monsoon 1986 season at the effluent discharge point were 1.5 times higher in comparison with the upstream levels. The

particulate copper at the effluent discharge point was 6.6 times higher during monsoon, 4.4 times higher during post-monsoon 1985 and 2.8 times higher during pre-monsoon 1986 seasons in comparison with the upstream levels.

The concentrations of copper in the fine grade suspended particulate matter from the effluent discharge point showed 3 to 4 times increase compared with its concentration in particulates observed in the upstream zone. Percentage of trace metal in particulates leached by treatment with 0.1 N Hcl with respect to its total metal content was found to be 90 to 100% for the study area.

3.1.3. Zinc

The values for dissolved zinc in the Cochin estuary ranged from 105 to 155 µg/L. during monsoon, 145 to 216 µg/L. during post-monsoon 1985 and 195--395 µg/L. during pre-monsoon 1986 seasons (Tables 3.4 to 3.6, Stations 1 - 18). Its concentration in particulates ranged from 125 to 140 ppm during monsoon, 150-2200 ppm during post-monsoon 1985 and 318 - 3100 ppm during pre-monsoon 1986 seasons (Tables 3.7 to 3.9, Stations 1 - 18). The

dissolved concentrations of zinc in the Cochin estuary ranged from 105 -155 µg/L., 145 - 216 µg/L. during monsoon, post-monsoon 1985 seasons, respectively and 226 - 385 µg/L. during pre-monsoon 1986 season at surface and at bottom the values were 105 - 155 µg/L. 150 - 213 µg/L. and 195 - 348 µg/L. during the respective seasons (Tables 3.4 - 3.6 Stations 1 - 18). The dissolved concentrations in the upstream zone were 24 µg/L. during monsoon, 40 µg/L. during post-monsoon 1985 and 65 µg/L. during pre-monsoon 1986 seasons. Hence, the reported concentrations were 4.37 - 6.45 times higher during monsoon, 3.62 - 5.50 times higher during post-monsoon 1985 and 3.47 - 5.92 times higher during pre-monsoon 1986 seasons at surface and at bottom the values were 4.37 - 6.45 times higher during monsoon, 3.75 - 5.32 times higher during post-monsoon 1985 and 3.0 - 5.35 times higher during pre-monsoon 1986 seasons in comparison with the upstream levels.

The particulate zinc concentrations in the Cochin estuary ranged from 125 - 410 ppm during monsoon, 170 - 1750 ppm during post-monsoon 1985 and 318 - 3100 ppm during pre-monsoon 1986 seasons at surface and at bottom the values were 142 - 1040 ppm, 150 - 2200 ppm, 790 -

3100 ppm during the respective seasons. The particulate zinc concentrations in the upstream zone were 48 ppm, 240 ppm and 450 ppm during monsoon, post-monsoon 1985 and pre-monsoon 1986 seasons, respectively. Hence, the reported concentrations were 2.6 - 8.5 times higher during monsoon, .70 - 7.29 times higher during post-monsoon 1985 and 0.70 - 6.80 times higher during pre-monsoon 1986 seasons at surface and at bottom 2.90 - 21.6 times higher during monsoon, 0.62 - 9.10 times higher during post-monsoon 1985 and 1.75 - 6.8 times higher during pre-monsoon 1986 seasons in comparison with the upstream levels.

The zinc concentrations in the fine grade suspended particulate matter near the industrial area was 1350 to 3800 ppm which was approximately 8 times higher when compared with the values observed in the upstream zone. The percentage of particulate metals leached by 0.1 N Hcl with total indicated that higher quantum was extracted in the Cochin estuary when compared with the upstream zone.

3.1.4. Cadmium

The dissolved concentration of cadmium in the

Cochin estuary ranged from 1.8 to 2.11 µg/L. during monsoon, 2.2 to 3.4 µg/L. during post-monsoon 1985 and 2.8 to 4.2 µg/L. during pre-monsoon 1986 seasons (Tables 3.4 - 3.6, Stations 1 - 18). Its concentration in particulates ranged from 58 to 91 ppm during monsoon, 50 to 150 ppm during post-monsoon 1985 and 65 to 180 ppm during pre-monsoon 1986 seasons (Tables 3.7 to 3.9, Stations 1 - 18). The dissolved concentrations of cadmium in the Cochin estuary ranged from 1.8 - 2.1 µg/L. during monsoon, 2.42 - 3.4 µg/L. during post-monsoon 1985 seasons and 3.12 - 4.20 µg/L. during pre-monsoon 1986 seasons at surface and at bottom the values were 1.8 - 2.1 µg/L. during monsoon, 2.20 - 3.23 µg/L. during post-monsoon 1985 and 3.12 - 4.20 µg/L. during pre-monsoon 1986 seasons. The dissolved concentrations in the upstream zone were constant (0.2 µg/L.) during the all the three seasons. Hence, the reported concentrations were 9 - 10.5 times higher during monsoon, 12.1 - 17.10 times higher during post-monsoon 1985 and 15.5 - 21.0 times higher during pre-monsoon 1986 seasons at surface and at bottom the values were 9.0 - 10.5 times higher during monsoon, 11 - 16 times higher during post-monsoon 1985 and 15.5 - 21.0

times higher during pre-monsoon 1986 seasons in comparison with the upstream levels.

The particulate cadmium concentrations were 58 - 70 ppm during monsoon, 50 - 150 ppm during post-monsoon 1985 and 65 - 160 ppm during pre-monsoon 1986 seasons at surface and at bottom the values were 60 - 90 ppm during monsoon, 55 - 150 during post-monsoon 1985 and 85 - 180 ppm during pre-monsoon 1986 seasons. The particulate concentrations in the upstream zone was 2.8 ppm during monsoon, 3.4 ppm during post-monsoon 1985 and 6.2 ppm during pre-monsoon 1986 seasons. Hence, the reported concentrations were 20.7 - 25.0 times higher during monsoon, 14.7 - 44.10 times higher during post-monsoon 1985 and 10.48 - 25.80 times higher during pre-monsoon 1986 seasons at surface and at bottom the values were 21.4 - 32.5 times higher during monsoon, 16.10 - 44.1 times higher during post-monsoon 1985 and 13.7 - 29.03 times higher during pre-monsoon 1986 seasons in comparison with upstream values.

The concentration of cadmium in the fine grade suspended particulate matter from the industrial zone was 6 to 12 ppm for all the seasons. The concentrations

of dissolved and particulate cadmium in the Cochin estuary was approximately 20 - 44 times higher in comparison with the values observed in the upstream zone.

3.1.5. Lead

The dissolved concentrations of lead in the Cochin estuary ranged from 8.8 to 10.6 µg/L. during monsoon 8.0 to 14.- µg/L. during post-monsoon 1985 and 10.0 to 14.0 µg/L. during pre-monsoon 1986 seasons (Tables 3.7 - 3.9, Stations 1 - 18). The dissolved concentrations of lead in the Cochin estuary ranged from 9.7 - 10.6 µg/L. during monsoon, 8 - 14 µg/L. during post-monsoon 1985, 10.1 - 14 µg/L. during pre-monsoon 1986 seasons at surface and at bottom the values were 8.8 - 10.7 µg./L. during monsoon, 8 - 13.8 µg/L. during post-monsoon 1985 and 10 - 13.2 µg/L. during pre-monsoon 1986 seasons. The dissolved concentrations in the upstream zones were 8 µg/L. during all seasons. Hence, the reported concentrations were 1.21 - 1.32 times higher during monsoon and 1 - 1.75 times higher during post-monsoon 1985 and 1.26 - 1.75 times higher during pre-monsoon 1986 seasons at surface and at bottom the values were 1.1 - 1.32 times higher during monsoon, 1.0 - 1.72

times higher during post-monsoon 1985 and 1.25 - 1.65 times higher during pre-monsoon 1986 seasons in comparison with the upstream levels. The particulate lead concentrations in the Cochin estuary ranged from 33 - 70 ppm during monsoon, 62 - 156 ppm during post-monsoon 1985 and 81 - 208 ppm during pre-monsoon 1986 seasons at surface and at bottom the values were 42 - 150 ppm during monsoon, 60 - 180 ppm during post-monsoon 1985 and 110 - 260 ppm during pre-monsoon 1986 seasons. The particulate lead concentrations in the upstream zone ranged from 84 ppm during monsoon 94 ppm during post-monsoon 1985 and 105 ppm during pre-monsoon 1986 seasons. Hence, the reported concentrations were 0.39 - 0.83 times higher during monsoon, 0.65 - 1.65 times higher during post-monsoon 1985 and 0.77 - 1.92 times higher during pre-monsoon 1986 seasons at surface and at bottom the values were 0.5 - 1.78 times higher during monsoon, 0.63 - 1.91 times higher during post-monsoon 1985 and 1.04 - 2.47 times higher during pre-monsoon 1986 seasons in comparison with the upstream levels.

The concentrations for the fine grade suspended particulate matter for the industrial effluent discharge

point was 400 to 850 ppm. The enrichment of dissolved and particulate lead was approximately 2 times higher in the Cochin estuary compared with the value observed in the upstream zone. The relation between salinity and dissolved lead was shown in Figs. 3.20 to 3.22.

3.1.6. Nickel

The dissolved concentration of nickel in the upstream zone was found to be constant during all the seasons which was 0.2 µg/L., whereas the particulate nickel was found to increase from monsoon to non-monsoon seasons (Tables 3.4 to 3.9, Stations 24 - 27).

The values of dissolved nickel in the Cochin estuary ranged from 0.3 to 0.4 µg/L. during monsoon, 0.4 to 0.6 µg/litre during post-monsoon 1985 and 0.3 to 0.4 µg/L. during pre-monsoon 1986 seasons (Tables 3.4 - 3.6, Stations 1 - 18). Hence, the reported dissolved concentrations in the Cochin estuary were 1.5 - 2.0 times higher during monsoon, 2.0 - 3.0 times higher during post-monsoon 1985 and 1.5 - 2.0 times higher during pre-monsoon 1986 seasons in comparison with the upstream levels. Its concentration in particulates in the Cochin estuary ranged from 45 to 65 ppm during

monsoon, 10 to 80 ppm during post-monsoon 1985 and 5 to 53 ppm during pre-monsoon 1986 seasons. The particulate concentrations in the Cochin estuary were found to be less in comparison with upstream levels.

3.1.7. Iron

Iron (both dissolved and that associated with particulate) in the upstream zone was found to decrease from monsoon to non-monsoon seasons (Tables 3.4 to 3.9). The values of dissolved iron in the Cochin estuary ranged from 0.6 to 0.8 µg/litre during monsoon, 0.2 to 0.8 µg/L. during post-monsoon 1985 and 0.2 to 0.55 µg/L. during pre-monsoon 1986 seasons. Its concentration in particulates ranged from 2.8 to 3.6 % during monsoon 1986, 7.4 to 8.1% during post-monsoon 1985, and 9.4 to9.8% during pre-monsoon 1986 seasons.

The reported metal concentrations form the world oceans were summarised in Table 3.20. The dissolved concentrations in the southern bight of the north sea (Duinker and Nolting, 1982) Cu, 0.22 - 0.3 µg/L. Zn 0.3 -0.4 µg/L. Cd. 0.02 - 0.03 µg/L. southern bight (Dutton et al., 1973) Cu 0.5 - 1. µg/L. Zn 2 - 4 µg/L. Cd 0.1 - 0.3 µg/L. western Atlantic shelf waters (Bruland and

Franks, 1981) Cu 0.26 µg/L. Zn 0.16 µg/L. Cd 0.023 µg/L. The highest dissolved concentrations of trace metals observed in the Puget sound (Paulson and Feely, 1985) Cu 1.6 µg/L. Ni .55 µg/L. Cd 0.39 µg/L. Zn 27 µg/L. and Pb 1.6 µg/L. The reported dissolved concentrations for the Laccadive sea (Sujatha and Moraces, 1979) Zn 2.9 - 29.7 µg/L. Ni 13 - 16 µg/L. Cu 13 - 16 µg/L. and particulate concentrations for Zn 1650 - 3085 ppm, for Ni 97 - 203 ppm and for Cu 163 - 420 ppm.

The relation between salinity and mercury concentrations in the Cochin estuary was shown in Fig.-3.1. For the monsoon season the estuary was almost full of fresh water with low mercury concentrations. This might be as a result of the dilution of mercury due to storm water input. The high content of mercury (both dissolved and associated with particulates) observed for the bottom water showed that mercury may be transferred from the bottom sediment to the over lying water. The effect of salinity on the removal of copper was 21.4% during monsoon, 44.6% during pre-monsoon 1986 and 33.33% during post-monsoon 1985 seasons (Tables 3.16). The dissolved copper was found

to be 2.2 to 4.0 times higher and particulate concentrations were comparable with the observed values in the Rhine estuary (Etcheber, 1979). The relation between salinity and dissolved copper (Figs.3.2 to 3.4) indicated that it was negatively correlated and this relationship increases with increase in salinity due to the seasonal change. Good interrelationship was observed for the particulate copper with salinity for all the seasons (Figs. 3.5 to 3.7). The effect of salinity on the removal of zinc is 32.25% during monsoon, 32.5% during post-monsoon 1985 and 49.35% during pre-monsoon 1986 seasons. The removal was almost constant during monsoon and post-monsoon 1985 seasons. The zinc concentrations were found to be 2 times higher for dissolved form and for particulates it was comparable with the observed values in the Rhine estuary (Etcher, 1979). Major quantum of particulate zinc was leached by 0.1N Hcl which showed that the particulate zinc was in such a form, that it can be easily removed by the biota. The relationship between salinity and dissolved zinc (Figs. 3.8 to 3.10) indicated that it was negatively correlated and this relationship increase with increase in salinity due to

the seasonal change. Good inter-relationship of particulate zinc with salinity (Figs.3.11 to 3.13) was observed for all seasons. Similar to copper the samples from the effluent discharge point showed enhanced levels of dissolved zinc during pre-monsoon 1986 season. The effect of salinity on the rate of removal of cadmium was 14.2% during monsoon 35.29%, during post-monsoon 1985 and 33.33% during pre-monsoon 1986 seasons. The rate of precipitation was almost constant in post-monsoon 1985 and pre-monsoon 1986 seasons. The relation between salinity and dissolved cadmium (Figs. 3.14 to 3.16) indicated that, it was negatively and particulate concentrations (Figs. 3.17 to 3.19)were positively correlated. The dissolved concentrations were comparable and particulate concentrations were 18 times higher when compared with the values reported in the Mersey estuary (Head & Jones, 1989). The percentage of cadmium which was leached by 0.1 N Hcl with the total indicated that higher quantum was extracted for Cochin estuary compared with the upstream zone. The effect of salinity on the rate of removal of lead was 16.9% during the monsoon, 42.85% during post-monsoon 1985 and 28.57% during pre-monsoon 1986 seasons. The rate of

removal of nickel was 25% during monsoon, 33.33% during post-monsoon 1985 and 25% during pre-monsoon 1986 seasons. High content of nickel was observed for the fine grade suspended matter from the industrial discharge point. The particulate leachable fraction of nickel in 0.1 N Hcl with the total metal was found to be 40 to 60% in the Cochin estuary. The relation between salinity and dissolved nickel was shown in Figs. 3.26 to 3.28 and with particulate nickel Figs. 3.29 to 3.31. The rate of removal of iron was 25% during monsoon, 75% during post-monsoon 1985 and 63.5% during pre-monsoon 1986 seasons. The relation between salinity with dissolved and particulate iron was shown in Figs. 3.32 to 3.37.

The steady decrease in the r value of copper from 0.60 - 0.95, from monsoon to non-monsoon seasons showed that the rate of removal of copper was enhanced with increase in salinity. For monsoon season, low salinity region showed high concentration of dissolved copper which proved that transport process of copper may be from fresh water sources. The decrease in the concentration of dissolved copper from monsoon to post-monsoon 1985 seasons, showed that the major removal

was taking place over a wide salinity region from 6 PPT to 24 PPT.

The negative correlation of dissolved lead was observed during non-monsoon season, but positive correlation was observed for particulate lead with salinity for all seasons. In the case of nickel, only particulate nickel showed positive correlation with salinity. In the case of iron, only particulate iron during post-monsoon 1985 season showed positive correlation with salinity.

The P^H alkalinity, salinity and the iron content play an important role in the precipitation as well as the removal of heavy metals in the water column. Metals were converted into their hydroxides or carbonates in the natural form, and this conversion was enhanced by the increased p^H or high alkalinity. Such hydroxides or carbonates which were more gelatinous in nature (like that of iron/aluminium) occlude the particulate matter thereby settles down fast. The concentrations of salinity, p^H and alkalinity were shown in Tables 3.17 to 3.19. Low p^H and low alkalinity were observed for the water samples collected near the effluent discharge

point. As the salinity increased the p^H and alkalinity were also found to be increased in the Cochin Harbour region. For the monsoon season the P^H ranged from 6.6 to 7.1 and iron removal was found to be 25%. During the post-monsoon 1985 the P^H ranged from 7.1 to 8.0 and the iron removal was maximum (75%) whereas during pre-monsoon 1986 the removal was found to be 66.66%. This change may be due to the fact that at high P^H conditions in pre-monsoon 1986 season, the depleted iron might have gone to the soluble form due to the high solubility product.

The high concentrations of iron (both dissolved and in particulates) during monsoon season in the upstream zone could be due to surface run off during heavy rain. Sankaranarayanan and Rosamma Stephen (1978) attributed to higher particulate iron in the Cochin estuary was due to land drainage, harbour activity and sewage. The trend of its decrease observed in post-monsoon 1985 and pre-monsoon 1986 seasons in the Cochin estuary indicated that iron was removed or precipitated from the water column under the influence of salinity and alkalinity.

Seasonally, the dissolved and particulate zinc

showed a conservative decrease in concentrations. The comparison of monsoon values of copper, cadmium and lead with pre and post-monsoon 1985 seasons indicated that salinity P^H, alkalinity and iron plays a major role in the removal of the above metals during estuarine mixing. The relation between salinity and dissolved concentrations during 1985 and 1986 survey were shown in Figs. 3.2 - 3.37. Salinity has a profound influence in the removal of particulate matter (Ouseph, 1986). In general surface samples were found to have more concentration compared with the bottom. As the salinity increases, the concentration of copper decreases. Zinc behaved in a similar way as copper. Pb, Cd, Fe had almost similar characteristics with salinity. The conservative nature of nickel was well noticed. The data revealed that large quantum of metals were removed from the water column and precipitated as suspended matter which may contaminate the bottom sediments.

The decrease in the concentration of heavy metals from surface to bottom and also with salinity showed contribution from fresh water sources and indicated that physical mixing was a significant factor in controlling the dissolved concentrations. High concentrations of

heavy metals were observed in the fine grade suspended matter from the industrial zone, even though no correction was made for the grain size. According to Paul and Pillai (1983) solubilisation of Cu and Cd from sediments under the influence of salinity may be regarded as one of the major mechanisms of trace metal transport to the sea. The enhanced levels of dissolved Cu and Zn observed during non-monsoon period in the upstream zone was attributed to the concentration by evaporation and increased dissolution from sediments due to higher pre-monsoon 1986 temperature and larger contact time in summer (Paul and Pillai, 1983). The steady increase in the concentration of particulate Cu, Zn, Cd, Pb and Ni from monsoon to the non-monsoon period indicated that the longer residence time of finer fractions of suspended solids in river water facilitates further build up by ion exchange processes. Similar behaviour was observed for the particulate Cu, Zn, Cd, Pb Ni and Fe from the effluent discharge point and also for Cu, Zn, Cd and Pb particulates from the Cochin estuary. The decrease in the concentration of particulate nickel from monsoon to non-monsoon season showed that the major mechanism may be solubilisation,

suspension, precipitation and subsequent incorporation in the sediment. The concentration in the fine grade suspended particulate matter from the effluent discharge point showed high concentration of heavy metal, which indicated that the transport route of heavy metal may be from industrial sources.

Metals leached by 0.1 N Hcl from particulates indicated that the major quantum of estuarine particulate Cu, Zn, Cd and Pb were in such a form which can selectively be removed by the biota (Ouseph, 1987). Similarity in the behaviour of particulate leachable metals with the total metal content from the effluent discharge point and Cochin estuary showed that the metals brought from the effluent discharge point can behave in a similar manner in the Cochin estuarine system for bio-geochemical uptake. High dissolved concentration in the surface water strongly suggests that anthropogenic inputs injected by industrial, harbour activity and sewage. Mixing curves have been shown to be useful in detecting the relative importance of physical and bio-geochemical reactions in controlling the distribution of dissolved constituents in estuaries. The balance between the physical and bio-geochemical

processes will dictate the fate of these anthropogenic sources in this estuarine environment.

The variation of heavy metals from season to season, station to station, relates to the characteristics of the estuarine system. Two models describing the mobilization of heavy metal can be suggested. One was the transport route of heavy metals through fine grade suspended particulate matter from river Periyar. The second was the removal of heavy metals during estuarine mixing. The survey revealed high concentrations of dissolved and particulate Cu, Zn and Cd in the waters of Cochin estuary. The removal of heavy metals with respect to estuarine mixing indicated that Lakshadweep Sea acts as a sink for heavy metals discharged from the Cochin Harbour. The study reveals that there was anthropogenic input of heavy metals to the Cochin estuary.

3.2. Semi-diurnal Variation of Dissolved Metals in the Cochin Estuary

The concentrations of heavy metals obtained during the semi-diurnal variation at station (Fig.1.3) was summarised in Table - 3.22. The percentage of removal

of dissolved elements under the influence of salinity was shown in Table - 3.23. The tides of this region were of a mixed type, predominantly semi diurnal with two high and two low waters. The low tide was observed on the day of experiment at 08.15 hrs. and the high tide at 15.00 hrs. The tidal range was approximately 60 cm.

3.2.1. Salinity

The variation of salinity ranged from 15.77 ppt to 32.50 ppt and was found to be in accordance with the tide. Bottom salinity was higher than the surface showing penetration of high saline sea water along the bottom.

3.2.2. Hydrogen ion concentration (p^H)

P^H variation for the surface and bottom waters was shown in Table - 3.18. The p^H vary between 7.25 to 8.15. During high tide, sea water intrudes into the estuary, the salinity increases accordingly p^H also increases.

3.2.3. Suspended particulate matter (SPM)

The suspended particulate matter ranged from 4.80 to 22.0 mg/litre and decreases with increase in salinity (Fig. 3.40).

3.2.4. Copper

The dissolved concentrations of copper in the Cochin estuary ranged from 8.1 to 15.4 µg/L. (Table - 3.22). In the concentrations of copper were 10.2 - 15.4 ug/L. at surface and 8.6 - 10.8 µg/L. at the bottom. The relation between salinity and dissolved copper was shown in Fig. 3.40.

3.2.5. Zinc

The concentrations vary from 68 to 101 µg/L. (Table - 3.22). The concentrations of zinc were 78 - 101 µg/L. at surface and 68 - 80 µg/L. at the bottom. During monsoon, 1985, the concentrations were found to be 105 to 155 µg/L.. The relation between salinity and zinc was shown in Fig. 3.40.

3.2.6. Cadmium

The concentrations ranged from 0.83 to 0.99 µg/L. (Table - 3.22). The concentrations were 0.86 - 0.99 µg/L. at surface and 0.82 - 0.89 µg/L. at the bottom. The rate of removal was 16.16% (Table - 3.23). The relation between salinity and dissolved cadmium shown in Fig. 3.40.

3.2.7. Lead

The dissolved concentrations ranged from 8.1 to 10.2 ug/L. (Table - 3.22). The concentrations were 8.1 - 10.2 µg/L. at surface and 8.12 - 9.10 µg/L. at the bottom. The rate of removal was found to be 20.58% (Table - 3.23). For monsoon, 1985 survey the concentrations were found to be 8.8 to 10.6 µg/L. and the rate of removal was 16.98%.

3.2.8. Nickel

The dissolved concentration of nickel ranged from 0.21 to 0.46 µg/L. (Table - 3.22) and found to be well agreement with the observed values during 1985 survey (Ouseph, 1992). The concentrations were 0.27 - 0.46 µg/L. at surface and 0.21 - 0.29 µg/L. at the bottom. The relation between salinity and dissolved nickel was shown in Fig. 3.41.

3.2.9. Iron

The dissolved concentration ranged from 0.21 to 0.48 µg/L. (Table - 3.22) and the rate of removal was found to be 56.25% (Table - 3.23). The concentrations were 0.29 - 0.48 µg/L. at surface and 0.21 - 0.31 µg/L. at bottom. The relation between and dissolved iron was

shown in Fig. 3.41.

3.2.10. Chromium

The dissolved concentration of chromium ranged from 0.30 to 0.40 µg/L. (Table - 3.22). The concentrations were 0.31 - 0.40 µg/L. at surface and 0.31 - 0.32 µg/L. at the bottom. The rate of removal was found to be 25% (Table - 3.23).

3.2.11. Silver

The concentration for silver ranged from 0.08 to 0.14 µg/L. The concentrations were 0.10 - 0.14 µg/L. at surface 0.08 - 0.10 µg/L. at the bottom.

Bottom water was having high P^H compared with the surface water and this indicated that the salinity play an important role in controlling the p^H of the estuarine system. The decrease in the concentration of particulate matter with increase in salinity showed that the input of particulate matter to the estuary was of river borne and the colloidal solids were precipitated and removed from the water column under the influence of salinity p^H and alkalinity. It was observed that the dissolved copper was removed by the intrusion of saline water to the estuary. The rate of removal was found to

be 48.34%. During monsoon, 1985 survey the concentration of copper for the entire harbour area was found to be 2.2 to 2.8 µg/L.. This indicated that higher concentrations were observed during the present study. The rate of removal of copper during monsoon, 1985 survey was found to be 21.4%. The concentrations were comparable with the maximum values observed in the Scheldt estuary (Baeyens et al., 1982) which was 12.9 µg/L.. The rate of removal of zinc during the 1985 and 1987 survey was 32.25% and 32.67%, respectively (Table - 3.23). This indicated that the rate of removal was almost constant. The observed values of zinc were comparable with the concentrations in the Scheldt estuary (Baeyens et al., 1982). For the monsoon season of 1985 the cadmium concentrations were found to be 1.8 to 2.1 µg/L. and the removal was 14.28%. The rate of removal of dissolved cadmium was between 14.28 to 16.66% during the earlier and the present study. The values of cadmium were comparable with the observed concentrations in the Scheldt estuary (Baeyens et al., 1982). The relation between salinity and dissolved lead was shown in Fig. 3.40. The observed values of lead were 1.6 to 2 times higher when compared with the

concentrations reported in the Scheldt estuary (Baeyens et al., 1982) which was 5 µg/L. The conservative nature of nickel was noticed for the high salinity range and also a hundred times increase in removal in comparison with the earlier study. Similar to nickel, iron was also found to have 100 times increase in removal in comparison with the earlier study.

The Figs. 3.40 and 3.41 show that p^H and salinity play an important role in the removal of heavy metals during estuarine mixing. This indicated that the transport route of heavy metals to the sea may be probably in the form of particulate matter by precipitation. The concentration versus time in hours (Figs.3.38 and 3.39) showed that copper and zinc behaved in a similar way. During high tide the bottom concentration for Cu, Zn, Cd and Pb show conservative nature compared with the surface. Among the metals under study, the conservative nature of Pb and Cr was well noticed for the entire tidal range. The major changes in the removal of trace metal and suspended matter were taking place between 24.0 to 32.5 salinity (Figs.3.40 and 3.41). This showed that the study area act as a removal zone for the heavy metals brought by

the rivers through the fresh water discharge. The results for the percentage of removal for Zn, Cd and Pb during the present study was found to be in well agreement with the monsoon, 1985 survey (Table - 3.19) and for Cu, Ni and Fe a 100% increase in removal was observed may be due to the high input from the fresh water zone. According to Paul and Pillai (1983) solubilisation of Cu and Cd from sediments under the influence of high salinity which may be regarded as one of the major mechanisms of trace metal transport to the sea. The study reveals that removal and subsequent sediment movement was the major mechanisms of trace metal transport to the sea.

Table - 3.1
Concentrations of Dissolved and Particulate Mercury in Cochin Estuary and River Periyar - July, 1985 (Monsoon)

Station No.		Salinity ppt	D ng/L.	PM µg/gm	P mg/L.	PM ng/L.
1.	S	1.8	130	4	15	60
	B	2.2	150	6	18	108
2.	S	1.9	85	5	16	80
	B	2.1	160	12	17	204
3.	S	3.2	150	6	15	90
	B	3.4	180	20	16	320
4.	S	1.6	85	5	18	90
	B	1.8	90	8	19	152
5.	S	1.2	80	5	18	90
	B	1.4	110	6	20	120
6.	S	1.1	80	5	15	75
	B	1.2	80	6	18	108
7.	S	0.8	90	5	15	75
	B	1.2	110	5	16	80
8.	S	1.4	40	4	17	68
	B	1.1	50	6	18	108
9.	S	1.4	60	4	16	64
	B	4.9	60	5	12	60
10.	S	3.2	120	6	14	84
	B	10.6	140	18	10	180
11.	S	3.6	100	5	12	60
	B	13.8	160	19	7	133
12.	S	3.4	85	6	10	60
	B	13.6	90	13	6	78

Table - 3.1

Station No.		Salinity ppt	D ng/L.	PM µg/gm	P mg/L.	PM ng/L.
13.	S	3.8	80	5	12	60
	B	16.9	160	12	6	72
14.	S	3.6	85	2	15	30
	B	16.5	180	20	6	120
15.	S	1.5	80	4	17	68
	B	1.6	110	6	18	108
16.	S	1.4	100	8	16	128
	B	1.9	120	10	15	150
17.	S	1.1	80	4	16	64
	B	1.1	90	6	15	90
18	S	2.2	110	5	14	70
	B	3.4	130	8	15	120
19.	S	<1.0	85	24.5	18	441
20.	S	<1.0	90	24.5	20	490
21	S	<1.0	95	24.5	19	465.5
22	S	<1.0	85	24.5	21	514.5
23.	S	<1.0	90	24.5	22	539
24	S	<1.0	15	2.0	12	24
25	S	<1.0	15	2.0	10	20
26	S	<1.0	15	2.0	8	16
27	S	<1.0	15	2.0	10	20

D = Dissolved Mercury

PM = Particulate Mercury

P = Particulate matter

Table - 3.2
Concentrations of Disoolved and Particulate Mercury in Cochin Eestuary and River Periyar November, 1985 (Post-monsoo)

Station No.		Salinity ppt	D ng/L.	PM µg/gm	P mg/L.	PM ng/L.
1.	S	16.2	140	8	8	64
	B	18.2	170	20	7	140
2.	S	17.2	160	6	9	54
	B	18.8	210	25	8	200
3.	S	15.2	180	5	9	45
	B	22.4	220	18	5	90
4.	S	17.4	130	7	5	35
	B	20.2	140	12	4	48
5.	S	12.3	100	5	7	35
	B	16.4	110	6	6	36
6.	S	11.5	50	3	10	30
	B	11.5	60	4	9	36
7.	S	10.8	70	3	10	30
	B	12.5	90	3	8	24
8.	S	12.5	50	2	9	18
	B	13.4	60	2	8	16
9.	S	21.3	80	2	8	16
	B	23.3	90	3	6	18
10.	S	22.5	150	6	4	24
	B	26.5	240	18	5	90
11.	S	18.5	170	7	4	28
	B	24.5	220	25	9	225
12.	S	17.4	180	3	5	15
	B	22.2	200	18	8	144

Table - 3.2

Station No.		Salinity ppt	D ng/L.	PM µg/gm	P mg/L.	PM ng/L.
13.	S	16.4	210	4	6	24
	B	18.5	230	15	7	105
14.	S	20.2	180	6	8	48
	B	21.5	240	12	5	75
15.	S	12.5	110	5	4	20
	B	16.4	140	5	12	60
16.	S	11.4	210	8	10	80
	B	15.2	230	13	8	104
17.	S	10.8	180	6	7	42
	B	11.2	180	7	9	63
18.	S	17.2	160	5	8	40
	B	18.5	210	16	7	112
19	S	<1.0	115	32	14	448
20	S	<1.0	120	32	15	480
21	S	<1.0	118	32	14	448
22	S	<1.0	120	32	15	480
23	S	<1.0	115	32	15	480
24	S	<1.0	15	2.5	8	20
25	S	<1.0	15	2.5	7	17.5
26	S	<1.0	15	2.5	8	20
27	S	<1.0	15	2.5	8	20

D = Dissolved Mercurry
PM = Particulate Mercurry
P = Particulate matter

Table - 3.3

Concentrations of Dissolved and Particulate Mercury in Cochin Estuary and River Periyar - April, 1986 (Pre-monsoon)

Station No.		Salinity ppt	D ng/L.	PM µg/gm	P mg/L.	PM ng/L.
1.	S	22.5	160	16	6	96
	B	28.3	200	20	5	100
2.	S	22.2	180	14	6	84
	B	29.2	180	18	5	90
3.	S	22.4	200	15	8	120
	B	28.2	230	16	7	112
4.	S	20.2	150	15	6	90
	B	26.2	210	18	6	108
5.	S	19.4	130	14	8	112
	B	26.2	150	19	5	95
6.	S	15.2	80	14	10	140
	B	18.2	100	14	8	112
7.	S	18.5	80	13	8	104
	B	22.4	120	15	6	90
8.	S	19.4	60	14	5	70
	B	28.2	80	15	7	105
9.	S	22.2	80	8	5	40
	B	29.9	130	6	6	36
10.	S	22.6	220	32	7	224
	B	33.2	240	36	5	180
11.	S	25.9	210	42	6	252
	B	34.2	250	28	4	112
12.	S	25.2	180	24	6	144
	B	32.2	200	25	5	125

Table - 3.3

Station No.		Salinity ppt	D ng/L.	PM µg/gm	P mg/L.	PM ng/L.
13.	S	26.1	220	16	6	96
	B	34.1	240	22	4	88
14.	S	28.4	180	28	6	168
	B	33.2	200	25	5	125
15.	S	22.1	100	34	7	238
	B	28.4	120	36	4	144
16.	S	18.2	230	26	5	130
	B	24.2	250	25	6	150
17	S	18.5	260	27	7	189
	B	19.2	280	22	7	154
18	S	21.4	180	17	8	136
	B	29.2	220	20	6	120
19	S	<1.0	120	36.8	25	920
20	S	<1.0	135	36.8	24	883.2
21	S	<1.0	132	36.8	22	809.6
22	S	<1.0	130	36.8	24	883.2
23	S	<1.0	128	36.8	22	809.6
24	S	<1.0	25	2.5	4	10.0
25	S	<1.0	25	2.5	6	15.0
26	S	<1.0	25	2.5	5	12.5
27	S	<1.0	25	2.5	8	20.0

D = Dissolved Mercury
PM = Particulate Mercury
P = Particulate matter.

Table - 3.4

Concentrations of Dissolved Metals µg/L. in Cochin Eastuary and River Periyar - July, 1985 (Monsoon)

Station		Salinity ppt	Cu	Zn	Cd	Pb	Ni	Fe
1.	S	1.8	2.7	139	2.10	10.6	0.3	0.80
	B	2.2	2.6	140	2.10	10.4	0.4	0.80
2.	S	1.9	2.7	145	2.00	10.6	0.32	0.83
	B	2.1	2.5	138	1.90	10.5	0.3	0.82
3.	S	3.2	2.8	130	1.80	9.8	0.38	0.79
	B	3.4	2.7	136	1.99	9.9	0.35	0.70
4.	S	1.6	2.78	155	2.10	10.2	0.41	0.71
	B	1.8	2.77	152	2.20	10.3	0.30	0.80
5.	S	1.2	2.62	150	1.98	10.6	0.30	0.84
	B	1.4	2.24	151	1.92	10.1	0.37	0.81
6.	S	1.1	2.20	154	1.91	10.5	0.42	0.69
	B	1.2	2.74	150	1.80	10.2	0.34	0.70
7.	S	0.8	2.79	152	2.05	10.6	0.43	0.78
	B	1.2	2.69	146	2.10	10.2	0.38	0.72
8.	S	1.4	2.6	148	2.00	10.1	0.43	0.73
	B	1.1	2.76	153	1.90	10.0	0.39	0.69
9.	S	1.4	2.6	132	2.40	10.1	0.37	0.60
	B	4.9	2.71	149	2.06	10.6	0.30	0.72
10.	S	3.2	2.62	147	1.92	9.7	0.40	0.75
	B	10.6	2.4	124	2.00	9.4	0.31	0.81
11.	S	3.6	2.73	140	2.00	9.8	0.40	0.85
	B	13.8	2.3	114	1.87	8.9	0.32	0.62
12.	S	3.4	2.76	138	-	9.6	0.37	0.60
	B	13.6	2.20	115	1.89	8.8	0.30	0.61

Table - 3.4

Station		Salinity ppt	Cu	Zn	Cd	Pb	Ni	Fe
13.	S	3.8	2.72	135	-	10.4	0.40	0.82
	B	16.9	2.22	114	1.8	8.8	0.28	0.65
14.	S	3.6	2.72	142	-	9.8	0.40	0.60
	B	16.5	2.45	105	1.79	8.8	0.29	0.64
15.	S	1.5	2.71	105	2.02	10.4	0.40	0.83
	B	1.6	2.8	136	2.01	10.2	0.40	0.71
16.	S	1.4	2.80	143	1.92	10.1	0.37	0.73
	B	1.9	2.79	137	2.10	10,7	0.39	8.83
17.	S	1.1	2.76	149	1.92	10.5	0.39	0.69
	B	1.1	2.74	155	1.89	10.2	0.38	0.83
18	S	2.2	2.73	151	1.9	10.4	0.40	0.75
	B	3.4	2.66	128	1.9	9.9	0.35	0.70
19	S	<1.0	0.80	24	0.20	8.0	0.20	1.10
20	S	<1.0	0.80	24	0.20	8.0	0.20	1.1
21.	S	<1.0	0.80	24	0.20	8.0	0.20	1.2
22.	S	<1.0	0.80	24	0.20	8.0	0.20	1.2
23.	S	<1.0	0.80	24	0.20	8.0	0.20	1.10
24.	S	<1.0	0.80	24	0.20	8.0	0.20	1.2
25.	S	<1.0	0.80	24	0.20	8.0	0.20	1.2
26.	S	<1.0	0.80	24	0.20	8.0	0.20	1.2
27.	S	<1.0	0.80	24	0.20	8.0	0.20	1.2

S = Surface
B = Bottom

Table - 3.5
Concentrations of Dissolved Metals ug/L. in Cochin Estuary and River Periyar - November, 1985 (Post-monsoon)

Station		Salinity ppt	Cu	Zn	Cd	Pb	Ni	Fe
1.	S	16.2	14.8	180	2.8	10.4	0.50	0.60
	B	18.2	13.4	179	2.4	10.4	0.6	0.70
2.	S	17.2	12.2	160	2.6	10.8	0.51	0.40
	B	18.8	11.6	170	2.5	10.4	0.41	0.64
3.	S	15.2	15.4	190	3.0	12.5	0.49	0.42
	B	22.4	12.4	155	2.3	9.8	0.52	0.68
4.	S	17.4	13.2	165	2.43	13.2	0.41	0.44
	B	20.2	11.4	150	2.20	13.1	0.52	0.80
5.	S	12.3	17.4	216	3.1	12.4	0.60	0.38
	B	16.4	15.1	180	2.7	11.0	0.40	0.30
6.	S	11.5	18.2	205	3.2	13.0	0.59	0.82
	B	11.5	18.4	195	3.15	12.8	0.55	0.85
7.	S	10.8	18.8	215	3.4	14.0	0.60	0.63
	B	12.5	17.9	213	3.23	13.1	0.45	0.69
8.	S	12.5	17.2	202	3.38	12.6	0.57	0.80
	B	13.4	17.1	192	3.14	13.3	0.53	0.65
9.	S	21.3	11.1	162	2.42	10.0	0.43	0.32
	B	23.3	10.9	176	2.52	9.1	0.45	0.20
10.	S	22.5	11.5	163	2.54	8.0	0.40	0.18
	B	26.5	10.4	145	2.2	8.0	0.46	0.24
11.	S	18.5	12.1	142	2.72	10.3	0.48	0.47
	B	24.5	10.9	179	2.45	10.4	0.49	0.36
12.	S	17.4	13.7	170	2.75	10.6	0.44	0.44
	B	22.2	12.5	158	2.56	10.4	0.59	0.45

Table - 3.5

Station		Salinity ppt	Cu	Zn	Cd	Pb	Ni	Fe
13.	S	16.4	14.2	161	2.83	11.30	0.46	0.53
	B	18.5	12.1	168	2.63	10.90	0.43	0.51
14.	S	20.2	11.9	177	2.54	10.1	0.60	0.53
	B	21.5	10.8	166	2.73	9.3	0.57	0.48
15.	S	12.5	16.4	197	3.40	13.7	0.45	0.35
	B	16.4	14.8	174	2.89	10.9	0.54	0.58
16.	S	11.4	10.6	202	3.12	12.1	0.39	0.78
	B	15.2	14.2	194	2.94	11.3	0.49	0.64
17.	S	10.8	18.8	193	3.35	13.4	0.60	0.67
	B	11.2	10.8	212	2.90	13.8	0.52	0.81
18.	S	17.2	12.6	165	2.86	11.0	0.58	0.69
	B	18.5	13.9	162	2.67	9.4	0.55	0.78
19.	S	<1.0	10	40	0.20	8.0	0.20	1.1
20	S	<1.0	10	40	0.20	8.0	0.20	1.1
21	S	<1.0	10	40	0.20	8.0	0.20	1.1
22	S	<1.0	10	40	0.20	8.0	0.20	1.1
23	S	<1.0	10	40	0.20	8.0	0.20	1.1
24	S	<1.0	10	40	0.20	8.0	0.20	1.1
25	S	<1.0	10	40	0.20	8.0	0.20	1.1
26	S	<1.0	10	40	0.20	8.0	0.20	1.1
27	S	<1.0	10	40	0.20	8.0	0.20	1.1

S = Surface
B = Bottom

Table - 3.6
Concentrations of Dissolved Metals µg/Ltr. in Cochin Estuary and River Periyar - April, 1986 (Pre-monsoon)

Station		Salinity ppt	Cu	Zn	Cd	Pb	Ni	Fe
1.	S	22.5	19.2	305	3.60	13.1	0.31	0.40
	B	28.3	17.6	240	3.10	10.0	0.40	0.25
2.	S	22.2	18.8	290	3.25	11.1	0.32	0.45
	B	29.2	16.8	215	3.12	10.0	0.35	0.28
3.	S	22.4	18.6	318	3.50	11.0	0.31	0.40
	B	28.2	17.5	262	2.98	11.1	0.30	0.28
4.	S	20.2	20.8	325	3.70	10.9	0.38	0.50
	B	26.2	17.6	230	3.05	11.2	0.40	0.32
5.	S	19.4	22.0	330	3.90	13.6	0.32	0.55
	B	26.2	17.8	225	3.15	10.8	0.30	0.30
6.	S	15.2	22.2	385	4.20	14.0	0.35	0.60
	B	18.2	21.8	340	3.86	13.2	0.39	0.51
7.	S	18.5	21.6	348	3.75	11.8	0.31	0.55
	B	22.4	19.8	305	3.50	11.2	0.32	0.35
8.	S	19.4	21.4	340	3.80	10.4	0.40	0.52
	B	28.2	16.8	242	3.15	10.2	0.40	0.29
9.	S	22.2	19.8	326	3.60	10.8	0.38	0.35
	B	29.9	15.4	232	3.08	10.8	0.32	0.32
10.	S	22.6	19.6	322	3.60	10.1	0.35	0.30
	B	33.2	15.1	195	2.90	10.6	0.38	0.28
11.	S	25.9	18.6	262	3.20	10.8	0.32	0.40
	B	34.2	14.8	208	2.80	10.5	0.31	0.20
12.	S	25.2	15.8	292	3.15	11.4	0.30	0.40
	B	32.2	15.1	210	3.00	11.7	0.39	0.24

Table - 3.6

Station		Salinity ppt.	Cu	Zn	Cd	Pb	Ni	Fe
13.	S	26.1	17.4	283	3.12	11.1	0.31	0.40
	B	34.1	14.8	205	2.94	10.2	0.32	0.20
14.	S	28.4	16.6	226	3.18	10.9	0.38	0.24
	B	33.2	15.2	195	2.96	10.2	0.34	0.20
15.	S	22.1	19.8	332	3.50	12.1	0.35	0.32
	B	28.4	17.4	208	3.16	10.2	0.38	0.30
16.	S	18.2	22.2	362	3.90	12.1	0.32	0.46
	B	24.2	17.8	200	3.10	10.9	0.38	0.28
17.	S	18.5	21.4	348	3.95	12.4	0.36	0.48
	B	19.2	21.0	362	3.78	13.2	0.34	0.51
18.	S	21.4	20.2	318	3.18	11.8	0.39	0.41
	B	29.2	16.8	218	3.12	10.9	0.30	0.23
19	S	<1.0	13.0	215	1.8	8.0	0.2	0.80
20	S	<1.0	15.0	168	1.5	8.0	0.20	0.80
21	S	<1.0	16.0	205	2.1	8.0	0.20	0.80
22	S	<1.0	13.0	208	2.8	8.0	0.20	0.80
23	S	<1.0	15.0	168	1.5	8.0	0.20	0.80
24	S	<1.0	8.0	65	0.20	8.0	0.20	0.80
25	S	<1.0	8.0	65	0.20	8.0	0.20	0.80
26	S	<1.0	8.0	65	0.20	8.0	0.20	0.80
27	S	<1.0	8.0	65	0.20	8.0	0.20	0.80

S = Surface
B = Bottom

Table - 3.7
Concentrations of Particulate Metals in Cochin Estuary and River Periyar - July, 1985 (Monsoon)

Station		Salinity ppt	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Ni ppm	Fe %
1.	S	1.8	68	190	62	33	46.0	2.90
	B	2.2	86	260	66	45	48.0	2.80
2.	S	1.9	91	125	64	46	47.0	2.80
	B	2.1	82	280	68	47	48.5	2.32
3.	S	3.2	94	310	69	48	51.0	3.10
	B	3.4	105	380	67	58	52.0	3.20
4.	S	1.6	65	140	61	62	54,0	2.30
	B	1.8	70	170	63	48	53.0	3.00
5.	S	1.2	55	129	62	40	46.5	2.80
	B	1.4	63	160	64	42	49.0	2.86
6.	S	1.1	64	130	59	38	45.5	2.80
	B	1.2	48	142	60	43	47.5	3.10
7.	S	0.8	44	125	58	35	45.0	2.78
	B	1.2	52	140	62	43	46.0	2.97
8.	S	1.4	60	160	65	44	47.0	3.12
	B	1.1	50	150	64	45	45.5	2.91
9.	S	1.4	49	160	70	41	45.0	2.92
	B	4.9	52	510	80	42	52.0	3.22
10.	S	3.2	96	360	65	52	48.5	3.10
	B	10.6	129	690	82	98	58.0	3.25
11.	S	3.6	107	390	66	60	50.5	3.20
	B	13.8	164	880	84	134	62.0	3.60
12.	S	3.4	111	340	68	64	48.0	3.24
	B	13.6	152	820	87	128	52.0	3.60

Table - 3.7

Station		Salinity ppt	Cu	Zn	Cd	Pb	Ni	Fe
13.	S	3.8	110	370	67	68	45.5	3.30
	B	16.9	197	1040	91	150	65.0	3.63
14.	S	3.6	101	410	68	70	49.5	3.40
	B	16.5	190	1035	90	148	64.0	3.50
15.	S	1.5	45	180	63	47	46.5	2.96
	B	1.6	50	195	64	48	47.5	2.43
16.	S	1.4	48	160	66	44	45.0	2.92
	B	1.9	57	165	69	49	49.3	3.04
17.	S	1.1	46	140	61	38	47.0	2.91
	B	1.1	48	142	63	43	48.0	2.97
18	S	2.2	80	210	67	45	48.5	2.94
	B	3.4	105	420	69	59	51.5	3.21
19	S	<1	240	1450	8.5	610	140	3.80
20	S	<1	250	1380	8.5	580	135	3.80
21	S	<1	260	2200	6.0	610	185	4.20
22	S	<1	320	2200	6.8	400	190	4.20
23	S	<1	260	1350	7.2	620	138	4.00
24	S	<1	48	180	2.8	84	88	9.2
25	S	<1	48	180	2.8	84	88	9.2
26	S	<1	48	180	2.8	84	88	9.2
27	S	<1	48	180	2.8	84	88	9.2

S = Surface
B = Bottom

Table - 3.8
Concentrations of Particulate Metals in Cochin Estuary and River Periyar - November, 1985 (Post-monsoon)

Station		Salinity ppt	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Ni ppm	Fe %
1.	S	16.2	108	918	88	104	38.0	7.90
	B	18.2	138	1170	100	120	46.0	7.80
2.	S	17.2	129	1045	95	113	41.0	7.01
	B	18.8	141	1250	105	124	49.0	8.00
3.	S	15.2	111	790	84	98	33.0	7.50
	B	22.4	174	1740	124	152	64.0	8.10
4.	S	17.4	132	1040	93	116	42.0	7.81
	B	20.2	156	1450	110	132	54.0	7.91
5.	S	12.3	88	450	62	78	19.0	7.43
	B	16.4	120	960	89	109	39.0	7.60
6.	S	11.5	80	290	58	63	16.4	7.80
	B	11.5	82	280	59	64	16.8	7.50
7.	S	10.8	65	260	54	62	10.0	7.45
	B	12.5	88	480	59	76	12.8	7.42
8.	S	12.5	92	470	69	76	16.0	7.42
	B	13.4	97	560	76	85	25.2	7.50
9.	S	21.3	169	1590	112	145	59.0	7.90
	B	23.3	186	1860	128	154	68.0	7.90
10.	S	22.5	179	1750	122	156	65.0	7.60
	B	26.5	230	2200	150	180	80.0	8.11
11.	S	18.5	142	1180	104	122	48.0	7.80
	B	24.5	198	2010	139	165	75.0	7.95
12.	S	17.4	133	1100	96	115	42.0	7.84
	B	22.2	178	1780	123	108	62.0	7.96

Table - 3.8

Station		Salinity ppt	Cu	Zn	Cd	Pb	Ni	Fe
13.	S	16.4	124	980	92	106	37.0	7.60
	B	18.5	145	1270	104	122	46.0	7.84
14.	S	20.2	142	1430	113	144	54.0	8.12
	B	21.5	170	1610	120	145	61.0	8.00
15.	S	12.5	88	470	64	67	21.0	7.50
	B	16.4	124	660	109	108	38.0	7.60
16.	S	11.4	79	330	50	62	16.0	7.46
	B	15.2	113	860	84	88	34.0	7.61
17.	S	10.8	66	170	58	66	12.0	7.45
	B	11.2	79	150	55	60	14.0	7.55
18.	S	17.2	139	1020	95	103	43.0	7.65
	B	18.5	142	1240	104	110	47.0	7.75
19	S	<1.0	380	2680	8.1	650	180	4.10
20	S	<1.0	350	2890	8.2	740	160	4.20
21	S	<1.0	400	3100	10.2	740	230	4.8
22	S	<1.0	400	3200	10.2	560	230	4.8
23	S	<1.0	380	2650	8.0	580	160	3.9
24	S	<1.0	85	240	3.4	94	110	8.8
25	S	<1.0	85	240	3.4	94	110	8.8
26	S	<1.0	85	240	3.4	94	110	8.8
27	S	<1.0	85	240	3.4	94	110	8.8

S = Surface
B = Bottom

Table - 3.9
Concentrations of Particulate Metals in Cochin Estuary and River Periyar - April, 1986 (Pre-monsoon)

Station		Salinity ppt	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Ni ppm	Fe %
1.	S	22.5	174	1410	108	149	24.5	9.40
	B	28.3	258	2210	145	210	38.0	9.50
2.	S	22.2	210	1660	160	165	28.6	9.41
	B	29.2	280	2390	152	212	42.0	9.60
3.	S	22.4	178	1400	110	149	25.0	9.80
	B	28.2	260	2250	148	205	39.0	9.70
4.	S	20.2	148	1078	98	130	18.0	9.81
	B	26.2	232	1950	130	132	35.0	9.62
5.	S	19.4	142	960	94	121	17.0	9.40
	B	26.2	235	1960	132	185	35.0	9.62
6.	S	15.2	76	318	65	81	5.0	9.40
	B	18.2	122	790	88	110	14.0	9.51
7.	S	18.5	124	798	85	108	14.0	9.82
	B	22.4	182	1410	112	152	25.0	9.82
8.	S	19.4	138	990	92	123	17.0	9.70
	B	28.2	265	2250	148	205	42.0	9.82
9.	S	22.2	128	1370	111	145	25.0	9.60
	B	29.9	285	2510	156	216	42.0	9.42
10.	S	22.6	176	1430	119	159	26.0	9.43
	B	33.2	278	2990	179	248	49.0	9.52
11.	S	25.9	288	1860	135	170	32.0	9.69
	B	34.2	296	3100	180	260	53.0	9.89
12.	S	25.2	285	1910	138	168	33.0	9.52
	B	32.2	314	2880	160	231	50.0	9.45

Table - 3.9

Station		Salinity ppt	Cu	Zn	Cd	Pb	Ni	Fe
13.	S	26.1	232	1950	128	188	38.0	9.65
	B	34.1	295	3100	180	257	53.0	9.60
14.	S	28.4	267	3100	140	208	52.0	9.45
	B	33.2	298	3053	178	258	51.0	9.55
15.	S	22.1	160	1350	109	160	28.0	9.88
	B	28.4	240	2270	154	215	51.0	9.45
16.	S	18.2	115	790	88	110	16.0	9.51
	B	24.2	204	1650	146	167	34.0	9.66
17	S	18.5	110	790	91	108	18.0	9.70
	B	19.2	150	930	99	122	16.0	9.86
18	S	21.4	168	1150	105	143	29.0	9.40
	B	29.2	276	2390	168	240	46.0	9.39
19	S	<1.0	410	3100	8.0	750	210	4.10
20	S	<1.0	390	2910	8.5	720	190	4.2
21	S	<1.0	420	3800	12.5	850	220	4.4
22	S	<1.0	420	3800	10.8	850	220	4.4
23	S	<1.0	380	2500	8.00	600	160	4.1
24	S	<1.0	140	450	6.2	105	142	6.5
25	S	<1.0	140	450	6.2	105	142	6.5
26	S	<1.0	140	450	6.2	105	142	6.5
27	S	<1.0	140	450	6.2	105	142	6.

S = Surface
B = Bottom

Table -3.10

Seasonal Distribution of Dissolved Metals in River Periyar Upstream

Season	Hg ng/L.	Cu µg/L.	Zn µg/L.	Cd µg/L.	Pb µg/L.	Ni µg/L.	Fe µg/L.
Monsoon July, 1985	15	0.8	24	0.2	8.0	0.2	1.2
Post-monsoon Nov., 1985	15	10.0	40	0.2	8.0	0.2	1.1
Pre-monsoon April, 1986	25	8.0	65	0.2	8.0	0.2	0.8

Table - 3.11

Seasonal distribution of particulate Metals in River Periyar Upstream

Season	Hg ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Ni ppm	Fe %
Monsoon July, 1985	2.0	48	180	2.8	84	88	9.2
Post-Monsoon Nov., 1985	2.5	85	240	3.4	94	110	8.8
Pre-Monsoon April, 1986	2.5	140	450	6.2	105	142	6.5

Table - 3.12
Seasonal Distribution of Dissolved Metals in Cochin Estuary

Season	Cu µg/L.	Zn µg/L.	Cd µg/L.	Pb µg/L.	Ni µg/L.	Fe µg/L.
Monsoon July, 1985	2.2-2.8	105-155	1.8-2.1	8.8-10.6	.3-.4	.6-.8
Post-Monsoon Nov., 1985	10.4-18.8	145-216	2.2-3.4	8.0-14.0	.4-.6	.2-.8
Pre-Monsoon April, 1986	14.8-22.2	195-385	2.8-4.2	10.0-14.0	.3-.4	.2-.6

Table - 3.13
Seasonal distribution of Particulate Metals in Cochin Estuary

Season	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Ni ppm	Fe %
Monsoon July, 1985	44-197	125-1040	58-91	33-150	45-65	2.8-3.6
Post-monsson Nov., 1985	65-230	150-2200	50-150	60-180	10-80	7.4-8.1
Pre-monsoon April 1986	76-298	318-3100	65-180	81-260	5-53	9.4-9.8

Table - 3.14
Concentration of Metals in Fine Grade Suspended Particulate Matter in River Periyar - Effluent Discharge point

Season	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Ni ppm	Fe %
Monsoon July, 1985	250-320	1350-2200	6-8.5	400-620	130-190	3.8-4.2
Post-monsoon Nov., 1985	350-400	2650-3100	8-10.2	560-740	160-230	3.2-4.8
Pre-monsoon April, 1986	380-420	2500-3800	8-12	600-850	160-220	4.2-4.4

Table-3.15
Percentage of Metals Leached by Treatment with 0.1 N Hcl with Respect to the Total Amount In Suspended Matter.

	Cu	Zn	Cd	Pb	Ni	Fe
River Periyar Unpolluted zone	100	40-70	45-60	50-60	40-60	38-47
Fine Grade suspended particulate matter effluent discharge point	85-90	80-90	60-80	80-90	40-60	55-68
Cochin Estuary	80-90	75-90	70-85	95-100	40-60	80-90

Table - 3.16
Percentage of Rduction In The Concentration of Metals in Water Column Consequent on Salinity Intrusion

Season	Cu %	Zn %	Cd %	Pb %	Ni %	Fe %	Salinity (ppt)	P^H
Monsoon July, 1985	21.4	32.25	14.2	16.9	25.0	25.0	1.1-16.0	6.6-7.1
Post-monsoon Nov.1985	44.6	32.5	35.2	42.8	33.3	75.0	10.8-26.5	7.1-8.0
Pre-monsoon April,86	33.33	49.3	33.3	28.5	25.0	66.6	19.4-34.2	7.8-8.4

Table - 3.17

Concentrations of Salinity, Alkalinity and p^H in Cochin Estuary and River Periyar - July, 1985 (Monsoon)

Station No.	Salinity ppt		Alkalinity mg/L..	p^H
1.	S	1.8	13	6.8
	B.	2.2	18	6.6
2.	S	1.9	15	6.6
	B	2.1	17	6.8
3.	S	3.2	20	6.6
	B	3.4	22	6.8
4.	S	1.6	12	6.7
	B	1.8	17	6.6
5.	S	1.2	14	6.7
	B	1.4	16	6.8
6.	S	1.1	12	6.8
	B	1.2	14	6.6
7.	S	0.8	8	6.6
	B	1.2	10	6.7
8.	S	1.4	14	6.7
	B	1.1	15	6.7
9.	S	1.4	12	6.7
	B	4.9	20	6.8
10.	S	3.2	18	6.8
	B	10.6	46	6.8
11.	S	3.6	14	6.7
	B	13.8	62	6.9
12.	S	3.4	16	6.7
	B	13.6	65	6.9

Table - 3.17

Station No.	Salinity ppt		Alkalinity mg/L..	pH
13.	S	3.8	18	6.8
	B	16.9	82	7.1
14.	S	3.6	20	6.8
	B	16.5	84	7.1
15.	S	1.5	14	6.7
	B	1.6	18	6.7
16.	S	1.4	18	6.7
	B	1.9	20	6.8
17.	S	1.1	12	6.6
	B	1.1	10	6.7
18.	S	2.2	16	6.7
	B	3.4	18	6.8
19.	S	<1	5	5.3
20	S	<1	4	5.2
21.	S	<1	4	5.3
22.	S	<1	5	5.2
23.	S	<1	6	5.3
24.	S	<1	20	7.1
25.	S	<1	22	7.1
26.	S	<1	25	7.1
27.	S	<1	22	7.1

S = Surface
B = Bottom

Table - 3.18

Concentrations of Salinity, Alkalinity and p^H in Cochin Estuary and River Periyar - November, 1985 (Post-monsoon)

Station No.	Salinity ppt		Alkalinity mg/L..	p^H
1.	S	16.2	84	7.8
	B.	18.2	90	7.4
2.	S	17.2	92	7.1
	B	18.8	95	7.4
3.	S	15.2	65	7.6
	B	22.4	95	8.0
4.	S	17.4	88	7.6
	B	20.2	92	7.9
5.	S	12.3	52	7.5
	B	16.4	80	7.6
6.	S	11.5	51	7.7
	B	11.5	52	7.8
7.	S	10.8	42	7.5
	B	12.5	48	7.4
8.	S	12.5	42	7.6
	B	13.4	48	7.6
9.	S	21.3	92	7.2
	B	23.3	95	7.9
10.	S	22.5	90	7.6
	B	26.5	92	8.0
11.	S	18.5	85	7.7
	B	24.5	90	7.9
12.	S	17.4	95	7.8
	B	22.2	100	7.9

Table - 3.18

Station No.	Salinity ppt		Alkalinity mg/L..	pH
13.	S	16.4	82	7.8
	B	18.5	88	7.4
14.	S	20.2	95	7.8
	B	21.5	98	8.0
15.	S	12.5	62	7.8
	B	16.4	88	7.8
16.	S	11.4	52	7.9
	B	15.2	65	7.8
17.	S	10.8	48	7.7
	B	11.2	55	7.6
18.	S	17.2	88	7.2
	B	18.5	90	7.6
19.	S	< 1	4	5.3
20	S	< 1	5	5.4
21.	S	< 1	5	5.4
22.	S	< 1	4	5.4
23.	S	< 1	4	5.4
24.	S	< 1	24	7.2
25.	S	< 1	28	7.3
26.	S	< 1	20	7.2
27.	S	< 1	24	7.3

S = Surface
B = Bottom

Table - 3.19

Concentrations of Salinity, Alkalinity and p^H in Cochin Estuary and River Periyar - April, 1985 (Pre-monsoon)

Station No.	Salinity ppt		Alkalinity mg/L..	p^H
1.	S	22.5	105	8.2
	B	28.3	110	8.1
2.	S	22.2	115	8.1
	B	29.2	116	7.8
3.	S	22.4	125	7.8
	B	28.2	128	7.9
4.	S	20.2	98	8.1
	B	26.2	110	8.0
5.	S	19.4	92	7.8
	B	26.2	112	7.9
6.	S	15.2	88	8.1
	B	18.2	95	8.2
7.	S	18.5	85	8.2
	B	22.4	110	8.1
8.	S	19.4	90	8.1
	B	22.2	115	8.1
9.	S	22.2	105	8.2
	B	29.9	120	8.1
10.	S	22.6	108	8.1
	B	33.2	125	8.3
11.	S	25.9	105	7.9
	B	34.2	110	8.4
12.	S	25.2	126	7.9
	B	32.2	128	8.1

Table - 3.19

Station No.	Salinity ppt		Alkalinity mg/L..	pH
13.	S	26.1	125	7.9
	B	34.1	128	8.4
14.	S	28.4	110	7.9
	B	33.2	125	8.3
15.	S	22.2	108	8.1
	B	28.4	118	8.2
16.	S	18.2	98	7.9
	B	24.2	110	8.1
17.	S	18.5	98	7.9
	B	19.2	110	8.1
18.	S	21.4	110	7.8
	B	29.2	128	8.2
19.	S	< 1	4	5.3
20	S	< 1	6	5.2
21.	S	< 1	5	5.4
22.	S	< 1	4	5.2
23.	S	< 1	4	5.3
24.	S	< 1	28	7.3
25.	S	< 1	30	7.4
26.	S	< 1	35	7.7
27.	S	< 1	30	7.6

S = Surface
B = Bottom

Table - 3.20
Concentrations of dissolved metals in sea water µg/L. from world oceans.

Elements					Area & Author
Cu	Zn	Cd	Pb	Ni	
-	49.1	1.2	2.4	9.8	Eastern Irish Sea - Preston, et al., 1972
0.5 - 1.0	2.0 - 4.0	0.023	-	-	Southern Bight of North Sea - Dutton et al, 1973
6.0	-	-	11.5	5.5	German Bight - Schmidt, 1976
13 - 16	2.9 - 29.7	-	-	-	Laccadive Sea - Sujatha & Caroline, 1979
5.0	50.1	-	-	-	Gironde Estuary - Etcheber, 1979
10.0	150.0	-	-	-	River Rhine - "
5.0	38.0	-	-	-	Scheldt - "
0.26	0.16	0.023	-	-	Western Atlantic Shelf Waters - Bruland & Franks, 1981
0.22 - 0.3	0.3 - 0.4	0.02 - 0.03	-	-	North Sea - Dginker & Nolting, 1982
1.6	27.0	0.39	1.6	-	Puget Sound - Paulson & Freely, 1985

TABLE - 3.21

Correlation-regression relationship of dissolved and particulate toxic metals with salinity.

Copper					
Dissolved Cu	= -0.032	Salinity PPT	+ 2.8	r = -0.60	July, 1985
Particulate Cu	= 8.44	"	+ 51.43	r = 0.91	"
Dissolved Cu	= -0.46	"	+ 21.64	r = -0.75	Nov., 1985
Particulate Cu	= 9.22	"	- 28.42	r = 0.99	"
Dissolved Cu	= -0.45	"	+ 29.69	r = -0.95	April, '86
Particulate Cu	= 12.50	"	-160.67	r = 0.94	"
Zinc					
Dissolved Zn	= -2.46	"	+148.88	r = -0.86	July, 1985
Particulate Zn	= 57.05	"	+102.39	r = 0.98	"
Dissolved Zn	= -3.86	"	+244.00	r = -0.84	Nov., 1985
Particulate Zn	=121.4	"	-1081.94	r = 0.99	"
Dissolved Zn	=-10.51	"	+ 538.72	r = -0.92	April, '86
Particulate Zn	=151.47	"	-1983.01	r = 0.98	"
Cadmium					
Dissolved Cd	= 0.01	"	+ 2.10	r = -0.86	July, 1985
Particulate Cd	= 1.82	"	+ 61.18	r = 0.94	"
Dissolved Cd	= -0.06	"	+ 3.98	r = -0.87	Nov., 1985
Particulate Cd	= 5.99	"	- 9.01	r = 0.98	"
Dissolved Cd	= -0.06	"	+ 4.94	r = -0.90	April, '86
Particulate Cd	= 5.62	"	- 13.78	r = 0.98	"
Lead					
Dissolved Pb	= -0.11	"	+ 10.47	r = -0.28	July, 1985
Particulate Pb	= 6.79	"	+ 34.15	r = 0.97	"
Dissolved Pb	= -0.31	"	+ 16.65	r = -0.87	Nov., 1985
Particulate Pb	= 7.37	"	- 17.46	r = 0.97	"
Dissolved Pb	= -0.13	"	+ 14.64	r = -0.66	April, '86
Particulate Pb	= 9.47	"	- 61.90	r = 0.99	"
Nickel					
Dissolved Ni	-0.006	"	+ 0.40	r = -0.28	July, 1985
Particulate Ni	= 1.01	"	+ 45.98	r = 0.88	"
Dissolved Ni	=-0.007	"	+ 0.63	r = 0.42	Nov., 1985
Particulate Ni	= 4.15	"	- 30.98	r = 0.94	"
Dissolved Ni	= 0.0005	"	+ 0.33	r = 0.07	April, '86
Particulate Ni	= 2.48	"	- 29.56	r = 0.95	"
Iron					
Particulate Fe	= 0.02	"	+ 3.11	r = 0.15	July 1985
Particulate Fe	= 0.04	"	+ 7.01	r = 0.94	Nov., 1985
Particulate Fe	= 0.0026	"	+ 9.54	r = 0.07	April, '8

Table - 3.22
Semi-diurnal variation of salinity, concentration of elements µg/L., alkalinity p^H particulate matter in Cochin harbour.

		Salinity PPT	Cu	Zn	Cd	Pb	Ni	Fe	Cr	Ag	Alka-linity mg/lit.	p^H	Parti-culate matter mg/lit.
06.00	S	16.9	15.4	99	0.99	10.1	0.46	0.42	0.31	0.10	65	7.30	22.0
	B	31.42	9.1	69	0.83	8.4	0.28	0.21	0.30	0.10	105	8.05	4.80
09.30	S	14.88	15.2	101	0.98	1012	0.42	0.43	0.40	0.10	62	7.25	20.10
	B	26.83	10.8	80	0.89	9.1	0.29	0.31	0.32	0.08	110	7.92	15.00
12.30	S	15.77	15.3	98	0.97	10.1	0.43	0.48	0.40	0.14	78	7.25	12.10
	B	32.29	8.1	68	0.83	8.2	0.21	0.21	0.32	0.10	125	8.15	4.80
16.00	S	28.59	10.2	78	0.86	9.1	0.27	0.29	0.32	0.10	95	7.62	13.20
	B	32.50	8.8	68	0.83	8.1	0.24	0.22	0.40	0.08	105	8.15	4.90
19.00	S	24.62	11.8	84	0.90	9.4	0.31	0.31	0.32	0.12	78	7.70	15.10
	B	32.29	8.6	68	0.82	8.5	0.21	0.24	0.31	0.10	115	8.15	4.80

S = Surface

B = Bottom

Table - 3.23
Percentage of reduction in the concentration of metals in water column consequent on salinity intrusion.

Period	Station	Cu	Zn	Cd	Pb	Ni	Fe	Cr
July, 1985 (Ouseph, 1992)	For entire Cochin harbour area.	21.40	32.25	14.28	16.98	25.0	25.0	25.0
July, 1987	Cochin Harbour diel variation studies	48.34	32.67	16.16	20.58	54.34	56.25	25.0

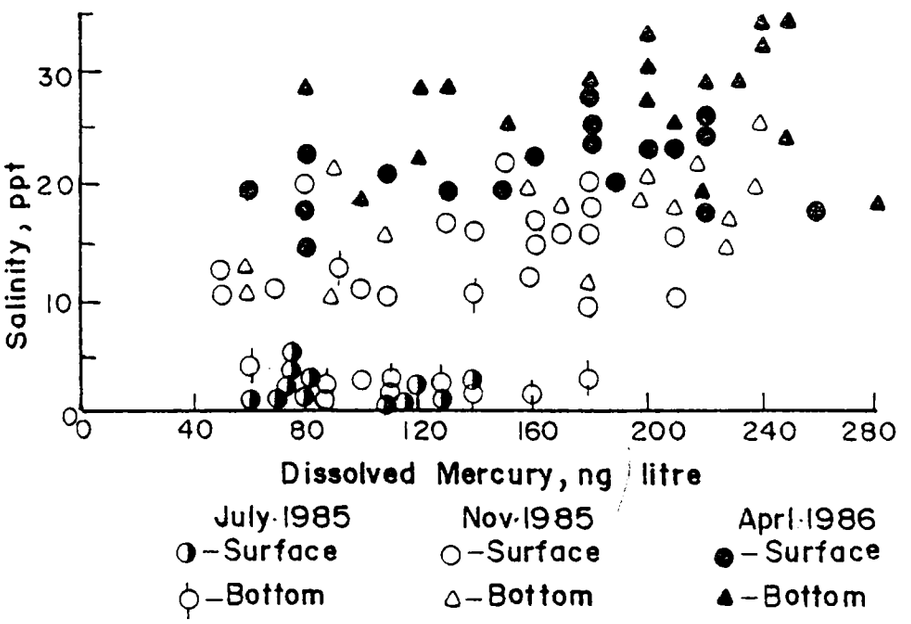


Fig. - 3.1
Relation between salinity and dissolved mercury.

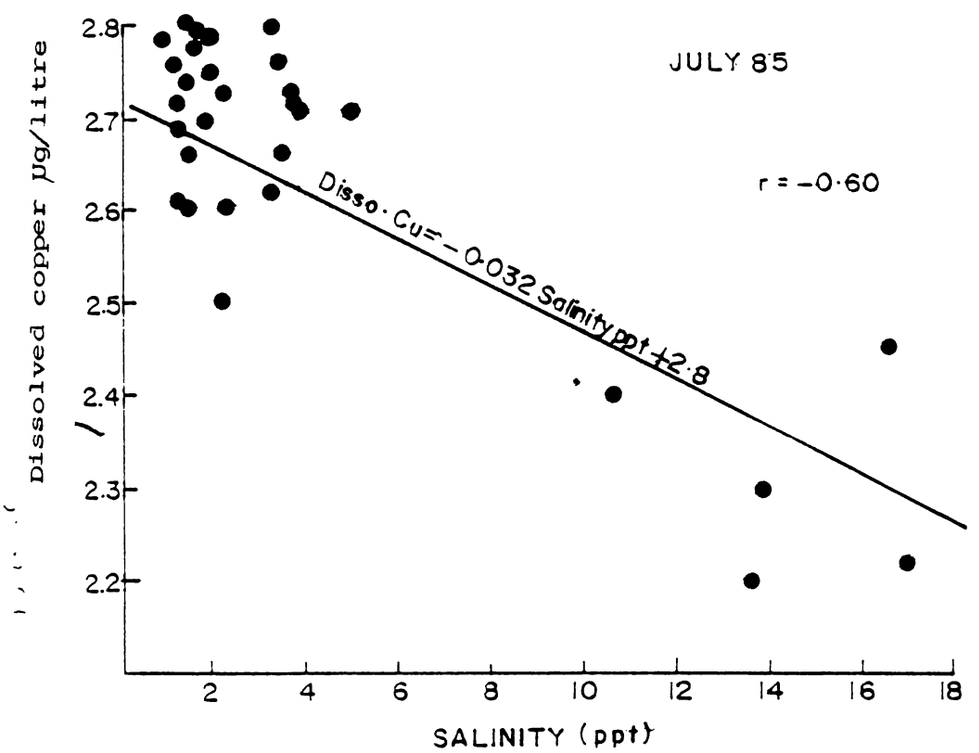


Fig. - 3.2
Relation between salinity and dissolved copper, July, 1985 (Monsoon).

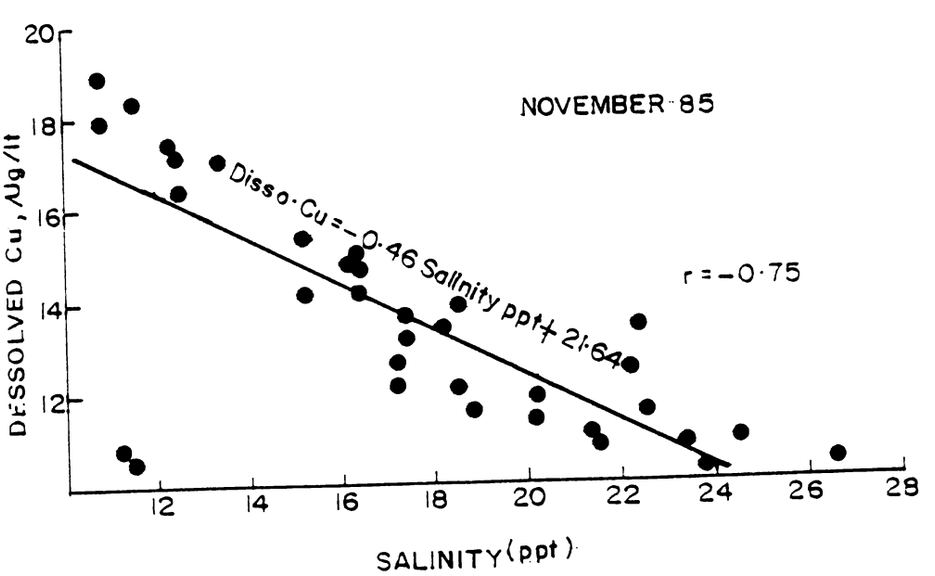


Fig. - 3.3
Relation between salinity and dissolved copper, November, 1985 (Post-monsoon).

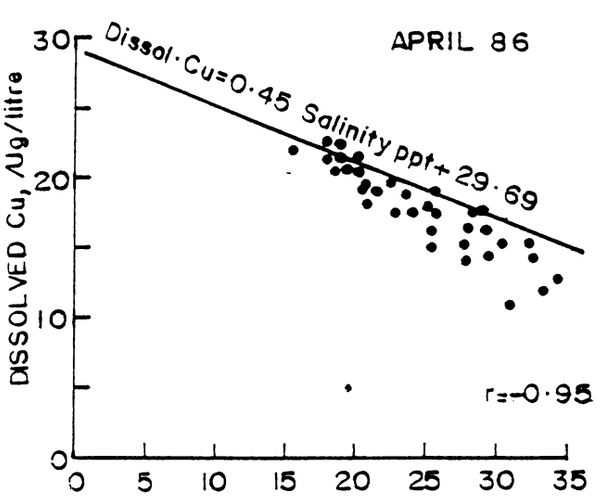


Fig. - 3.4
Relation between salinity and dissolved copper, April, 1986 (Pre-monsoon).

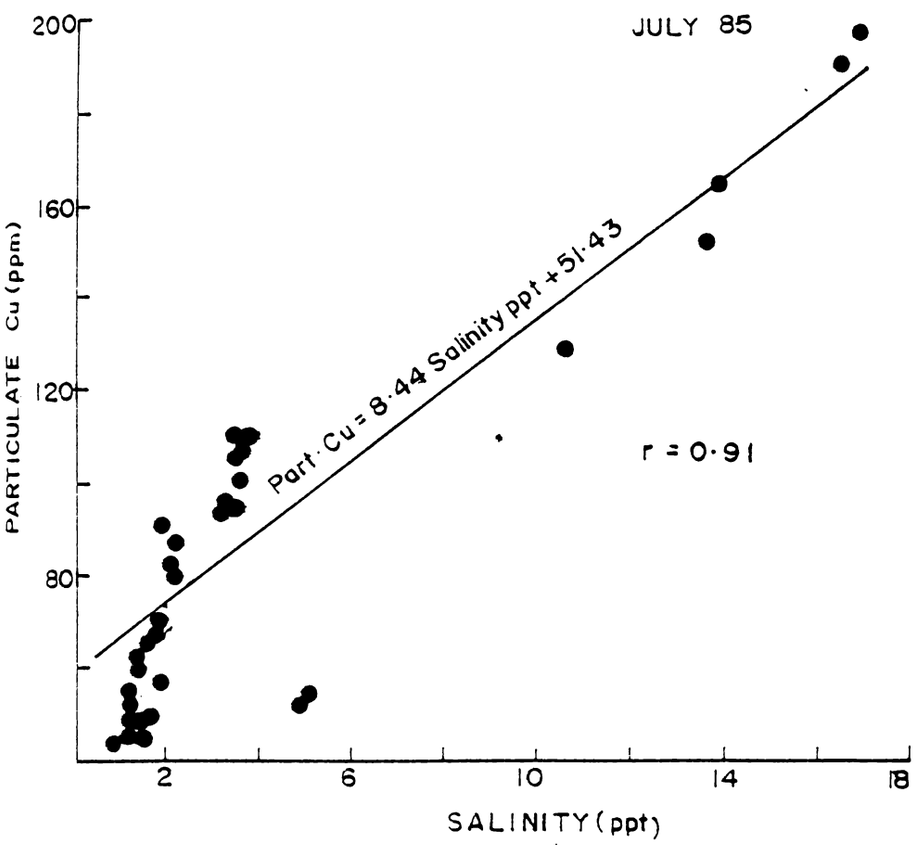


Fig. - 3.5
Relation between salinity and particulate copper, July, 1985 (Monsoon).

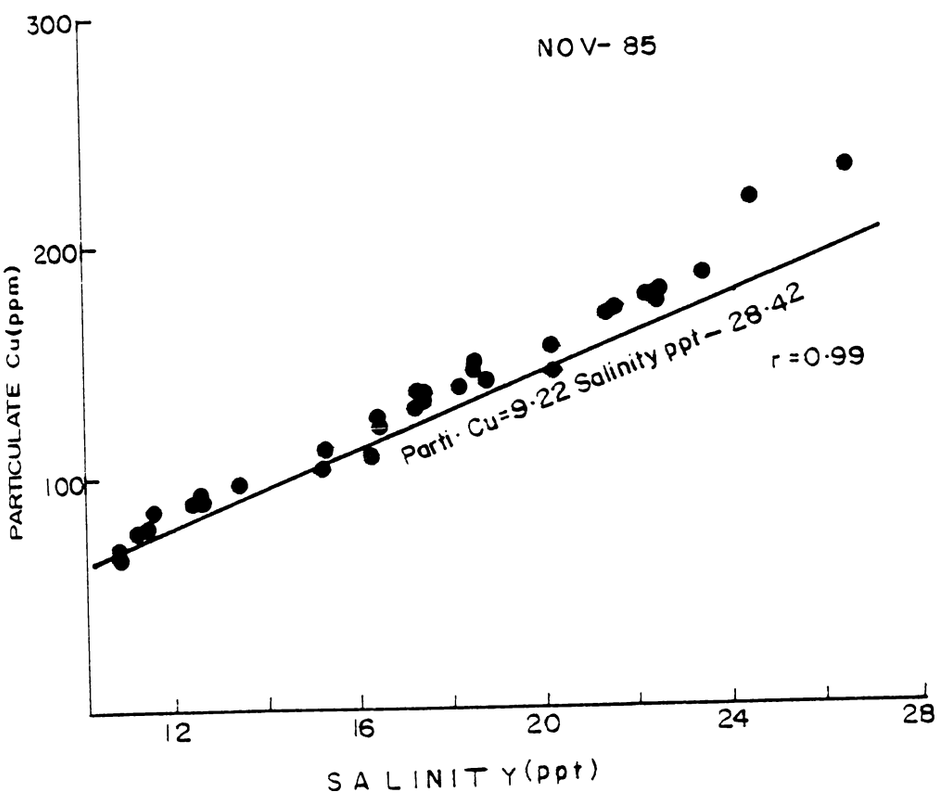


Fig. - 3.6
Relation between salinity and particulate copper, November, 1985 (Post-monsoon).

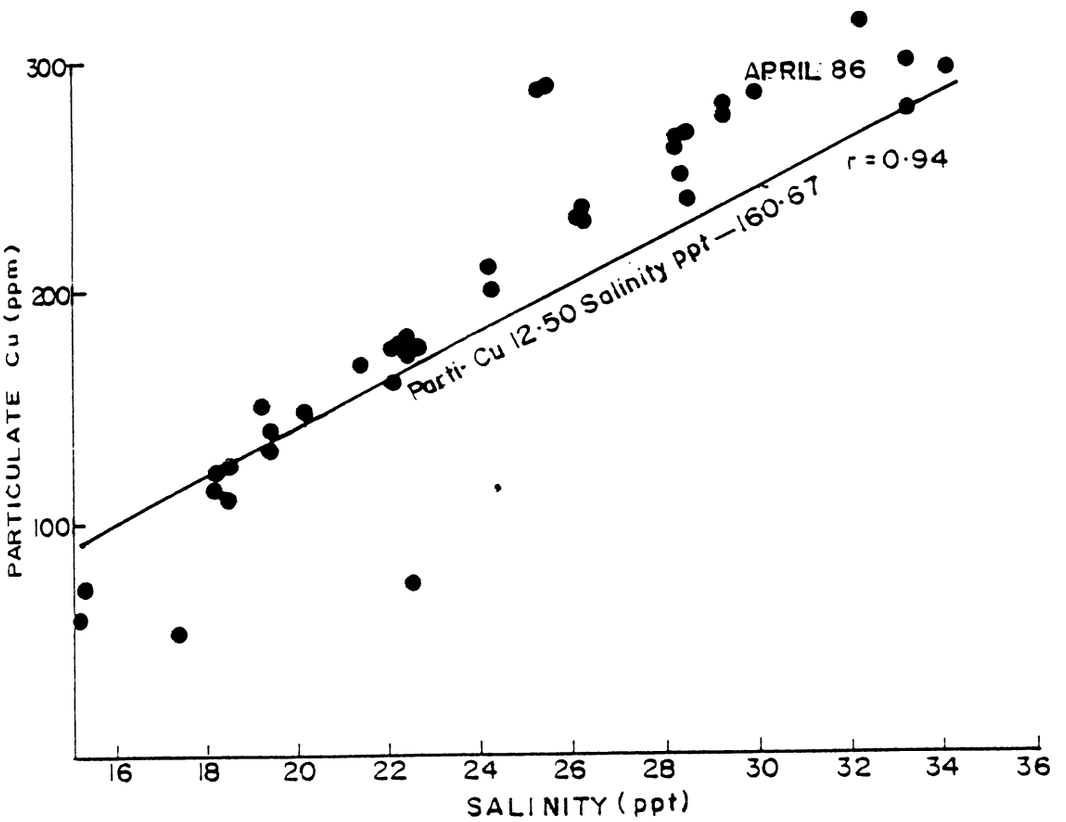


Fig. - 3.7
Relation between salinity and particulate copper, April, 1986 (Pre-monsoon).

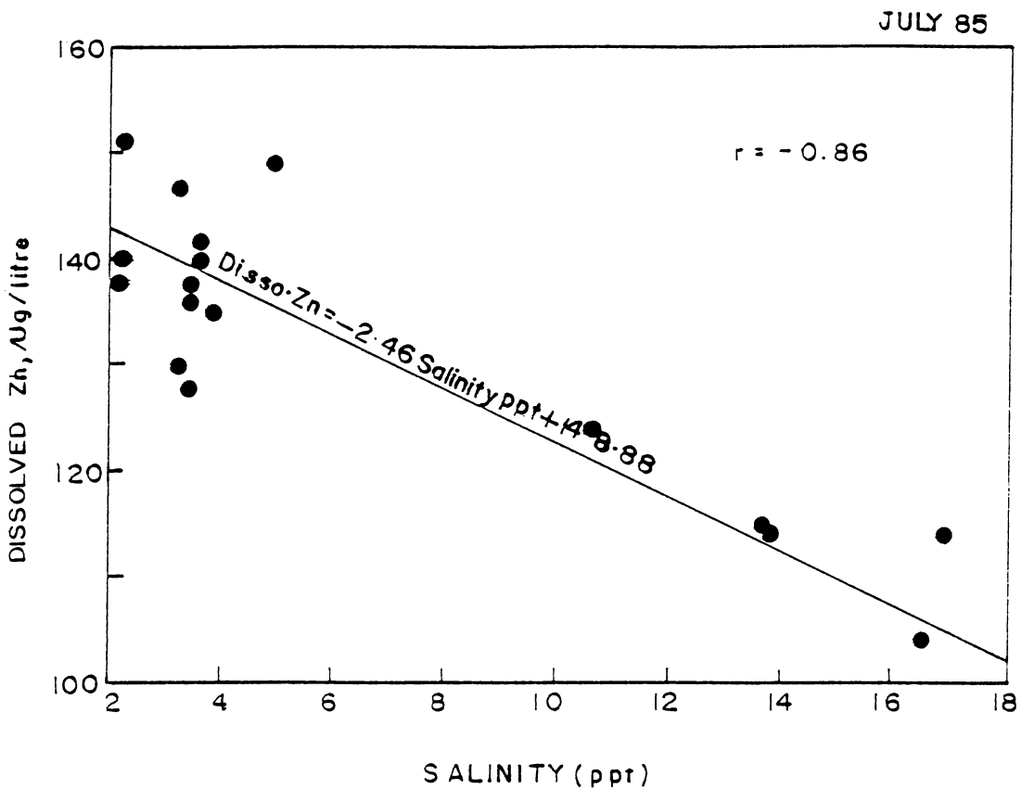


Fig. - 3.8
Relation between salinity and dissolved zinc, July, 1985 (Monsoon).

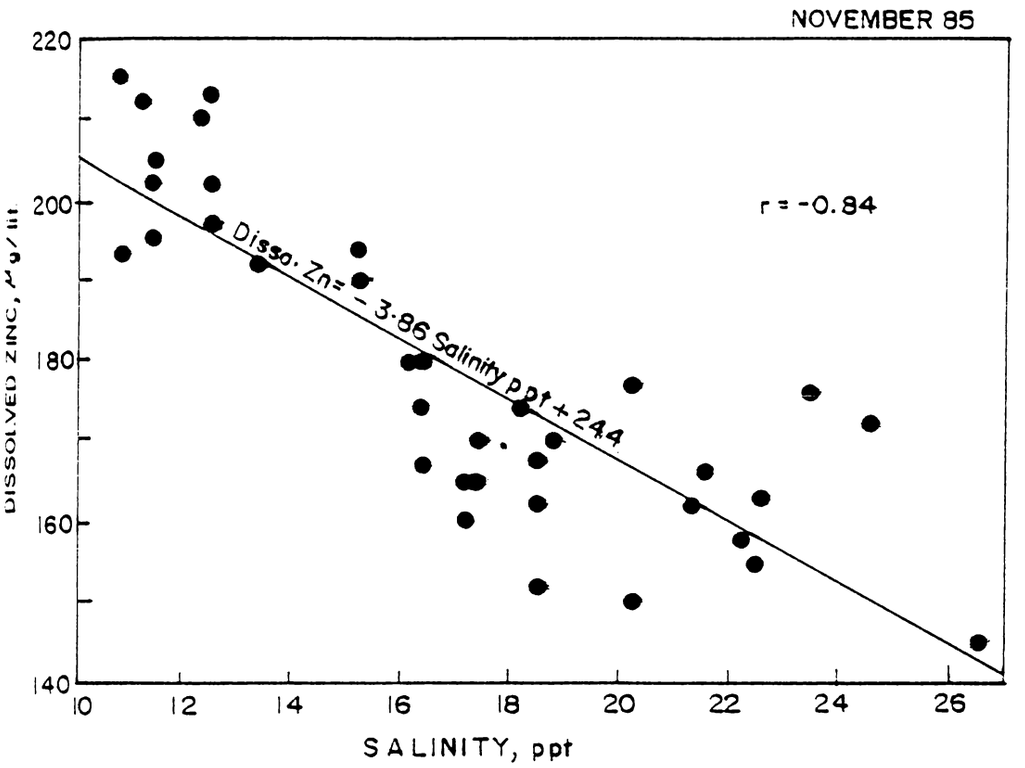
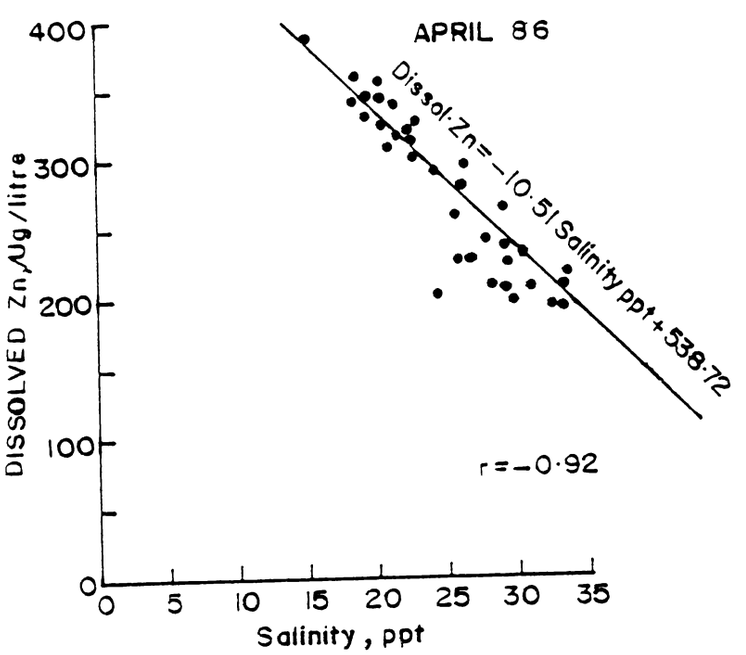


Fig. 3.10

Fig. - 3.9
Relation between salinity and dissolved zinc,
November, 1985.



F3. - 3.10

Relation between salinity and dissolved zinc, April, 1986 (Pre-monsoon).

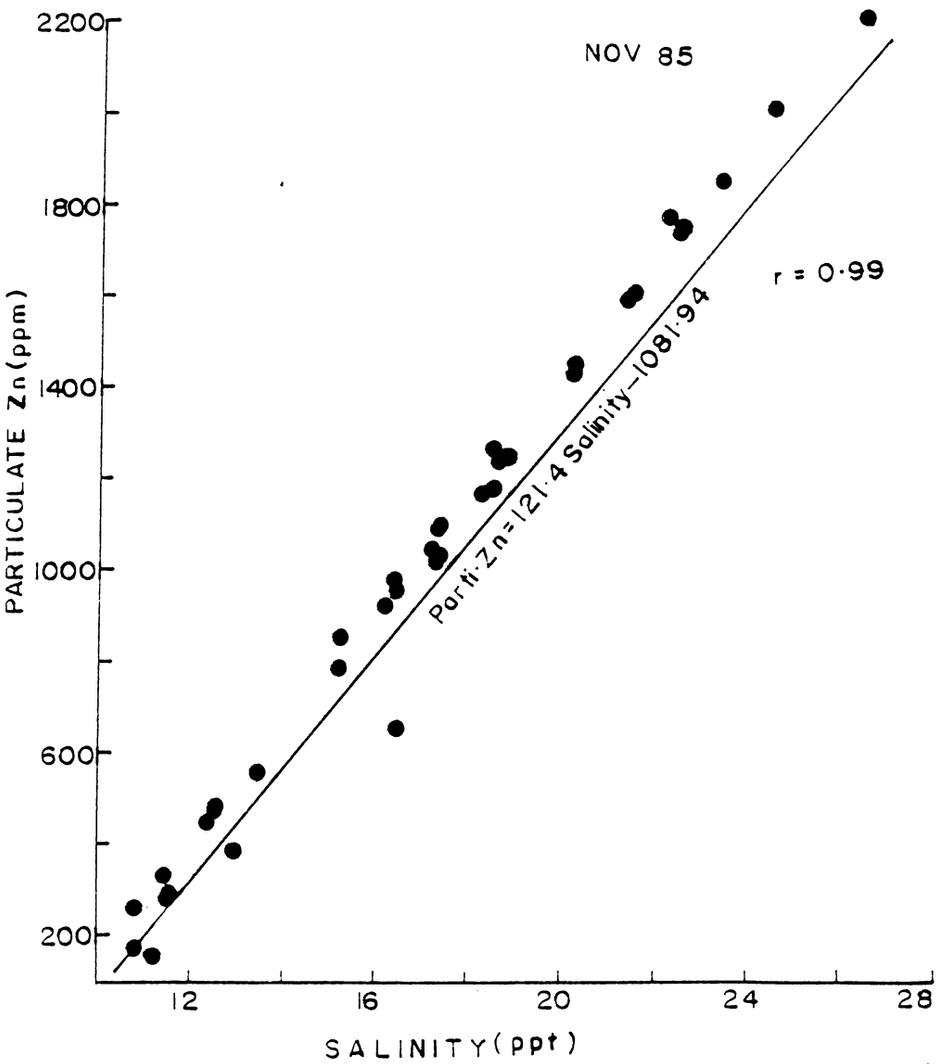


Fig. - 3.12
Relation between salinity and particulate zinc, November, 1985 (Post-monsoon).

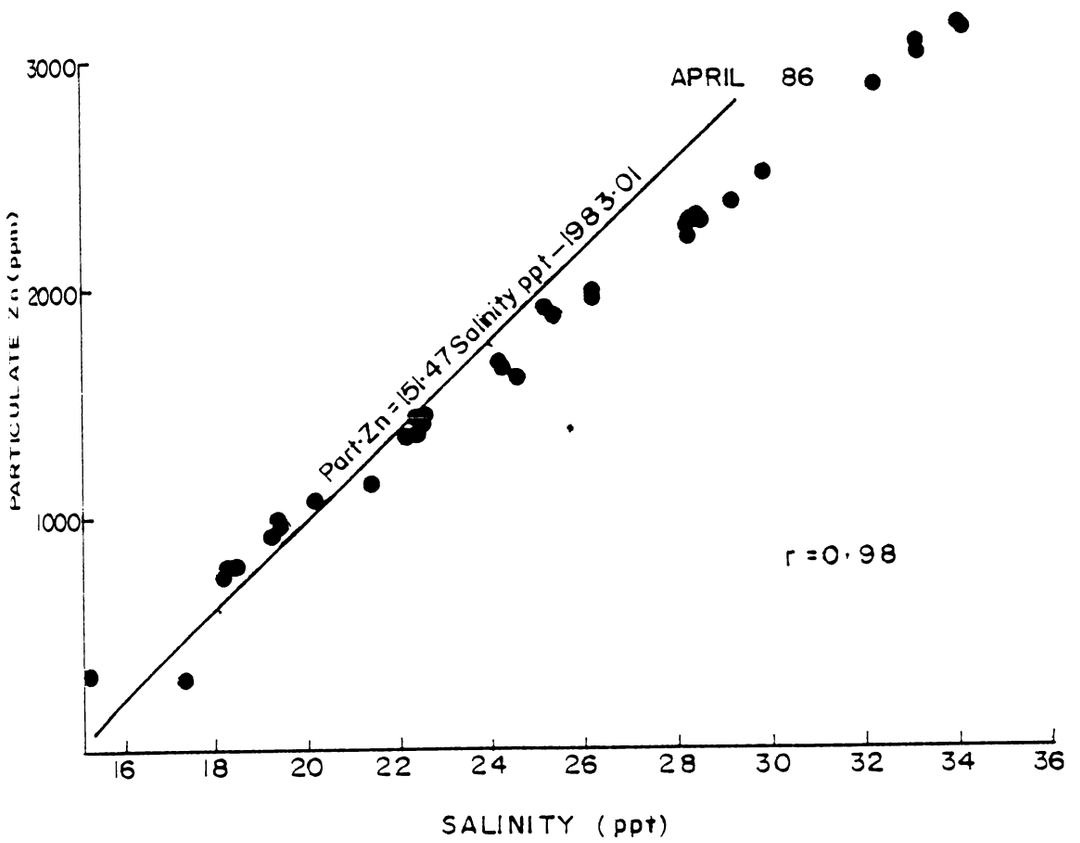


Fig. - 3.13
Relation between salinity and particulate zinc, April, 1986 (Pre-monsoon).

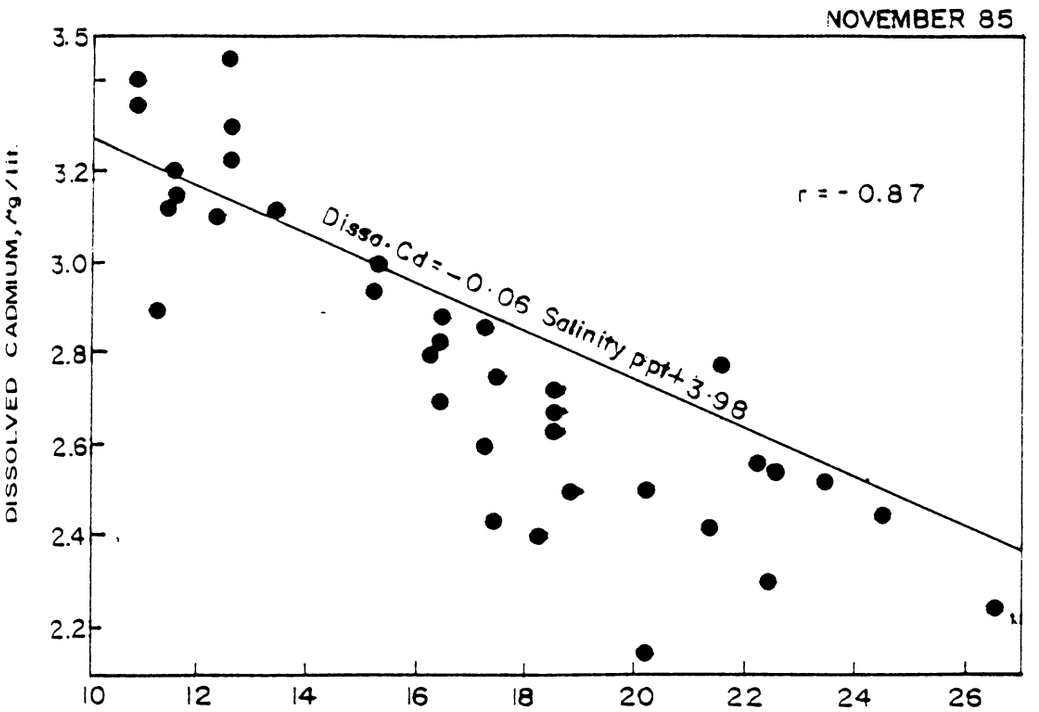


Fig. - 3.15

Relation between salinity and dissolved cadmium, November, 1985 (Post-monsoon).

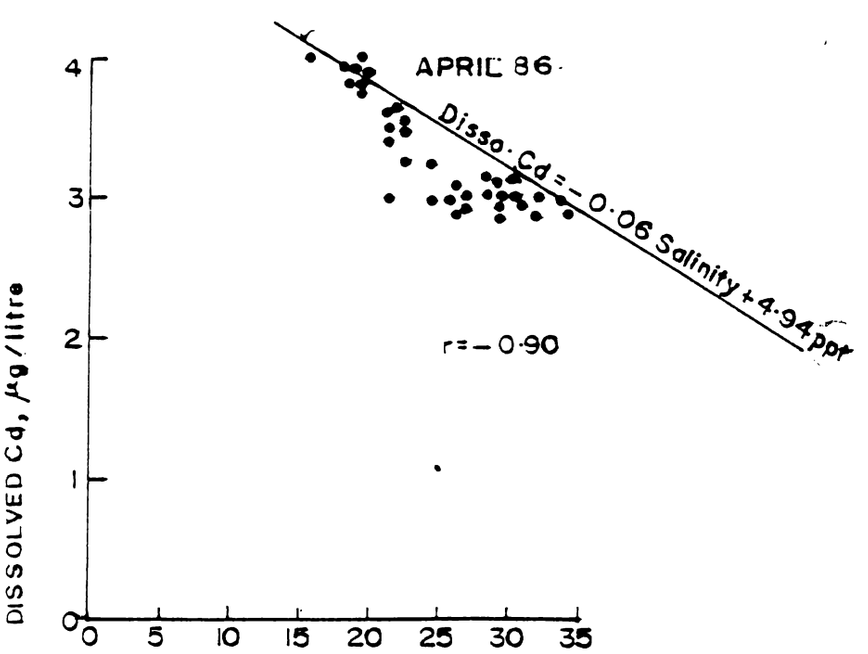
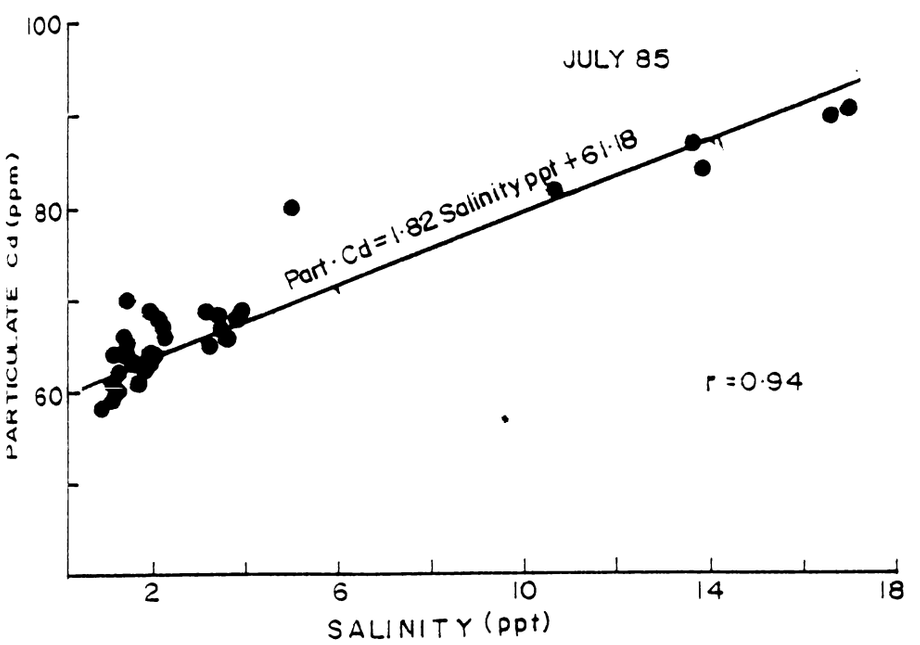


Fig. - 3.16

Relation between salinity and dissolved cadmium, April, 1986 (Pre-monsoon).



F3. - 3.17

Relation between salinity and particulate cadmium, July, 1985 (Monsoon).

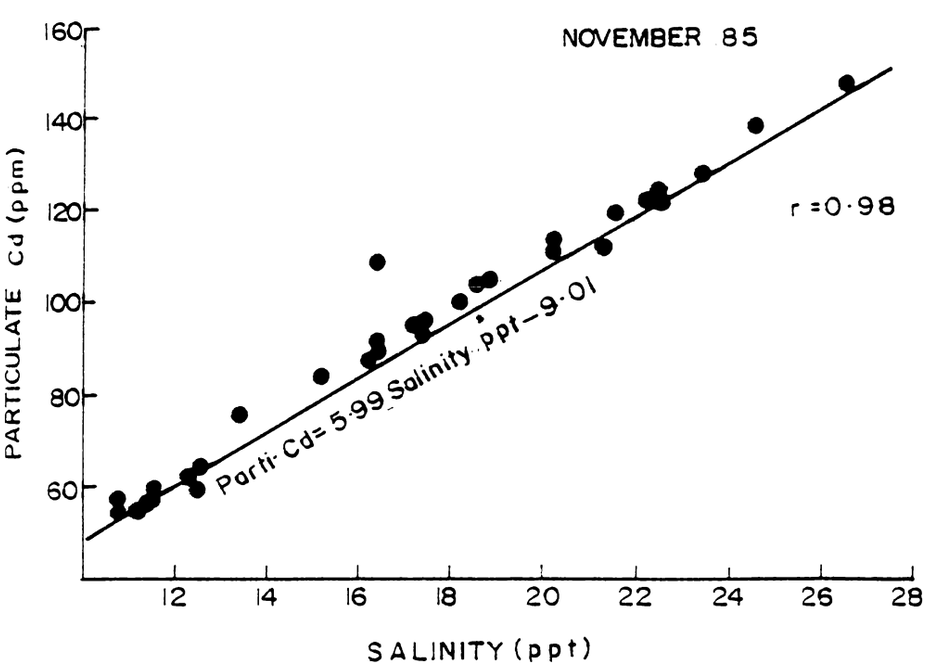


Fig. - 3.18
Relation between salinity and particulate cadmium, November, 1985 (Post-monsoon).

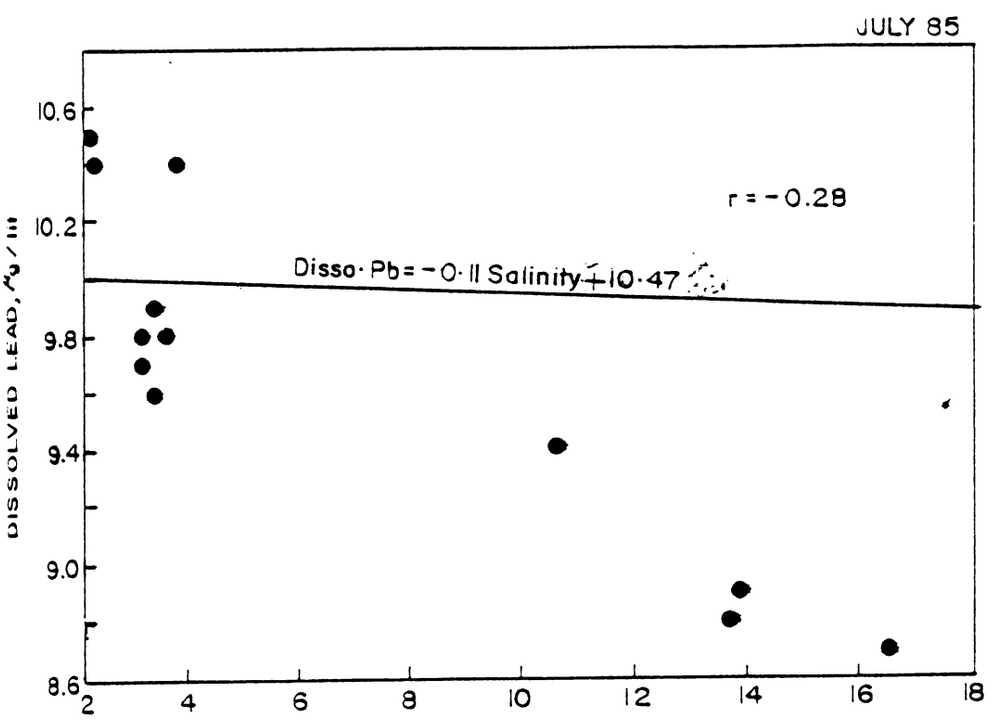


Fig. - 3.20
Relation between salinity and dissolved lead, July, 1985 (Monsoon).

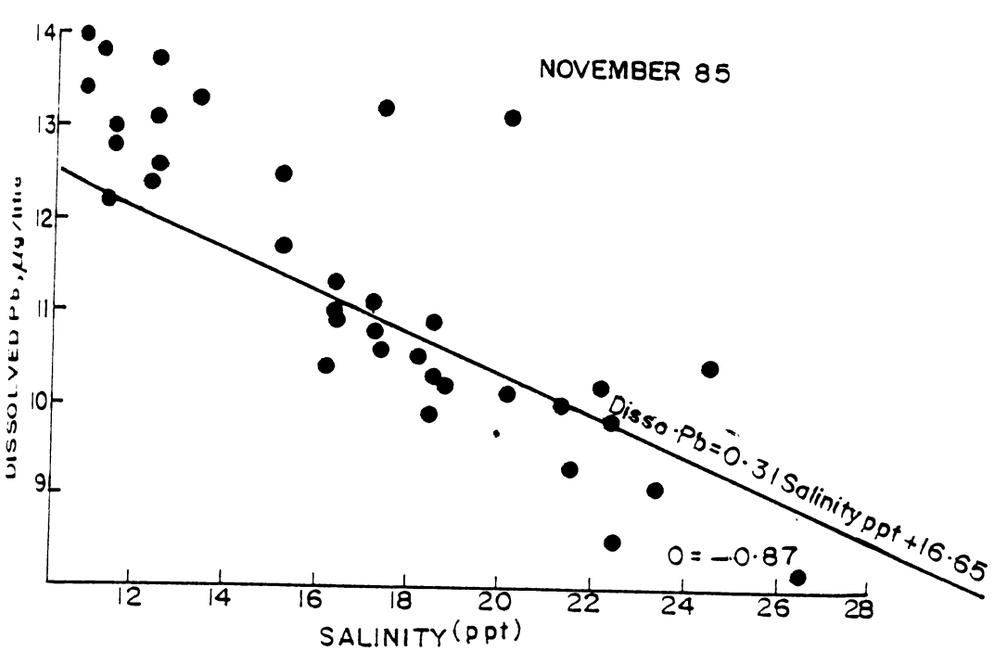


Fig. - 3.21
Relation between salinity and dissolved lead, November, 1985 (Post-monsoon).

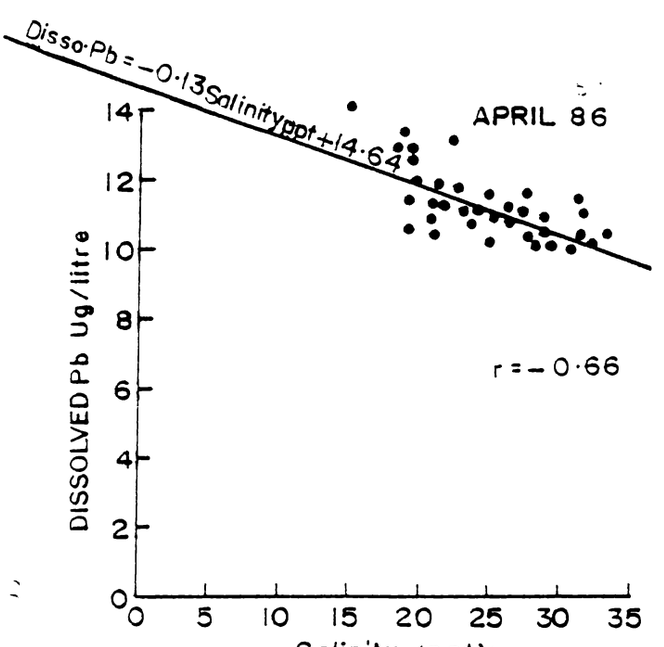


Fig. - 3.22

Relation between salinity and dissolved lead, April, 1986 (Pre-monsoon).

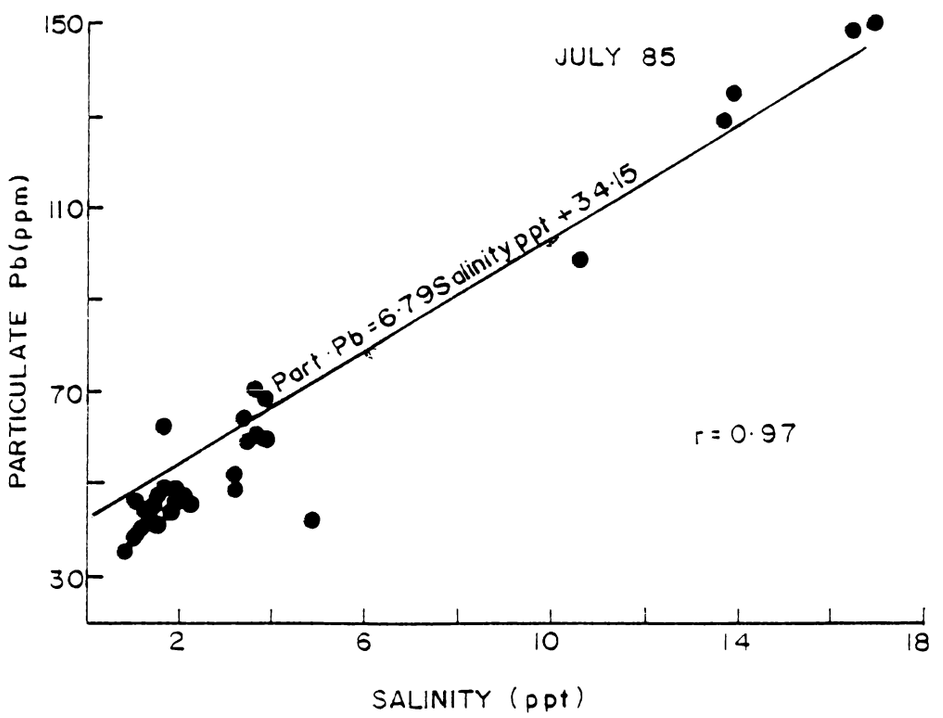


Fig. - 3.23
Relation between salinity and particulate lead, July, 1985 (Monsoon).

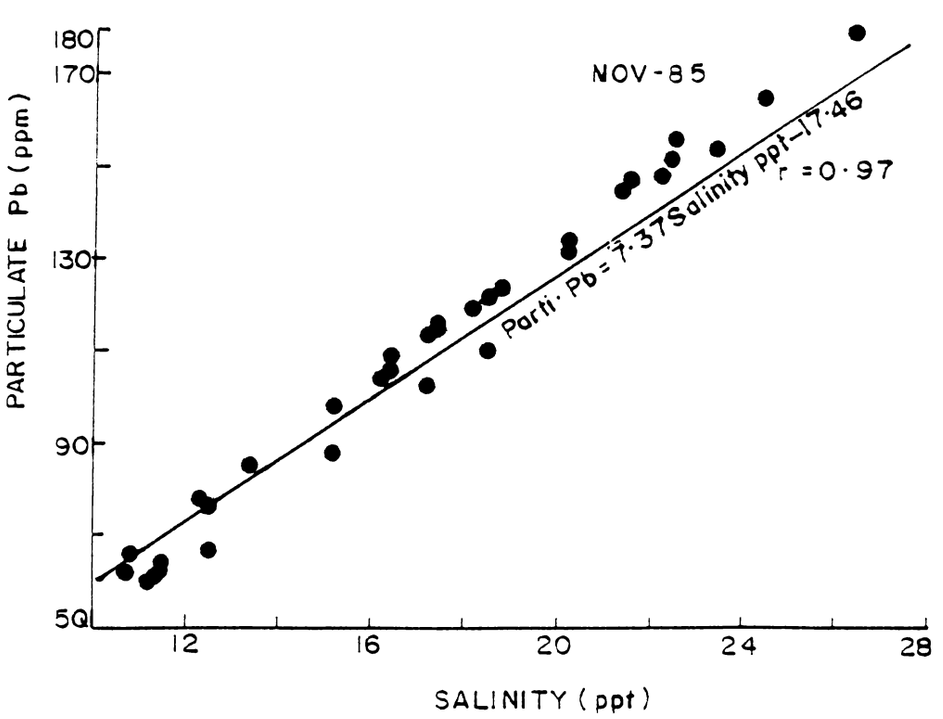


Fig. - 3.24
Relation between salinity and particulate lead November, 1985 (Post-monsoon).

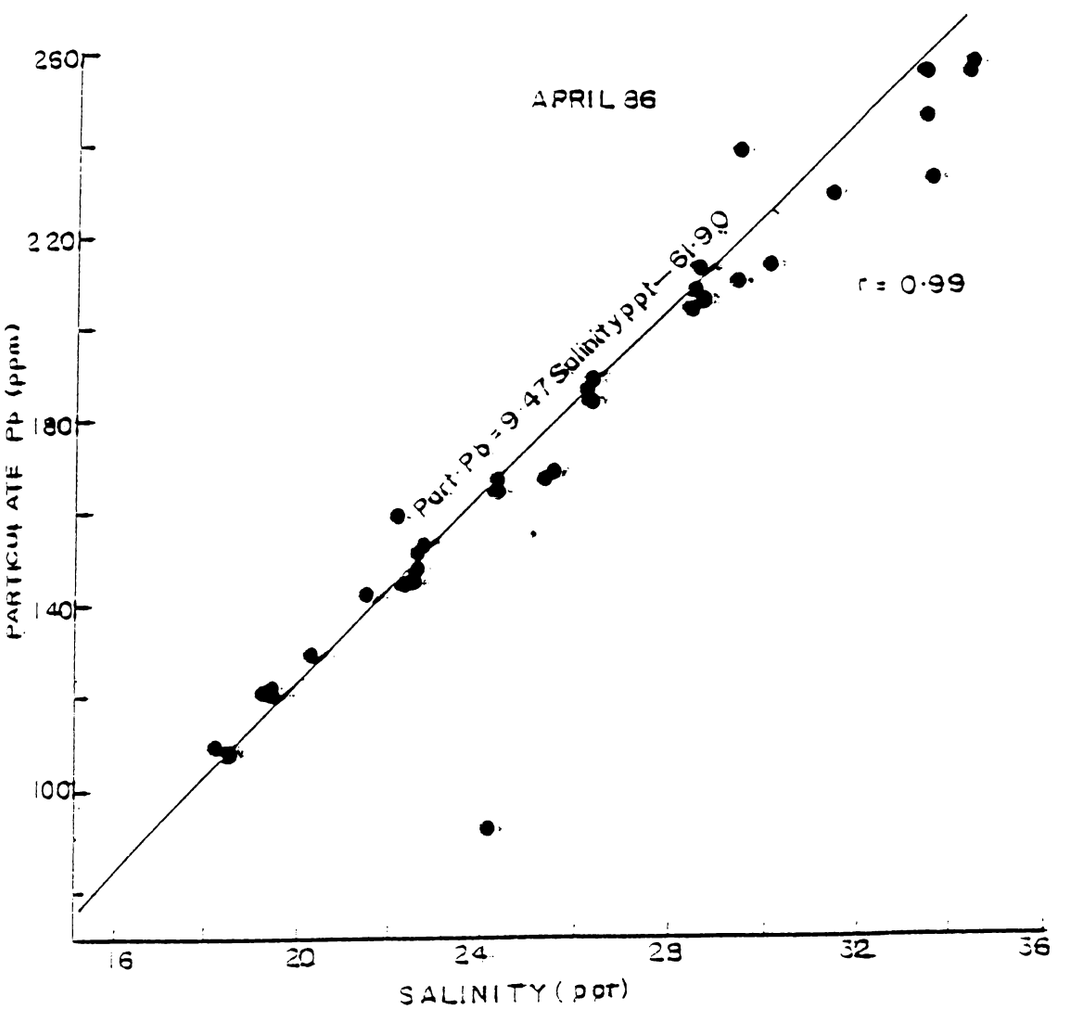


Fig. - 3.25
Relation between salinity and particulate lead, April, 1986 (Pre-monsoon).

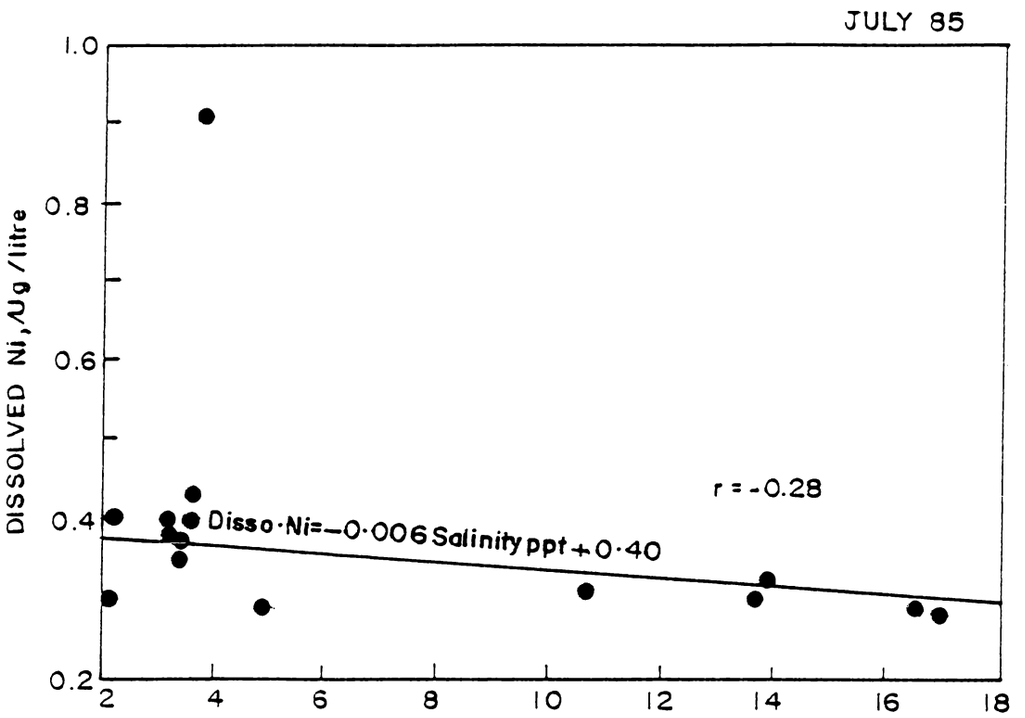


Fig. - 3.26

Relation between salinity and dissolved nickel July, 1985 (monsoon).

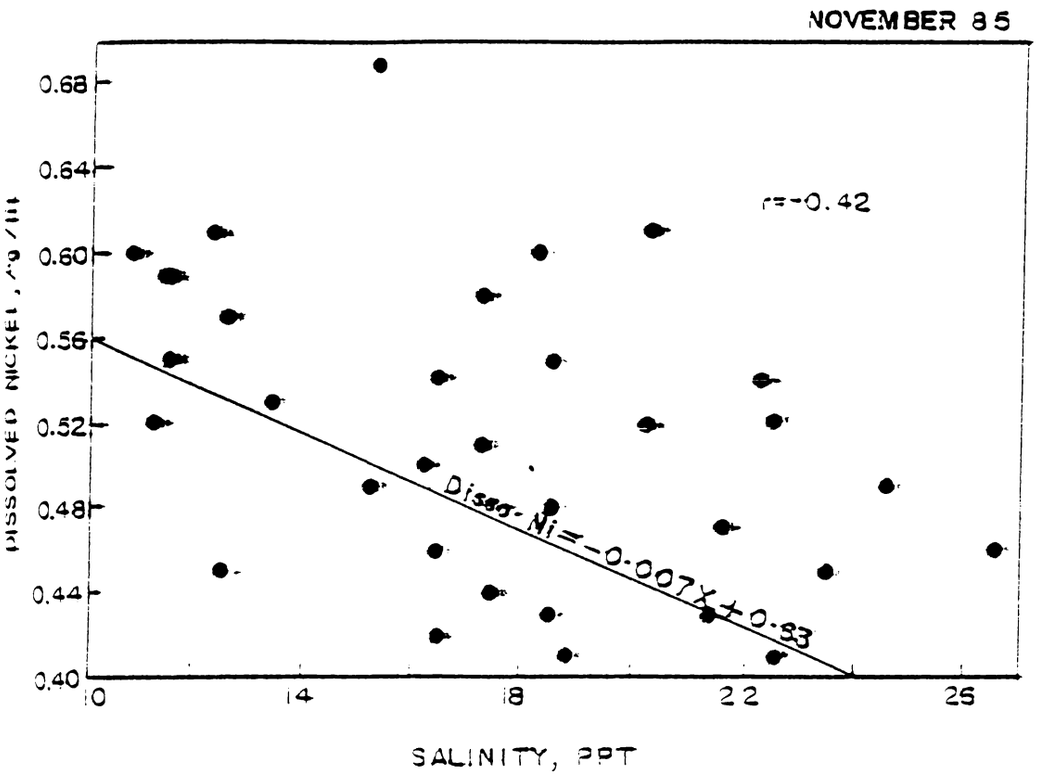


Fig. - 3.27
Relation between salinity and dissolved nickel
November, 1985 (Post-monsoon).

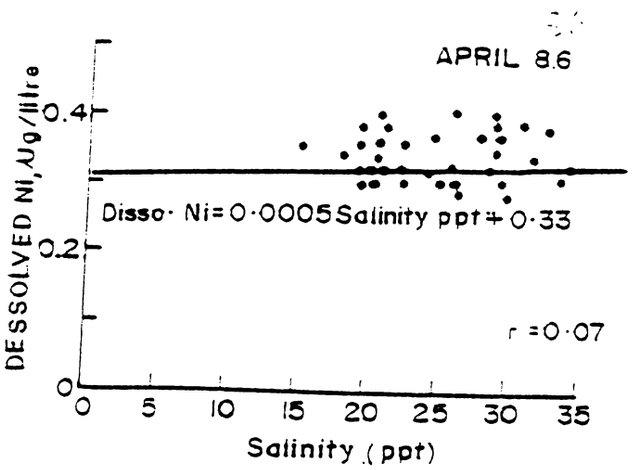


Fig. - 3.28

Relation between salinity and dissolved nickel April, 1986 (Pre-monsoon).

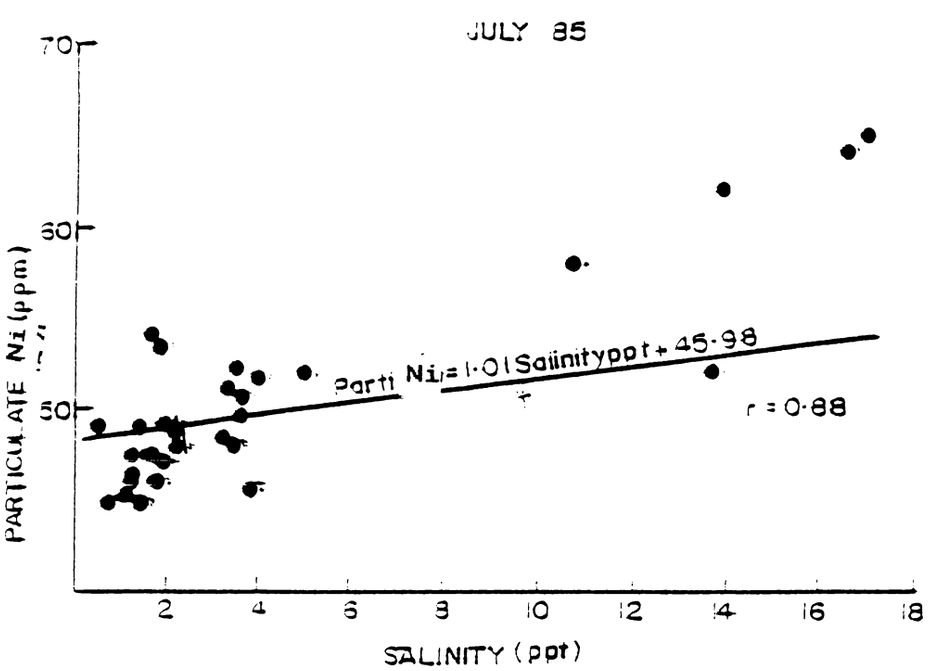


Fig. - 3.29
Relation between salinity and particulate nickel July, 1985 (Monsoon).

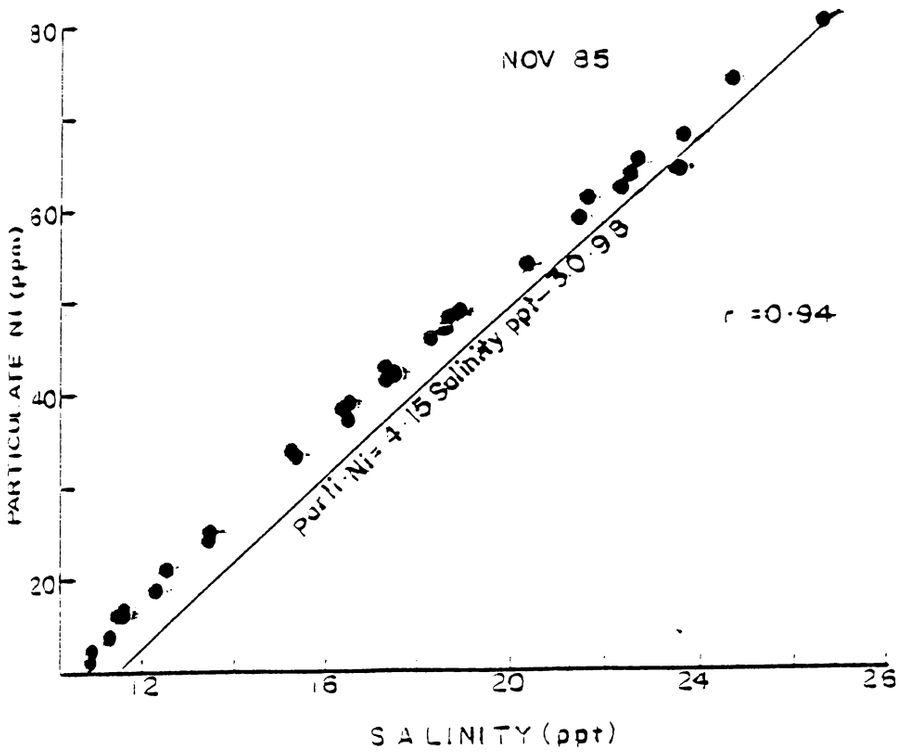


Fig. - 3.30
Relation between salinity and particulate nickel November, 1985 (Post-monsoon).

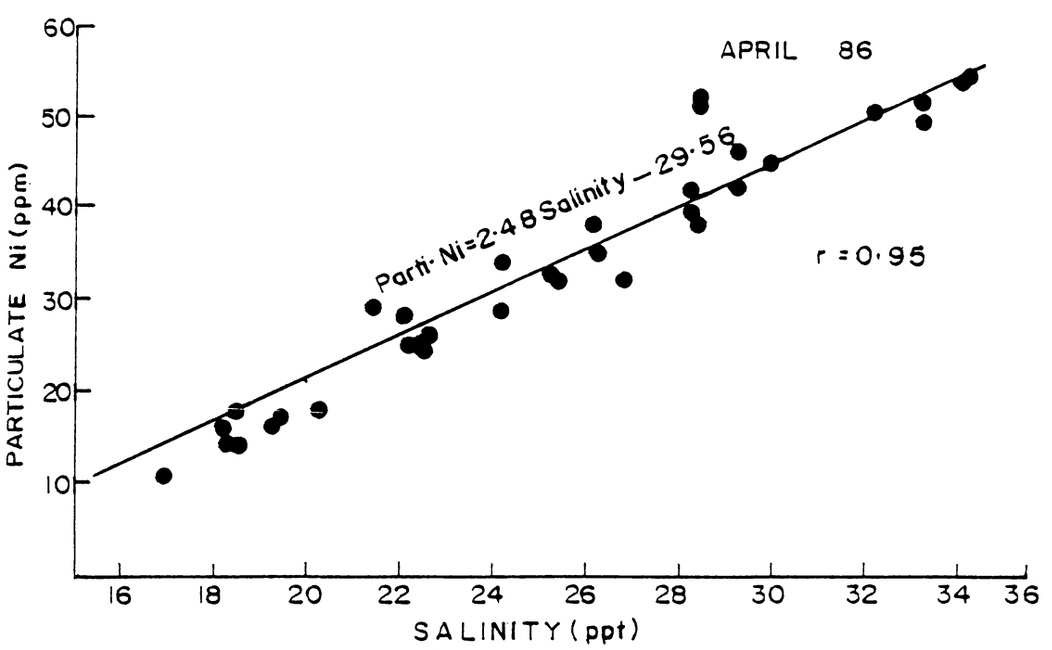


Fig. - 3.31
Relation between salinity and particulate nickel April, 1986 (Pre-monsoon).

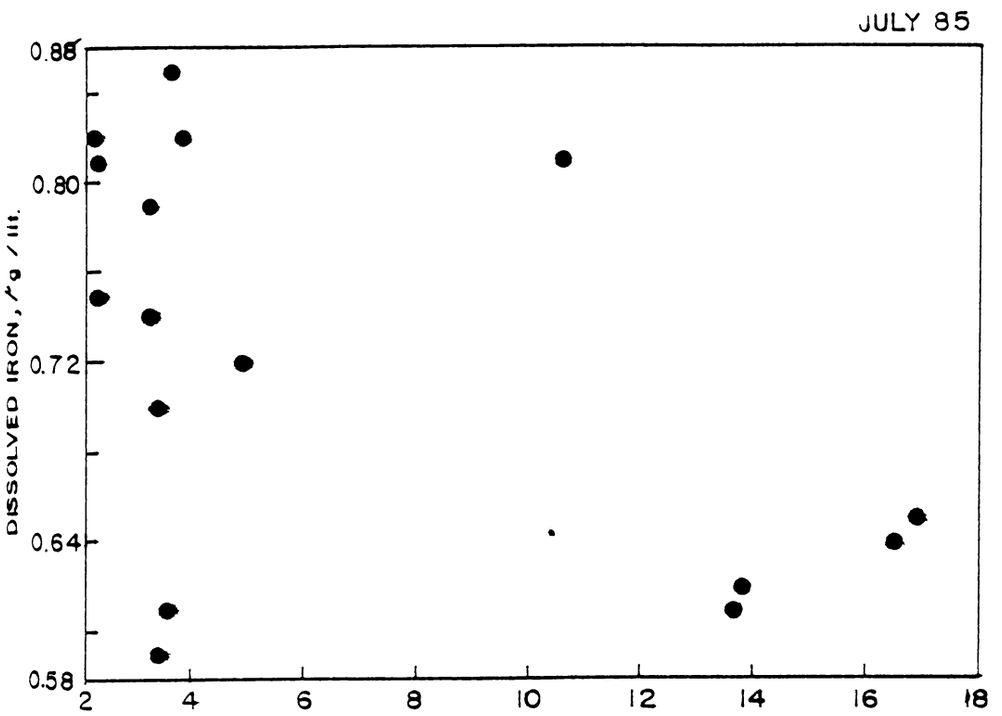


Fig. - 3.32
Relation between salinity and dissolved iron
July, 1985 (Monsoon).

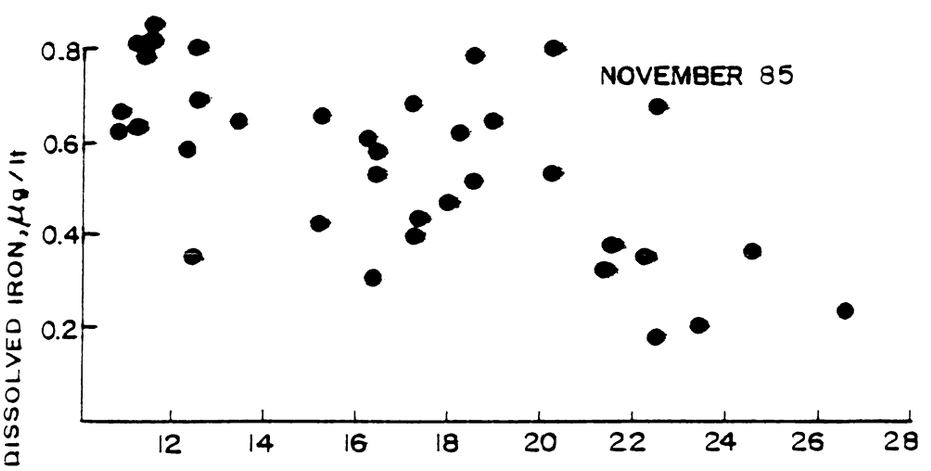


Fig. - 3.33

Relation between salinity and dissolved iron

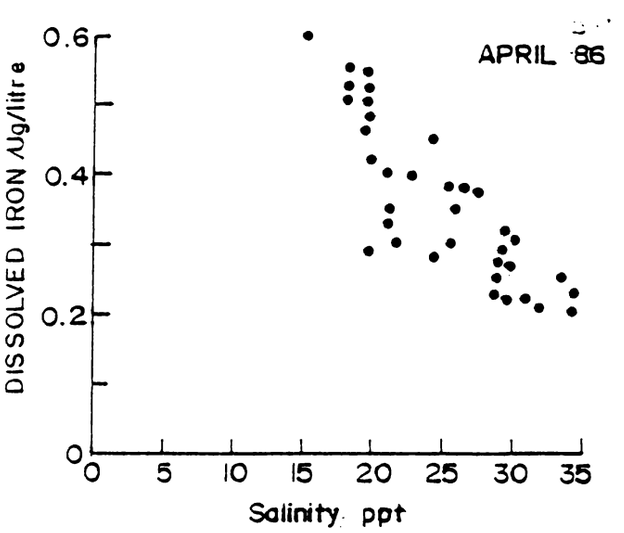


Fig. - 3.34

Relation between salinity and dissolved iron April,1986.

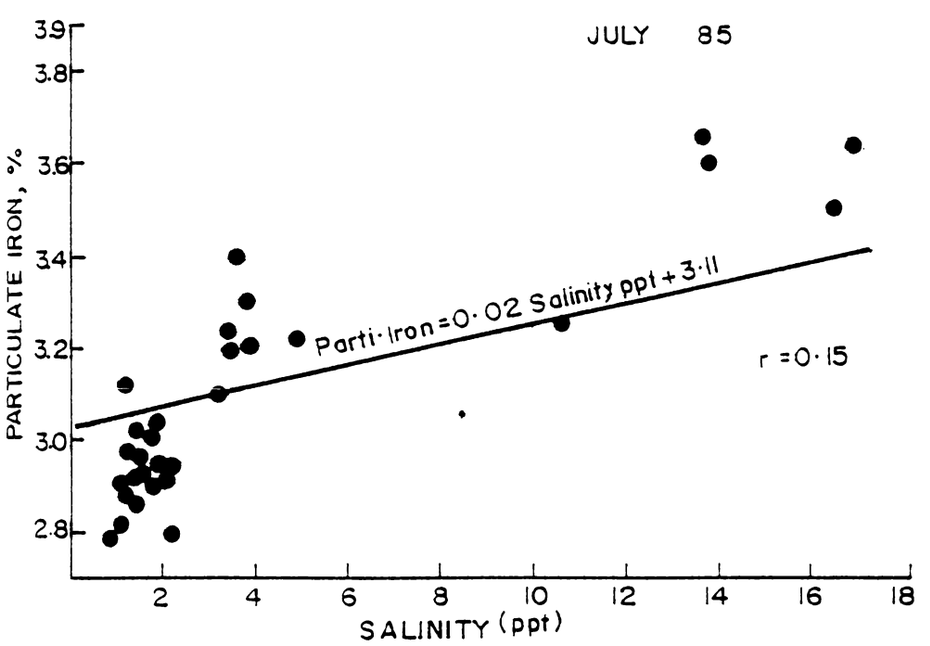


Fig. - 3.35
Relation between salinity and particulate iron July, 1985 (Monsoon).

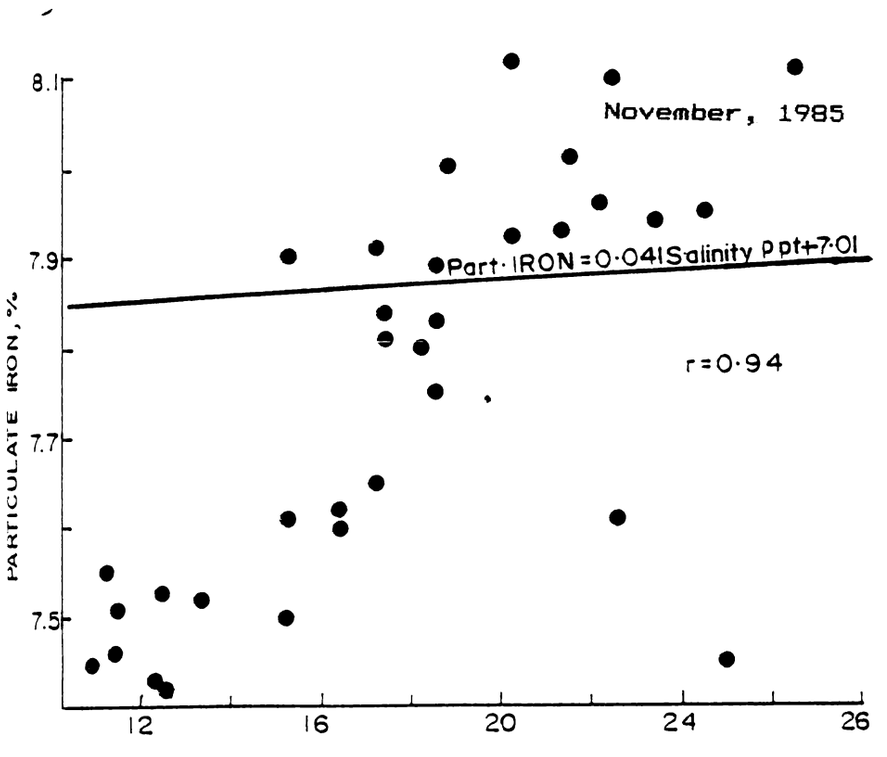


Fig. - 3.36
Relation between salinity and particulate iron November, 1985 (Post-monsoon).

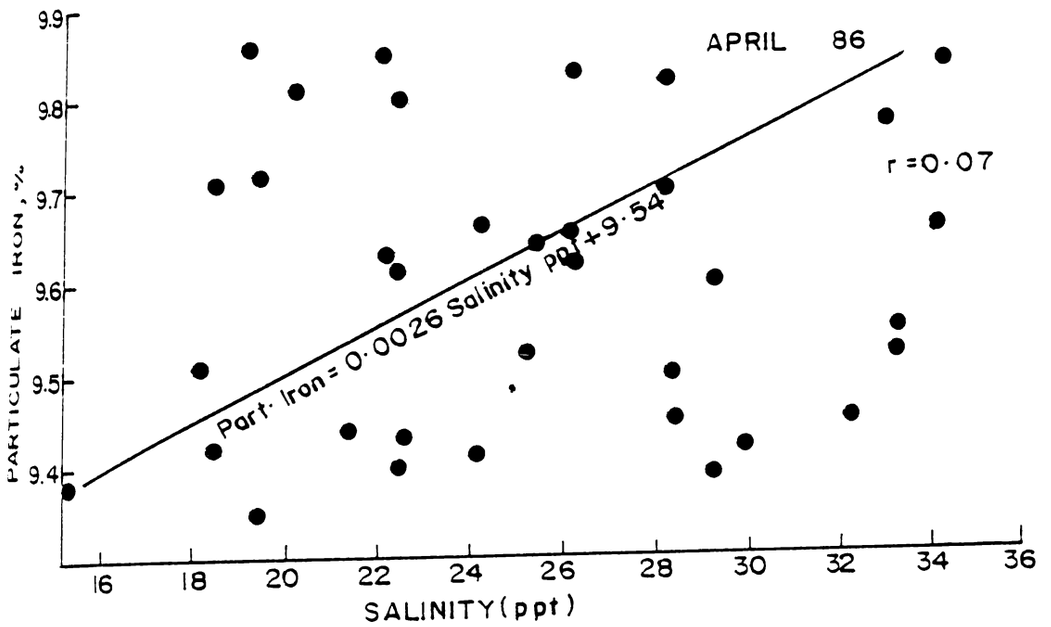


Fig. - 3.37

Relation between salinity and particulate iron, April, 1986 (pre-monsoon).

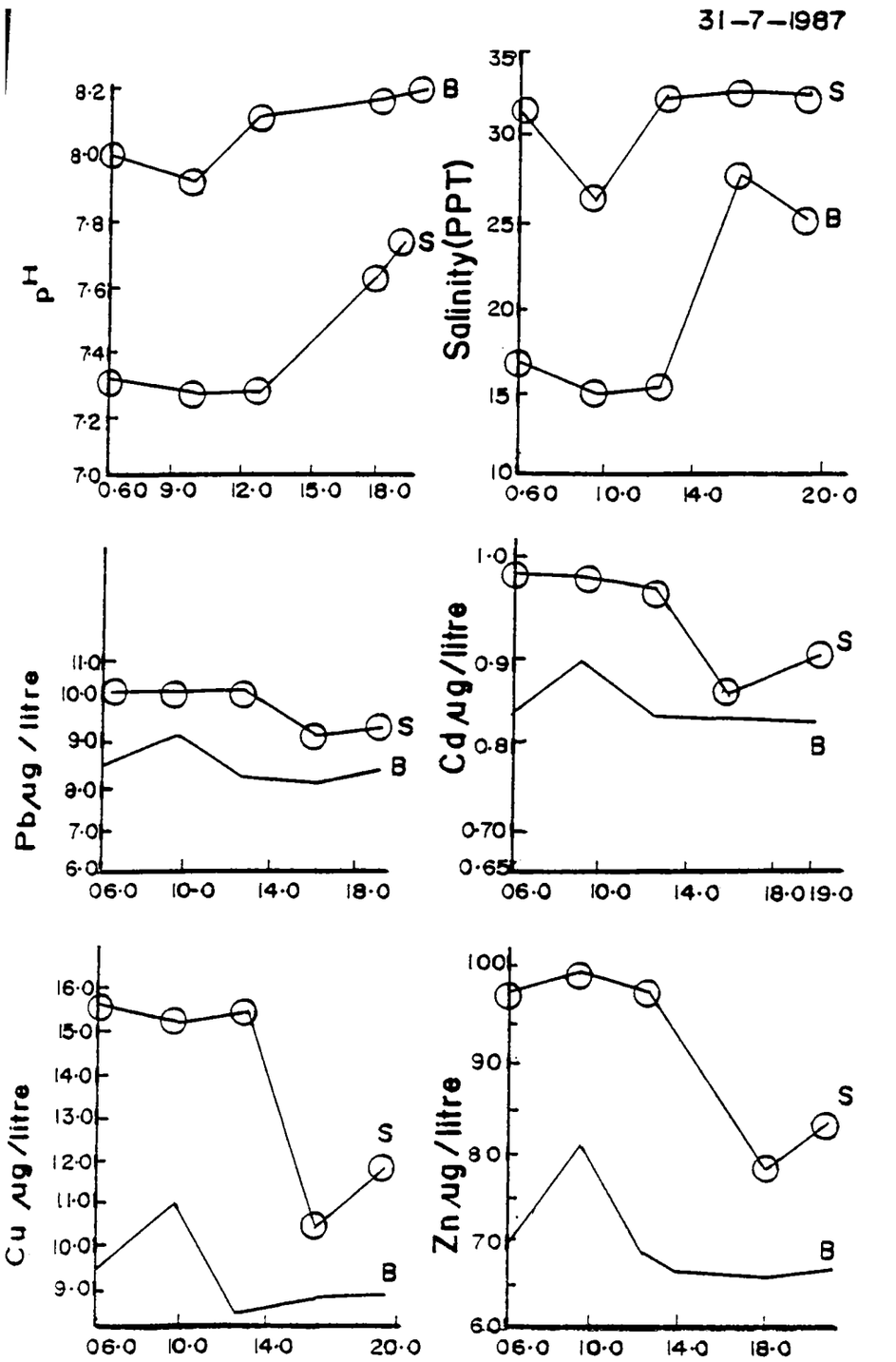


Fig. - 3.38

Distribution of dissolved Cu, Zn, Pb and Cd versus time in hours in Cochin estuary.

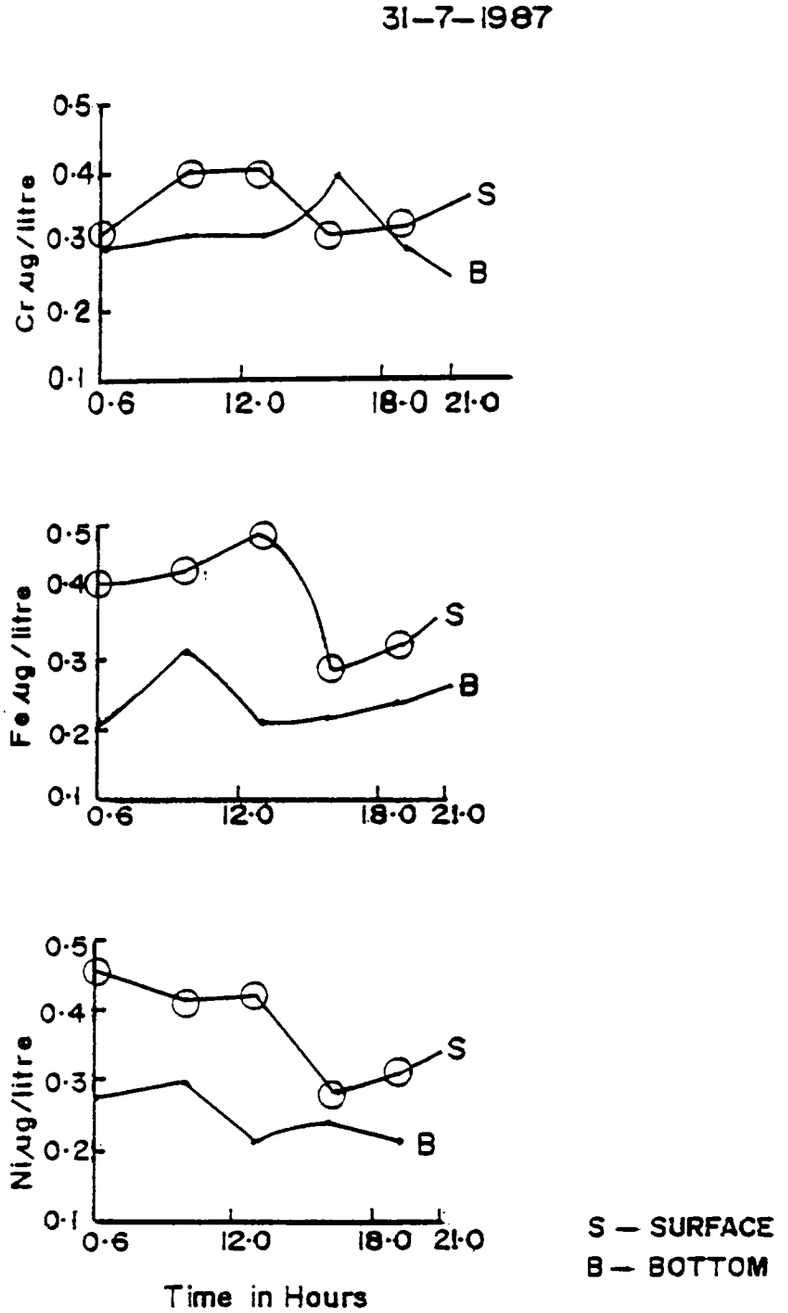


Fig. - 3.39
Distribution of dissolved Ni, Fe and Cr versus time in Cochin estuary.

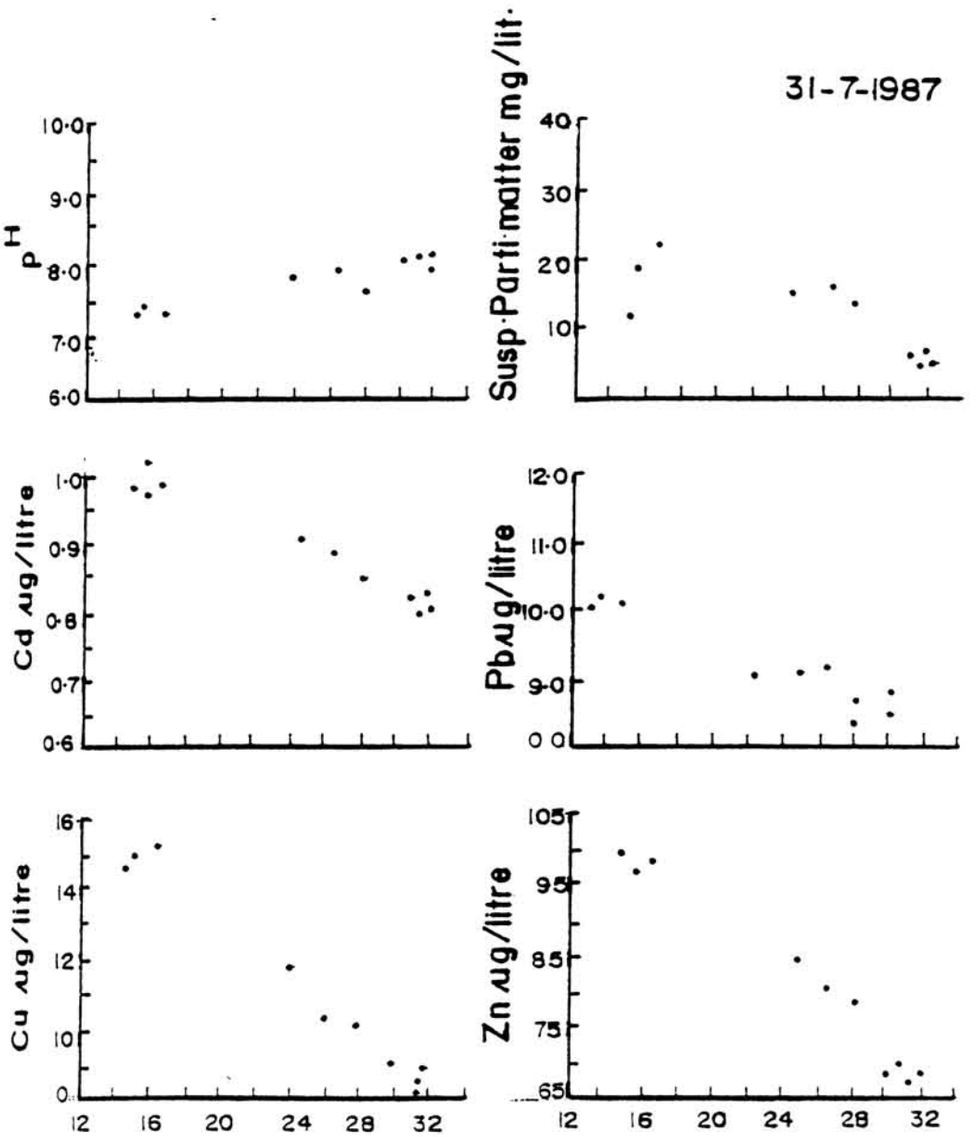


Fig. - 3.40

Relation between salinity and dissolved Cu, Zn, Cd, Pb, pH and suspended particulate matter in Cochin estuary.

31-7-1987

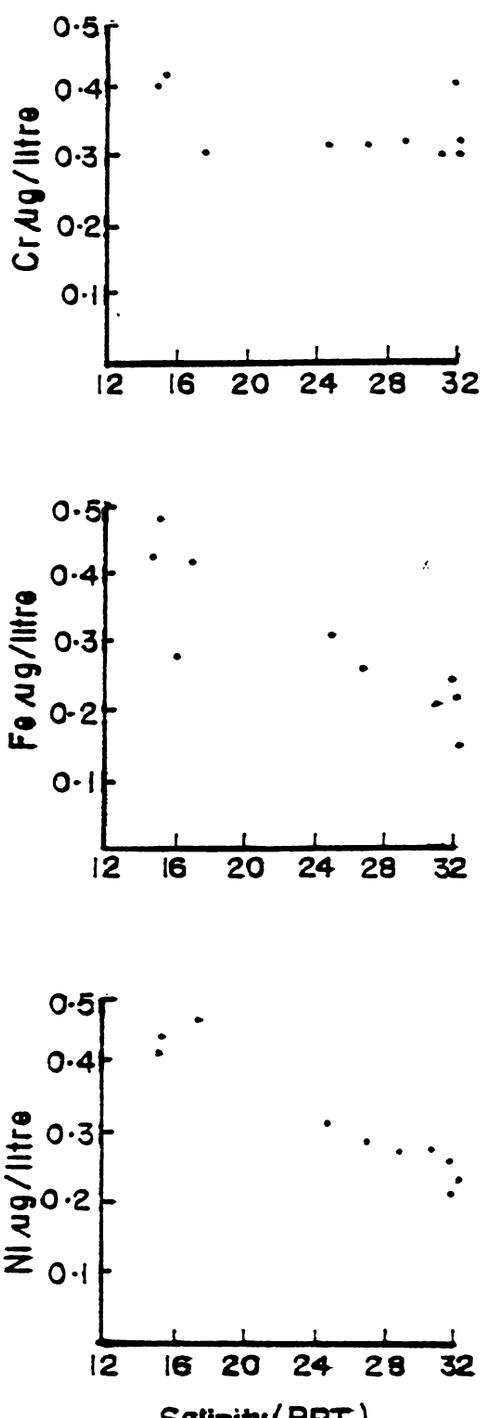


Fig. - 3.41
Relation between salinity and dissolved Ni, Fe and Cr in Cochin estuary.

CHAPTER - 4

RESULTS AND DISCUSSIONS PART - B

4.1. Metals Present In Sediments

Sediments are widely used as indicators of environmental contamination by trace metals in rivers lakes estuaries and the oceans. (Hirst, 1962; Chester and Hughes, 1967; Perkins et al., 1973; Helz et al., 1975; Loring, 1975; Kemp and Thomas, 1976; Bertine and Goldberg, 1977; Malo, 1977; Bewers and Yeast, 1977; Dixit and Witcomb, 1983) . The distribution of various environmental parameters in the Ashtamudi estuary have been reported by Balan, 1979; Nair et al., 1983, 1984, 1985 and 1987. The effect of titanium effluents on the biota was reported by Nair and Rajan, 1974; Vijayamohan et al. 1985; and Abdul Azis and Sheela, 1987. The importance of heavy metal studies has generated interest among ecologist to study the heavy metal concentrations in the bottom sediments of aquatic biotopes exposed to pollution and environmental degradation (Lu and Chen, 1977; Forstner and Pachineelam, 1980; Badri and Aston, 1981 and 1983; Rippey, 1982 and Talbot, 1983). Data on the concentration of heavy metals in sediments of the continental shelf along the west coast of India have

been reported by Rao & Setty 1976 and Murthy et al. 1978.

This chapter reports in detail the regional distribution and potential bio-availability of heavy metals in sediments at the effluent discharge point (Stations 19 - 23), upstream zone (Stations 24 - 27) and harbour area (Stations 1 - 18). The seasonal distribution in the concentrations of elements were shown in Tables 4.1 -4.3. The size distribution and major element concentrations were shown in Tables - 4.4 - 4.6. The relationship of trace metals with silt and major elements were presented in Figs.4.1 - 4.29.

4.1.1. Mercury

The sediment mercury concentrations in the Cochin estuary ranged from 0.15 to 1.10 ppm during monsoon, 0.1 - 0.95 ppm during post-monsoon 1985 and 0.11 - 0.98 ppm during pre-monsoon 1986 seasons. The concentrations in the upstream zone was constant for all the seasons which was 0.04 ppm. The concentrations at the effluent discharge point varied from 5.5 - 11.5 ppm during monsoon, 5.2 - 9.8 ppm during post-monsoon 1985 and 5.5 - 11.5 ppm during pre-monsoon 1986 seasons. The base line level of mercury was 0.08 ppm estimated based on a

90 cm core sample collected at station No.13. The core profile for total mercury was shown in Fig.4.1. The observed concentrations were 1.5 to 11.8 times higher in the Cochin estuary compared with the baseline levels, suggesting recent anthropogenic activity. The relationship between mercury with silt, iron, and organic carbon were shown in Figs. 4.2 - 4.4.

4.1.2. Copper

The levels of copper ranged from 40 - 160 ppm in the Cochin Harbour, 260 - 280 ppm at the effluents discharge point and 2 - 25 ppm in the upstream zone Tables 4.1 - 4.3. Seasonally the concentrations in the Cochin estuary were 40 - 160 ppm during monsoon, 48 - 145 ppm during post-monsoon 1985 and pre-monsoon 1986 seasons. The base line level of copper was found to be 40 ppm at station No.13 (Table - 4.7 and Fig. 4.5). Hence the reported concentrations were 1 - 4 times higher in the Cochin estuary, and 6.5 - 7 times higher at the effluent discharge point in comparison with the baseline levels. The size distribution and major element concentrations were shown in Tables 4.4 - 4.6. The results showed that higher concentrations of copper were present at the effluent discharge point.

The relation between total copper and silt, iron organic carbon and aluminium were shown in Figs. 4.6 - 4.9.

4.1.3. Zinc

The observed concentrations ranged from 60 to 380 ppm in the Cochin Harbour, 420-780 ppm near the effluent discharge point and 40-60 ppm in the upstream zone (Tables 4.1 - 4.3.). The baseline level of Zn at station No.13 (Fig.4.10) was 55 ppm. The baseline levels of zinc average for the Newark Bay sediments was found to be 35 ppm (Lee Meyerson, 1981). Hence, the reported concentrations were 1 to 7 times higher in Cochin Harbour and 7 to 14 times higher at the effluent discharge point in comparison with the baseline levels. The relation between zinc and silt, iron, organic carbon and aluminium were shown in Figs. 4.11 - 4.14.

4.1.4. Cadmium

The concentrations of cadmium ranged from 0.5 to 4.5 ppm in the Cochin Harbour and 6 - 8.4 ppm near the effluent discharge point (Tables 4.1 - 4.3). The baseline level of cadmium at station No.13 was found to be 0.15 ppm (Fig. 4.15). The levels of cadmium in sediments of Bay of Faundy was 0.2 ppm (Loring, 1982).

The observed results were 3-30 times higher in Cochin Harbour and 40-57 times higher at the effluent discharge point in comparison with the baseline level concentrations observed for Cochin Harbour area. The relation between cadmium and silt, iron, organic carbon and aluminium were shown in Figs. 4.16 - 4.19.

4.1.5. Lead

The observed concentrations ranged from 30 to 165 ppm in harbour area, 160-190 ppm near the effluent discharge point and 10-65 ppm in the upstream zone (Tables 4.1 - 4.3). The base line level of lead was found to be 40 ppm at station No. 13 (Fig.4.7). Hence the reported concentrations were 1 to 4 times higher in the Cochin estuary and 4-4.5 times higher at the effluent discharge point compared with the observed baseline values. The natural values of lead in sediments in the Bay of Naples was found to 25 ppm (Griggs & Johnson, 1978). The relation between total lead and silt, iron, organic carbon and aluminium during post-monsoon 1985 seasons were shown in Figs. 4.21 - 4.24.

4.1.6. Chromium

The levels of chromium ranged from 20 to 130 ppm in

Cochin Harbour, 85 to 120 ppm at the effluent discharge point and 7 to 20 ppm in the upstream zone (Tables 4.12 - 4.3). The baseline level of chromium was found to be 60 ppm at station No.13. (Fig. 4.25) The levels of chromium in the study area were comparable with the background values observed from other marine environment (Carmody et al., 1973 and Griggs & Johnson, 1978). The relation between chromium and silt, iron, organic carbon and aluminium shown in Figs. 4.26 - 4.29.

The silt (less than 0.062 mm) ranged from 28.5 to 87.5%, T/Fe 0.4 to 6.8%, T/Org. C, 0.2 to 3.50 and T/Al 4.5 to 11.5%. The data were processed for Pb, Zn, Cr,Cd & Hg with silt, T/Fe, T/Org. C and T/A1 by the least square method of linear regression. The results were presented in Table - 4.8, Figs. 4.2 - 4.4, 4.6 - 4.9, 4.11 - 4.14, 4.16 - 4.19, 4.21 - 4.24 and 4.26 - 4.29. The core profile of mercury (Fig.4.1) showed that the concentration was maximum (1.0 ppm) at about 5 cm and it decreased to 0.1 ppm at 30 cm. and afterwards it gradually decreased to 0.08 ppm at 90 cm. The positive correlation of organic carbon with mercury indicated that organic carbon plays a major role in the incorporation of mercury in sediment. The results were

comparable with the correlation equation obtained for Mersey estuary (Bartlet and Craig, 1981).

Mersey estuary:

Silt % = 8.9 Hg (ppm) + 8.17, r = 0.84

Org.C% = 1.4 Hg (ppm) + 2.7, r = 0.77

Cochin estuary:

Silt % = 61.85 Hg (ppm) + 28.12, r = 0.65

Org.C% = 2.93 Hg (ppm) + 2.49, r = 0.93

For Mersey sediments the slope and intercept were lower compared with the Cochin estuary. The silt fraction was better correlated compared with org. carbon which indicated that the texture of sediment played an important role in the incorporation of mercury in Mersey sediments. In the case of Cochin estuary the order of correlation was found to decrease from organic carbon to silt. The reported values from other marine environments ranged from 0.06 to 2.57 ppm in coastal British Columbia (Thompson, 1980), 1.3 to 11.3 ppm in River Mersey England (Bartlet, 1978), 0.1 to 4.8 ppm in British estuarine sediment (Bartlet and Craig, 1981), 0.1 to1.2 ppm in Ems estuary (Essink, 1980) etc.

The core profile of copper showed that the concentrations decreased from 130 ppm to 75 ppm upto a

depth of 40 cm and afterwards it further decreased to 40 ppm at 45 cm (Fig.4.5). The relation with major elements (Table - 4.8 and Figs.4.6 - 4.9) showed that iron and organic carbon behaved in a similar way in the incorporation of copper in sediments. In the core profile of zinc it is observed that the decrease in the concentration was steep from 0 to 40 cm depth and afterwards it was constant. The zinc concentrations found to decrease from 280 ppm to 175 ppm upto a depth of 10 cm and it gradually decreased to 55 ppm at 40 cm depth. The relation between silt, total iron, aluminium and organic carbon with lead showed that silt was better correlated and these parameters play a better role in the incorporation of zinc in sediments. The core profile of cadmium showed a steep decrease in concentration from 0 to 60 cm. depth. The concentration of cadmium found to decrease from 3.2 ppm to 2.0 ppm upto a depth of 50 cm and it gradually reduced to 0.3 ppm at 60 cm depth. No correlation existed for cadmium with silt, total iron, total aluminium and organic carbon.

The concentrations of lead found to decrease from 120 ppm to 80 ppm upto 10 cm depth and it gradually reduced to 60 ppm at 40 cm depth. This showed that

there was anthropogenic input of lead into the study area and accumulation of lead in sediments. The relation between total silt and lead showed no relationship exists and the accumulation of lead in sediments were not influenced by grain size. In the case of lead (Fig.4.17), it showed positive correlation with iron in sediments. As iron increased the lead concentration also increased. Total organic carbon, aluminium also behaved in a similar way.

The chromium core profile was quite different from lead and zinc. There was steep decrease in concentration of chromium from 0 to 60 cm depth and afterwards it was constant. The concentrations found to decrease from 110 ppm to 90 ppm upto a depth of 10 cm and gradually reduced to 60 ppm upto a depth of 60 cm No correlation exists in the incorporation of chromium in sediments with silt, total iron, total organic carbon, and aluminium.

Estuaries and coastal waters all over the world were increasingly exposed to heavy metal contamination in recent times. The sediments in the Princes Royal Harbour, Albany, W. Australia contained 12.7 - 180.6

ppm of lead against 30 - 165 ppm in Cochin Harbour, 6.4 - 122.1 ppm of zinc against 60 - 380 ppm and 6.4 - 122.1 ppm of copper against 40 - 160 ppm (Talbot V., 1983). While studying the heavy metal burden in the polluted river Ireweil (England) it was reported that the mean concentration for Zinc 0.55 ppm and that for Pb 0.6 ppm (Dixit & Witcomb 1983). In Ravenglass estuary, the mean concentrations of Zn, 90 ppm, of pb, 37 ppm and of Cu, 10 ppm, in Wyre estuary the values were Zn, 82 ppm, Pb, 35 ppm and Cu, 97 ppm and in Mersey estuary, the values of Zn, Pb and Cu were 236 ppm 57 ppm 41 ppm, respectively (Badri and Aston, 1983). In the Ashtamudi estuary the reported sediment concentrations on Fe 1200 to 3900 ppm, Zn - 109.7 ppm, Ni 10 - 49 ppm, Pb 69 - 92 ppm and Hg 0.002 to 0.010 ppm, (Nair et al., 1987). The role of river as a source of trace metal contamination has been properly brought out in the Bay of Lough Neagh northern Ireland (Rippy 1982). In the Ottawa river the concentrations of Cu, Pb and Zn in sediments were ten times higher in the down stream of the sewage out fall than in the upper zone (Oliver, 1973). The trace metal levels in sediments of Cochin backwater has been reported by Venugopal, 1982. The highest value for Cu,

Ni, Zn recorded were 70.80, 85.90 and 663.5 ppm, respectively. Several authors have reported that fine grained sediments normally have higher concentrations and greater sorptive capacity for trace metals (Pitta and Hyne, 1975; Hakanson, 1977; Murthy and Veerayya, 1981). In the Cochin Harbour the above statement appears to be in agreement in the case of Hg and Zn.

The input of mercury and other metals to the study area may be from the chemical industries situated near the banks of the river Periyar and Chitrapuzha which includes a major chlor alkali plant by a zinc, cadmium processing unit and many other industries using mercury and chlorine gas, caustic soda, hydrochloric acid in their process. The variation of mercury and other metals observed from station to station, may be due to the hydrographic conditions of the estuarine environment and also in the particle size of the sediments.

4.2. Estimation of bioavailability of metals in sediments

The sediment chemistry broadly reflects the contamination history of the area. Metals were associated with the composition of sediments like

hydroxides, carbonates which can be quite different from natural and anthropogenic levels. In general the anthropogenic inputs of metals will necessarily be associated with non-lattice fractions. Total dissolution of sediment was analytically demanding and in many monitoring purposes sediments were leached to remove the non-lattice held material. The non-lattice held contribution usually constitutes a small but bio-geochemically important fraction. It represents some proportion of the element that was initially leached from the source rocks or supplied in dissolved form from industrial sources. This fraction of the elements that were most easily available to the biota and constitutes the greatest danger to them, if it present in excessive quantities, particularly if the elements were in such a form that can be selectively removed by the biota from the sediment or in particulate matter in the water column. In fact the total metal and the easily extractable metal extraction techniques give useful information in such analysis.

The study reveals that high contents of Hg, Zn, Cd, and Cu were reaching the estuary from the river Periyar through industrial discharge. The chlor-alkali plant

and zinc-cadmium factory situated near the banks of river Periyar discharge effluents which contain Hg, Zn, Cu and Cd into the coastal waters. The samples from the effluent discharge point showed that 46 - 64% of total copper 83-89% of total zinc and 83-95% of total cadmium occur in the acetic acid soluble fraction (Table - 4.9). Similarly in the estuarine environment 5-60% of the total zinc, 10-80% of total cadmium and 10 - 40% of total copper were potentially available to the biota. The above results clearly indicated that most of the zinc and cadmium in sediments appears to be originated from industrial wastes. The results also showed that there was an anthropogenic input of Pb and Cr to the estuarine environment (Table 4.9) and the data was comparable from upstream zone. Moreover, 90% of the total lead and 85% of the total chromium in sediments were not potentially available to the biota being insoluble in Acetic acid medium. Earlier studies of Sankaranarayanan et al. (1978), Remani (1979), Nair and Nair (1986) indicated that biota from Cochin Harbour area contains, Hg, Zn, Cd etc. This confirm the present finding that this environment contains high concentrations of heavy metals in which few elements were in a form that can be selectively removed by biota.

Table - 4.1
Concentrations of Metals in Sediments of Cochin Estuary and River Periyar - July, 1985 (Monsoon)

Station Location	Hg ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Cr ppm
1	0.15	40	128	1.8	85	105
2	0.35	65	35	0.5	30	20
3	0.25	38	46	0.8	78	115
4	0.12	42	65	0.5	65	65
5	0.22	45	68	0.6	39	78
6	0.15	52	78	0.8	48	98
7	0.62	130	130	2.8	128	112
8	0.58	128	280	3.5	132	115
9	0.42	135	360	4.5	165	130
10	1.10	128	380	3.8	118	115
11	0.68	128	220	2.4	135	108
12	0.54	142	218	3.2	105	125
13	0.58	160	138	2.8	128	132
14	0.59	120	220	2.2	135	104
15	0.62	132	214	2.8	128	115
16	0.54	128	240	3.2	155	130
17	0.52	160	212	2.8	118	116
18	0.48	128	238	2.2	108	125
19	5.80	210	525	6.0	165	90

Table - 4.1

Station Location	Hg ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Cr ppm
20	5.5	260	420	6.5	190	85
21	10.5	240	430	8.4	185	115
22	11.5	230	420	8.2	160	120
23	5.8	280	410	8.4	165	105
24	0.04	25	60	--	15	7.0
25	0.04	20	40	--	10	15
26	0.06	25	40	--	65	20
27	0.05	15	60	--	40	18

Table - 4.2
Metal Concentrations in Sediments of Cochin Estuary and River Periyar - November, 1985 (Post-monsoon).

Station Location	Hg ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Cr ppm
1.	0.25	48	165	1.5	85	65
2.	0.45	55	170	0.5	70	90
3.	0.95	60	280	2.5	165	130
4.	0.15	58	60	2.5	65	95
5.	0.45	78	70	1.0	30	20
6.	0.65	85	180	1.5	65	70
7.	0.65	120	140	2.5	105	65
8.	0.85	135	190	3.5	180	130
9.	0.90	118	380	3.5	160	110
10.	0.35	105	210	2.5	115	85
11.	0.65	125	340	2.0	145	130
12.	0.55	145	260	4.5	55	85
13.	0.95	128	280	3.5	120	110
14.	0.85	145	230	2.8	95	70
15.	0.95	130	280	2.5	70	45
16.	0.20	128	220	1.0	90	105
17.	0.68	142	290	1.5	135	115
18.	0.55	138	240	1.5	125	105
19.	6.2	258	580	4.2	162	98

Table - 4.2

Station Location	Hg ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Cr ppm
20	5.2	129	650	6.5	158	105
21	5.5	190	625	6.2	185	116
22	9.8	195	780	5.6	185	85
23	6.5	168	696	4.8	190	120
24	0.04	15	45	--	38	15
25	0.04	18	60	--	40	18
26	0.04	16	55	--	45	18
27	0.04	20	48	--	38	20

Table - 4.3
Metal concentrations In Sediments of Cochin Esutaryand River Periyar - April, 1986 (Pre-monsoon)

Station Location	Hg ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Cr ppm
1	0.12	65	75	0.8	40	25
2	0.22	40	105	0.6	45	30
3	0.10	48	295	2.5	108	78
4	0.11	50	35	0.6	35	20
5	0.18	55	115	0.7	68	48
6	0.25	65	65	0.8	108	55
7	0.52	95	220	1.1	120	108
8	0.88	105	238	1.2	118	85
9	0.92	118	380	2.8	125	130
10	0.98	108	315	3.8	165	125
11	0.68	118	275	3.5	155	118
12	0.95	115	268	2.8	148	108
13	0.92	128	220	4.5	150	115
14	0.89	116	245	3.6	156	120
15	1.10	125	238	3.1	158	108
16	0.85	130	245	4.2	125	115
17	0.86	145	220	3.6	118	98
18	0.95	135	195	3.2	150	110
19	5.50	230	680	8.1	182	118

Table - 4.3

Station Location	Hg ppm	Cu ppm	`Zn ppm	Cd ppm	Pb ppm	Cr ppm
20	5.50	280	785	7.8	180	108
21	11.5	275	765	8.2	190	115
22	10.8	265	780	7.5	185	120
23	10.2	280	760	7.9	190	115
24	0.04	20	40	0.15	25	10
25	0.04	18	45	0.10	20	15
26	0.04	15	45	0.10	45	14
27	0.04	18	40	0.18	40	15

Table - 4.4

Size Fraction and Major Element Concentrations in Sediments of Cochin Estuary and River Periyar - July, 1985 (Monsoon).

Station location	Sand %	Silt %	T/Fe %	T/Org.C %	T/Al %
1	68.5	31.2	0.58	0.15	2.9
2	27.5	72.5	0.38	1.80	8.8
3	11.5	88.5	6.8	3.2	9.8
4	70.2	29.8	2.80	1.6	3.8
5	32.18	67.6	3.9	1.2	8.8
6	35.8	64.7	3.9	2.8	8.5
7	22.5	77.5	3.6	2.1	8.6
8	13.5	86.4	4.2	2.8	9.8
9	12.8	87.6	4.8	2.6	10.2
10	33.8	66.2	3.9	2.1	8.2
11	28.5	62.2	4.1	2.3	8.1
12	23.5	75.8	3.10	1.8	8.8
13	13.2	86.8	4.8	2.9	10.8
14	17.2	82.5	6.2	2.2	10.2
15	16.8	83.1	6.2	3.1	10.2
16	75.2	24.6	1.4	1.6	2.8
17	12.9	87.1	4.2	2.5	10.8
18	22.1	77.6	5.8	2.4	8.9
19	35.2	64.5	3.5	0.8	8.2

Table - 4.4

Station Location	Sand %	Silt %	T/Fe %	T/Org.C %	T/Al %
20	32.8	68.5	3.9	3.2	8.5
21	36.7	62.3	3.8	3.5	8.6
22	35.8	64.2	3.2	3.2	7.8
23	32.5	67.5	3.6	3.2	8.9
24	88.2	11.8	1.2	0.2	2.8
25	89.5	10.5	1.1	0.6	3.2
26	90.1	9.5	1.3	0.6	2.9
27	88.5	11.5	1.5	0.2	3.1

Table - 4.5
Size Fraction and Major Element Concentrations in Sediments of Cochin Estuary and River Periyar, November, 1985 (Post-monsoon)

Station location	Sand %	Silt %	T/Fe %	T/Org.C %	T/Al %
1.	71.5	28.5	0.65	0.2	3.4
2.	30.2	69.8	0.40	2.1	8.9
3.	12.5	87.5	6.2	3.4	10.8
4.	68.8	31.2	2.1	1.2	4.10
5.	28.5	71.5	4.6	1.8	9.8
6.	30.5	69.5	4.1	2.6	8.8
7.	26.5	73.5	3.8	2.4	9.4
8.	15.6	84.4	4.8	2.9	10.2
9.	13.8	83.8	5.2	2.9	10.4
10.	35.5	64.5	4.2	1.75	8.4
11.	29.0	61.0	4.6	2.5	8.1
12.	24.4	73.6	3.2	2.2	9.8
13.	14.6	85.4	5.2	3.2	11.3
14.	16.8	83.2	6.4	2.8	10.6
15.	17.5	82.5	6.8	3.3	10.66
16.	76.8	23.5	1.2	1.2	3.4
17.	13.8	86.2	4.5	2.65	11.5
18.	22.6	77.4	6.2	2.25	9.0
19.	28.4	71.6	2.8	3.5	9.4

Table - 4.5

Station location	Sand %	Silt %	T/Fe %	T/Org.C %	T/Al %
20	29.2	70.8	3.2	3.2	8.9
21	31.5	68.5	3.5	3.4	9.2
22	30.2	69.8	3.2	3.5	8.6
23	26.2	63.8	3.2	3.2	8.2
24	88.2	11.8	1.6	0.6	2.8
25	89.5	10.5	1.4	0.6	2.8
26	87.2	12.8	1.2	0.6	3.2
27	88.5	11.5	1.4	0.6	2.8

Table -4.6

Size fraction and major element concentrations in sediments of Cochin Estuary and River Periyar - April 1986.

tion ation	Sand %	Silt %	T/Fe %	T/Org.C %	T/Al %
1	67.5	32.2	0.85	0.40	3.6
2	26.5	62.8	0.65	1.80	8.2
3	10.4	89.8	6.4	3.2	10.2
4	65.2	34.8	2.4	1.8	5.2
5	25.2	74.8	4.8	2.2	9.8
6	28.8	31.2	4.2	2.8	9.2
7	25.8	72.1	3.8	2.9	9.1
8	14.2	85.8	5.1	2.8	9.8
9	12.5	87.5	5.8	2.9	10.2
10	32.10	67.8	4.8	2.2	9.2
11	26.2	63.8	4.9	2.6	9.1
12	22.1	78.0	3.8	2.9	10.2
13	12.2	87.2	5.1	3.1	10.2
14	14.5	85.5	6.5	3.1	10.2
15	14.5	85.5	6.8	3.2	10.2
16	17.2	29.9	2.1	1.8	4.2
17	12.1	88.1	4.8	2.8	10.9
18	20.1	79.4	6.1	2.8	10.8
19	32.2	68	3.2	3.2	8.6

Table -4.6

Station Location	Sand %	Silt %	T/Fe %	T/Org.C %	T/Al %
20	30.5	69.5	3.5	3.5	8.8
21	28.5	71.5	3.8	3.2	8.5
22	35.5	64.5	3.9	3.2	8.2
23	31.8	68.2	3.9	3.2	8.0
24	88.5	11.5	1.3	0.2	2.5
25	89.5	10.5	1.4	0.4	2.4
26	90.1	9.8	1.2	0.2	2.4
27	92.2	7.8	1.1	0.4	2.2

Table - 4.7

Distribution of Metals in ppm (Mini. & Max.) at Surface and at 90 cms Depth of a Core Sample From Cochin Harbour Area

Element	Minimum ppm	Maximum ppm
Hg	0.08	1.10
Cu	40.00	130.00
Zn	55.00	280.00
Cd	0.15	3.50
Pb	40.00	120.00
Cr	60.00	110.00

Table-4.8

Correlation-regression relationship of metals with silt fraction and major elements in sediments of Cochin estuary - November, 1985 (Post-monsoon).

Hg					
Silt	=	61.85 T/Hg	+	26.12	r = 0.65
T/Fe	=	5.78 T/Hg	+	0.55	r = 0.78
T/Org.C	=	2.93 T/Hg	+	0.49	r = 0.93
Cu					
Silt	=	0.24 T/Cu	+	42.28	
T/Fe	=	0.03 T/Cu	+	1.13	
T/Org.C	=	0.01 T/Cu	+	1.16	
T/Al	=	0.033 T/Cu	+	5.26	
Zn					
Silt	=	0.100 T/Zn	+	43.44	r = 0.65
T/Fe.	=	0.010 T/Zn	+	1.78	r = 0.55
T/Org.C	=	0.005 T/Zn	+	1.10	r = 0.53
T/Al	=	0.013 T/Zn	+	5.87	r = 0.42
Cd					
Silt	=	8.84 T/Cd	+	47.50	r = 0.39
T/Fe	=	0.71 T/Cd	+	2.48	r = 0.39
T/Org.C	=	0.33 T/Cd	+	1.53	r = 0.42
T/Al	=	0.89 T/Cd	+	6.81	r = 0.36

Pb.

Silt	=	0.19T/Pb	+	49.13	r = 0.14
T/Fe	=	0.02T/Pb	+	2.03	r = 0.40
T/Org.C	=	0.01T/Pb	+	1.32	r = 0.43
T/Al	=	0.02T/Pb	+	6.74	r = 0.30

Cr

Silt	=	0.05T/Cr	+	62.61	r = 0.12
T/Fe	=	0.03T/Cr	+	3.77	r = 0.18
T/Org.C	=	0.008 T/Cr	+	1.62	r = 0.27
T/Al	=	0.005 T/Cr	+	8.32	r = 0.07

Table-4.9. Concentration of metals in sediments (PPM) and organic carbon (%) (Minimum and maximum values during monsoon, post-monsoon 1985 and pre-monsoon 1986).

Location	No. of samples		Hg	Cu	Zn	Cd	Pb	Cr	T/Org. Carbon
Cochin Barbour area	18	A	0.12-1.10	40-160	35-380	0.5-4.5	30-165	20-130	0.2-3.4
		B	--	10-45	2-230	0.05-3.6	1.5-17	6.5-20	--
		C	--	(25-28%)	(5-60%)	(10-80%)	(5-10%)	(2-15%)	--
Effluent discharge point	5	A	5.5-11.5	260-280	420-780	6-8.4	160-190	85-120	0.8-3.5
		B	--	120-180	350-700	5-8.0	15-40	15-42	--
		C	--	(46-64%)	(83-89%)	(83-95%)	(9-21%)	(17-35%)	--
Fresh water zone (upstream)	4	A	0.04-0.06	15-25	40-60	N.D.	10-65	7-20	0.2-0.6
		B	--	2-5	10-24	--	2-15	2-8	--
		C	--	(13-20%)	(25-40%)	N.D.	(20-23%)	(28-40%)	--

A = Total attack
B = Acetic acid attack
C = % of potentially bio-available elements
N.D. = Not detected.

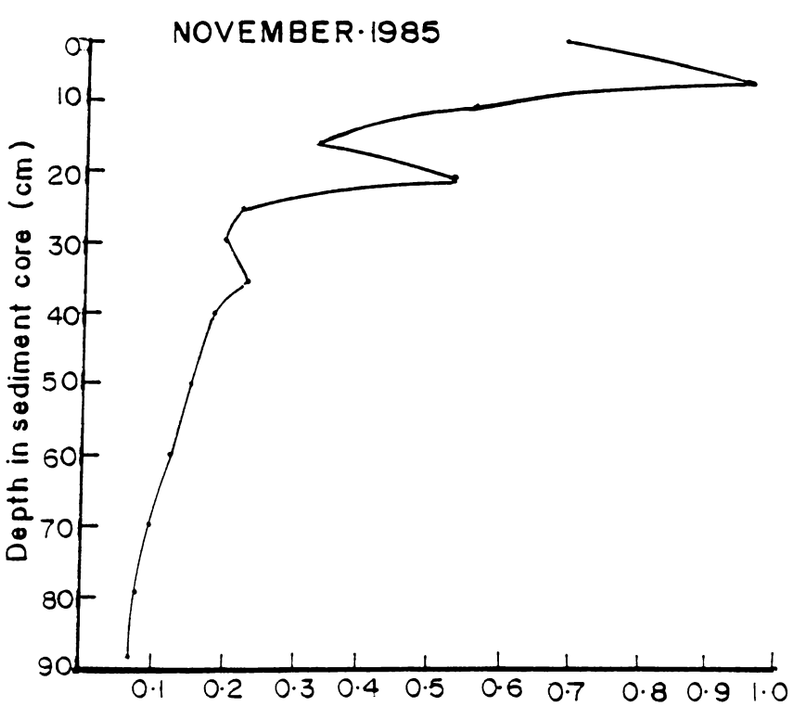


Fig. - 4.1
Representative core profile of total mercury at station No.13.

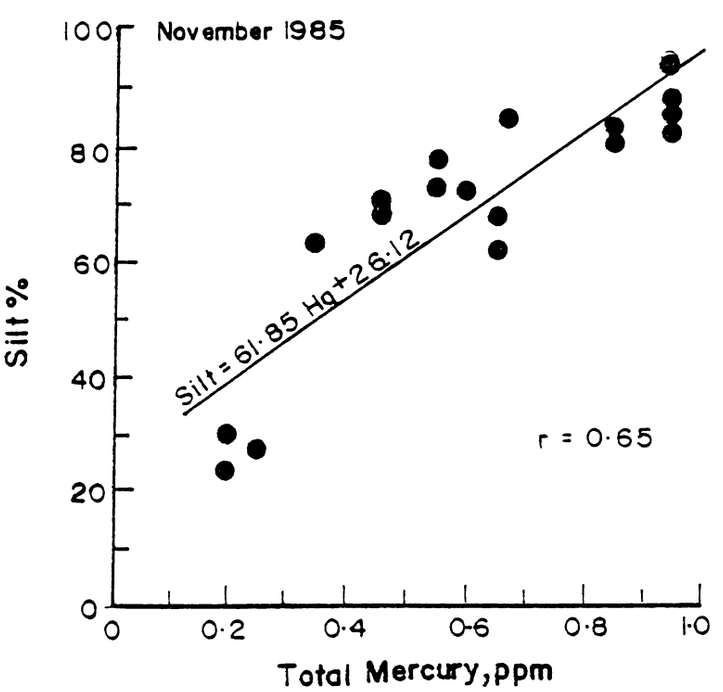


Fig. - 4.2
Relation between silt and total mercury in sediments.

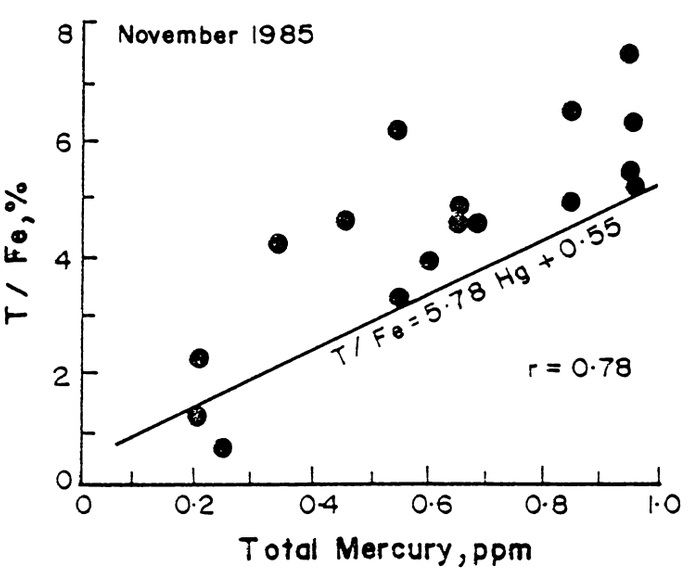


Fig. - 4.3
Relation between total iron and total mercury in sediments.

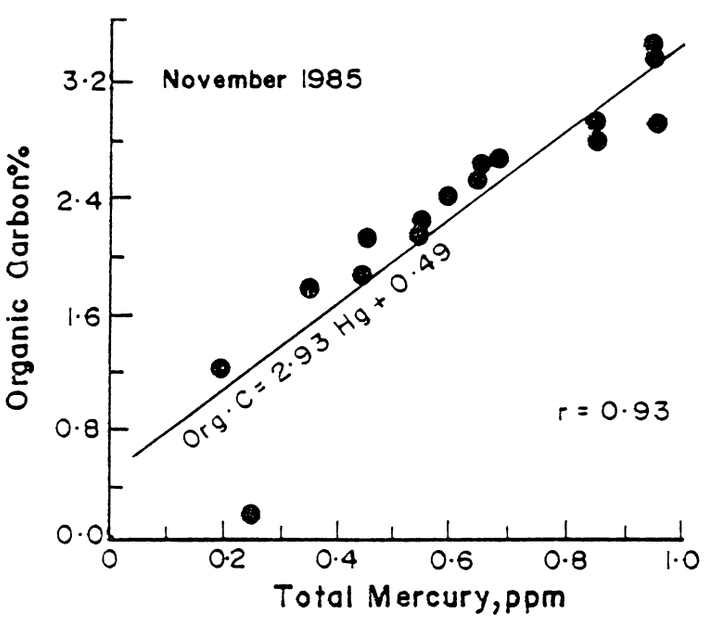


Fig. - 4.4
Relation between total organic carbon and total mercury in sediments.

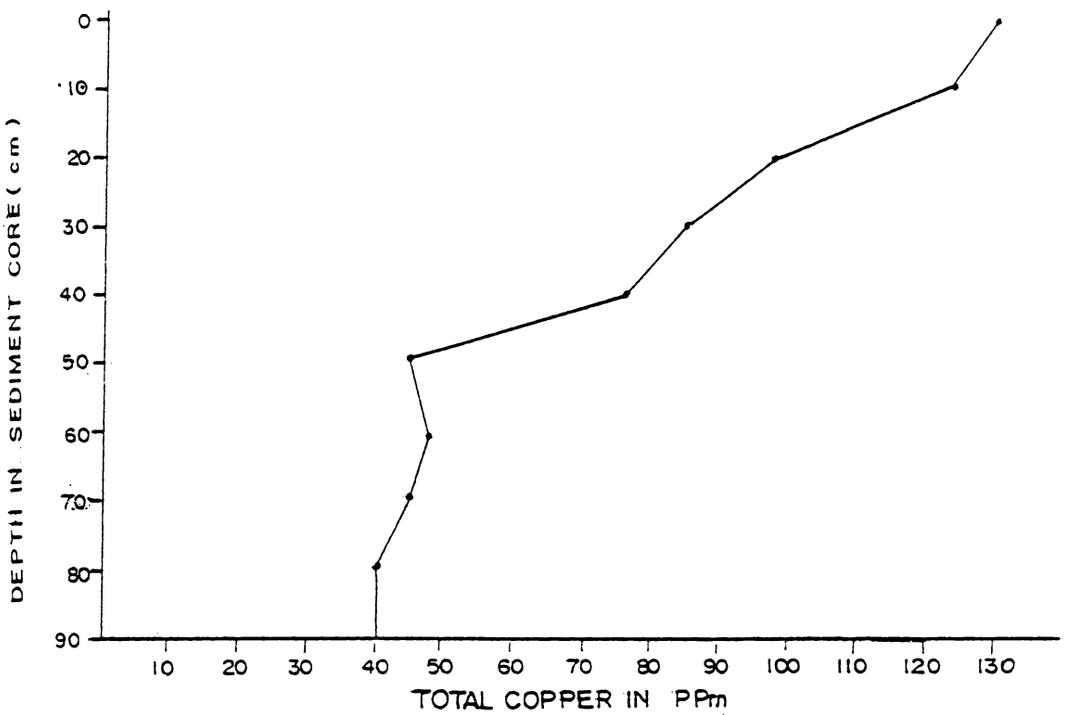


Fig. - 4.5
Representative core profile of total copper at station No.13.

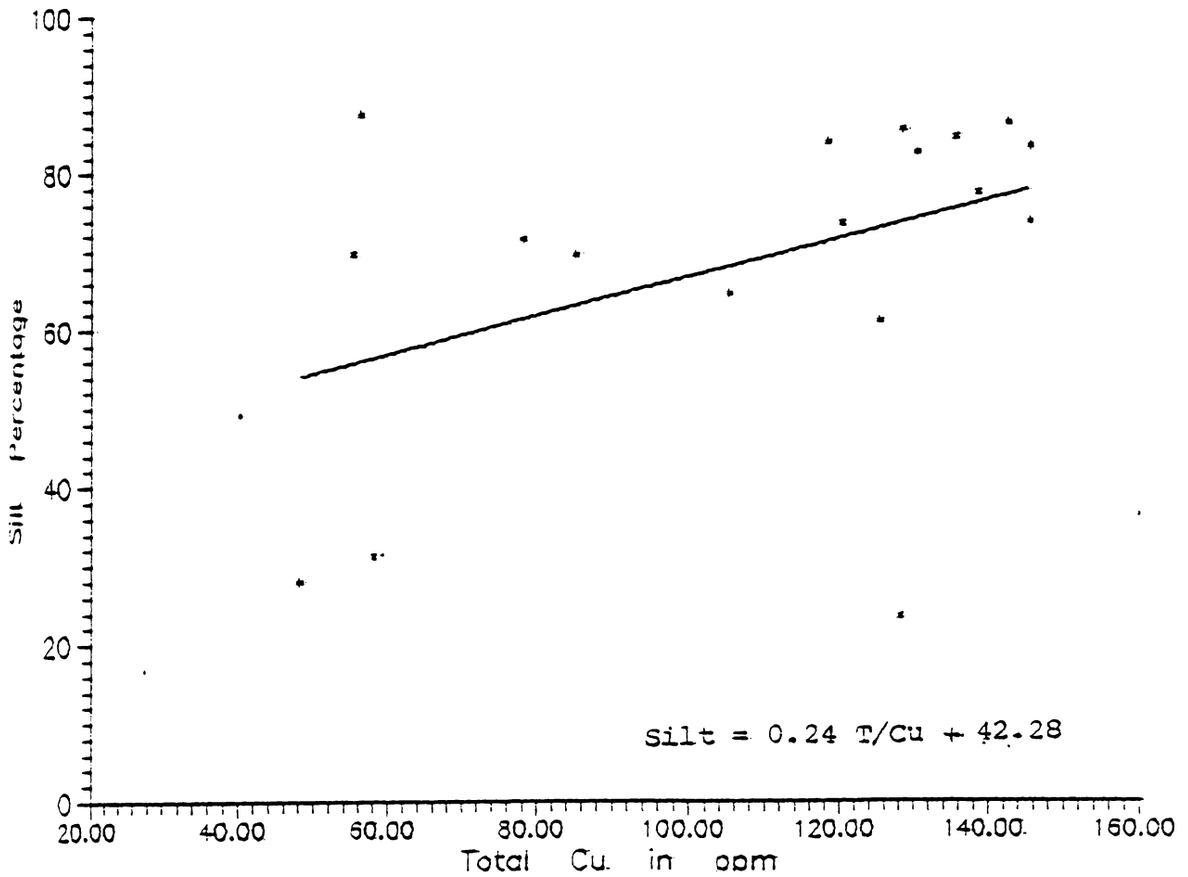


Fig. - 4.6
Relation between silt and total copper in sediments

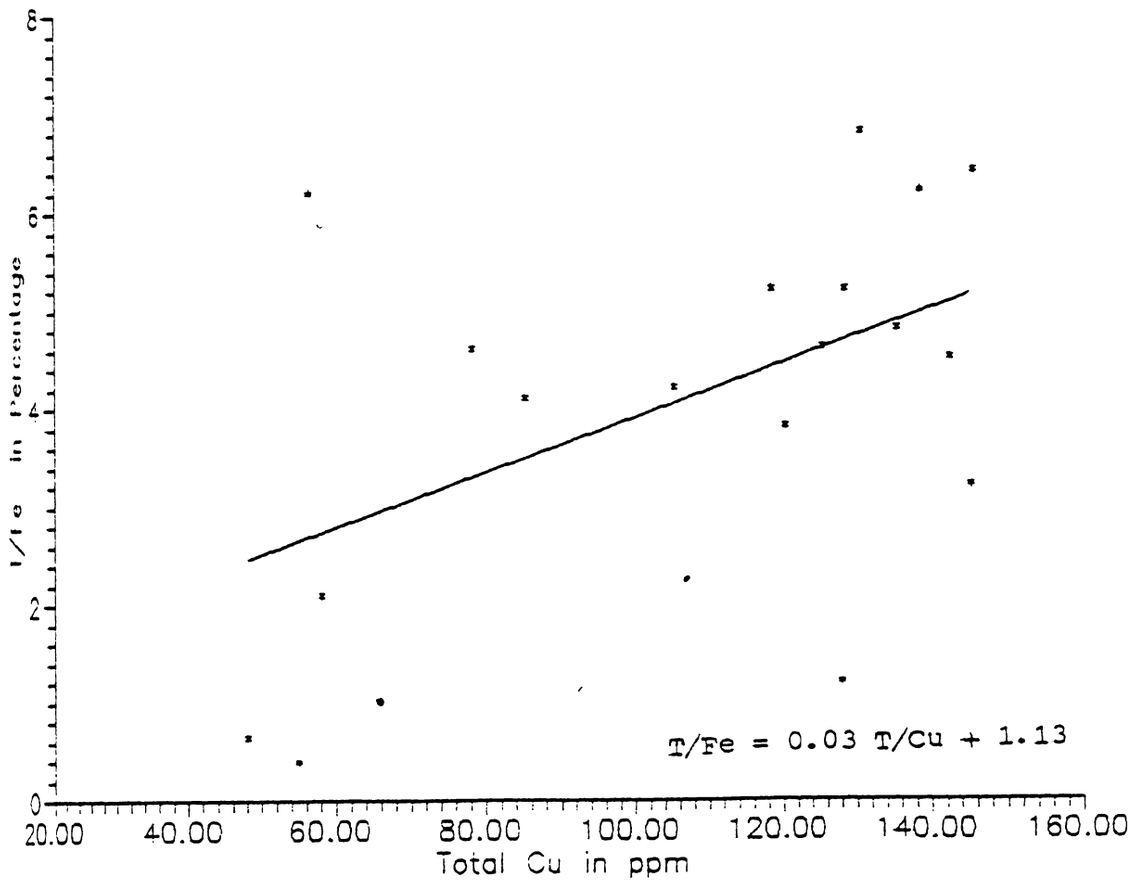


Fig. - 4.7
Relation between total iron and total copper in sediments.

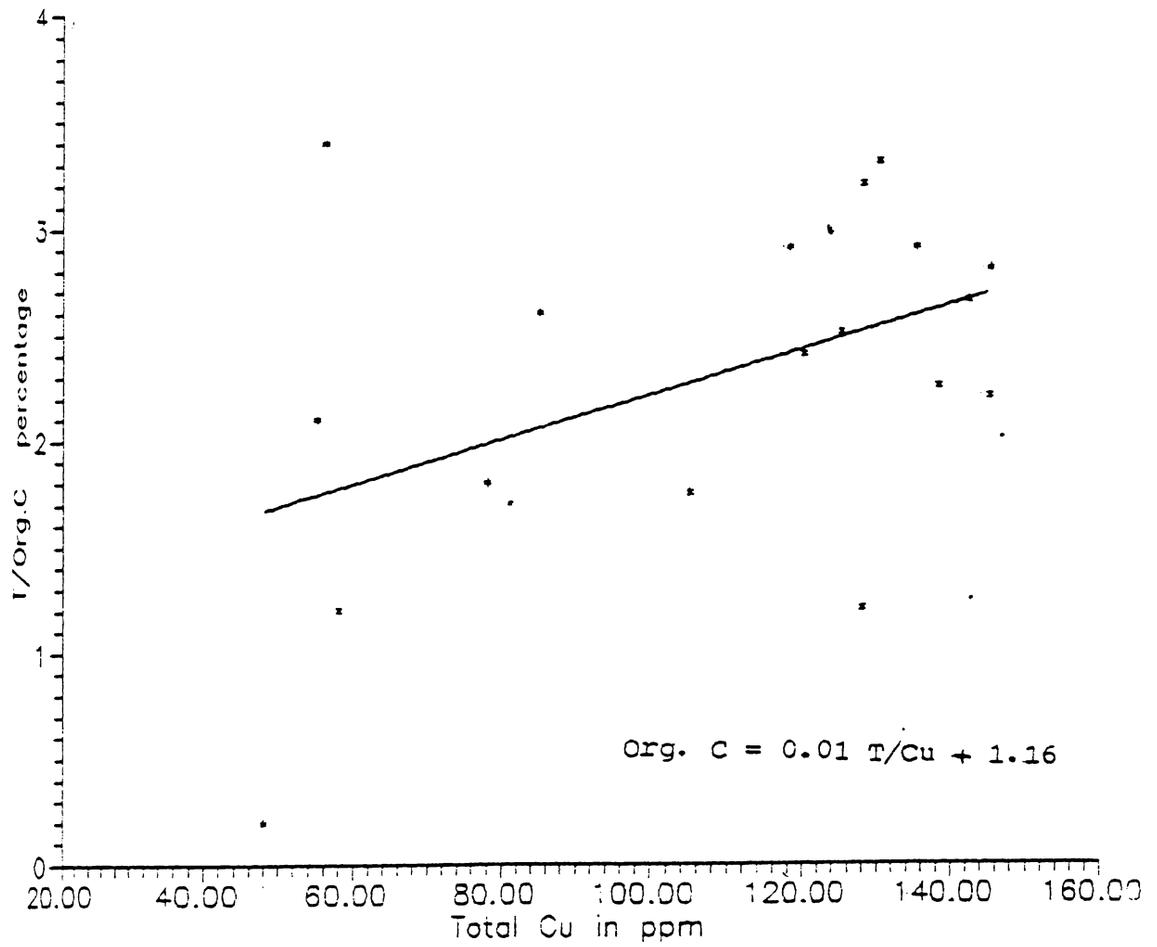


Fig. - 4.8
Relation between total organic carbon and total copper in sediments.

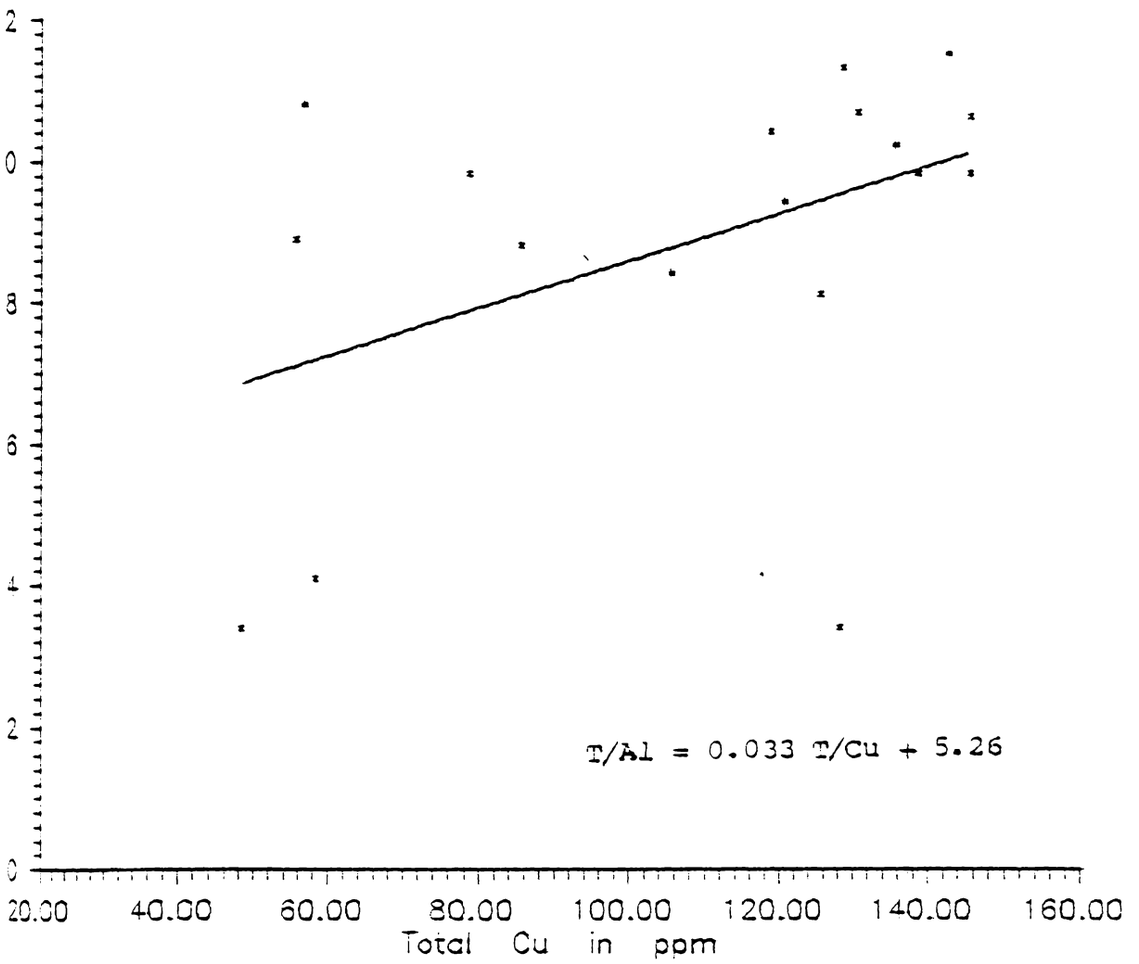


Fig. - 4.9
Relation between total aluminium and total copper in sediments.

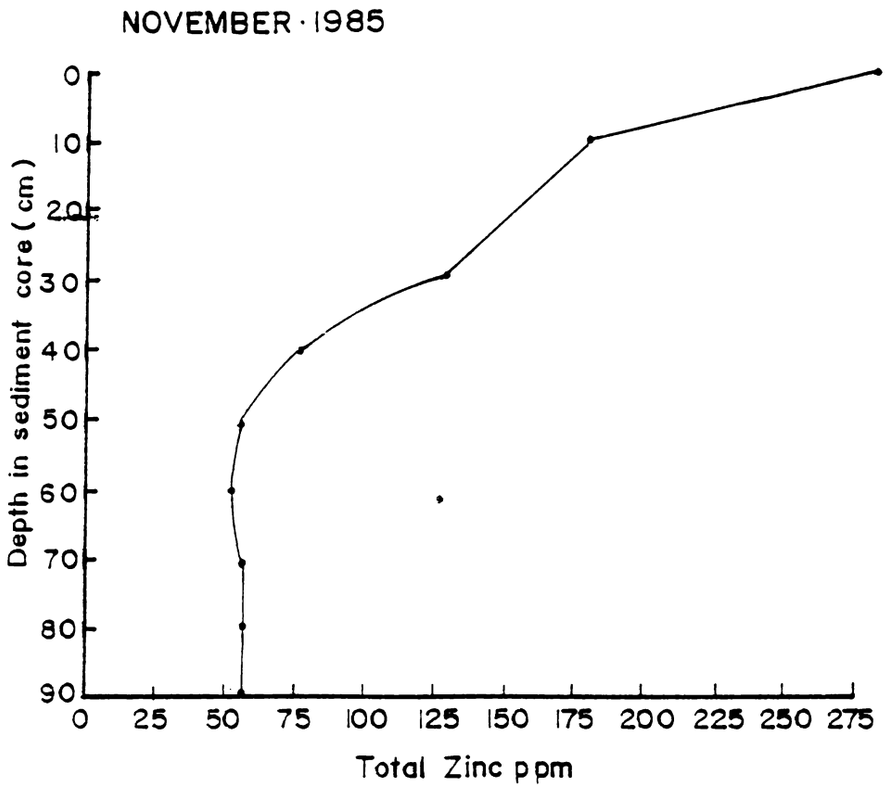


Fig. - 4.10
Representative core profile of total zinc at station No.13.

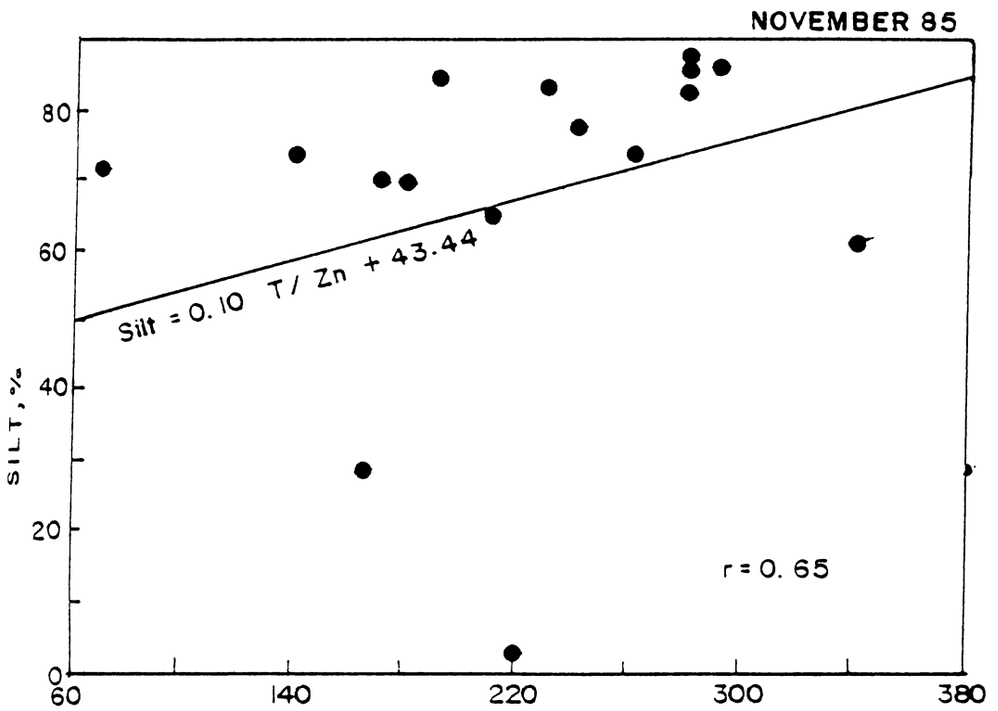


Fig. - 4.11
Relation between silt and total zinc in sediments.

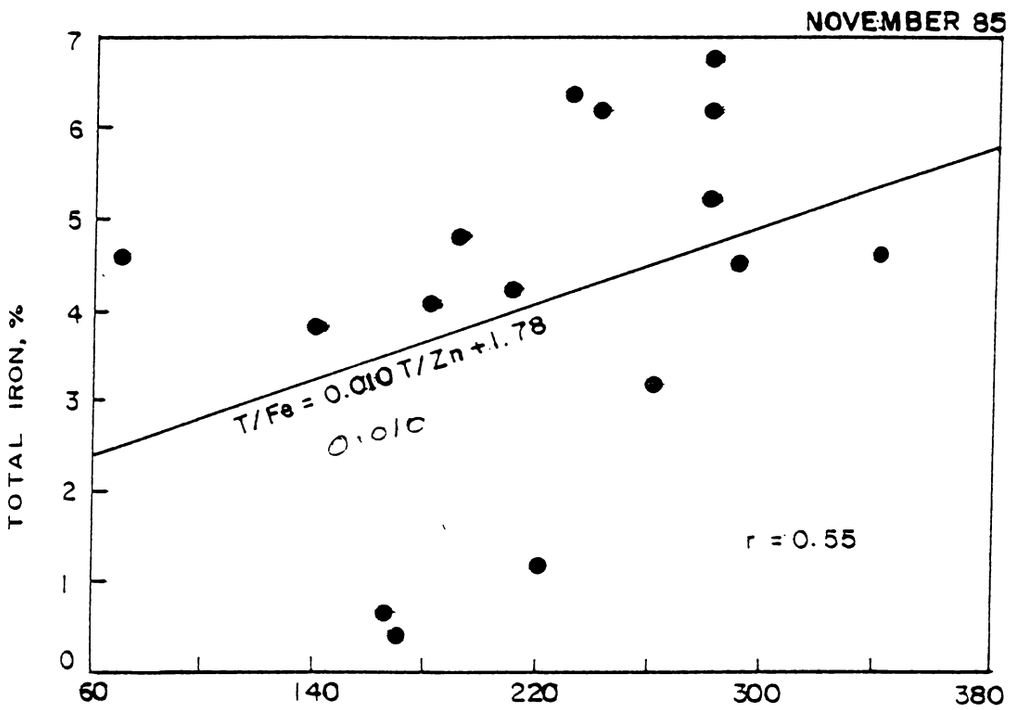


Fig. - 4.12
Relation between total iron and total zinc in sediments.

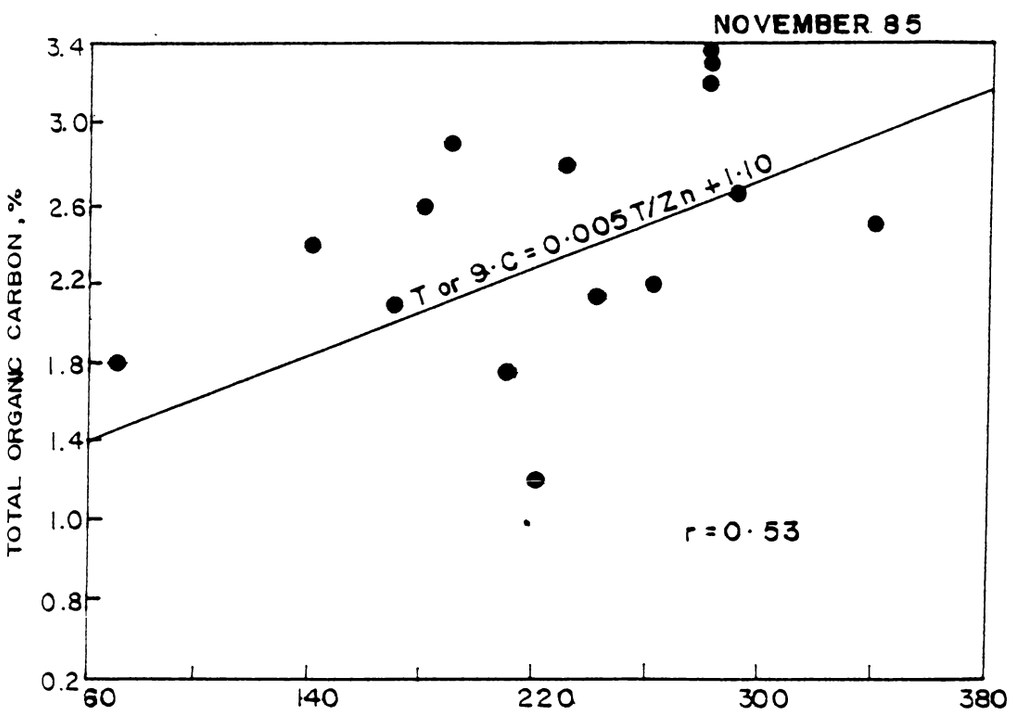


Fig. - 4.13

Relation between total organic carbon and total zinc in sediments.

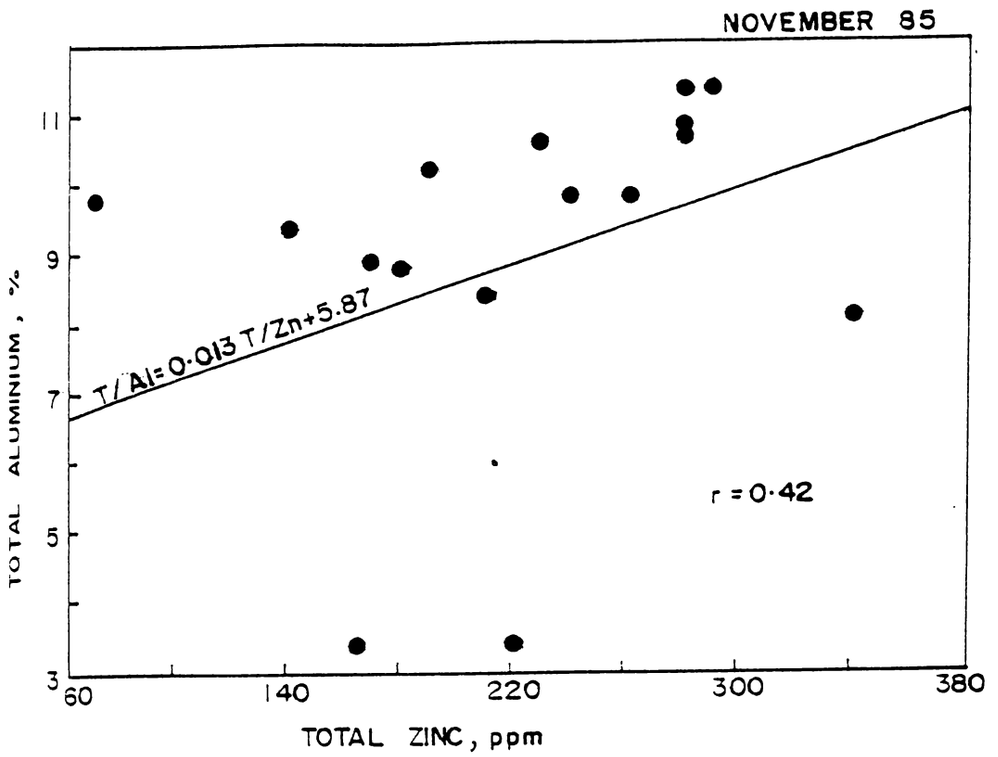


Fig. - 4.14
Relation between total aluminium and total zinc in sediments.

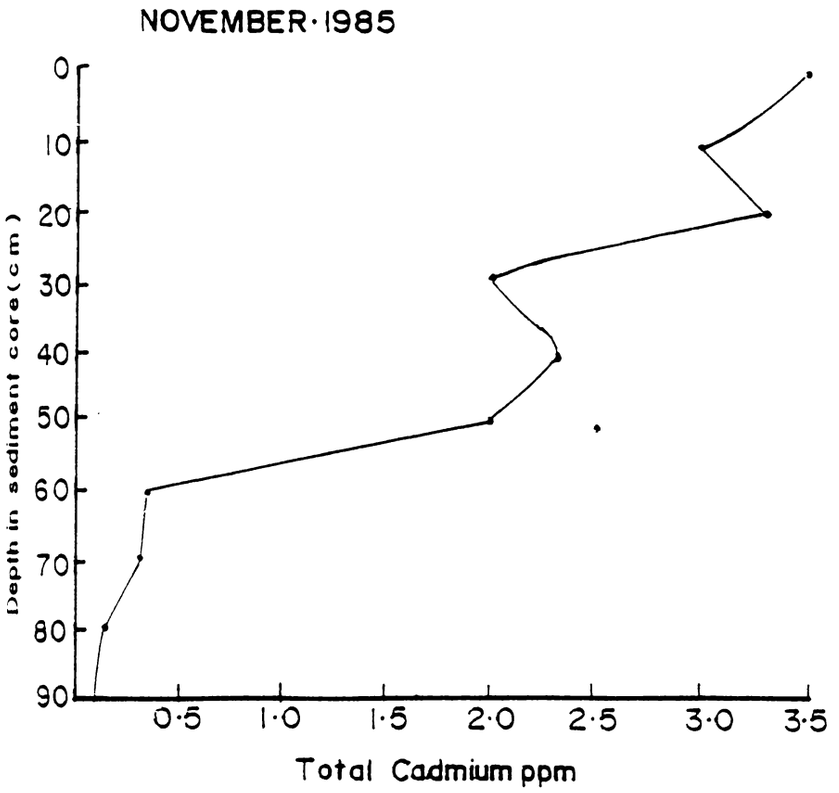


Fig. - 4.15
Representative core profile of total cadmium at station No.13.

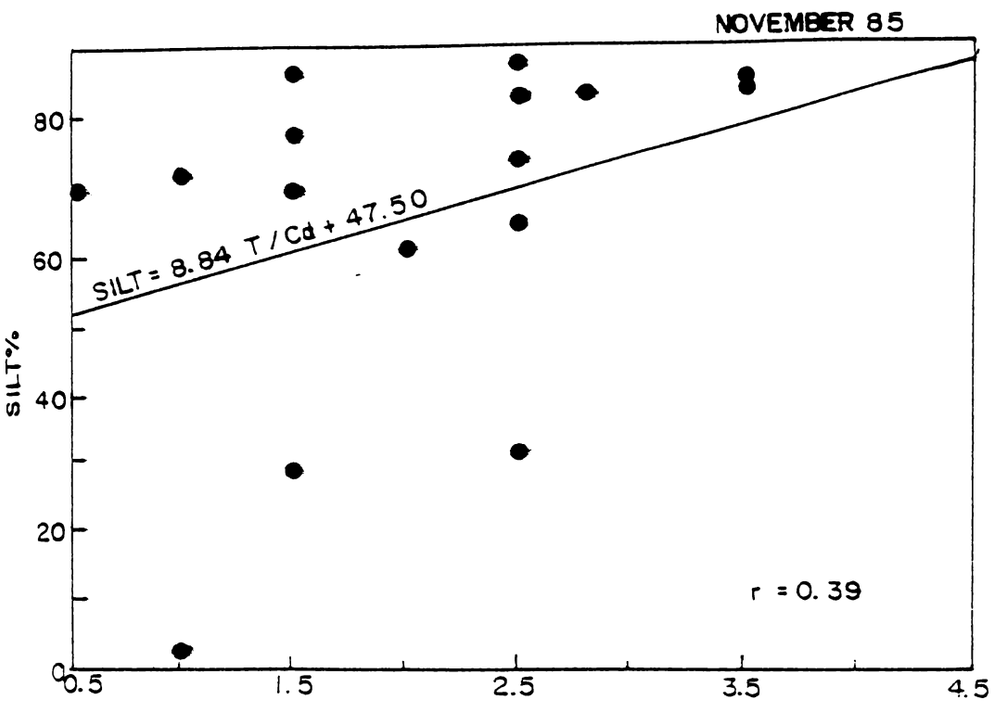


Fig. - 4.16
Relation between silt and total cadmium in sediments.

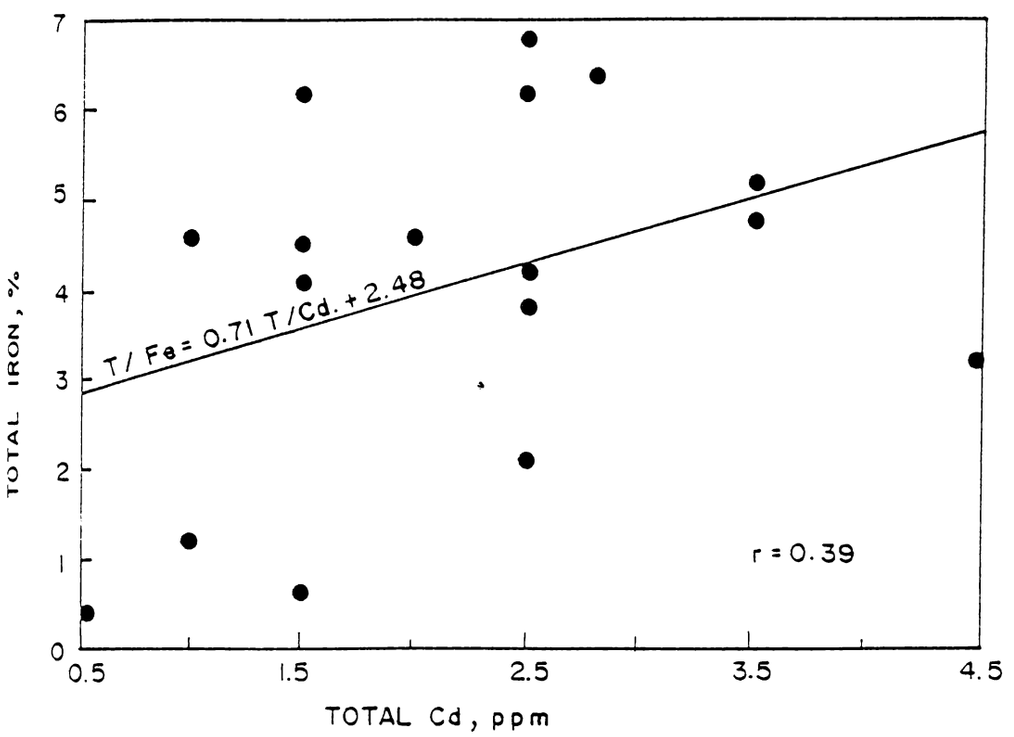


Fig. - 4.17
Relation between total iron and total cadmium in sediments.

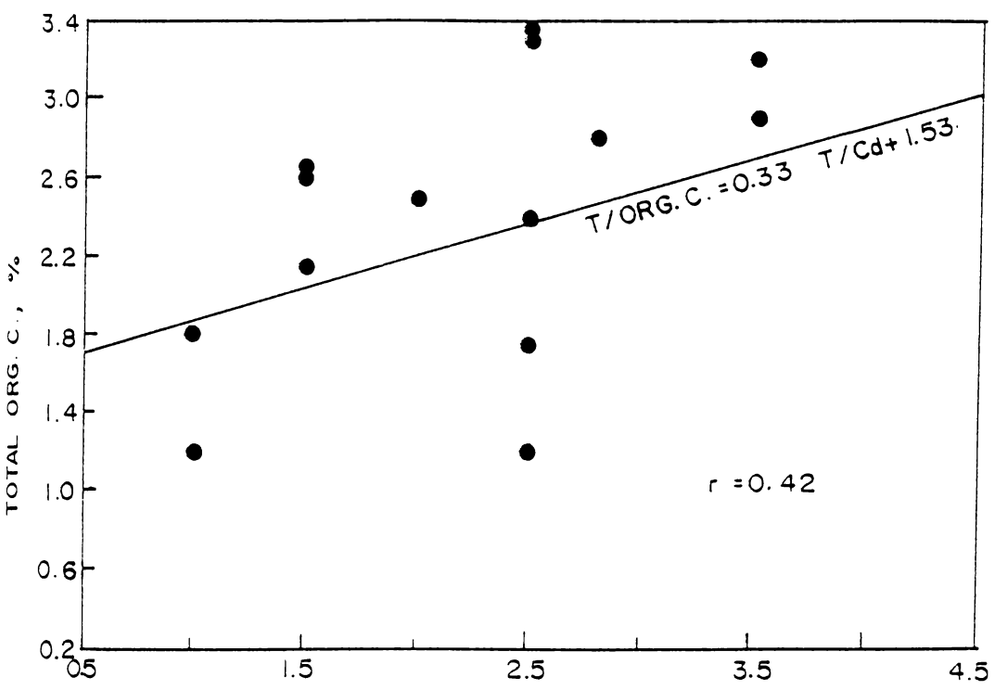


Fig. - 4.18
Relation between total organic carbon and total cadmium in sediments.

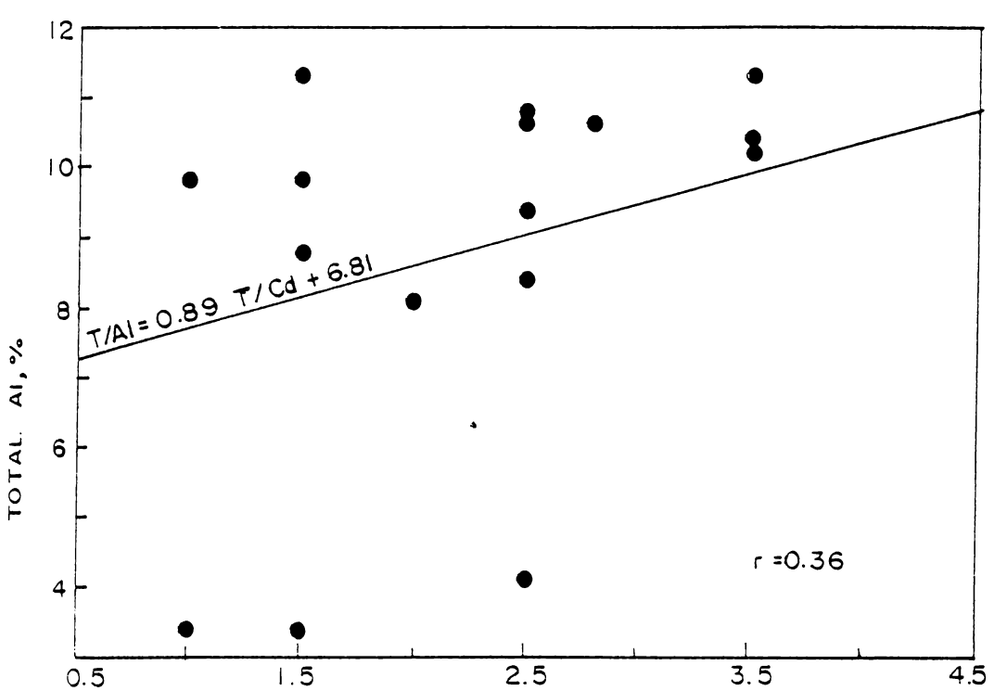


Fig. - 4.19

Relation between total aluminium and total cadmium in sediments.

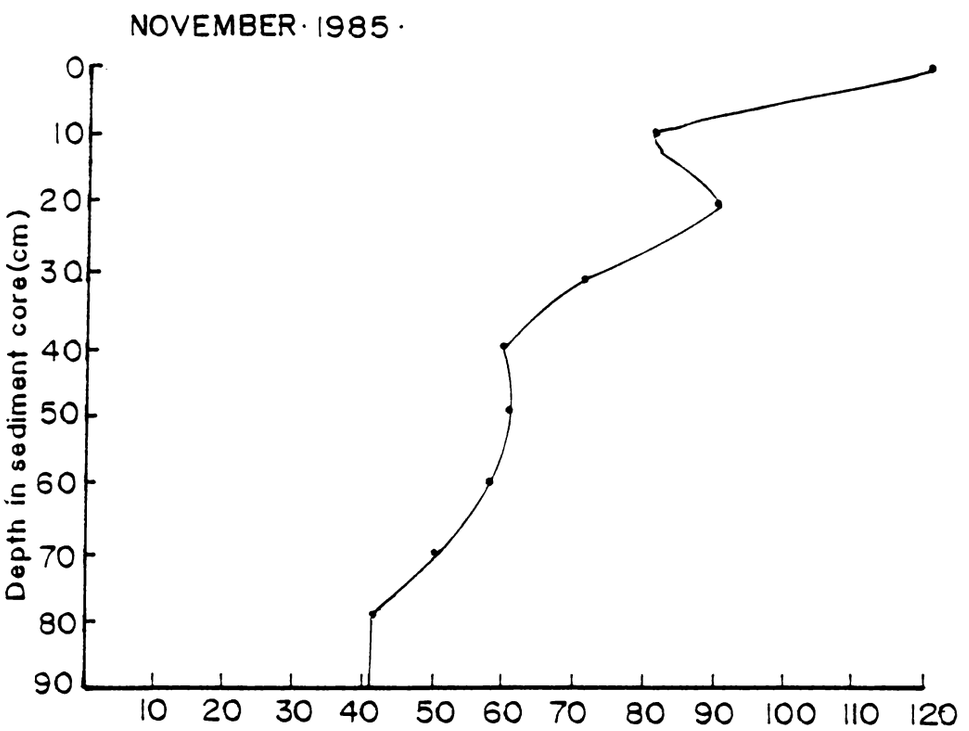


Fig. - 4.20
Representative core profile of total lead at station No.13.

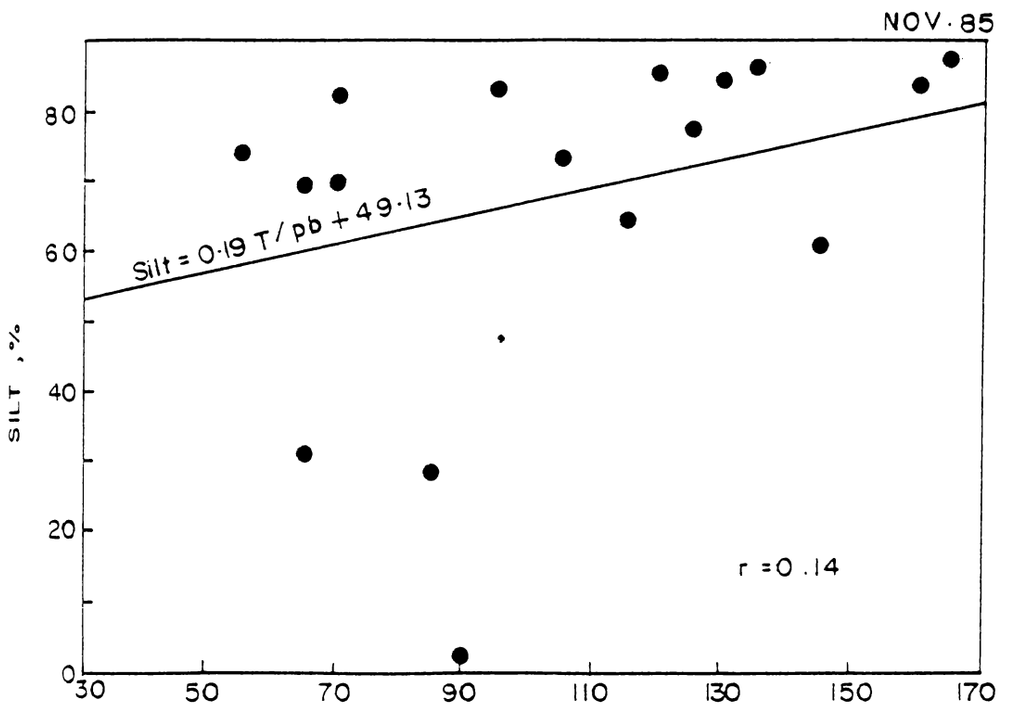


Fig. - 4.21
Relation between silt and total lead in sediments.

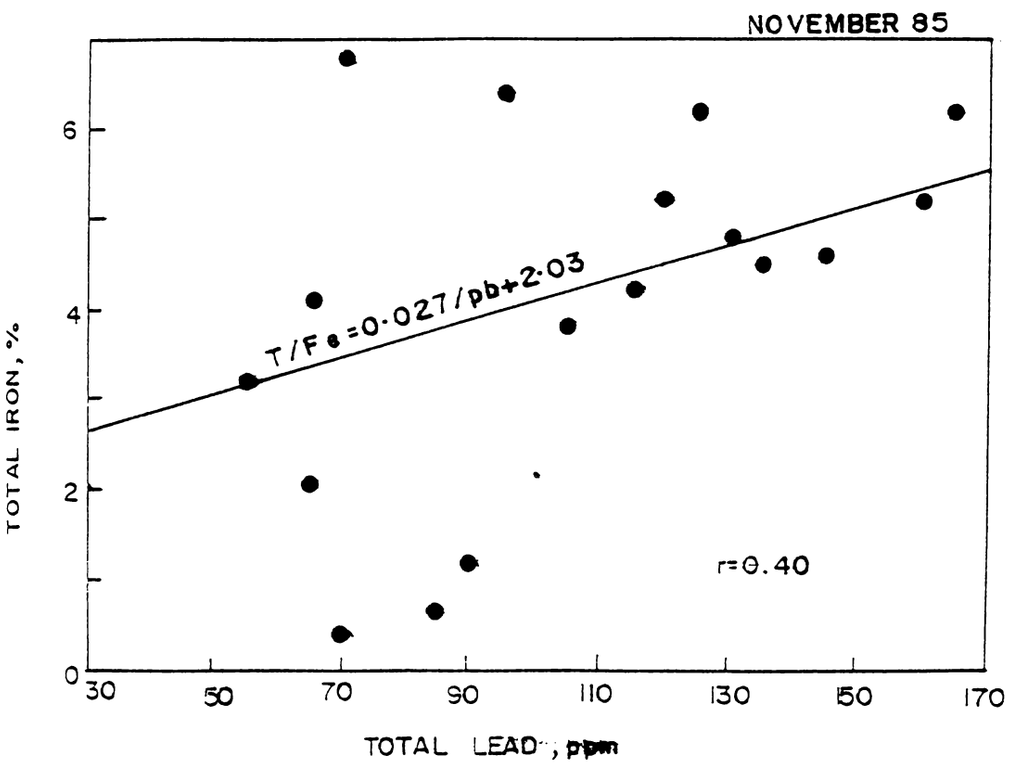


Fig. - 4.22
Relation between total iron and total lead in sediments.

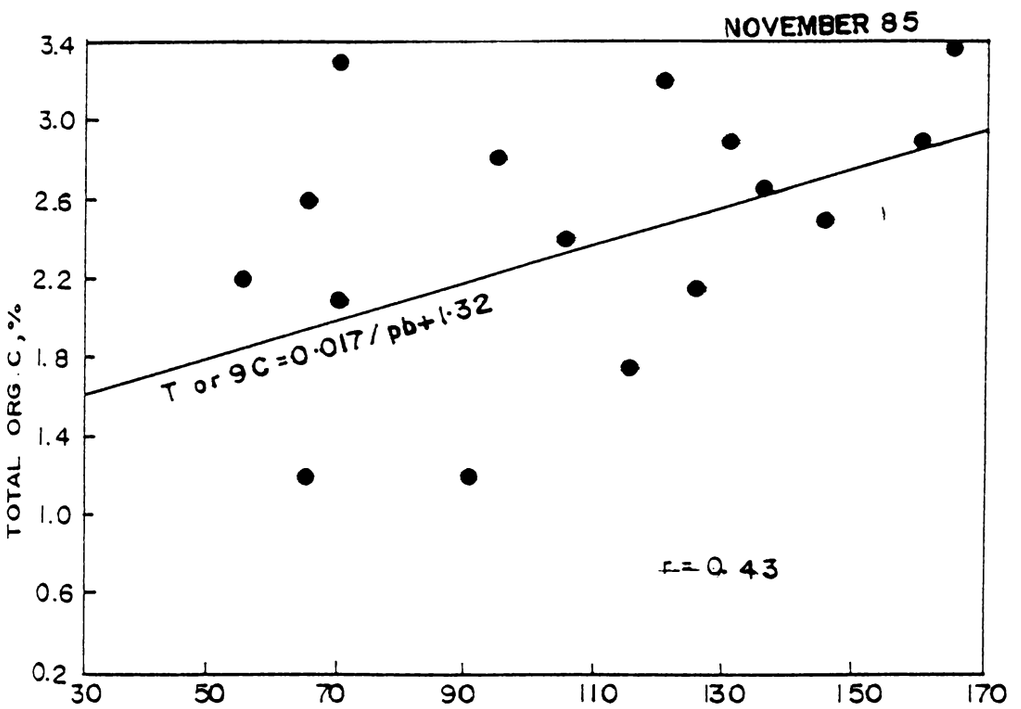


Fig. - 4.23
Relation between total organic carbon and total lead in sediments.

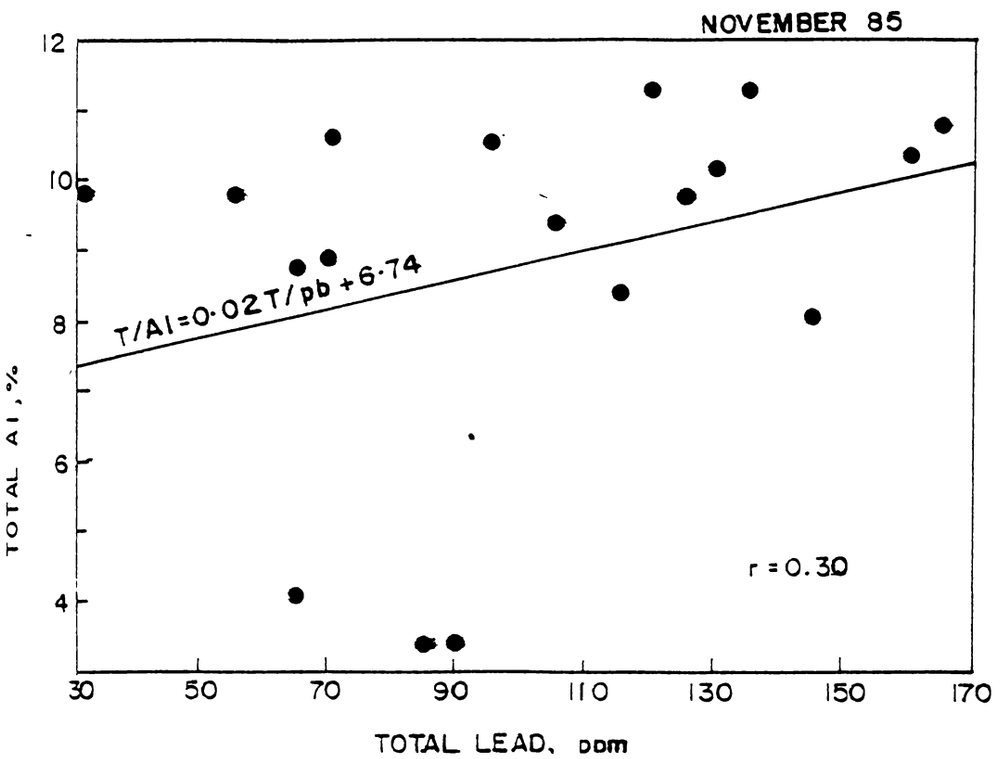


Fig. - 4.24
Relation between total aluminium and total lead in sediments.

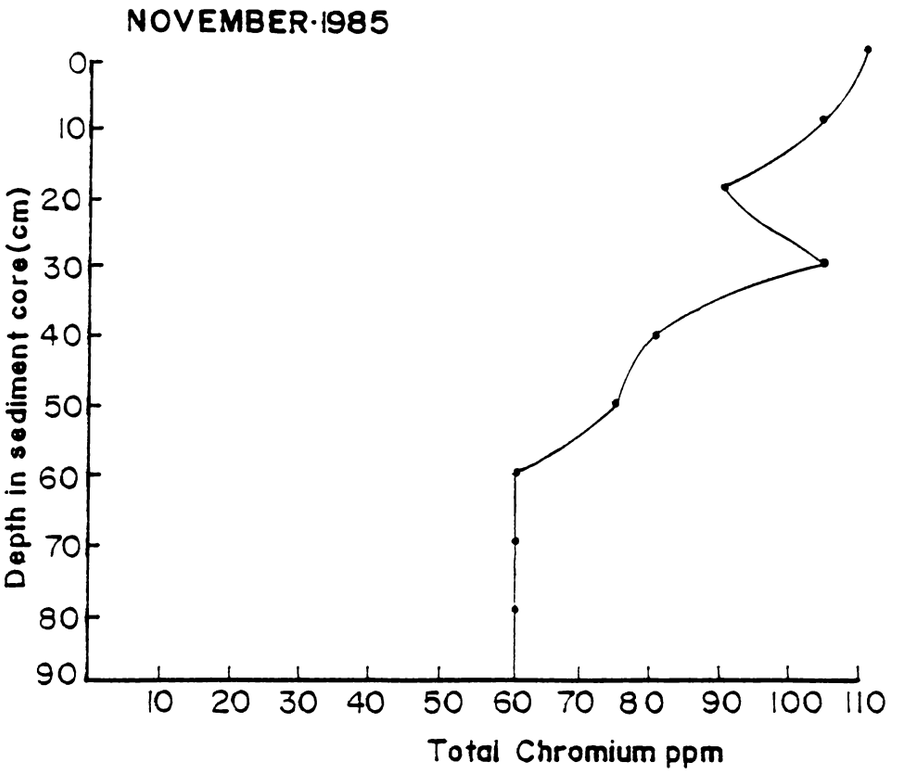


Fig. - 4.25
Representative core profile of total chromium at station No.13.

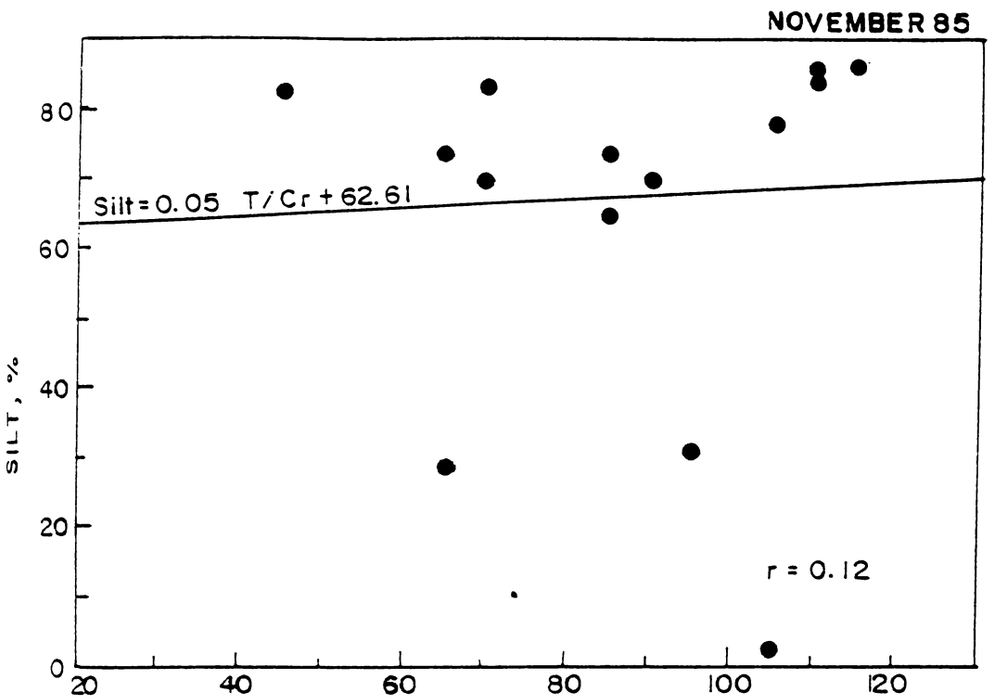


Fig. - 4.26

Relation between silt and total chromium in sediment.

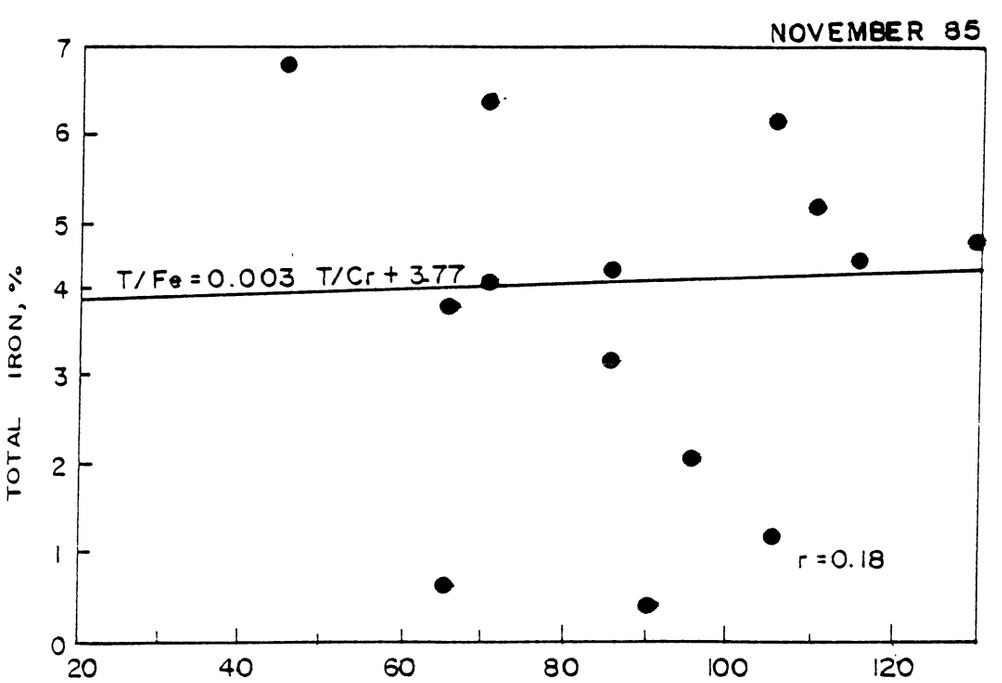


Fig. - 4.27
Relation between total iron and total chromium in sediments.

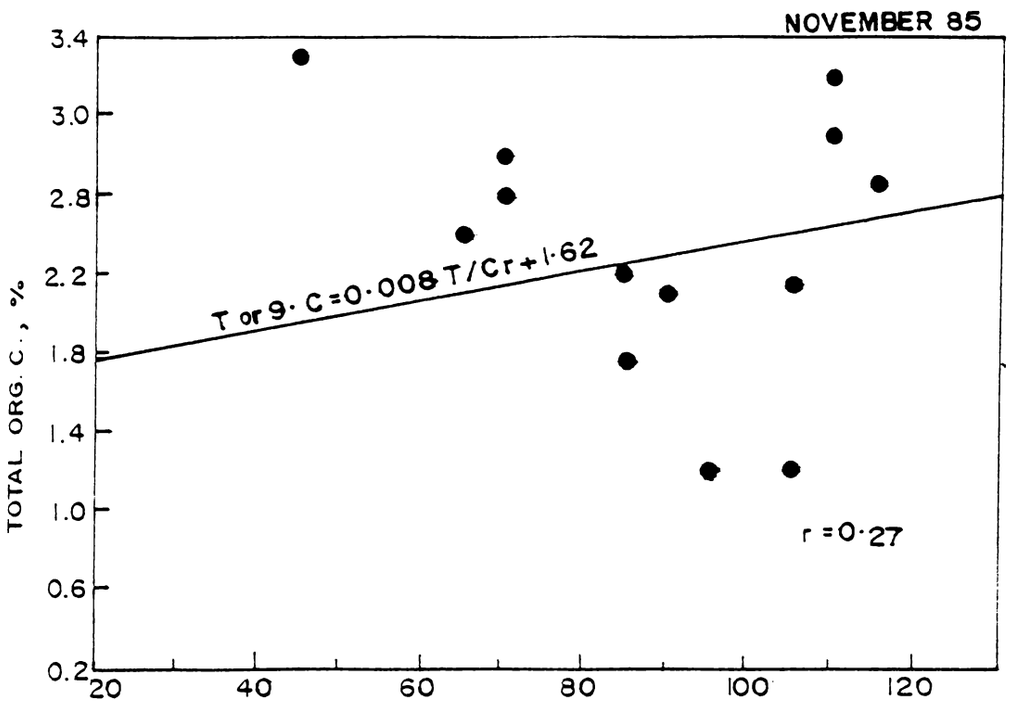


Fig. - 4.28
Relation between total organic carbon and total chromium in sediments.

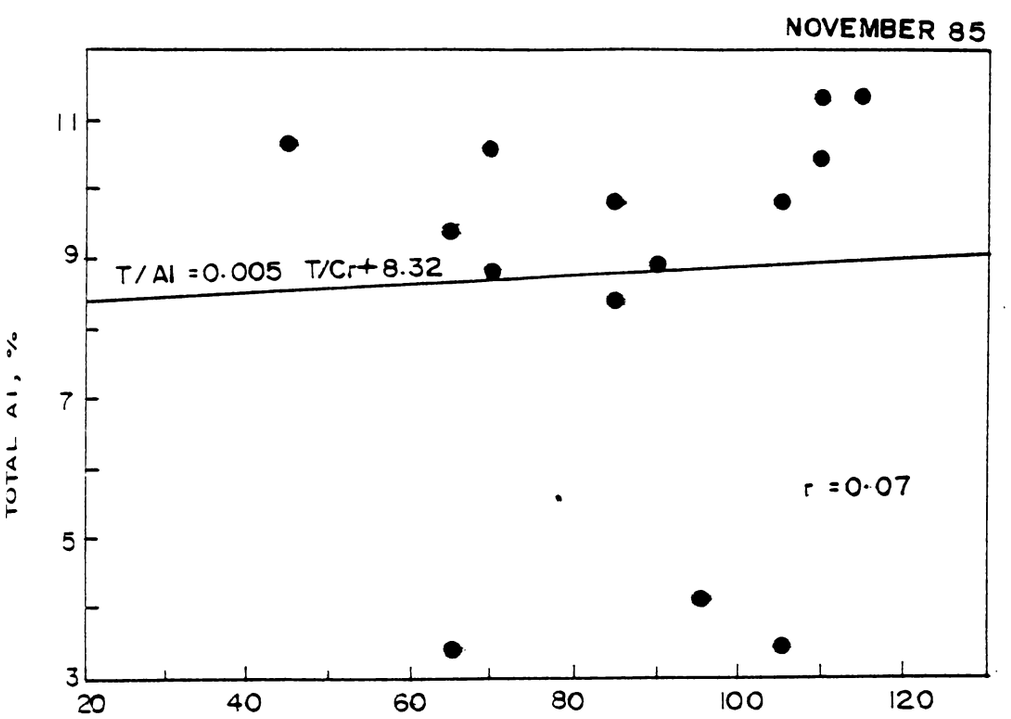


Fig. - 4.29
Relation between total aluminium and total chromium in sediments.

CHAPTER - 5

Summary and Conclusions

The environment is contaminated naturally due to the biotic and abiotic activities. The contamination mainly arises consequent on the accumulation of waste. Any waste can become a resource or a resource can become a waste. The judicious use of resources is therefore, should be the motto of human activity, but for easy gains and circumstantial constraints motivates the man to dump materials in place and out of place leading to toxic contamination or pollution of the environment. It is, in this context, that investigations on the distribution and the abundance of waste discharged into the various ecosystems are becoming relevant and mandatory.

The aquatic environment which receives the waste impregnated with toxic metals and other noxious particulate originating from processing concerns of various magnitude and formulations, besides the municipalities, when attains a level beyond their carrying capacity transforms it into a degraded one. Water gets deteriorated and becomes useless for the purpose for which it is meant (drinking, agriculture,

fishery and industries). In the rivers, lakes, estuaries and seas the bottom sediments also get charged with toxic materials particularly those which are not easily degraded. The metals being nondegradable pose a long term threat to the aquatic community including benthic forms.

The metals in trace quantities discharged into the aquatic environment remain biologically available and are capable of being stored up in ensymes and disrupt the natural chemical equilibrium of the system. The quantification and identification of the trace metals in the environment is a powerful tool in the planning and the administrative circles to initiate and prescribe statutory levels, for the effluents before they are discharged into the different systems - aquatic, terrestrial or aerial. Indian water bodies are not yet dead but are deteriorating at stupendous rate towards this end, due to indiscriminative programmes and policies adopted in the disposal of wastes. For the successful management, monitoring of environment is a must. Monitoring will also provide appropriate action to be followed for addition or deletion of any component whenever and wherever necessary based on the prevailing

ambient levels. It will be helpful, if models are worked out to understand the the complex relationship in the ecosystem prior to granting permission for the discharge of effluents into the system. Protection of environment is never antagonistic in the developmental programmes and it should never be, but it should be the mirror image of development.

The reported heavy metal concentrations of the near shore water in the Bay of Bengal were higher than that in the Lakshadweep Sea. Kureishy et al. (1978 & 1979) have observed the presence of Cu, Fe, Mn, Zn, Ni, Co in considerable quantities in zooplankton as well as fishes from Indian waters. Among the non-essential metals lead was detected in high quantities in zooplankton collected from the Bay of Bengal. Detailed study on mercury contamination in crab muscles, sediments and water samples from shore creek to sea near Bombay has been carried out by Ganesan et al. (1980), which showed that the Hg concentration decreases with increase in distances from the shore. Several food fishes from inshore waters of Bombay have also been found laden with high concentrations of Hg (Tejam & Halder, 1975). In Japan the minamatta disease which broke out in 1953 was

due to consumption of high Hg contaminated fin and shell fish affected by effluents discharged from chemical plant in the Minamatta Bay (Nitta, 1972).

In the Visakhapatanam Harbour mass mortality of fish has been attributed to a combination of factors beginning with the sudden and large scale discharge of acid waste water, incidence of appreciable amount of free Co_2 and drastic depletion of dissolved oxygen (Ganapathy and Raman, 1976). Recently Rao et al. (1985) have proved that the zinc smelter effluent containing copper, lead, zinc and other heavy metal concentrations can affect the growth of sheletonema costatum in about 3% level and kill the alga from 5% level. Another study in the port and coastal areas around the Visakhapatanam has revealed that the industrial wastes enhanced the biochemical oxygen demand of the system thereby resulting in eutrophication (Sarma et al., 1982). The concentration of metal was found to decrease from harbour to inshore water due to the discharge of domestic sewage and industrial effluent which gradually diluted and dispersed in coastal water. Thus there have been a few mass mortalities reported from Indian waters (Ganapathy and Raman, 1976) due to natural causes,

discharge of industrial effluents to which lethal effects could be attributed. Most of the pollutants, therefore, might be imparting contamination and thereby causing sublethal effects on organisms, especially, in the estuarine and near shore marine ecosystem. A marked increasing trend over the years in growth rate of Plaice in Scottish coastal waters was observed to be associated with pollution or changes in benthos due to pollution (Johnston, 1976). The north sea which was supposed to be one of the most polluted seas in the world has been studied to a great extent for effects of pollution with regard to its hydrography, chemistry, water quality, plankton, fish, shell fish, benthos, sediments and geology. In spite of the above fact that none was certain whether fisheries of the north sea were affected by pollution alone (Johnston, 1976). The same applies to the Indian seas although it was established that the backwaters and estuaries with limited circulation have definitely been affected by various kinds of pollution. Effluents from industries were probably the most important sources of trace metals in the estuary. Although sediment analyses do not furnish quantitative data on the absolute degree of pollution they do

indicate their role in ascertaining relative factors of enrichment whereby source of pollution in the aquatic environments may be traced and monitored. Abiotic parameters such as salinity, temperature, alkalinity and p^H may affect the heavy metal absorption in the sediment, depletion of dissolved metals from the water column. It has shown that Pb, Ni and Zn become relatively immobile under such conditions in sediment and metallic sulphide solids were formed (Lu and Chen, 1977). The spatial distribution of metals observed in the estuary showed that the levels of metals were very high, at the effluent discharge point and also in the harbour area. Among trace metals mercury was regarded as a serious toxic metal followed by cadmium, lead and others. Mercury was considered as a non-essential element for living organism. Even at low level mercury and its compounds, present potential hazards due to the enrichment in the food chain. Monomethyl mercury being the most toxic mercury compound known until recently was not tightly bound to sediment and was somewhat water soluble and volatile. It was rapidly assimilated by living organism and then returned relatively stable.

Preventive measures can be adopted to solve water

pollution problems, such as, clean up operations, which were meant for treatment of the polluted water environment. Results of research activities on the estuarine pollution issues were another significant approach for identifying and solving problem of estuarine pollution. Such research activities were particularly significant in contributing and exchanging ideas on environmental issues relating to the estuarine areas and the measures for improving the water quality management.

The present study is an attempt to evaluate some of the metals contained the water column and sediments of Cochin Harbour area. Hg, Pb, Cr, Ni, Fe have been introduced into the estuary either in soluble form or associated with suspended particulate matter. The results suggest that Hg is firmly bound with organic matter in sediments of Cochin estuary. Fine grain particulate matter provides extensive surface area for the adsorption and a suitable medium for retention during transport and deposition. The concentrations of Zn and Cd in sediments were potential contaminants in the river Periyar at the effluent discharge point and behaved in a similar way in the estuarine environment.

These metals are potentially available for the biotic community whereas lead and chromium in sediments were not available to the biota as the metals were not found dissolved in acetic acid fraction. In addition to the heavy metals, large quantities of organic matter was also reaching the estuary from industrial discharge point. Except mercury for all other metals surface water samples were found to have high concentration compared with bottom. This showed that the metals were from storm water or agricultural run off. The higher values observed for dissolved mercury in bottom suggests that solubilisation of mercury from sediments to the overlying water of salinity was the mechanism of mercury transport to the sea. Decrease in the concentration of dissolved metals with salinity showed that the physical mixing was a significant factor in controlling the dissolved concentrations. Dissolved levels were depleted in the high salinity range and particulate contaminant concentrations showed the highest values during summer. The small range of dissolved nickel in the study area suggest that the anthropogenic input of nickel do not alter its distribution significantly. In the case of dissolved and particulate mercury, the

concentrations were found to be less at Stations 4 - 8 and the reverse trend was observed for the Stations 10 - 16. The particulate Cu, Zn, Cd and Pb also showed the same behaviour. The trace metal level in sediments were found to be less at Stations 1 - 6 in comparison with the levels observed for Stations 10 - 16. The Stations 4 - 8 receive water from Chitrapuzha where refinery and fertilizer plants exist. The Stations 10 - 16 on the northern side of the harbour area receive effluents from various industrial complexes situated on the banks of river Periyar. These stations are also under the influence of high tide and low tide from two directions namely Cochin and Munambam guts. It is likely that at these stations the velocity of water movement might have been much reduced because of opposite drag enriching both water column and sediment. The peculiar situation at Station 10 - 16 is reserved for future studies.

In comparison with the baseline levels, the metal concentrations were relatively high in the Cochin estuary, and the threat to the aquatic resources appears to be of high magnitude. Depletion of benthic organisms and fishes may be attributable to the contamination by metals either in water or in

sediments along with other parameters. The study proved that large amount of dissolved metals were removed from the water column, enrich the suspended particulates and get incorporated with the food chain. Even low levels of metal concentrations might lead to accumulation and biomagnification.

The large inventory of trace metals found in the chemically and biologically active surface water may accelerate biogeochemical reactions. The strong sea ward surface flow of the estuarine system may also tend to disperse these pollutants rapidly. Examination of the difference in the concentration between oceanic and Cochin estuarine waters provide insight into the importance of physical processes in controlling the fate of dissolved trace metals in this estuarine system.

It was well known fact that no organic life can develop and survive without the participation of metal ions and these trace metals were essential to sustain biological life. The increasing metal contamination in the river Periyar and the Cochin estuary pose a serious threat to the living aquatic resources and appropriate measures have to be taken to abate total destruction.

The effect of these heavy metals in the environment may be mutagenic, teratogenic and or carcinogenic. At higher dozes even nutritionally essential metals may cause diverse effects. All these suggest further indepth studies for understanding the nature and role of the metals in the context of living aquatic resources and the vast population living in and around this estuary.

BIBLIOGRAPHY

Abdul Aziz, P.K. and Sheela, R. (1987) on the influence of titanium effluents in the composition and distribution of interstitial fauna of Trivandrum Coast. Advances in aquatic biology and fisheries, 337-351.

Agemian, H. and Chau. A.S.Y. (1976) Evaluation of extraction techniques for the determination of metals in aquatic sediments. The Analyst 101. 761-767.

Ansari, Z.A.(1977) Macrobenthos of Cochin backwaters. Mahasagar - Bull. Nat. Inst. Oceanogr. 10, 169-171.

Armansson,H.(1979) Dithizone extraction & flame Atomic Absorption Spectrometry for the determination of Cd, Zn, Cu, Ni Co & Ag in sea water and biological samples. Analy.Chemi. Acta. 110, 21-28.

Badri, M.A. and S.R. Aston (1981) A comparative study of geochemical fractionation of heavy metals in marine sediments. Proceedings of the International Conference on Heavy metals in the Environment, WHO 705 - 8, Amsterdam, 15-18.

Badri, M.A. and S.R. Aston, (1983) Observations on heavy metal geochemical associations in polluted and non-polluted estuarine sediments. Environmental Pollution Ser B. 6: 181-183.

Baeyens, W., Wartel, S., Dehatrs, F., Decadt, G., Bogaert, M., Gillain, G., Dedeurwaerder, H. (1982 a) Distribution, transport and fate of B1, Cd, Cu, Hg, Pb, Sb and Zn in the Belgian coastal marine environment part IV the river Scheldt as a transport route for heavy metals to the sea in programatic van, het wetenschapsbeleid, I. Elskens & A. Distcehe (Ed) Brussel (Belgium).

Balan, A. (1979) The polluted Kallada River. The Malayala Manorama, April, 29.

Bartlet, P.D. (1978). Total mercury and methyl mercury levels in British Estuarine and Marine sediment. The Science of the Total Environment 10: 245-251

Bartlet, P.D. and Craig, P.J.(1981). Total mercury and methyl mercury levels in British Estuarine Sediments. Water Res.15, 37-47.

Bertine, K.K. and E. D. Goldberg, (1977) History of heavy metal pollution in Southern California Coastal Zone - Environmental Science & Technology, 11: 297-299.

Bewers, J.M. Macauley I.D. and Sundly. B. (1974) Trace metals in the waters of St. Lawrence estuary Can. J. Earth Sci. 11: 939-950.

Bewers, J.M. and Yeast, P.A. (1977) Oceanic residence times of trace metals nature 268, 595-598.

Bruland R.W. (1983) Trace metal in sea water. Chemical Oceanography (J.P. Riley and R. Chester edn.) 8, 157-218.

Bruland, K.W. and Franks, R.P.(1979) Sampling & Analytical methods for the determination of Cu, Cd, Zn & Ni at nanogram/litre level in sea water Anal. Chem. Acta 1-5, 23-243.

Bruland K.W. and Franks R.P. (1981) Mn, Ni, Cu, Zn and Cd in the western north Atlantic Nato Advanced Research Institute Conference "Trace Metals in Sea Water" Erice Italy.

Burton, .D.(1978). Chemical processes in estuaries and coastal waters. Environmental and analytical aspects. J.Instn.Wat.Engg.Sci., 32, 31-44.

Carmody, D.J., Pearce, J.B. and Yasso, W.E.s,(1975) Trace metals in sediments of New York Bight. Mar. Pollut. Bull.4.132-135.

Chester, R. and Hughes, M.J. (1967) A chemical technique for the separation of feromanganese mineral, carbonate minerals and adsorbed trace elements from pelagic sediments, Chem. Geo. 2, 249-262.

Chester, R., and Stoner, J.H.(1974) The distribution of Zn, Ni, Mn, Cd, Cu and Fe in some surface waters, from the world oceans. Mar. Chem. 2 17-32.

Cosma, B., Drago, M., Scarponi, G. and Tucci, S. (1977). Heavy metals in Ligurian Sea sediments, Mar. Chem. B, 125-142.

Cosma,B., Contradi, V., Zeniiech, G. and Capelli, R., (1983). Heavy metals in superficial sediments from the Ligurian sea, Italy, Chemist. In. Eco. 1, 331-344.

Devassy, V.P. and Bhattathiri, P.M.A.(1974) Phytoplankton ecology of the Cochin Backwater. Ind. J. Mar. Sci.4 46-50.

Dixit, S.S. and D. Witcomb. (1983) Heavy metal burden in water, substrata and macroinvertebrate body tissue of a polluted river Irwell (England), Environmental Pollution, Ser B. 6: 161-172.

Drago,M., Cosma, B., and Contradi, V.(1981) Distribution of Heavy metals in superficial marine sediments of Savanna Harbour and Vado Ligure Bay (Ligurian Sea). Atti Soc. Tosc. Sci. Nat. Series A. 88, 117-136.

Duinker, J.C. and Kramir, C.J.M.(1977) An experimental study of the speciation of dissolved Zn, Cd, Pb and Cu in river Rhine and north sea by diferential pulse anodic stripping yoltametry. Mar. Chem. 5: 207-228.

Duinker, J.C. and Nolting, R.F.(1977). Disolved and particulate trace metals in the Rhine estuary and southern Bight Mar.. Pollu. Bull. 8(3) 65-71.

Duinker, J.C. and Nolting, R.F. (1982) Dissolved copper, zinc and cadmium in the southern bight of the north sea. Mar. Pollu. Bull. 13, 3, 91-96.

Dutton, J.W.R., Jefferies, D.F. Folkard, A.R. and Jones, P.G.W. (1973) Trace metals in the north sea. Mar. Pollu. Bull. 4, 135-138.

Essink, K. (1980). Mercury pollution in the Ems Estuary. Helgolander Meeresunters 33, 111-121.

Etecheber, H. (1979) repartition et compartment du, Zn, Pb, Cu et Ni dans 1' estuarine de La Gironde. Bul Institute, Geol, Bassin d' Aquintaine,s Bordeaux 25, 121-147.

Forstner, V. and S.R. Patchinneelam (1980) Chemical association of heavy metals in polluted sediments from the lower Rhine River. American Chemical Society Advances Chemical Series, 189: 177-193.

Ganapathy, R.N. and Raman, A.V. (1976) Mass mortality of fish in the Visakhapattanam harbour, Ind. J. Mar. Sci. 5, 134-135.

Ganesan, R., Sha, P.K., Turel, Z.R., and Halder, B.C. (1980) Study of heavy elements (Cd, He, and Se) in the environment around, Bombay by radio chemcial netron activation analysis. Transaction of fourth international conference on environment and environmental research, University of Missouri.

Goldberg, E.B., and Johnson, S. (1958) Chemistry of Pacific pelagic sediments Geochem, Cosmochimi Acta 13, 153-212.

Gopalan, U.K. and Sreekumaran Nair, S.R. (1975) Ecological studies on the floating weed Salviniea

auriculata in Cochin Backwaters and adjacent areas. 1. Associated fauna. Bull dept. Mar. Sci. Uni. Cochin 367-375.

Gore, P.S., Ravindran, O., Unnithan, R.V., (1979) Pollution in Cochin backwater with reference to indicator bacteria. Ind. J. Mar. Sci.8(1) 43-46.

Grasshoff, K; Kremling, K; Olaffson, J; Andreae O.M., and Koroleff, F, (1983) Methods of sea water analysis verlag chemi. New Yourk. pp.189-213.

Griggs, G.B., and Johnson, S. (1978) Botom Sediment Contamination in the Bay of Naples Italy. Mar. Pollut. Bull. 9, 208-214. Hakanson, L. (1977) Sediments as indicators of contamination investigations in the four largest swedish lakes. SNVPM Naturrardsverkets Limnologioka Undersokning Rapport, 92

Haridas, P., Madhupratap, M. and Rao, T.S.S.(1975) Salinity temperature, oxygen and zooplankton biomas of the Backwaters from Cochin to Alleppey. Ind.. J. Mar. Sci. 94-102.

Hashmi, N.H., Kidwai, R.M., and Nair, R.R. (981) Comparative study of the topography and sediments of the western and eastern continental shelves around Cape Comerin. Ind. J. Mar. Sci. 10, 45-50.

Hatch, N.R. and Ott, W.L. (1968) Determination of submicrogram quantity of mercury by atomic absorption spectrophotometry, Anal. Chem. 40,

2085-2087.

Head P.C. and Jones P.D. (1989) Fluxes of waters, solids, and metals through the Mersey estuary, (U.K.) as measured by a continuous data recording station (MIDAS). Proceedings of the International Conference on Estuarine Water Quality Management Geesthacht. Federal Republic of Germany 141 - 146.

Helz, G.R., R.J. Huggett and J.M. Hill, (1975) Behaviour of Mn, Fe, Cu, Zn, Cd and Pb discharged from a wasterwater treatment plant into an estuarine environment, Water Research, 9: 631-636.

Hershalman, G.P., Schafer, H.A., Jan, T.K., and Young, D.K.(1981) Metals in marine sediments near a large California munici al outfal. Mar. Pollut. Bull. 7, 244-250.

Hirst, D.M. (1962) The geochemistry of modern sediments from the gulf of Paria. Geochem. Cosmochem. Acta 26, 1147-1187.

Johnston, R. (1976) Mechanism and problems of marine pollution in relation to commercial fisheries. R. Johnston (ed), Academic press, London 3-156.

Joysingh, J.N. (1976) Industrial water pollution in Kerala. Proceedings of the national seminar on environmental pollution. May 6 - 8, 79-84.

Kemp. A.L.W. and R.L.Thomas, (1976) Impact of man's activities on the chemical compostiion in the

sediments of lakes Onatario, Erie and Huron. Water, Air and Soil Pollution, 5: 469-490.

Kremling, K., and Petersen, H. (1977) The distribution of zinc, cadmium, copper and iron in sea water of the Iceland-Faroe Ridge area 'Meteor' Forsch-Ergcbnisse A-19, pp.10-17.

Kureishy, T.W., George, M.D. and Sen Gupta, R. (1978) DDT concentrations in Zooplankton from the Arabian Sea. Ind.J. Mar. Sci. 7, 54-55.

Kureishy, T.W., George, M.D. and Sen Gupta, R.(1979) Total mecury content in some marine fishes from the Ind. Ocean. Mar. Poll. Bulltn. 10, 357-360.

Kurian, C.V. (1972) Ecology of Benthos in a tropical estuary Proc. Ind. Nat. Sc. Aca 38, 156-163.

Lakshmanan, P.T. Shyanamma, C.S., Balachand, A.N. Kurup, P.G., and Nambisan, P.N.K. (1982). Distribution and seasonal variation of temperature and salinity in Cochin backwaters Ind. J. Mar. Sci. 11(2).

Lee Meyerson, A., Luther, W.G. Krajewaski, J., and Hans, I.R. (1981) Heavy metal distribution in Newark bay sediment.Mar. Pollut. Bull. 7, 244-250.

Loring, D.H. (1975) Mercury in the sediments of the Gulf of St. Lawrence. Canadian jour. of Earth Sciences 12, 1219-1237.

Loring, D.H.(1982) Overview of trace metals in eastern Canadian coastal and estuarine sediments.

International Council for the Exploration of the Sea. 1-30.

Loring, D.H. and Bewers, J.M. (1978) Geochemical Mass balances for mercury in Canadian Ford chemi. geo.22, 309-330.

Lu, J.S.C. and K.Y. Chen, 1977. Migration of trace metals in interface of seawater and polluted surficial sediments. Environmental Science & Technology, 11: 174-182.

Madhupratap, M., Rao T.S.S., and Haridas, P. (1977) Secondary production in the Cochin backwaters, a tropical estuary. Proc. Symp. Warm Water Zoopl. Spl. Publi. UNESCO/NIO 515-519.

Madhusudana Rao; Murthy P.S.N. and Reddy C.V.G.(1972). Distribution of uranium in the shelf sediments along the west coast of India. Ind. Nat. Sci.Aca.38A 114-119.

Malo, B. (1977) Partial extraction of metals from aquatic sediments. Env. Sci. and Tech. 11, 277-282.

Mathew K.J. (1978) Health problems of Kuttanad. Kerala Medical J.. V.18, 77-84.

Michaelis, W. (1989). The Bilex concept - Research supporting public water quality surveliance in estuaries. Proc. Int. Conf. Estuarine Water Quality Management Geesthacht, Federal Republic of Germany

79-88.

Murthy, P.S.N. Rao C.H.M., and Reddy, C.V.G.(1973) partition patterns of Fe, Mn, Ni and Co in the shelf sediments of west coast of India Ind. J. Mar. Sci. 2, 6-12.

Murthy, P.S.N., Rao C.H.M., Paropakari, A.L. and Topgi, R.S.(1976) Distribution pattern of Al, Ti, Mn, Cu and Co in sediments of the northern half of the western continental shelf of India. Ind. J. Mar. Sci. 7, 67-71.

Murty, P.S.N., Rao C.H.M., Paropkari, A.L. and R.S. Topgi, (1978) Distribution patterns of Aluminium. Titanium, Manganese, Copper and Nickel in sediments of the Northern half of the western continental shelf of India. Ind. J. Mar. Sci., 7: 67-71.

Murty, P.S.N. and M. Veerayya, (1981) Studies on the sediments of Vembanad Lake, Kerala State. Part IV - Distribution of trace elements. Ind. J. of Marine Sci.s, 10: 165-172.

Nair, N.B., Abdul Aziz, P.K., Dharmaraj, K., Arunajalam, M., Krishna Kumar, K. and Balasubramoniam, N.K. (1983) Ecology of Indian estuaries Part-I. Physico-chemical features of water and sediment, nutrients of Ashtamudi estuary. Ind. Jor. Mar. Sciencs, 12, 143-150.

Nair, N.B., Abdul Azis, P.K., Arunachalam, M., Krishnakumar, K. and Dharmaraj, K. (1984) Ecology of Indian estuaries. Distribution of total phosphorus, total nitrogen and total pottasium in The sediments of Ashtamudi estuary, Mahasagar Bulletin of the National Institute of Oceanography, 17, 33-39.

Nair, N.B., Abdul Azis, P.K., Arunachalam, M, Dharmaraj, K. and Krishnakumar, K. (1985) Ecology of Indian Estuaries. Ecology and distribution of benthic macrofauna in the Ashtamudy estuary. Mahasagar Bullentin of the National Institute of Oceanography, 17, 89-101.

Nair, N.B., Abdul Azis, P.K., Suryanarayanan, H., Arunachalam, K., Krishnakumar, K. and Treasa V. Fernandez (1987) Distribution of heavy metals in the sediments of the Ashtamudi estuary. Dr. S.Z. Qasim, Sastyaboapurti, Falicitations volume 269-298.

Nair, N.B., and Rajan, K.C. (1974) Observation on the effect of the effluents from a titanium plant on the interstitial fauna. Biol. Inst. Oceanogr. Univ. Oriento, 13, 107-124.

Nair, U.N. and Nair, B.K. (1986).Seasonality of trace metals in crassostrea madarasensis (Preston) inhabiting in Cochin Backwaters, NationalSeminar on Mussel watch, Cochin Vol.1, 6-12.

Nitta. T. (1972) Marine pollution in Japan. In. Marine Pollution and Sea Life (Mario Ruivo ed.) FAO 77 - 81.

Oliver, B.G (1973) Heavy metal levels of Ottawa and Ridean river sediments. Environmental Science and Technology 7, 135-137.

Ouseph, P.P. (1986) Status report on marine pollution along Kerala coast. Proc. Interdepartmental Seminar on Status of marine pollution in Ind., Department of Ocean Development, New Delhi, 86-105.

Ouseph, P.P. (1987) Heavy metal pollution in the sediments of Cochin estuarine system. Proc. Nat. Sem. Estuarine Management, Trivandrum 123-126.

Ouseph, P.P. (1989) Dissolved particulate and sedimentary mercury in the Cochin estuary. Proc. Int. Sem. Estuarine Water Quality Management, Geessthatch, Federal Republic of Germany 461-465.

Ouseph, P.P. (1992) Dissolved and particulate trace metals in the Cochin estuary. Mar. Polu. Bull. 24, 4, 181-192.

Ouseph, P.P; Jayan, K.G; Johny Joseph and Jayasankar, C.U. (1989) A method for the extraction of large number of dissolved heavy metals from sea water. Presented at the nat. conf. Aquatic Pollution, Trivandrum. (in press).

Papakostidis, G., Grimanis, A.P., Zafiropoulos, D., Griggs, G.B. and Hopbins, T.A.(1975) Heavey metals in sedisments from the Athens sewage out fall area. Mar. Pollut. Bull. 6, 136-139.

Paropakari, A.L., Topgi,R.S., Rao, Ch.M., and Murthy,P.S.N.(1980) Doistribution of Fe, Mn, Co, Ni and Zn in the non-lithogenious fractions of the gulf of Cutch. Ind. J. Mar. Sci. 189-200

Pattersen,C.C and Schaule, B.K. (1981) lead concentrations in the north east pacific. Evidence for global anthropogenic perturbations. Earth & Planetary Science letters 54, 97-116.

Paul, A.C. and Pillai, K.C. (1983) Trace metals in a tropical river environment - distribution. Water, air, soil pollu. 19, 63-73.

Paulson, A. J. and Feely, R.A. (1985) Dissolved trace metals in the surface waters of puget sound. Mar. Pollu. Bull. 16, 7, 285-291.

Perkins, E.J. Gilchrist, J.R.S., Abbott, O.J. and Halcrow, W (1973) Trace metals in solway firth sediments Mar. Poll. Bull. 4, 59-61.

Pita, F.W. and N.J. Hyne, (1975) The depositional environment of zinc, lead and cadmium in reservoir sediments. Water Research, 9: 701-706.

Presten,A; Jeffenis, D.F; Dutton, J.W.R; Harvey, B.R. and Steele. A.K. (1972) British Isles Coastal Waters, The concentrations of selected heavy metals in sea water, suspended matter and biological indicators - a pilot survey, Envi. Poll. 3, pp.69-82.

Qasim, S.Z. (1980) Adaptations in phytoplankton to changing conditions in tropical estuaries. Mahasagar - Bull. Nat. Inst. Ocean. 13, 117-124.

Qasim, S.Z., and Madhuprathap, M.,(1981) Changing ecology of Cochin backwaters. Contribution to Marine Sciences dedicated to Dr. C.V. Kurian 138-140.

Rajan, K.C. (1972) Studies of the interstitial fauna of the southwest coast of India. Ph. D. thesis.

Rajendran, N. and Kurian, C.V. (1986) Cressostres Madrasensis (Psreston)-Indicator of metal pollution in Cochin backwaters. National Seminar on Mussel Watch, Cochin Vo.I, 121-126.

Rao, C.M. and M.G.A.P. Setty, (1976) Distribution of iron maganese, cobalt and nickel in sediment cores of the Nnorthern Arabian Sea. J. of Geological Society of Ind., 17: 252-261.

Rao. U., Mohan, V. and Murthy S.B.K. (1985) Effect of zinc smelter effluents on the growth of skeletonema costatum in marine plants, their biology, chemistry and utilisation. V. Krishnamurthy (ed)., All Ind. Sypm. Mar. Plants, Dona Paula, Goa, 109-114.

Remani, K.N.(1979) Studies on the effect of pollution with special reference to benthos in Cochin backwaters. Ph. D. thesis submitted to the University of Cochin.

Remani K.N., Venugopal, P., Saraldevi, K. Lalitha, S and Unnithan R.V. (1980). Sediments of Cochin backwaters in relation to pollution Ind. J. Mar. Sci. 9 (2).110-116.

Rippey. B. (1982) Sediment - Water interactions of Cu, Cn and Pb discharged from a domestic waste water, source into a Bay of Lough Neagh, Northern Ireland. Environmental Pollution Ser B. 3: 199-214.

Robert Bristow (1959) Cochin Saga, Pico Publishing Company, Ernakulam.

Sankaranarayanan, V.N., Purushan, K.S. and Rao, T.S.S. (1978) Concentrations of some of the heavy metals in the oyster crassostrea madrasensis (preston) from the Cochin region. Ind. J. Mar. Sci. 7, 130-131.

Sankaranarayanan, V.N., and Rosamma Stephen (1978) particulate iron, manganese, copper and zinc in water of the Cochin backwaters. Ind. J. Mar. Sci. 7, 201-203.

Santhakumari, V., and Vannucci, M. (1977) Variability of Hydromedusae from Aroor, Cochin backwaters. Proc. Symp. Warm water Zool. spl. Pubnl.UNESCO/NIO 354-361.

Sarala Devi, K., Venugopal, P., Remani, K.N., Lalitha, S., and Unnithan, R.V., (1979). Hydrographic features and water quality of Cochin backwaters in relation to industrial polltion. In. J. Mar. Sci. 8, 141-145.

Sarala Devi, K., Venugopal, P., Remani, K.N., Lalitha, S. and Unnitha, R.V. (1979) Hydrographic features and water quality of Cochin backwaters in relation to industrial pollution. Ind. J. Mar. Sci. 8 (3), 141-145.

Sarma, V.V., Raju, G.R.K. and Bose Babu, J. (1982) Pollution characteristics and water quality in the Visakhapattanam harbour, Mahasagar Bulltn. Nat. Instt. Ocephy. 15, 1, 15-22.

Scmidt, D., (1976) Distribution of seven trace metals in sea water of the inner German Bight. ICES.DOC.C.M. 1976/C; 10 (Mimco).

Sen Gupta, R., Qasim, S.Z., Fondekar, S.P., and Topgi, T.S. (1980). Dissolved Petroleum Hydrocarbons in some regions in the northern Indian Ocean. Mar. POll. Bull. 11, 65-68.

Sen Gupta, R., Singbal., S.Y.S., Sanzgri, S. (1978) Atomic Absorption analysis of a few trace metals in Arbaian Sea. Ind. J. Mar. Sci. 7, 295-299.

Silas, E.G. and Pillai, V.K. (1976) Water pollution and fish mortality in the Cochin backwaters. Proce. Nat. Semi. Env. Pollu. May 6-8, 323-327..

Spencer, D.W., and Bewer, P.G. (1969) The distribution of copper, zinc, and nickel in sea water of the gulf of Marine and Sargasso sea. Geochm. & Cosmoch. Acta 33, 325-339.

Sujatha Sanggiri and Colorine Moraces (1979) Trace metals in the Laccadives Sea Ind. J. Mar. Sci 4, 254-257.

Talbot, V. (1983) Lead and other trace metals in the sediments and selected biota of Princes Royal Harbour. Albany, Western Australia. Environmental Pollution. Ser. B. 5: 35-49.

Tejam, B.M. and Halder, B.C. (1975) Preliminary survey of Hg in fish from Bombay and Thana environment. Ind. J. Envtl. Health, 17, 9-16.

Tessier, A., Combell, P.G.C., and Bisson, M. (1979) Sequential extraction procedures for the speciation of particulate trace metals. Analy chemist 51, 44-85.

Thomson,J.A.J., Macdonald, R.W. and Wong, C.S. (1980) Mercury geochemistry in sediments of a contaminated fjord of coastal British Columbia. Geochem. J. 14: 71-82.

Unnithan, R.V., Viayan, M., and Remani, K.N. (1975) Organic pollution in Cochin backwaters. Ind.J.Mar.Sci.4, 39-42.

Unnithan, R.V., Gore, P.S, Revindran, O., Venugopal, P., Sarala Devi, K., and Ramesh, K.N. (1981) Deposition of tar like residue in beaches of Kerala. Ind. J. Mar. Sci.10, 371-372.

Venugopal, P., Sarla Devi, K., Remani, K.N. and Unnithan, R.W. (1982) Trace metal levels in the sediments of the Cochin backwaters. Bull. of the National Instt. of Ocenography, 15, 205-214.

Vijalakshmi Nair, R., (1975) Distribution of Chaetognaths along the salinity gradient in the Cochin backwaters an estuary connected to the Arabian sea. J. Mar. Biol. Ass.Ind. 721-730.

Vijayamohan, T.G., Nair, G.A., Nair, N.B., and Suriyanarayana, H. (1985) Dirunal variation of interstitial fauna in Trivandrum beach exposed to effluents from the Titanium dioxide factory. Aquatic biology, 5, 1889-191.

Vijayan, M., Remani, K.N., and Unnithan, R.V. (1976) Effect of organic pollution on some hydrographic features of Cochin backwaters. Ind. J. Mar. Sci.5, 196-200.

Vogel, A.L. (1978) A text book of quantitative inorganic analysis E L B S and Longman.

Walkey, A. (1947) A critical examination of a rapid method for the estimation of organic carbon in soil. Soil science 63: 251-263.

Appendix

In connection with the thesis the following research papers are published:

(1) OUSEPH, P.P. (1986) Status report on marine pollution along Kerala coast. Inter-departmental seminar on status of marine pollution in India. Department of Ocean Development, New Delhi, 86 - 105.

(2) OUSEPH, P.P.(1987) Heavy metal pollution in the sediment in Cochin estuarine system. Proceedings of National Seminar, Estuarine Management, Trivandrum - 123 - 126.

(3) OUSEPH, P.P. 1989) Dissolved particulate and sedimentary mercury in the Cochin estuary. Proceedings of the International Seminar on Estuarine Water Quality Management, Geesthacht, Federal Republic of Germany, 461 - 465.

(4) OUSEPH, P.P.(1992) Dissolved and particulate trace metals in the Cochin estuary. Marine Pollution, Bulletin, Vol. 24, 4, 186 - 192.

Proceedings of the Interdepartmental Seminar on Status of Marine Pollution in India organised by the Department of Ocean Development, New Delhi.

STATUS REPORT OF MARINE POLLUTION ALONG KERALA COAST

P.P. Ouseph
Regional Centre
Centre for Earth Science Studies
St. Vincent Street, Cochin

INTRODUCTION

Marine pollution, as defined by the U.N. Conference on Human Environment is "the introduction by man, directly or indirectly, of substances or energy into the marine environment resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fisheries, impairment of quality for use of sea water and reduction of amenities".

Kerala has a coast line of 560 km length extending from Manjeshwar in the north to Poovar in the south, being 14 km in length per 100 sq. km of land territory. Parallel to the coast, there is a chain of backwater lagoons, interconnected with natural or artificial canals. There are in all 29 major river basins consisting of 41 west flowing rivers, which reach the Arabian Sea directly or through the backwaters, which in turn join the sea. Since the rivers, backwaters and the sea are inter-connected, pollution of one water body causes pollution of the next body ultimately resulting in marine pollution.

CAUSES OF MARINE POLLUTION

Following are the major sources of marine pollution in Kerala regions.

Population related pollution

The population density of Kerala is 655 persons per sq. km as per 1981 census. The arrangements for disposal of sewage and sullage from the settlements are far from adequate. Only about one seventh of the population has access to sanitary modes of disposal of waste. Table 1 gives daily pollution load in terms of BOD per day, that may reach the marine environment, calculated on the basis of 1981 census. The quantum of pollution caused by direct/indirect discharge of untreated sewage into our water bodies is alarming. It is

estimated that the organic putriable matter exerting a BOD of 630 metric tonnes per day is reaching our marine environment.

TABLE - 1

Pollution Load into Marine Environment from Municipalities/Corporations along the Coast Line of Kerala.

Sl. No.	Municipality/ Corporation	Population (as per 1981 census)	Population Load Kg/day of B.O.D.
1.	Trivandrum	483086	144925.80
2.	Varkala	34009	10202.70
3.	Quilon	137943	41382.90
4.	Alleppey	169940	50982.00
5.	Vaikom	21097	6329.10
6.	Cochin	513249	153974.70
7.	Chavakkad	34344	10303.20
8.	Kodungalloor	28334	8500.00
9.	Ponnani	43226	12967.80
10.	Calicut	394447	118334.10
11.	Badagara	64174	19252.20
12.	Tellicherry	75561	22668.30
13.	Cannanore	60904	18271.20
14.	Kasargod	43137	12941.10
	Total Pollution load (Kg/day of B.O.D.)		631035.30

TABLE - 2

Direct Discharge of Trade Effluent into Coastal Zone of Kerala (m^3/day)

Receiving body	Food & drink industries effluents	Engineering industries effluents	Chemical industries effluents	Other organic effluents	Total
Sea	-	-	41,600	-	41,600
Tidal waters	1,150	41,437	1,27,985	54,850	2,25,422
Total	1,150	41,437	1,69,585	54,850	2,67,022

Industries

There are over 200 medium and large scale industries and about 2000 small scale industries which contribute to the marine pollution. Approximately, two third of the industrial effluents generated in the State is discharged into the sea or into the tidal waters. These effluents are generated from chemical and engineering industries, food and drug manufacturing as well as industries related with paper, rayon, rubber, textiles, plywood and tanneries. Some of these major industries are identified in Fig.1 and estimated direct discharge of the effluents into the coastal zone is included in table 2.

Agriculture

The extensive use of fertilisers and insecticides/fungicides etc. causes considerable damage to the quality of water in rivers ultimately adding to the marine pollution problem and seriously affecting human beings as well as aquatic flora and fauna. Additionally, retting of coconut in the backwaters causes deterioration of the water quality. Retting is a bio-chemical process inducing salt organic material into water bodies. This causes depletion of dissolved oxygen thereby degenerating aquatic flora and fauna. The major retting zones along the Kerala coast are identified in Fig.1.

Oil tankers, mechanised fishing and related operations

The operation of large scale oil tankers and other oil connected activities considerably add to the problem of marine oil pollution. Apart from the oil spills from the tankers, fishing boats operated in various backwaters and sea also contribute to oil pollution.

Air pollution

The major air pollutants are suspended matters, oxides of nitrogen, sulphur and carbon monoxide which are emitted from power generating stations, industrial plants, construction projects, smoke discharges from vehicles and solid waste disposal operations. These pollutants reach the sea through rain and atmospheric transport of particulate matter.

MONITORING OF MARINE POLLUTION IN THE VICINITY OF KERALA COAST

The monitoring of Marine Pollution can be broadly classified by the detection and estimation of the following parameters in water, sediment, particulate matter and selected marine organisms.

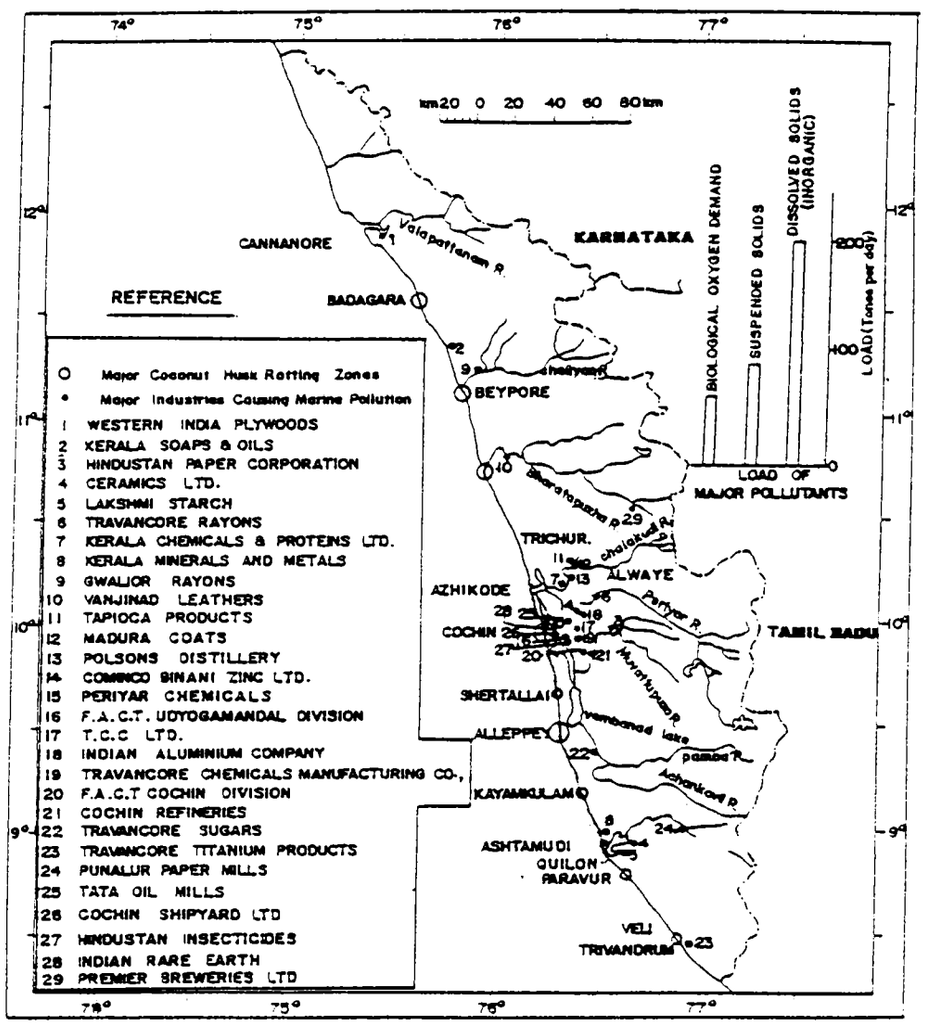


Fig. 1 : MAJOR INDUSTRIES CAUSING MARINE POLLUTION IN KERALA

1. Biological oceanography

2. Heavy metallic contaminents

3. Pesticides/insecticides

4. Petroleum hydrocarbon

Biological Oceanography

The increasing loads of sewage and industrial waste in the Cochin estuary have created conditions which are extremely

destructive to plants and animals (Qasim and Madhupratap 1981). Benthos of the Cochin backwaters has been studied by Kurian (1972) and more recently by Ansari (1977). From these studies, it has become clear that the density of bivalves, gastropods and isopods in the backwaters has been considerably reduced with time. These are attributed to the increasing pollution (Qasim and Madhupratap,1981). Study by Ramani (1979) indicates that in some of the polluted areas, the BOD values reach 513.76 mg/litre, sulphide 4.97 mg/litre and oxygen content less than 0.05 ml/litre. The effects of industrial pollution are clearly seen in the form of depletion of biota especially benthic organisms, fish mortality and presence of high ammonia in water hydrobiological conditions of Cochin backwaters are greatly influenced by sea water intrusion and influx of river water as shown by the distribution of salinity and temperature (Lakshman et al.,1982). The organic carbon in the sediments are higher in the monsoon season due to the contribution from land run off (Ramani et al.,1980). The study with reference to the indicator bacterial revealed that the principal source of faecal pollution is non-human type originating from land drainage, sewage and organic discharge (Gore et al.,1979). The higher C.O.D. values observed are probably due to domestic sewage and wastes discharged into the harbour area (Sarala Devi et al., 1979).Previous studies have shown appreciable degree of organic pollution in Harbour area (Unnithan et al.,1975; Vijayan et al.,1979).

Heavy metallic contaminents

Study of particulate matter of water from Cochin backwater for trace metals indicated that this environment contain high content of Zn, Cr etc. due to industrial pollution (Sankaranarayanan and Rosamma Stephen, 1978).High concentrations of Zn, Cu, Fe, Mn,Zn and Hg in the backwater, oyster (Crassostrea madrasensis)(Preston) of Cochin harbour indicated that high metal load in the tissue was observed during the breeding period and also when the estuary maintained high salinities from October to April. The suitability of the oyster as an indicator organism for metal pollution in Cochin backwater has been discussed by Rajendran and Kurian (1986). Some of the benthic organisms, such as mussels and oysters, have accumulation of zinc higher than the permitted limit (Ramani, 1979).

Pesticides/Insecticides

Very limited work has been taken up in monitoring pesticides and insecticides.

Petroleum Hydrocarbon

Unnithan et al (1981) reported that tar like deposits from 14 beaches of Kerala appear to be derived from oil

spills and oil tanker washings. The concentration of dissolved hydrocarbons in the Cochin region of the Arabian Sea is between 14.6to18.1 microgram/litre (Sengupta et al., 1980). Out of 5.5 million tons of cargo handled by Cochin Port, mor than 4 million tons is oil. Better control measures are required to prevent spillage of oil inside the port area while being loaded or unloaded as well as to control pollution by discharge of waste mixed with oil from ballasting tanks into the sea.

MARINE POLLUTION FROM RIVER DISCHARGE

It is known for the past several years that some of the rivers of Kerala, viz. Chaliyar, Periyar, Chitrapuzha, Kallada etc. have polluted the estuarine flora and fauna. It has been estimated that 183 m^3 of trade effluents are being dumped into our rivers and tidal waters every year (Nair, 1984). It has been recognised that a greater potential hazard exists in estuarine and nearshore areas because of their proximity to sites of industrial and domestic activity, resulting in concentration of specific pollutants by run-off or by biological activity.

THE IMPORTANCE OF COCHIN ESTUARINE SYSTEM

The Centre for Earth Science Studies has undertaken a major work for the monitoring of the heavy metallic contaminents in the Cochin harbour area where the major industrial discharge to the coastal environment of Kerala is envisaged.

The Cochin estuarine system receives industrial effluents from various factories which include metallurgical, fertilizer, chemical, rare earth, newsprint, etc. The shipping facilities, trade effluents, land drainage and also the sewage disposal makes the estuary more polluted. There are also inorganic compounds such as arsenic salts, copper oxychloride, copper sulphate etc. used in agriculture as pesticides, insecticides and fungicides which reach the estuary on its way to sea.

Estuaries are one of the most productive and biologically active areas in the marine environment. The infantile stages of the fishes and shellfish are spent in these environments. Heavy metals are biologically non-degradable and tend to accumulate in these marine organisms to pass on finally to man. Hence a knowledge of the heavy metal distribution is of extreme importance in order to understand the bioavailability and toxicities in the marine environment.

The study initiated by Centre for Earth Science Studies related to the monitoring of heavy metallic contaminents in the Cochin harbour and river Periyar by establishing 46 stations as shown in Fig. 2. Preliminary inves-

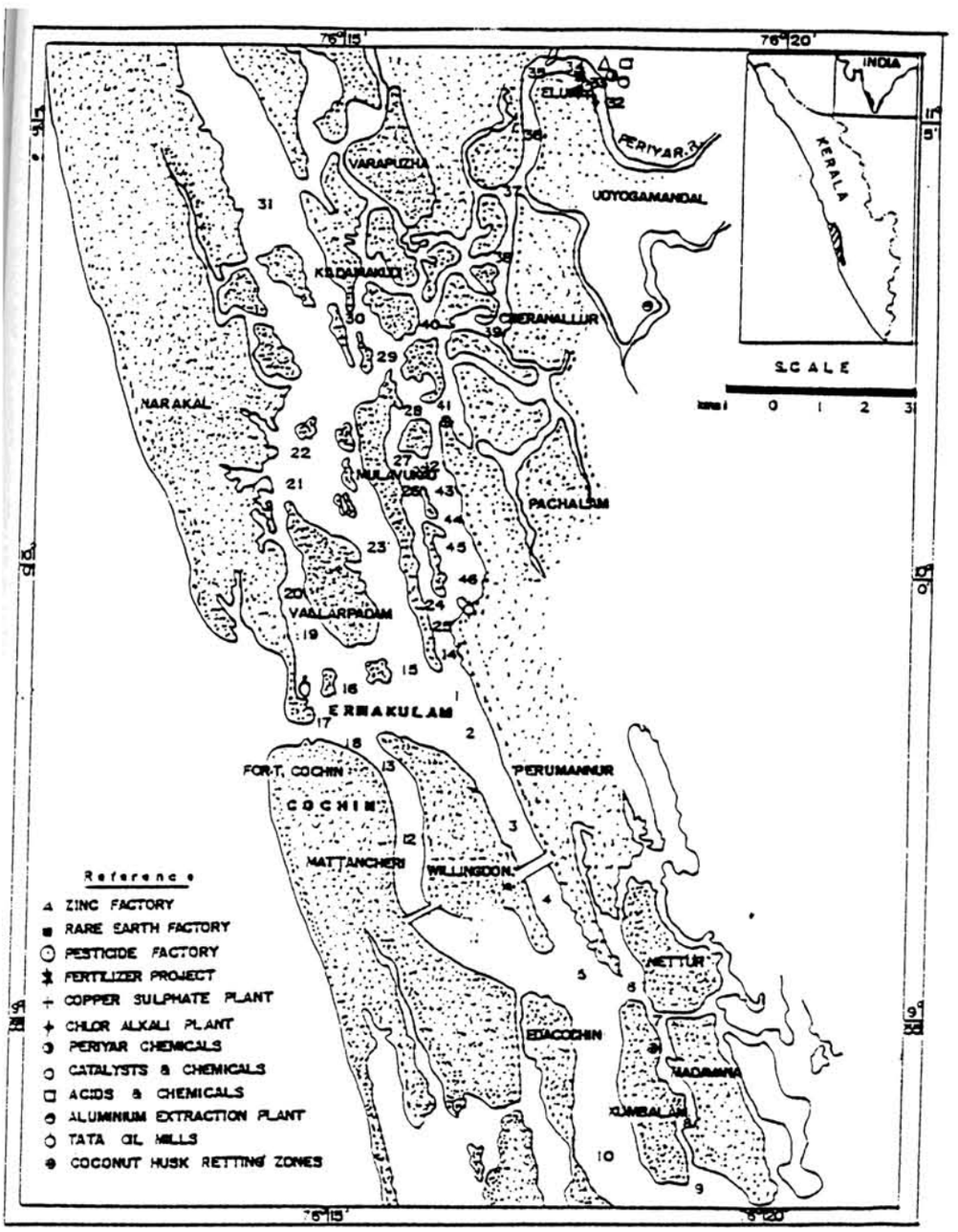


Fig-2 : LOCATION MAP WITH DETAILS OF SAMPLING STATIONS AND MAJOR INDUSTRIES

tigations were carried out in July 1985, Nov. 1985 and April 1986. From all stations sediment samples were collected using a Van Veen Grab. Water samples were collected for 28 station locations for the estimation of dissolved and particulate mercury.

Analysis: The samples were dried at 60°C to a constant weight. Before drying the rock fragments, shells and visible organisms were removed by hand picking. The dried samples were manually powered and homogenised as per the method of Hershelman et al. (1981). The following extraction procedures were employed. The total metal content (Drago et al.1981) and the potential bio-availability of metals (Loring,1982). The extracts were analysed for Pb, Zn, Cr, and Cd by AAS. Five replicate analysis of one sample gave a coefficient of variation of 4.8% for Pb, 6.5% for Zn, 5.5% for Cr and 7.5% for Cd.

Mercury: Wet sediment samples were digested with a mixture of nitric and sulphuric acids (Thomson et al., 1980). Cold vapour AAS technique was used for the estimation of mercury as described by Batch and Ott, 1968.

Surface samples were collected using a plastic bucket and Van Dorn Sampler was used for bottom samples. The samples were acidified with excellar grade conc. HNO_3 20 ml/ litre (Freemann and Schmidt, 1982) and a small amount of Potassium persulphate was added in order to oxidise the interfearing organics (Thomson and MacDonald,1980). Millipore filter paper used for filtering the samples and the filtrate was acidified for dissolved mercury estimation. Total mercury was determined by directly acidifying the sample. The amount of suspended matter was determined by the gravimetric procedure by filtering a bulk volume of the sample and the values were computed from the known concentration of dissolved and total mercury. After acidification the samples were kept in the freezed condition. The above preservation done within six hours and the analysis of mercury carried out within eight days of sample collection. In each case the values for the blanks were determined. Five replicate determinations done for one sample from each set of samples collected seasonally gave coefficient of variation of 3.8 to 4.6% at concentrations between 5 to 100 mg/litre. The detection limit was about 5 ng/litre. High purity reagents were used for mercury analysis. Mercury was determined by using the cold vapour atomic absorption technique described by Batch and Ott, 1968. Analytical reagent grade (Sarabhai M. Chemicals) Mercuric chloride was used for the preparation of standard solutions.

6. RECENT FINDINGS ON HEAVY METAL POLLUTION

6.1. Total metal content

The concentration of heavy metals in the sediments of river Periyar and Cochin harbour are shown in Fig. 3-7. Total metal

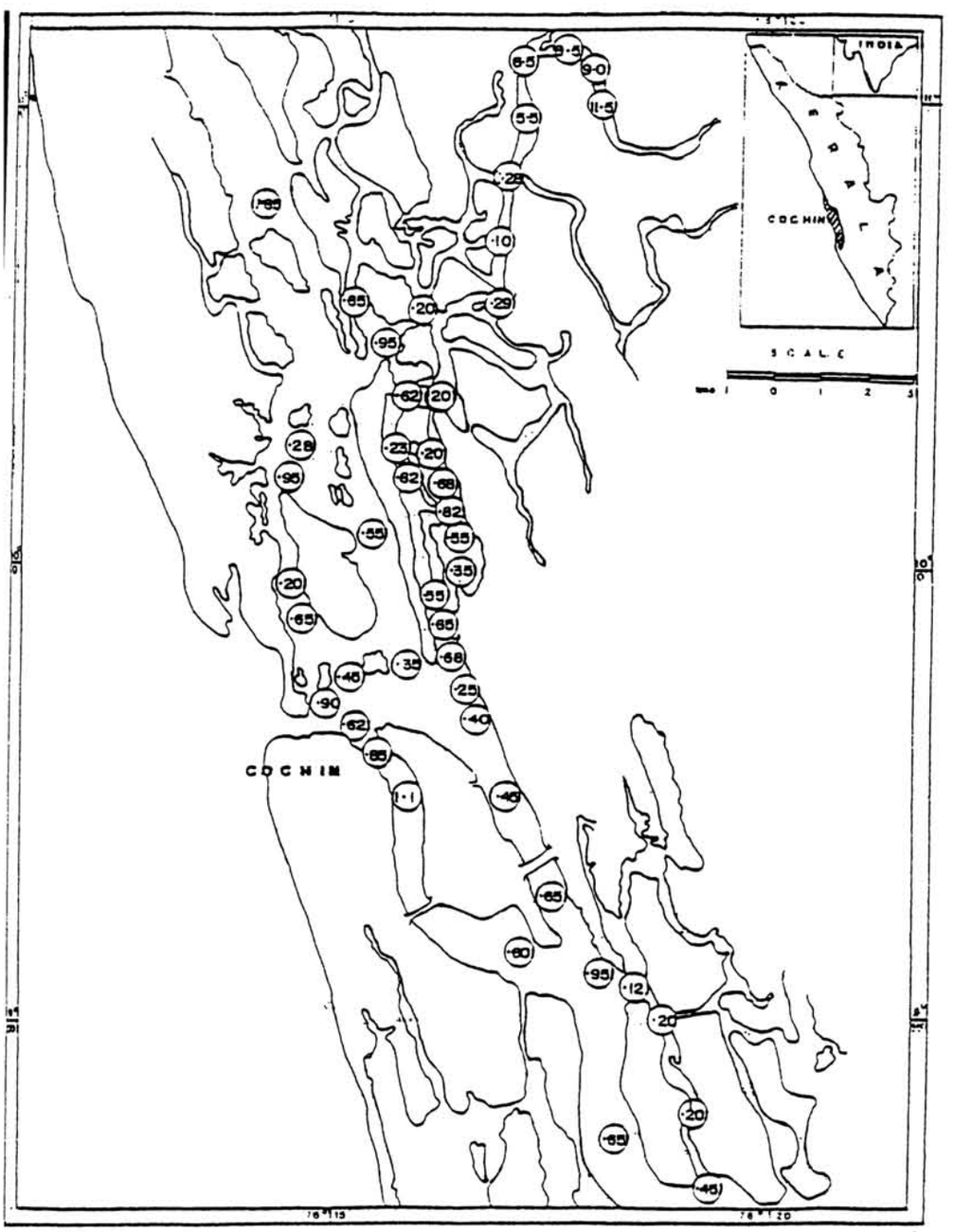


Fig. 3 - MERCURY DATA IN SEDIMENTS (ppm)

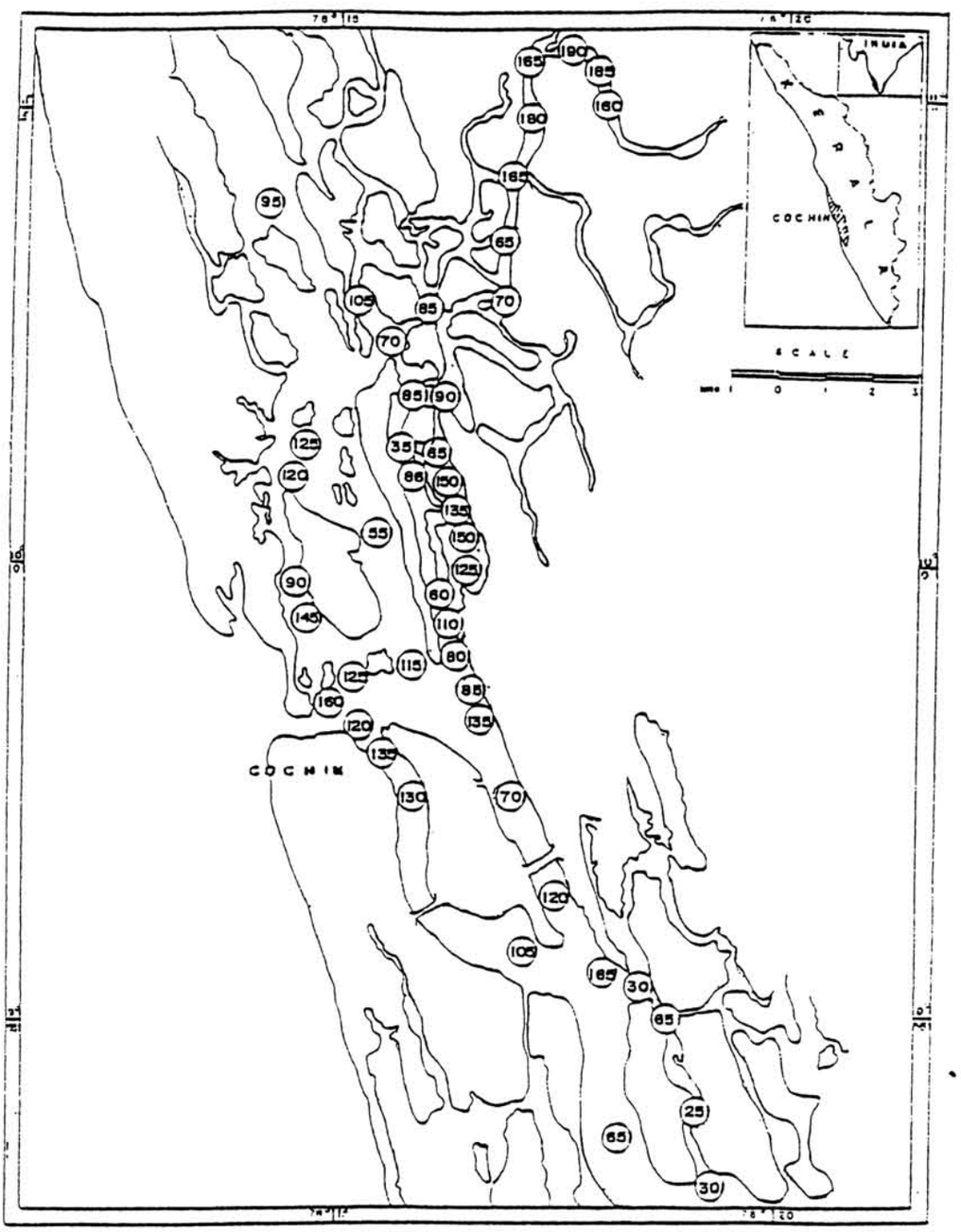


Fig. 4 - LEAD DATA IN SEDIMENTS (ppm)

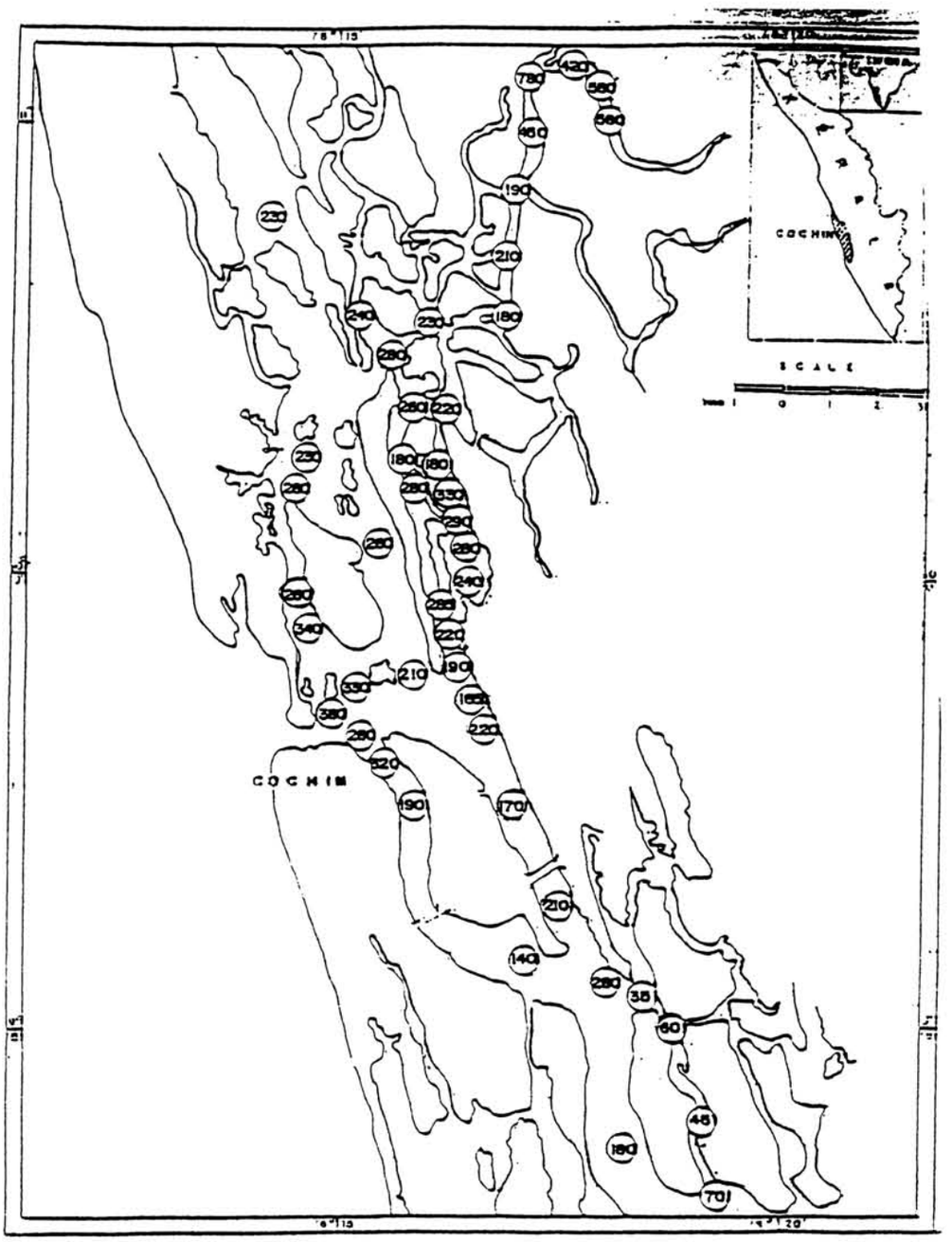


Fig. 5 · ZINC DATA IN SEDIMENTS (ppm)

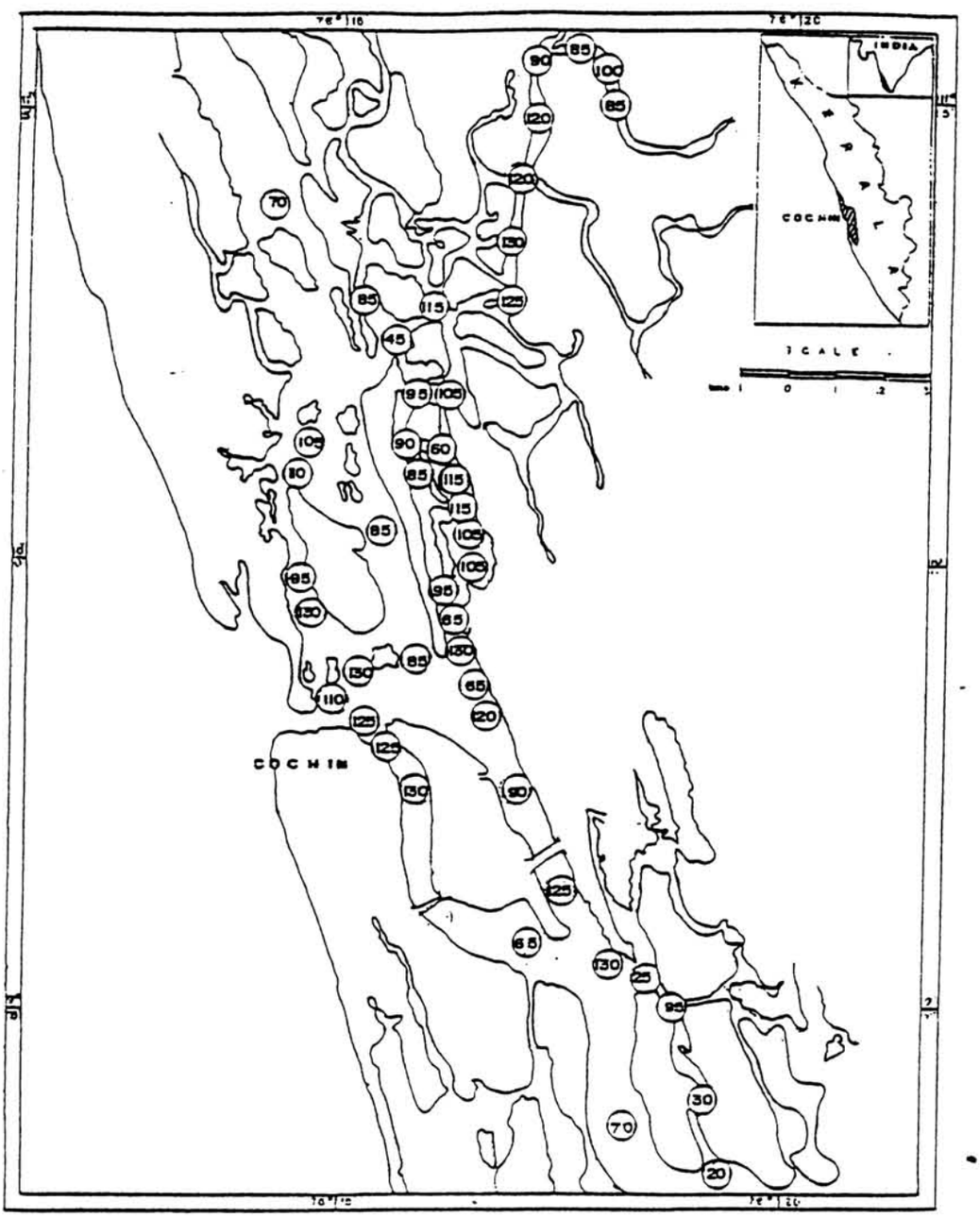


Fig - 6 - CHROMIUM DATA IN SEDIMENTS (ppm)

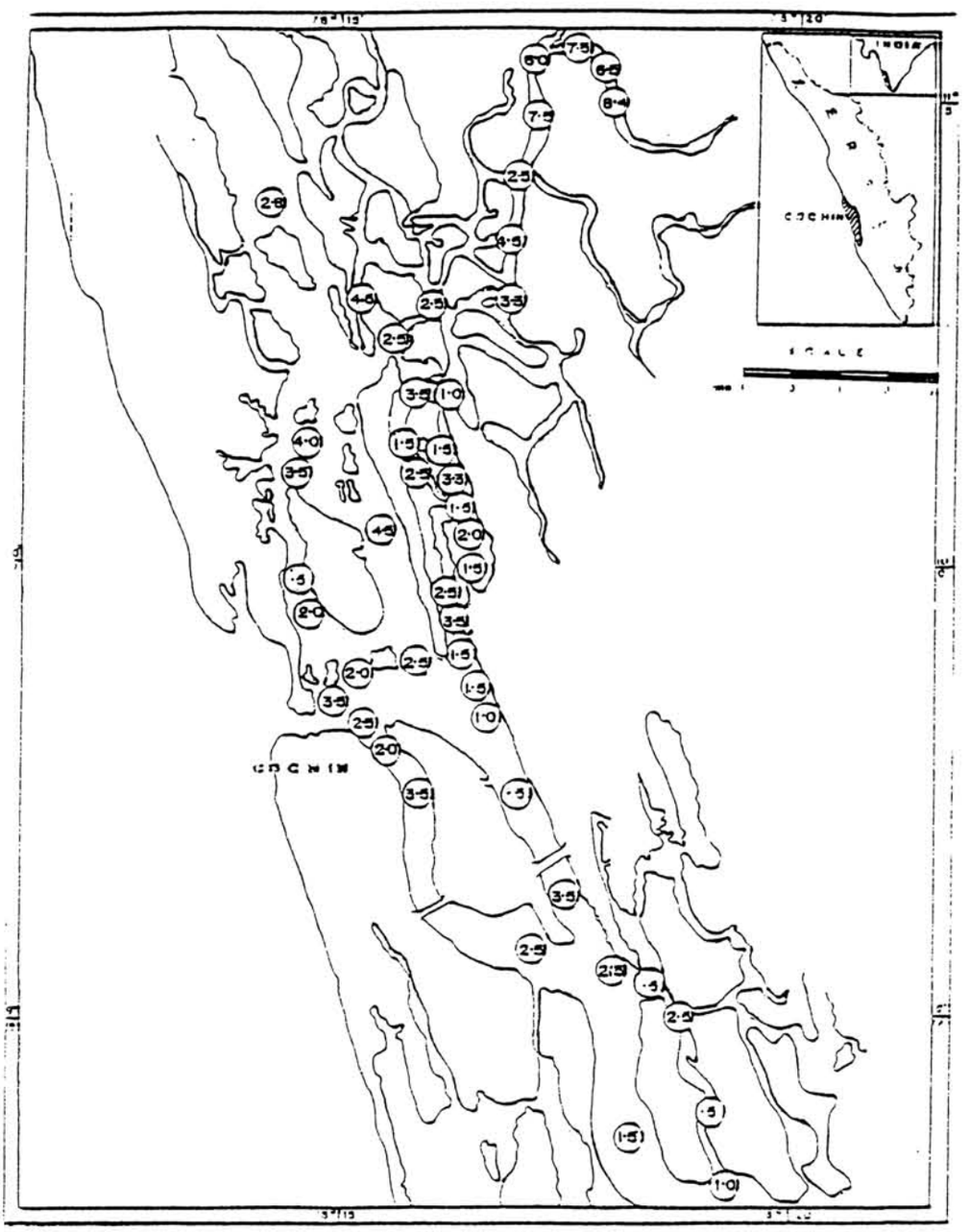


Fig. 7 CADMIUM DATA IN SEDIMENTS (ppm)

concentrations measured in the sediments are Hg 0.12 - 11.5 ppm, Pb 30 - 190 ppm, Zn 35 - 780 ppm, Cr 20 - 145 ppm, Cd 0.5 - 8.4 ppm. In general, the concentrations are higher at the point of effluent discharge and decreases towards the estuarine environment. The base line level for Hg is found to be 0.08 ppm. This is based on the analysis of a 90 cms core sample taken at station location No. 22. The enrichment of mercury in the sediments are 1.5 to 143 time higher compared to the natural level. The baseline levels of other metals are not known the data is being compared with the reported metal concentrations from other parts of the world. The observed concentrations for lead is 1.2 to 7.6 time higher compared to the natural values for lead for the sediments of Bay of Naples which is 2-25 ppm (Griggs & Johnson, 1978). The background values for the Zinc average for the Newark Bay sediments is 35 ppm (Lee Meyerson, 1981). Hence the reported values are 1 to 22 times higher in compared to Newark Bay sediments. The levels of chromium ranges from 20 to 130 ppm are comparable to the background values observed from other marine environments (Griggs and Johnson, 1978; Carmody, 1973). The concentration observed for Cd is higher when compared to the values reported for the sediments of Bay of Aundy (Loring, 1982). The high values reported might be partly due to the industrial and domestic pollution. For example a zinc factory located near the bank of river Periyar discharges effluents which contain zinc and cadmium to the coastal waters. Similarly a chlor-alkali plant situated near the bank of Periyar discharges effluents which contains mercury to the coastal waters.

Chemical partition and bio-availability of metals

Although high levels of metals in sediments are a general indication of industrial and urban contamination, the total metal concentrations are a poor means of assessing the potential or actual availability of a given element to the Biota. It is well established by various workers that in understanding the distribution and ecological implications of heavy metals, knowledge on the total metal concentration is not sufficient but it is necessary to know the elemental concentration present in different phases (Goldberg and Arhenius 1958; Loring, 1982; Tesser et al., 1979; Cosma et al., 1979; Cosma et al; 1983). In fact the total metal and the easily extractable metal extraction techniques are most informative for environmental purposes. We have employed as 25%V/V Acetic Acid to make an assessment of the available concentration of metals as suggested by Loring, 1982. This method was chosen because it is one of the weakest chemical treatments that can be effectively used to remove a certain part of the total metal concentration in the sediments that could be potentially available to the biota. Chemical partitions of the sediments from the study area shows that 5-10% of the total Pb, 5-60% of total Zn, 2-15% of

Table 3

Mean concentration for surface and bottom sample

	Monsoon 1985	Postmonsoon 1985	Premonsoon 1986
Dissolved mercury ng/litre	130	169	213
Particulate mercury µg/gm	9.64	17.13	24.68

total Chromium and 10-80% of total Cadmium occur in the acetic acid soluble fraction. This fraction may represent some portion of the element that was initially leached from the source rocks or supplied in the dissolved form from industrial sources.

Dissolved and particulate mercury

The mean concentration of dissolved and particulate mercury in water samples are shown in table 3. Bottom samples contain high particulate matter as compared to the surface samples. The concentration of dissolved mercury is found to be high in the bottom compared to the surface samples. This observation indicates that the origin of dissolved mercury may be partly from the bottom sediments and bottom sediment contaminates the marine environment. The highest concentration observed in the innermost northern part of the harbour area and at the effluent discharge point near the chloralkali plant. In general, the concentration of dissolved mercury decrease with increasing distance from the point of effluent discharge towards the estuarine environment. This indicates that Arabian Sea acts as a sink for the discharge of mercury through Cochin harbour by River Periyar. In the monsoon season the quantum of particulate matter found to be high and the concentration of dissolved and particulate mercury was low may be due to the influx of high amount of freshwater input from the rivers along with land run off. In the river Periyar the premonsoon season observed highest concentration of dissolved mercury. During the premonsoon season a bundh was constructed across Periyar river just above the effluent discharge point in order to block the entry of the saline and effluent waters to the upper reaches of river Periyar. This blockage might have created a high concentration of dissolved mercury in the river Periyar during the premonsoon season. The concentration of mercury in Cressostrea madrasensis (Preston) from Cochin backwater was found to be 18-72 ppb (Nair U.N. and Nair B.N.,1986). This suggests that mercury is being transferred to the biota through water sediment and particulate matter. The relation between particulate matter and salinity are shown

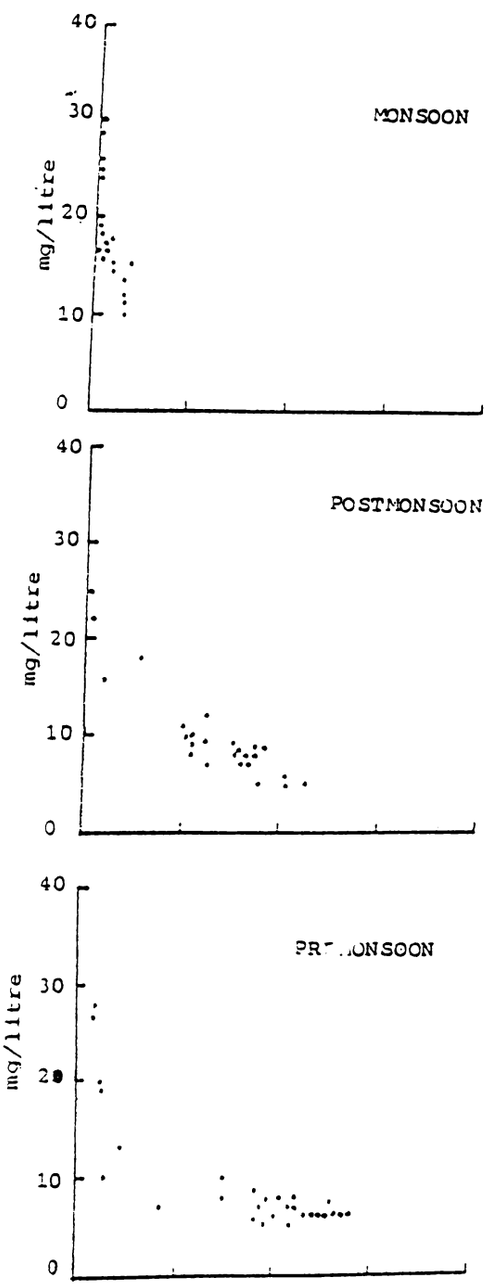


Fig. 8 : Relation between surface salinity and particulate matter.

in Fig. 8. This shows that the maximum precipitation of particulate matter is taking place above 10 ppt salinity. Present data are not sufficient to explain the vertical distribution, particulate association and mobilisation even-though bottom sample contain higher concentrations of dissolved and particulate mercury. The mercury concentration in the investigated waters varied through the year and showed an observable seasonal variation. The assayed values may be severely influenced by several factors such as rain, wind, sudden changes in the surface streams, influx of fresh water, tidal phenomena etc., eventhough much care has been taken in minimising errors in collection and storage, pretreatment and analysis of samples.

The above results indicate that the areas under study are affected by heavy metal pollution.

POLLUTION CONTROL

Pollution control systems can be broadly divided into three sections: (a) identification (b) solution (c) implementation. The first step in any system to control pollution is identification. The pollutant may be identified either directly, qualitatively or quantitatively. The solution is to be found out only after a lot of evaluation of technical and technological aspects of the pollutants and these technical and technological solutions should be viable in terms of financial aspects. Once the identification is completed and the solution is selected, the question of implementation of the schemes for the prevention of pollution naturally arises. Experts familiar with all technical and technological aspects of the solutions are to be utilised. They should be well experienced, qualified and capable of understanding the implementation of the schemes.

RECOMMENDATIONS

(a) Marine pollution baseline and monitoring studies for the pollutant levels, the sources and pathways may be initiated.

(b) An evaluation of the various methods currently employed for the collection, storage, pre-treatment and analysis of samples to identify the optimum overall procedure to be used for pollution assessment and trend monitoring may be done.

(c) Action plan for the protection and development of the marine environment and coastal areas of Kerala may be initiated.

ACKNOWLEDGEMENTS

I am thankful to Dr. Harsh K. Gupta, Director, Centre for Earth Science Studies for the keen interest shown in the

above studies and to Dr. M. Baba, Scientist-in-Charge, Regional Centre for his encouragements and useful discussion. I am obliged to S/Shri M.N.Muraleedharan Nair and N.R. Prakasan for the assistance given to me in the field and laboratory and to Shri D. Raju for the preparation of the drawings and to Shri K.P. Shaskaran for typing the manuscript.

REFERENCES

Ansari, Z.A. (1977) Macrobenthos of Cochin backwaters. Mahasagar - Bull. Nat. Inst. Oceanogr. 10, 169-171.

Cosma, B., Drago, M., Scarponi, G. and Tucci, S. (1979) Heavy metals in Ligurian sea sediments. Mar. Chem. B, 125-142.

Cosma, B., Contradi, V., Zeniech, G. and Capelli, R., (1983). Heavy metals in superficial sediments from the Ligurian sea, Italy, Chemist. In. Eco. 1, 331-344.

Carmody, D.J., Pearce, J.E. and Yasso, W.E., 1973. Trace metals in sediments of New York, Bight. Mar. Pollut. Bull. 4, 132-135.

Drago, M., Cosma, B. and Contradi, V. (1981) Distribution of heavy metals in superficial marine sediments of Savanna Hartour and Vado Ligure Bay (Ligurian sea). Atti. Soc. Tosc. Sci. Nat. Series A, 88, 117-136.

Freemann, P. and Schmidt (1982). The determination of mercury in sea water by cold vapour Atomic Absorption Spectrophotometry. Anal. Chem. 299, 97-102.

Gore, P.S, Ravindran, O, Unnithan, R.V., (1979) Pollution in Cochin backwater with reference to indicator bacteria. Ind. J. Mar. Sci. 8(10), 43-46.

Goldberg, E.D. and Arnenius, G.O.S. 1958. Chemistry of Pacific Pelagic Sediments. Geochem Cosmochimi Acta 13, 153-212.

Griggs, G.B. and Johnson, S. (1978). Bottom sediment contamination in the Bay of Napples Italy. Mar. Pollut. Bull. 9, 208-214.

Hershalman, G.P., Schafer, H.A., Jan, T.K. and Young, D.K. 1981. Metals in marine sediments near a large California Municipal Outfall, Mar. Pollut. Bull. 7, 244-250.

Hatch, N.R. and Ott, W.L. (1968) Determination of submicrogram quantity of mercury by atomic absorption spectrophotometry, Anal. Chem. 40, 2085-2087.

Kurian, C.V. (1972) Ecology of Benthos in a tropical estuary. Proc. Indian Nat. Sci. Acid., 38, 156-163.

Lakshmanan, P.T., Shyanamma, C.S., Balchand, A.N., Kurup, P.G., and Nambeesan, P.N.K. (1982). Distribution and seasonal variation of temperature and salinity in Cochin backwaters. Ind. J. Mar Sci. 11(2).

Lee Meyerson, A., Luthen W.G., Krajewaski, J. and Hans, I.R. (1981). Heavy metal distribution in Newark Bay sediment. Mar. Pollut. Bull. 7, 244-250.

Loring, D.G. and Bewers, J.M. (1978) Geochemical mass balances for mercury in Canadian Ford Chemical Geology 22, 309-330.

Loring, D.H. (1982) Overview of trace metals in eastern Canadian coastal and estuarine sediments. International Council for the Exploration of the Sea, 1-30.

Nair, U.N. and Nair, B.N. (1986) Seasonality of trace metals in (Crassostrea madrasensis) (Preston) inhabiting in Cochin Backwaters. National Seminar on Mussel Watch, Cochin, Vol.I, 6-12r

Nair, V.J. (1984) Status paper on water pollution including pollution caused by industrial operation, municial wastes and agricultural operation.

Qasim, S.Z. and Madhupratap, M. (1981) Changing ecology of Cochin backwaters. Contribution to Marine Sciences dedicated to Dr. C.V. Kurian, 137-142.

Remani, K. N., Venugopal, P., Saraladevi, K., Lalitha, S. and Unnithan, R.V. (1980) Sediments of Cochin backwaters in relation to pollution. Indian J. Mar. Sci. 9 (2).

Rajendran, N. and C.V. Kurian. (1986) (Crassostrea madrasensis) (Preston) - Indicator of metal pollution in Cochin backwaters. National Seminar on Mussel Watch, Cochin, Vol. I. 121-126.

Sarala Devi, K., Venugopal, P., Ramani, K.N., Lalitha, S. and Unnithan, R.V. (1979) Hydrographic features and water quality of Cochin backwaters in relation to industries pollution. Ind. J. Mar. Sci. 8(3), 141-145.

Sankaranarayanan, V.N. and Rosamma Stephen (1978) Particulate iron, maganese, copper and zinc in water of the Cochin backwaters. Ind. J. Mar. Sci. 7, 201-203.

Sengupta, R., Qasim, S.Z., Fondekar, S.P. and Toppi, T.S. (1980) Dissolved petroleum hydrocarbon in some regions

in the northern Indian Ocean. Mar. Poll. Bull. 11, pp.65-68.

Thomson, J.A.J., MacDonald, R.W. and Wong, C.S. (1980) Mercury Geochemistry in sediments of a contaminated fjord of coastal British Columbia. Geochemical Journ. 14, 71-82.

Tessier, A., Compbell, P.G.C. and Bisson, M. (1979), Sequential extraction procedures for the speciation of particulate trace metals. Analyst. Chem. 51, 44-85.

Unnithan, V.C., Gore, P.S., Ravindran, O., Venugopal, P., Sarada Devi, K., Ramesh, K.N. (1981) Deposition of tar like residue in beaches of Kerala. Ind. Jour. Mar. Sci. 10, 371-372.

Unnithan, R.V., Vijayan, M. and Remani, K.N. (1975) Organic pollution in Cocnin backwaters backwaters. Ind. J. Mar. Sci., 4, 39-42.

Vijayan, M., Ramani, K.N. and Unnithan, R.V. (1976) Effect of organic pollution in some hydrographic features of Cochin backwaters. Ind. J. Mar. Sci. 5, 196-200.

Proc. Nain. Sem. Estuarine Management, 1987, Trivandrum. pp. 123–127

EC-01

Heavy metal pollution in the sediments of Cochin estuaries system

P P OUSEPH
Centre for Earth Science Studies. Cochin 682 018. India

Abstract. The present study concerns with typical pollutants such as Hg. Pb. Zn. Cr. and Cd. The concentrations of heavy metals such as Hg. Pb. Zn. Cr and Cd in the sediments of the Cochin estuarine system have been analysed by atomic absorption spectrometry. Total element concentrations (Hg 0.12–1.1 ppm. Pb 30–165 ppm. Zn 35–380 ppm. Cr 20–130 ppm. Cd 0.5–4.5 ppm) in the estuarine region vary with sediment texture. High total metal load (Hg 5.5–11.5 ppm. Pb 160–170 ppm. Zn 420–780 ppm. Cr 85–120 ppm. Cd 6–8.4 ppm) is observed in the sediments near the point of effluent discharge. Low total metal content was noticed (Hg0.04–0.06 ppm. Pb 10–25 ppm. Zn 40–60 ppm. Cr 7–20 ppm. Cd not detected) for the fresh water sediment samples collected from the upstreams of river Periyar. An assessment has been made for the potential bio-availability of these elements by extraction with 25% v/v acetic acid. It is found that in the estuarine environment 5–10% of total Cd are potentially available to the biota. The organic carbon vary from 0.2 to 3–5%. The observed results are compared with the concentrations for the unpolluted sediments and also from other marine environments. The concentrations showed an observable seasonal variation.

Keywords. Heavy metal pollution: sediments: effluents.

1. Introduction

The southwest coast of India bordering the state of Kerala is connected by a chain of backwater systems and rivers. There is a growing concern over the last decades regarding the effect of industrial discharges in estuarine and nearshore environments. The major river systems causing marine pollution are the Chaliar. Periyar. Chitrapuzha and Kallada. In Kerala. Ernakulam District accounts for more than 70% of the chemical industries in the State and these are situated in the banks of Periyar and Chitrapuzha. The major chemical industries can be classified as metallurgical. fertilizer. rare earths. newsprint etc.. and the effluents from these industries are drained to the Arabian sea through Cochin estuary. The shipping facilities. trade effluents. land drainage. sewage disposal. construction of super tanker berth. reclamation of wet lands for housing, dreding operations etc.. makes the estuary more polluted. In addition to the above organic pesticides and insecticides used by farmers which reach the estuary on its way to sea.

The Cochin estuarine system receives effluents containing a large dose of heavy metals. Table (1) and (2) gives an estimate about the type and quantity of heavy metals discharged into the environment through river Periyar. A knowledge on the distribution of heavy metals in the marine environment is immportant in studying the environmental pollution since such elements can be toxic even in traces and cause harmful effects. Heavy metals are biologically nondegradable and through the food chain. it may finally pass on to the man. The distribution pattern of Fe. Mn. Ti. Ni. Co and Cu in the sediments of Vembanad lake has been extensively studied by Murthy and Veereyya (1981). Few trace metal levels in the sediments of Cochin backwaters were studied by Venugopal (1981). Particulate matter of water from Cochin backwater for trace metals indicated that this environment contains high conent of Zn. Cr. etc. due to industrial pollution (Sankaranarayanan and Rosamma Stephan. 1978). Some of the benthic organisms such as mussels and oysters have accumulation of Zinc higher than the permitted limit (Remani 1979). High concentrations of Zn. Cu. Fe etc. were observed in *Crassostrea madrasensis* from Cochin region is considered to be due to the industrial and domestic pollution (Sankaranarayanan *et al* 1978). The seasonality in the distribution of trace metals such as Cd Cu. Fe. Mn. Zn and Hg in the backwater oyster *Crassostrea madrasensis* (Preston) of Cochin Harbour is studied by Nair and Nair (1986). The suitability of the oyster as an indicator organism for metal pollution in Cochin backwater is discussed by Rajendran and Kurian (1986).

Table 1: **Quantity of wastes and nature of pollutants discharged into the river periyar (Jovsingh 1976)**

Factories discharging wastes	*Quantity of wastes lakh litres per day*	*Pollutants*
M/s. Travancore Rayons.		Suspended Solids.
Indian Aluminium Co..		Mercury, Zinc.
F. A. C. T.. T. C. C..	1722.00	Copper. Cadmium.
Hindustan Insecticides.		Lead. Hexavalent
Indian Rare Earths.		Chromium. Radio-
Periyar Chemicals.		active material etc.
T. C. M. Co. Limited		

Table 2: **Quantity and nature of heavy metalic pollutant discharged into the River Periyar**

Factories discharging wastes	*Type of Heavy Metalic contaminent*	*Quantity per year in tonne*
1. Travancore Cochin Chemicals	Mercury	2.0
2. Fertilisers and Chemicals Travancore Limited (FACT)	Hexavalent Chromium	1.1
3. Cominco–Binani Zinc Limited	Zinc	7.5
4. Catalysts and Chemicals Ltd.	Hexavalent Chromium	0.32
	Zinc	2.45
	Copper	0.33
	Iron	30.0
5. Travancore Chemicals	Zinc	0.15

A series of environmental geochemical studies have been undertaken by the Centre for Earth Science Studies (CESS) to determine the levels, behaviour dynamics of heavy metals in the sediments of Cochin estuarine system. In an earlier paper Ouseph (1987) a general description of the total and potentially available metal content for Mercury (Hg), Lead (Pb), Zinc (Zn), Chromium (Cr) and Cadmium (Cd) has been presented. This paper reports in detail the regional distribution and potential bioavailability of heavy metals in the sediments at the point of effluent discharge and estuarine environment. The data is compared with the results observed for the sediments collected from unpolluted area and from other marine environment.

2. Materials and methods

The study initiated by CESS in the Cochin harbour and river Periyar by establishing 46 stations as shown in (Figure 1). The station location for the unpolluted zone is not shown in the figure but samples were collected 0.5 km upstream from the point of effluent discharge. Preliminary investigations were carried out in July and November 1985 and March 1986. From all stations sediment sampls were collected using a Vanveen grab. Since high concentrations are expected at the point of effluent discharge, the collection of samples has been done by taking three sampling points across the river. A composite sample was made for carrying out the analysis. The samples were dried at 60°C to constant weight. Before drying the rock fragment, shells and visible organisms were removed by hand picking. The dried samples were manually powdered and homogenised as per the method of Hershalman, *et al* (1981). Organic carbon was estimated by the wet oxidation method Wakeel and Relay (1957). The following extraction techniques were employed. The total metal content Basso & Mazzoccotelli (1975) and the potential bioavailability for metals Loring (1982). The extracts were analysed for Pb, Zn, Cr and Cd by AAS. Five replicats analysis of one sample gave a coefficient of variation of 4.8% for Pb, 6.5% for Zn, 5.5% for Cr and 7.5% for Cd.

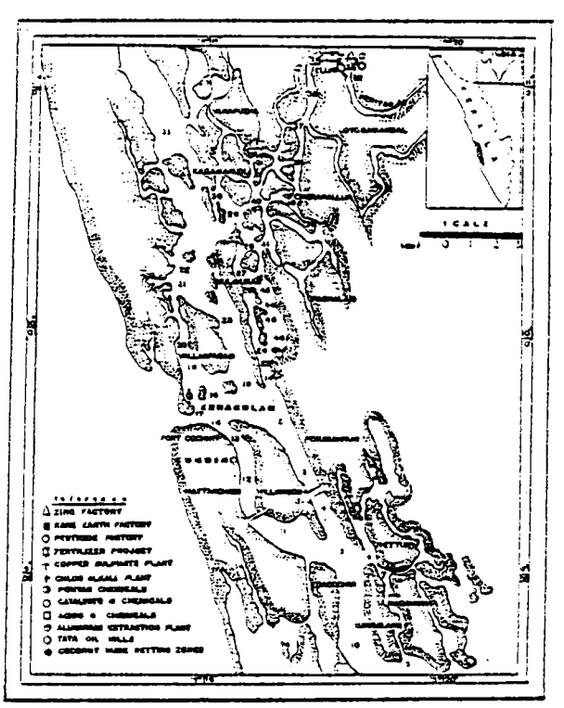


Fig. 1 Location map with details of sampling stations and major industries

For the estimation of Mercury, wet sediment samples were digested with a mixture of nitric and sulphuric acids (Thomson *et al* 1980) in Bethge apparatus. The digested samples were made upto a known volume. Cold vapour Atomic Absorption Technique was used for the estimation of mercury as described by Hatch and Ott (1968). A known weight of the wet sediment sample was dried, and the moisture was calculated.

The results were computed to get the concentrations of Mercury on dry weight basis.

A 25% V/V acetic acid extraction method for the estimation of the percentage of potentially available elements in the sediment. This method was chosen because it is one of the weakest chemical treatments that can be effectively used to remove the non-residual element from sediments without the danger of releasing elements from structural positions or those strongly complexed with organic matter (Agemian and Chau 1976, Malo 1977, Loring 1982).

3. Results and discussion

3.1. *Total metal content*

The total concentrations measured in the sediments are presented in Table 3. In general, the concentration are higher at the point of effluent discharge and decrease towards the estuarine mouth.

(i) *Mercury*: The base line levels for Hg is found to be 0.08 ppm. This is based on the analysis of a 90 cm core sample taken at station location No. 22. The enrichment of Hg is 68 — 142 times higher at the point of effluent discharge and 1.5 — 13 times higher in the Cochin Harbour area. The values observed for the unpolluted zone is less than the background levels.

(ii) *Lead*: The observed concentrations are 6–7 times higher at the point of effluent discharge and 1 – 6 times higher in the Cochin Harbour area when compared to the natural values for the sediments of Bay of Naples, which is 2 — 25 ppm (Griggs and Johnson 1978). The values for the fresh water zone showed little higher concentrations when compared to the natural level.

(iii) *Zinc*: The background levels for the Zinc average for the Newark Bay sediments is 35 ppm (Lee Meyerson 1981). Hence the reported values are 12 — 22 times higher at the point of effluent discharge and 1–10 times higher in the Cochin Harbour area. Just like, lead, zinc also showed little higher concentrations for the freshwater sediments. This observation is under further investigation.

(iv) *Chromium*: The levels of chromium in the study areas are comparable to the background values observed from other marine environments (Griggs and Johnson 1978, Carmody *et al.* 1973). Table 2 shows a major input of hexavalent chromium into the ecosystem, but our study does not indicate any such enrichment, probably the element might be in the soluble form in the aquatic system, and could not come down to the sediment by the usual estuarine processes.

(v) *Cadmium*: The levels of cadmium for the sediments of Bay of Faundy is 0.2 ppm (Loring 1982). The observed results are 30 — 42 times higher at the point of effluent discharge and 2 — 22 times higher for the Cochin Harbour area when compared to the Bay of Faundy sediments.

3.2. *Discussion of concentration of total metal content*

Total element concentration vary with location and sediment texture. High concentration of Hg, Pbs, Zn, Cr and Cd occur in fine grained sediments. Sandly sediments showed low concentrations of metals. High organic carbon content observed a the point of effluent discharge and also in the estuarine region. The concentrations of total metal content showed seasonal variation with station location. In general monsoon season showed the lowest and premonsoon season the highest concentration in the sediments. The results were predominent a the effluent discharge point when compared to the Cochin Harbour area. During the monsoon season, high influx of fresh water from the rivers makes the sediment to exchange a part of the exchangable phase of the metals to the water column. A better understanding of this phenomenan will be known by a study on the water sediment interface chemistry. During the premonsoon season of 1986 a bundh was constructed across the river Periyar just above the effluent discharge point, in order to block the entry of the saline and effluent mixed water to the upper reaches of Periyar. This might have created a high concentration of elements at the effluent discharge point. The high concentrations observed in Cochin Harbour area during the premonsoon season, may be due to the intrusion of high saline waters and precipitation of particulate matter. Due to this the sediment may have high content of fine grade fraction which leads to the high concentration of elements. Moreover our study of salinity versus particulate matter, (Figure 2) showed that maximum precipitation occurs for more than salinity 10 ppt. The variation in the concentrations observed in the Cochin Harbour area can also be attributed to the transport of fine grade sediment towards the seaward and back, due to the tidal and seasonal influence.

3.3. *Chemical partition and potential bio-availability*

The sediment chemistry will broadly reflect the contamination history of the area. Heavy metals are associated to different extents with the various components of sediment and these associations can be quite different for natural and anthropogenic material. In general the anthropogenic inputs of metals will necessarily

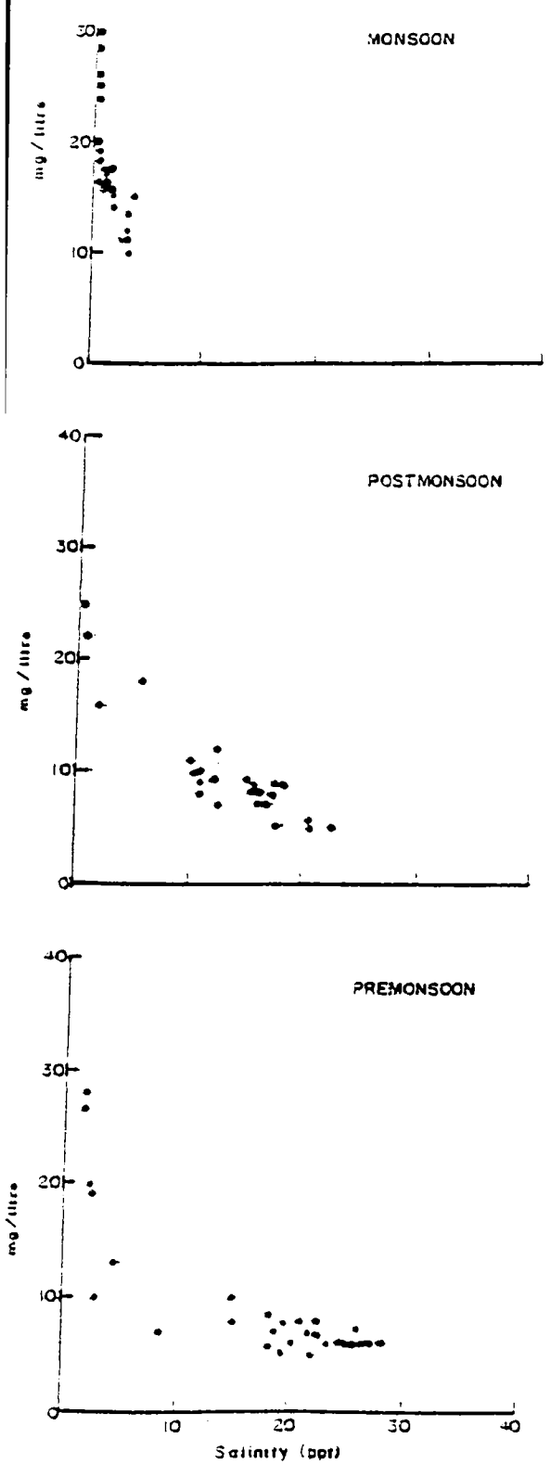


Fig. 2 Relation between salinity and particulate matter

be associated with non-lattice fractions. Total dissolution of sediment is analytically demanding and many monitoring purposes sediments are leached to remove the non-lattice held material. The non-lattice held contribution usually constitutes a small but biogeochemically important fraction. It represents some proportion of the element that was initially leached from the source rocks or supplied in dissolved from industrial sources. This refraction of the elements that are most easily available to the biota and constitutes the greatest danger to them if present in excessive quantities, particularly if the elements are of a form that can be selectively removed by the biota from the sediment or in particulate matter in the water column. In fact the total metal and the easily extractable metal-extraction technique give maximum information in such analysis.

The study reveals that high contents of Hg, Zn, Cd are reaching the estuary from the river Periyar through industrial discharge. For example a chloral-kali plant and zinc factory situated near the banks of river Periyar discharge effluents which contain Hg, Zn and Cadmium into the coastal waters. The samples from the effluent discharge point showed that 83–89% of total zinc and 83–95% of total cadmium occur in the acetic acid soluble fraction. Similarly in the estuarine environment 5–60% of the total zinc and 10–80% of total cadmium are potentially available to the biota. The above results clearly indicate that most of the zinc and cadmium in the sediments appears to originate from industrial wastes. From the results it is observed that there is an anthropogenic input of Pb and Cr to the estuarine environment and the data is comparable from unpolluted marine environment. Moreover, 90% of the total lead and 85% of the total chromium in the sediments are not potentially available to the biota. Earlier studies of Sankaranaravanan *et al* (1978), Remani (1979), Nair and Nair (1986) indicated that biota from Cochin Harbour area contains, Hg, Zn, Cd etc. This confirm our finding that this environment contains high concentrations of heavy metals in which few elements are in a form that can be selectively removed by biota.

4. Conclusions and recommendations

(i) High content of Hg, Zn, and Cd are reaching estuary through industrial wastes.

(ii) Zn and Cd are potential contaminents of the estuarine sediments.

(iii) A detailed investigation on the speciation and sediment water interface chemistry of heavy metals in the Cochin Estuarine system is recommended.

Table 3: **Concentration of some heavy metals in the sediments (ppm) and organic carbon (%)**

Location	*No. of samples*		*Hg*	*Pb*	*Zn*	*Cr*	*Cd*	*T/Org. carbon*
Fresh water		A	0.04–0.06	10–65	40–60	7–20	N.D.	0.2–0.6
zone	4	B	—	2–15	10–24	2–8	—	—
(unpolluted)		C	—	(20–23%)	(25–40%)	(28–40%)	N.D.	—
Effluent		A	5.5–11.5	160–190	420–780	85–120	6–8.4	0.8–3.5
discharge	5	B	—	15–40	350–700	15–42	5–8.0	—
point		C	—	(9–21%)	(83–89%)	(17–35%)	(83–95%)	—
Cochin		A	0.12–1.1	30–165	35–380	20–130	0.5–4.5	0.2–3.4
Harbour	34	B	—	1.5–17	2–230	6.5–20	0.05–3.6	—
area		C	—	(5–10%)	(5–60%)	(2–15%)	(10–30%)	—

(A = Total attack. B = Acetic Acid attack. C = % of Potentially bio-available elements. N. D. = Not Detected)

Acknowledgement

The author is grateful to Dr. Harsh K. Gupta, Director CESS for this interest and for providing the facilities. He is thankful to Dr. M. Baba, Scientist-in-charge, Regional Centre for his continuous encouragement and useful discussions. He is obliged to S/Shri M. N. Muraleedharan Nair, N. R. Prakasan, P. P. Simon for the assistance given in the field and laboratory to G. Balasubramonian for capably performing the heavy metal analysis and to K. P. Bhaskaran for typing the manuscript.

References

Agemain and Chau A S Y 1976 *The Analyst* 191 76 Basso R and Mazzanceotelli A 1975 *Di Roccee Minerali* 44 5

Carmody D S, Pearce J B and Yasso W E 1973 *Mar. Pollut. Bull.* 4 132

Griggs G B and Jonnson S 1978 *Mar. Pollut. Bull.* 9 208

Hersnaiman G P Schafer H A Jan T K and Young D K 1981 *Mar. Pollut. Bull.* 7 244

Hatch N R and Ott W L 1968 *Anal. Chem.* 40 2085

Lee Mayerson A. Luther W G. Krajeswaski J and Hans I R 1981 *Mar. Pollut. Bull.* 7 244

Loring D H and Bewers J M 1978 *Chem. Geology* 22 309

Loring D H 1982 *International Council for the exploration of the sea* 1

Maio B 1977 *Envt. Sci. & Techno.* II 227

Murthy P S N and Veerayya M 1981 *Ind. J. Mar. Sci.* 10 3 221

Nair G N and Nair B N 1986 *Nat Sem. on Mussell Watch Cochin* I 6

Qusepn P P 1987 *Proc. of the Interdepartmental Seminar on Status of Marine Pollution in India*. Dept. of Ocean Development. New Delhi (in press)

Rajendran N and C V Kurian 1986 *National Seminar on Mussel Watch Cochin* I 121

Remani K N 1979 PhD Thesis submitted to the University of Cochin

Sankaranarayanan V N and Rosamma Stephen 1978 *Ind. J. Mar. Sci.* 7 201

Sankaranarayanan V N, Purushan K S and Rao T S S 1978 *Ind. J. Mar. Sci.* 7 130

Thomson J A J, Macdonald R W and Wong C S 1980 *Geochem. J.* 14 71

Wakeel E L and Relay J F 1957 *J. Cons. Perm. Int. Explor. Mar.* 22 180

Coastal and Estuarine Studies

formerly Lecture Notes on Coastal and Estuarine Studies

36

W. Michaelis (Ed.)

Estuarine Water Quality Management

Monitoring, Modelling and Research

Springer-Verlag

Berlin Heidelberg New York London Paris Tokyo Hong Kong

DISSOLVED, PARTICULATE AND SEDIMENTARY MERCURY IN THE COCHIN ESTUARY SOUTHWEST COAST OF INDIA

P.P Ouseph
Centre for Earth Science Studies
Cochin - 682018, India

ABSTRACT

The Cochin estuary is subjected to the discharge of effluents from the major industrial units situated on the banks of the rivers Periyar and Chitrapuzha. Since mercury and its compounds are highly toxic, a study has been initiated for understanding its distribution and seasonal variations. The concentration of mercury in the sediments varied with sediment texture and showed good correlation with organic carbon. The bottom waters are found to have higher concentrations compared to the surface. Total mercury for particulate matter was high in relation to the sediment concentrations.

1. INTRODUCTION

The southwest coast of India bordering the state of Kerala is connected by a chain of backwaters and rivers. The region surrounding Cochin accounts for more than 70 % of the chemical industries situated near the banks of the rivers Periyar and Chitrapuzha, and the effluents containing a heavy load of metals are discharged into the Cochin estuarine systems. The particulate matter of water in Cochin backwaters indicated that this environment contains high contents of Zn, Cr, and other metals (Sankaranarayanan and Rosamma Stephen, 1978). High concentrations observed in Crassostrea madrasensis is considered to be due to industrial and domestic pollution (Sankaranarayanan et al., 1978). A series of environmental-geochemical studies have been undertaken to determine the levels, behaviour and dynamics of heavy metals in the Cochin estuarine system. This paper reports on the dissolved, particulate and sedimentary mercury determined during the surveys undertaken in July and November 1985, and April 1986.

2. MATERIALS AND METHODS

Samples were collected from 18 locations as shown in Fig. 1. Sediment samples were taken using a van veen grab, surface water samples were collected with a plastic bucket and bottom water samples with a van dorn sampler. The analytical

method for total mercury in sediment employs oxidative digestion (Thomson et al., 1980) and cold vapour atomic absorption (Hatch and Ott, 1968). Filtered and unfiltered water samples were used for the estimation of dissolved and particulate mercury (Ouseph, 1987). The method was further modified by a dithizone/CCl_4 extraction technique using 800 ml samples. The organic layer was extracted back by means

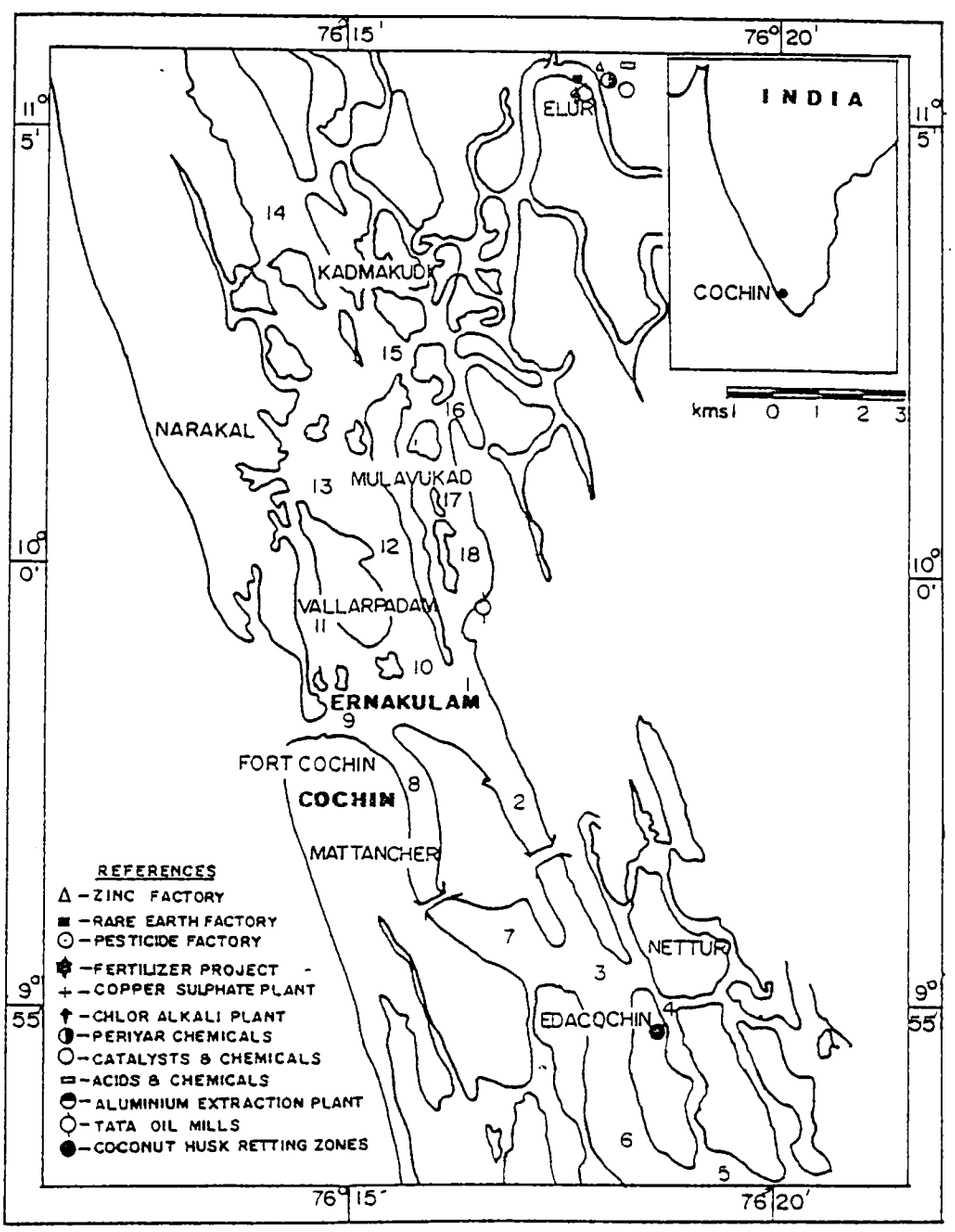


Figure 1: Location map with details of sampling stations and major industries

of sodium nitrite and hydroxylamine hydrochloride. The extracts served to estimate the mercury concentration by cold vapour AAS. In each case the blank values were determined. Five replicate determinations, done for one sample from each set of samples collected seasonally, gave a variation coefficient of 3.8 to 4.2 % for water samples at concentrations between 5 to 100 ng/l and 5.2 to 6.8 % for sediment samples. Silt is defined as the fraction < 0.062 mm.

3. RESULTS AND DISCUSSION

The mercury concentration in sediments ranged from 0.12 to 0.95 ppm and varied regionally with sediment texture. The background level of mercury was estimated on the basis of a 90 cm core sample collected at station 13 and found to be 0.08 ppm. Hence, the observed sediment concentrations are 1.5 to 11.8 times higher compared to the background levels, indicating an anthropogenic orgin. In order to find out whether mercury is held up in the silicate or non-silicate extractable fraction, the sediment samples were subjected to 8N HNO_3 attack (Cosma et al., 1983) and the extracts were used to estimate the mercury concentration. It was found that 80 to 90 % of the mercury is held in the non-silicate extractable fraction.

The total iron concentration ranged from 0.4 to 6.8 % and organic carbon from 0.26 to 3.2 %. Results of linear regression analysis are presented in Figs. 2, 3 and 4. The good interrelationship of organic carbon with mercury indicates that organic carbon plays a major role in the incorporation of mercury in the sediment compared to silt and iron. The correlation studies confirm that mercury appears to be trapped in the finer sediment. Reported values from other marine environments range, for example, from 0.06 to 2.57 ppm (Thomson et al., 1980) and from 0.2 to 4.4 ppm (Bartlett, 1978).

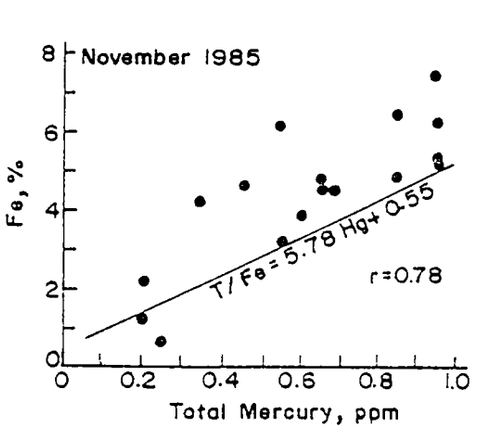


Figure 2: Total Fe and Hg in sediments

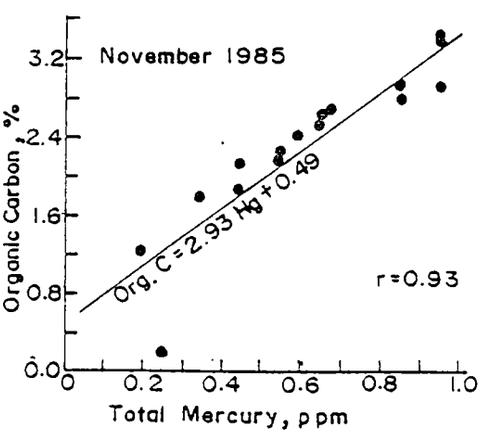


Figure 3: Organic C and Hg in sediments

The seasonal distribution of dissolved mercury ranged from 40 to 180 ng/l during southwest monsoon, 50 to 240 ng/l in the post-monsoon and 80 to 280 ng/l in the pre-monsoon season. For all seasons the concentration in the surface samples was found to be lower than in the bottom samples. This may indicate that mercury is released from the sediment or suspended particulate matter to the bottom water. To examine the possible contamination during sampling and analysis, water samples from unpolluted reaches of the upper Periyar river were analysed. The results were in the range between 15 to 25 ng/l. These values are approximately 2 to 10 times higher compared to the natural background levels. The relation between salinity and mercury concentration is shown in Fig. 5. During the SW monsoon season there is a strong input of fresh water and the mercury concentrations are low. This might be the result of dilution by fresh water.

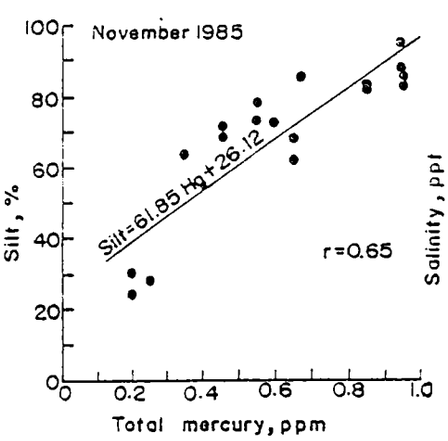


Figure 4: Silt and Hg in sediments

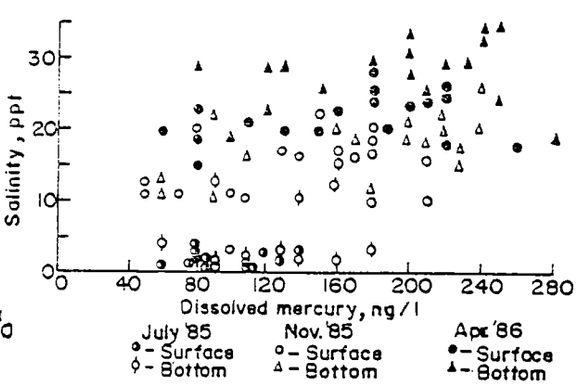


Figure 5: Salinity and dissolved Hg

The particulate mercury concentrations ranged from 2 to 20 ppm during SW monsoon, 2 to 25 ppm during post-monsoon, 6 to 36 ppm during pre-monsoon seasons. Particulate mercury is almost uniform for bottom samples except at a few stations. Bottom particulate matter has a higher content compared to the surface which is similar to dissolved mercury. Salinity has a profound influence on the precipitation of particulate matter. The relation between salinity and particulate matter indicates that the precipitation takes place with salinity > 10 ppt (Ouseph, 1987).

ACKNOWLEDGEMENT

The author is thankful to Dr. M. Ramakrishnan, Director in-charge, Centre for Earth Science Studies, for providing facilities, to Dr. M. Baba, Head RC, for his encouragement, to Dr. K. Premchand for useful discussions, and to Shri D. Raju for the preparation of the drawings.

REFERENCES

Bartlett PD (1978) Total mercury and methyl mercury levels in British estuarine and marine sediment. The Science of the Total Environment 10: 245-251

Cosma B, Contradi V, Zaniceni G, Capelli R (1983) Heavy metals in superficial sediment from the Ligurian Sea, Italy. Chemist in Ecol 1: 331-344

Hatch NR, Ott WL (1968) Determination of submicrogram quantity of mercury by atomic absorption spectrophotometry. Anal Chem 40: 2085-2087

Ouseph PP (1987) Status report on marine pollution along Kerala coast. Proc of the Interdepartmental Seminar on Status of Marine Pollution in India, Dept of Ocean Development, New Delhi, pp 86-105

Sankaranarayanan VN, Purushan KS, Rao TSS (1978) Concentrations of some of the heavy metals in the oyster Crassostrea madrasensis (Preston) from the Cochin region. Ind J Mar Sci 7: 130-131

Sankaranarayanan VN, Rosamma Stephen (1978) Particulate iron, manganese, copper and zinc in water of the Cochin backwater. Ind J Mar Sci 7: 201-203

Thomson JAJ, Macdonald RW, Wong CS (1980) Mercury geochemistry in sediments of a contaminated fjord of coastal British Columbia. Geochem J 14: 71-82

REPORTS

Marine Pollution Bulletin, Volume 24, No. 4, pp. 186–192, 1992.
Printed in Great Britain.

0025-326X/92 $5.00+0.00

Dissolved and Particulate Trace Metals in the Cochin Estuary

P. P. OUSEPH
Centre for Earth Science Studies, Trivandrum-31, India

The Cochin estuary located at 9°58'N latitude and 76°15'E longitude is subjected to various types of effluents discharged from the Eloor and Chitrapuzha industrial belts. The present study reports the concentrations of dissolved and particulate copper, zinc, cadmium, lead, nickel, and iron based on three consecutive surveys conducted during July (monsoon), November (post-monsoon) 1985 and April (pre-monsoon) 1986. The concentrations of dissolved and particulate copper, zinc and cadmium showed high seasonal variation. Seasonal variation in the concentrations of nickel and lead was negligible. Iron was found to be removed from the dissolved state. Surface water samples contained higher concentrations as compared to the bottom. The study revealed that salinity plays an important role in the precipitation of particulate matter and heavy metals with respect to estuarine mixing.

Ernakulam district in Kerala accounts for more than 70% of the chemical industries situated on the banks of the rivers Periyar and Chitrapuzha. The effluents from these industries reach the estuary by tides and fresh water discharges. Pesticides, insecticides, fungicides, oil spills from ships and boats, land drainage, trade effluents, sewage disposal, etc. make the estuary more polluted.

The hydrography/flow regime/geochemistry has been described by Sankaranarayanan & Rosamma Stephen (1978), Sankaranarayanan *et al.* (1978), Remani *et al.* (1980), Paul & Pillai (1983), Nair & Nair (1986), Rajendran & Kurian (1986), Ouseph (1987), and Joseph & Kurup (1990).

To understand the effect of toxicities of heavy metals in the marine environment, it is important to distinguish between particulate and dissolved species. The river Periyar brings heavy metals in the form of fine grade

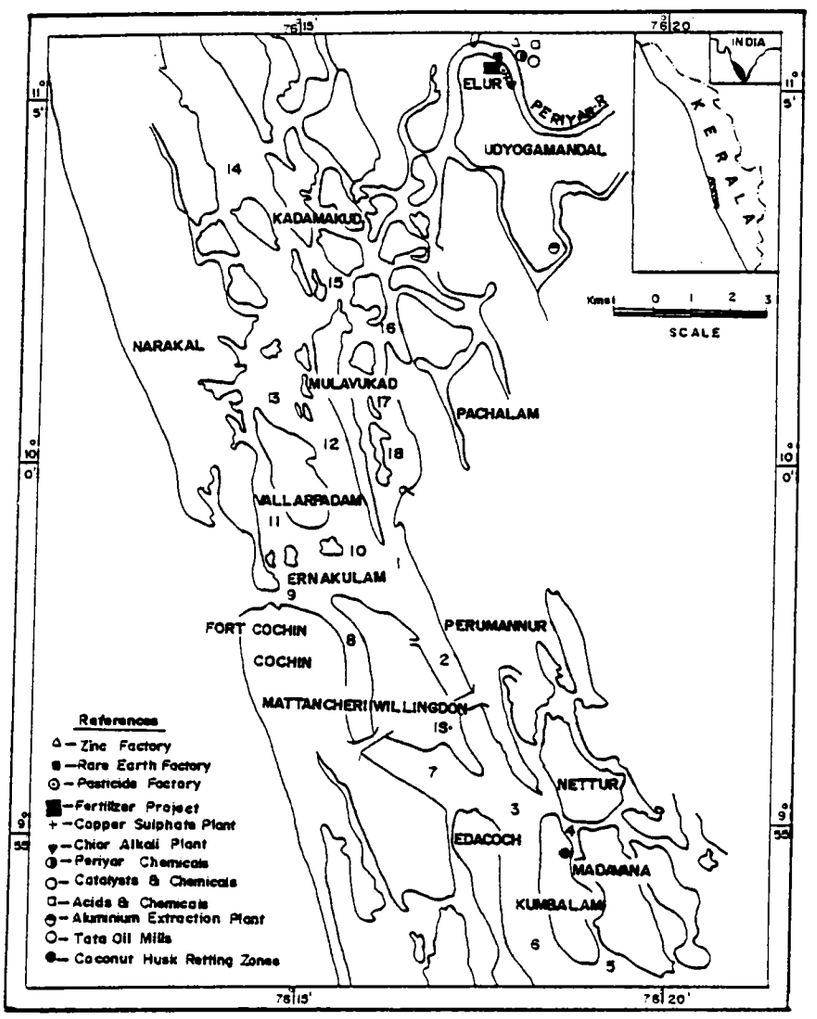


Fig. 1 Location map with details of sampling stations and major industries.

suspended particulate matter from the effluent discharge point.

Materials and Methods

Surface and bottom water samples were collected from 18 locations (Fig. 1) in the Cochin estuary. Collection of surface samples was done by a plastic bucket and bottom samples by a Van Dorm sampler. Surface water samples were collected from a location 0.5 km upstream of the industrial effluent discharge point in the river Periyar. The blackish, effluent rich, fine grade suspended particulate matter samples were collected from the sides of the river Periyar at the effluent discharge point. Samples were collected during July (1985), November (1985), and April (1986) representing monsoon, post-monsoon, and pre-monsoon respectively. 500 to 1000 ml of the water samples were filtered using a millipore filter paper and the particulate matter was estimated by the gravimetric method. For the total metal content, the particulate matter was digested as described by Sen Gupta *et al.* (1978). Duplicate filtration of the water samples was undertaken and the particulate matter was digested with 0.1 N HCl for the estimation of leachable heavy metals (Duinker *et al.*, 1974). This method was chosen because it is one of the weakest chemical treatments that can be effectively used to remove the non-residual elements from particulate matter without the danger of releasing elements from structural positions or those strongly complexed with organic matter (Agemian & Chau, 1976; Malo, 1977).

For the determination of dissolved trace metals, a larger volume of filtered water was required. For this purpose, a prefiltration by GFC and a subsequent millipore filtration was undertaken. Prior to filtration the GFC filter papers were cleaned with 0.01 N HCl and rinsed with distilled water. 800 ml of water sample was used for the pre-concentration of metals by APDC/MIBK at pH 4 as described by Sen Gupta *et al.* (1978). The organic extract was back extracted with HNO_3 and the aqueous layer (A) collected. The organic layer, after back extraction was treated with Perchloric acid, evaporated to dryness and redissolved in 0.1 N HCl (B). Both the extracts (A+B) were taken in a beaker, evaporated to dryness and made to a volume of 8 ml using 0.1 N HCl and the heavy metals were determined using AAS. Metal free sea water was prepared by

TABLE 1

Dissolved trace metals—River Periyar, Unpolluted Zone.

Season	Cu $\mu g\,l^{-1}$	Zn $\mu g\,l^{-1}$	Cd $\mu g\,l^{-1}$	Pb $\mu g\,l^{-1}$	Ni $\mu g\,l^{-1}$	Fe $\mu g\,l^{-1}$
Monsoon July 1985	0.8	24	0.2	8.0	0.2	1.2
Post-monsoon Nov. 1985	10.0	40	0.2	8.0	0.2	1.1
Pre-monsoon April 1986	8.0	65	0.2	8.0	0.2	0.8

TABLE 2

Particulate trace metals—River Periyar, Unpolluted Zone.

Season	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Ni ppm	Fe %
Monsoon July 1985	48	180	2.8	84	88	9.2
Post-monsoon Nov. 1985	85	240	3.4	94	110	8.8
Pre-monsoon April 1986	140	450	6.2	105	142	6.5

TABLE 3

Dissolved trace metals—Cochin Estuary.

Season	Cu $\mu g\,l^{-1}$	Zn $\mu g\,l^{-1}$	Cd $\mu g\,l^{-1}$	Pb $\mu g\,l^{-1}$	Ni $\mu g\,l^{-1}$	Fe $\mu g\,l^{-1}$
Monsoon July 1985	2.2–2.8	105–155	1.8–2.1	8.8–10.6	0.3–0.4	0.6–0.8
Post-monsoon Nov. 1985	10.4–18.8	145–216	2.2–3.4	8–14	0.4–0.6	0.2–0.8
Pre-monsoon April 1986	14.8–22.2	195–385	2.8–4.2	10–14	0.3–0.4	0.2–0.6

TABLE 4

Particulate trace metals—Cochin Estuary.

Season	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Ni ppm	Fe %
Monsoon July 1985	44–197	125–1040	58–91	33–150	45–65	2.8–3.6
Post-monsoon Nov. 1985	65–230	150–2200	50–150	60–180	10–80	7.4–8.1
Pre-monsoon April 1986	76–298	318–3100	65–180	81–260	5–53	9.4–9.8

TABLE 5

Heavy metal concentration in fine grade suspended particulate matter.

Season	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Ni ppm	Fe %
Monsoon July 1985	250–320	1350–2200	6–8.5	400–620	130–190	3.8–4.2
Post-monsoon Nov. 1985	350–400	2650–3100	8–10.2	560–740	160–230	3.2–4.8
Pre-monsoon April 1986	380–420	2500–3800	8–12	600–850	160–220	4.2–4.4

TABLE 6

Percentage of trace metal, leached by treatment with 0.1 N HCl with respect to the total amount in suspended matter.

	Cu	Zn	Cd	Pb	Ni	Fe
River Periyar, Unpolluted Zone	100	40–70	45–60	50–60	40–60	38–47
Fine grade suspended particulate matter	85–90	80–90	60–80	80–90	40–60	55–68
Cochin Estuary	80–90	75–90	70–85	95–100	40–60	30–90

TABLE 7

Percentage of depletion of heavy metals with respect to estuarine mixing.

Season	Cu %	Zn %	Cd %	Pb %	Ni %	Fe %	Salinity (PPT)	pH
Monsoon July 1985	21.4	32.25	14.2	16.9	25.0	25.0	1.1–16.9	6.6–7.1
Post-monsoon Nov. 1985	44.6	32.5	35.29	42.85	33.33	75.0	10.8–26.5	7.1–8.0
Pre-monsoon April 1986	33.33	49.35	33.33	28.57	25.0	66.66	19.4–34.2	7.8–8.4

extracting twice using this technique. Spiked metal standards were added to the metal free sea water and extractions were done as described for water samples. For each set of spiked standards, three replicate analyses were conducted and calibration curve drawn. Five replicate analyses were done for one sample from each set collected during different seasons. These gave coefficients of variation of 4.2–7.8% for Cu, 6.4–8.2% for Zn, 5.2–6.8% for Cd, 2.3–4.4% for Pb, 6.4–9.3% for Ni, 3.1–5.2% for Fe.

Results and Discussion

The heavy metal concentrations in dissolved, particulate and fine grade suspended particulate matter are shown in Tables 1–5. The percentage of trace metals leached by treatment with 0.1 N HCl with respect to the total amount of metal is shown in Table 6. The seasonal changes in the percentage of depletion of heavy metals, salinity and pH are shown in Table 7.

Copper

The dissolved concentrations of copper for the unpolluted zone is 0.8 μg l^{-1} for the monsoon, 10 μg l^{-1} for the post-monsoon, and 8.0 μg l^{-1} for the pre-monsoon seasons. The particulate concentration is 48 ppm for the monsoon, 85 ppm for the post-monsoon, and 140 ppm for the pre-monsoon seasons. Non-monsoon seasons showed enhanced level of dissolved and particulate copper concentrations for the unpolluted zone.

The dissolved concentration for the Cochin estuary is 2.75–3.5 times higher for monsoon, 1.0–1.88 times higher for the post-monsoon, and 1.85–2.77 times higher for the pre-monsoon seasons in comparison to the values observed for the unpolluted zone. Similarly the particulate concentrations are 1.0–4.0 times higher for monsoon, 1.0–2.7 times higher for the post-monsoon, and 0.5–2.1 times for the pre-monsoon seasons.

Percentage of trace metals leached by treatment with 0.1 N HCl with respect to the total amount for the metal is found to be 80–100% for the study area. The dissolved copper is found to be 2.2–4.0 times higher and particulate concentrations are comparable to the values observed in the Gironde estuary (Etechaber, 1979).

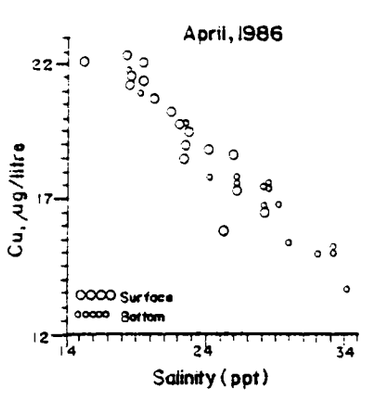


Fig. 2 Relation between salinity and dissolved copper.

Zinc

The dissolved concentrations for the unpolluted zone is 24 μg l^{-1} for the monsoon, 40 μg l^{-1} for the post-monsoon, and 65 μg l^{-1} for the pre-monsoon seasons. The particulate concentration is 180 ppm for the monsoon, 240 ppm for the post-monsoon, and 450 ppm for the pre-monsoon seasons. Similar to copper enhanced dissolved and particulate zinc is observed for the non-monsoon seasons.

The dissolved zinc is 4.37–6.45 times higher for the monsoon, 3.62–5.4 times higher for the post-monsoon, and 3.0–5.92 times higher for the pre-monsoon, and the particulate zinc is 0.60–5.77 times higher for the monsoon, 0.62–9.1 times higher for the post-monsoon, 0.70–6.8 times higher for the pre-monsoon seasons for the Cochin estuary in comparison to the values observed for the unpolluted zone. In general the concentrations are found to be 2 times higher for dissolved zinc and the particulate concentrations are comparable to the observed values in the Gironde estuary (Etecheber, 1979). Percentage of particulate trace metal leached by 0.1 N HCl with the total, indicated that higher amount is extracted for the Cochin estuary compared to the unpolluted zone.

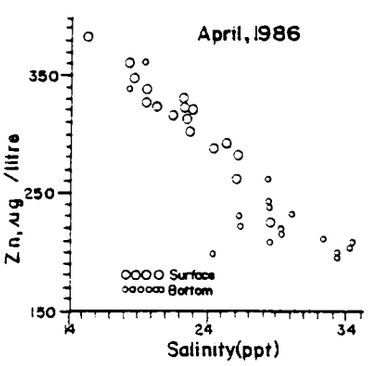


Fig. 3 Relation between salinity and dissolved zinc.

Cadmium

The concentrations of dissolved cadmium for the unpolluted zone is found to be constant for all the three seasons which is 0.2 μg l^{-1} and the particulate concentration is 2.8 ppm for the monsoon, 3.4 ppm for the post-monsoon, and 6.2 ppm for the pre-monsoon seasons. The dissolved concentration for the Cochin estuary is 9.0–10.5 times higher for the monsoon, 11.0–17.0 times higher for the post-monsoon, 14.0–21.0

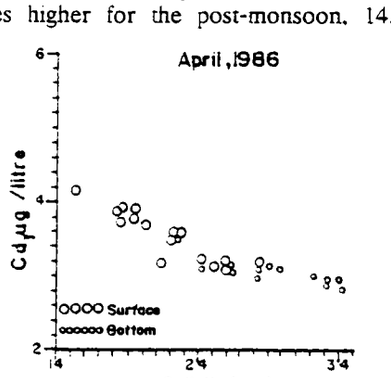


Fig. 4 Relation between salinity and dissolved cadmium.

times higher for the pre-monsoon, and the particulate concentrations are 20.7–32.5 times higher for the monsoon, 14.7–44.11 times higher for the post-monsoon, 10.48–29.0 times higher for the pre-monsoon seasons in comparison to the values observed for the unpolluted zone. Similar to zinc, the percentage of particulate trace metals leached by 0.1 N HCl with the total indicated that higher amount is extracted for the Cochin estuary compared to the unpolluted zone.

Lead

For all the three seasons, the dissolved concentration of lead is constant for the unpolluted zone which is 8 μg l^{-1} and the particulate lead concentration is 84 ppm for the monsoon, 94 ppm for the post-monsoon, and 105 ppm for the pre-monsoon seasons.

The dissolved concentrations are 1.1–1.32 times higher for the monsoon, 1.0–1.75 times higher for the post-monsoon, and 1.25–1.75 times higher for the pre-monsoon, and the particulate concentrations are 0.38–1.78 times higher for the monsoon, 0.63–1.91 times higher for the post-monsoon, and 0.77–2.4 times higher for the pre-monsoon seasons for the Cochin estuary, in comparison to the values observed for the unpolluted zone. 95–100% of the particulate lead in the estuarine region is leached by 0.1 N HCl.

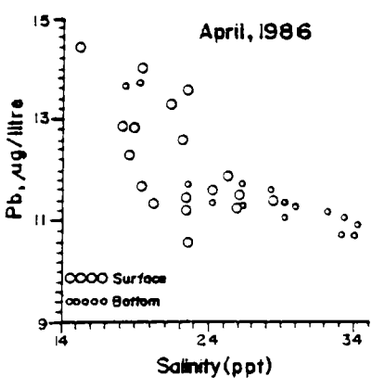


Fig. 5 Relation between salinity and dissolved lead.

Nickel

The dissolved concentration of nickel for the unpolluted zone is found to be constant for all the seasons which is 0.2 μg l^{-1}, whereas the particulate nickel is found to increase from monsoon to non-monsoon seasons.

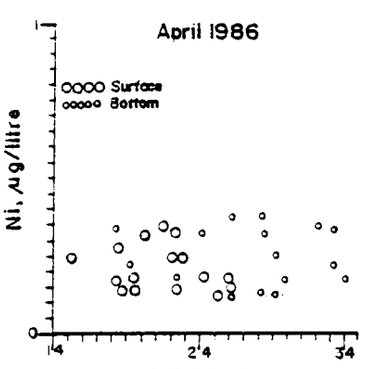


Fig. 6 Relation between salinity and dissolved nickel.

The dissolved concentrations for the Cochin estuary is 0.3 to 0.4 μg l^{-1} for the monsoon, 0.4–0.6 μg l^{-1} for the post-monsoon, and 0.3–0.4 μg l^{-1} for the pre-monsoon seasons. The particulate concentration of nickel is found to decrease from monsoon to non-monsoon seasons. High content of nickel is observed for the fine grade suspended matter from the industrial discharge point. The particulate leachable fraction in 0.1 N HCl with the total metal is found to be 40–60% for the Cochin estuary.

Iron

The dissolved and particulate concentrations of iron for the unpolluted zone is found to decrease from monsoon to the non-monsoon seasons. The dissolved concentrations of iron for the Cochin estuary vary from 0.6–0.8 μg l^{-1} for the monsoon, 0.2–0.8 μg l^{-1} for the post-monsoon, and 0.2–0.6 μg l^{-1} for the pre-monsoon seasons, and the particulate iron concentration is found to increase from monsoon to non-monsoon periods. The percentage of leachable iron with 0.1 N HCl is found to be 80–90% for the study area.

The depletion of heavy metals are governed by pH, iron content and salinity of the water column. Among the metals under study, iron has the maximum percentage of depletion which indicates that iron plays an important role in scavanging the heavy metals from the water column. For the monsoon season the pH ranges from 6.6–7.1 and iron depletion is found to be 25%. During the post-monsoon the pH ranges from 7.1–8.0 and the iron depletion is maximum (75%) whereas for the pre-monsoon the depletion is found to be 66.66%. This change may be due to the fact that at high pH conditions in pre-monsoon season, the depleted iron might have gone to the soluble form due to the high solubility product.

The high concentrations of dissolved and particulate iron for the monsoon season for the unpolluted zone could be due to the land drainage. Sankaranarayanan & Rossamma Stephen (1978) attributed the higher particulate iron in the Cochin estuary is due to land drainage, harbour activity and sewage. The decrease in the concentration of dissolved and particulate iron observed from monsoon to the non-monsoon period in the Cochin estuary indicates that iron is removed from the water column under the influence of salinity.

Seasonally the dissolved and particulate zinc shows a conservative decrease in concentrations. The com-

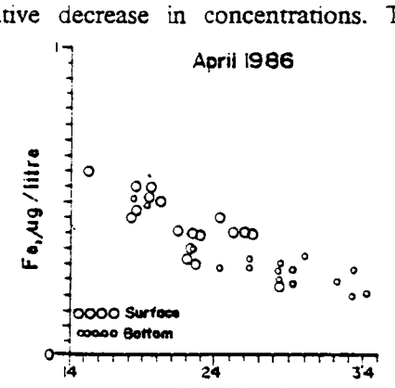


Fig. 7 Relation between salinity and dissolved iron.

parison of monsoon values of copper, cadmium and lead with pre- and post-monsoon seasons indicate that salinity, pH and iron plays a major role in the depletion of the above metals during estuarine mixing. The relation between salinity and dissolved concentrations for the April, 1986 survey are shown in Figs 2–7. Salinity has a profound influence in the precipitation of particulate matter (Ouseph, 1987). In general surface samples found to have more concentration compared to the bottom. As the salinity increases, the concentration of copper decreases. Zinc behaves in a similar way as copper. Pb, Cd, Fe have almost similar characteristics with salinity. The conservative nature of nickel is well noticed. The above data reveals that large quantum of metals are removed from the water column and precipitated as suspended matter which may contaminate the bottom sediments.

The decrease in the concentration of heavy metals with salinity shows contribution from fresh water sources and indicates that physical mixing is a significant factor in controlling the dissolved concentrations. High concentration of heavy metals are observed for the fine grade suspended matter from the industrial zone, even though no correction has been made for the grain size. According to Paul & Pillai (1983) solubilization of Cu and Cd from sediments under the influence of salinity may be regarded as one of the major mechanisms of trace metal transport to the sea. The enhanced levels of dissolved Cu and Zn observed during the non-monsoon period for the unpolluted zone is attributed to the concentration by evaporation and increased dissolution from sediments, due to higher summer temperature and larger contact time in summer (Paul & Pillai, 1983). The steady increase in the concentration of particulate Cu, Zn, Cd, Pb, and Ni from monsoon to the non-monsoon period indicate that the longer residence time of finer fractions of suspended solids in river water facilitates further build up by ion exchange processes. Similar behaviour is observed for the particulate Cu, Zn, Cd, Pb, Ni, and Fe from the effluent discharge point and also for Cu, Zn, Cd, and Pb particulates from the Cochin estuary. The decrease in the concentration of particulate nickel from monsoon to non-monsoon season shows that the major mechanism may be solubilization, suspension, precipitation and subsequent incorporation in the sediment. The concentration for the fine grade suspended particulate matter from the effluent discharge point showed high concentration of heavy metal, which indicates that the transport route of heavy metal may be from industrial sources.

Metals leached by 0.1 N HCl with the total, indicate that major quantum of estuarine particulate Cu, Zn, Cd, and Pb are in such a form which can selectively be removed by the biota (Ouseph, 1989). Similarity in the behaviour of particulate leachable metals with the total metal content from the effluent discharge point and Cochin estuary shows that the metal brought from the effluent discharge point can behave in a similar manner in the Cochin estuarine system for bio-geochemical uptake. The high dissolved concentration in the surface water strongly suggests anthropogenic inputs injected by industrial, harbour activity, and sewage. Mixing curves have been shown to be useful in detecting the relative importance of physical and bio-geochemical reactions in controlling the distribution of dissolved constituents in estuaries. The balance between the physical and bio-geochemical processes will dictate the fate of these anthropogenic sources in this estuarine environment.

The variation of heavy metals from season to season, station to station, relates to the characteristics of the estuarine system. Two models describing the mobilization of heavy metal can be suggested. One is the transport route to heavy metals through fine grade suspended particulate matter from river Periyar. The second is the removal of heavy metals during estuarine mixing. The survey revealed high concentrations of dissolved and particulate Cu, Zn, and Cd in the waters of Cochin estuary. The removal of heavy metals with respect to estuarine mixing indicates that Arabian Sea acts as a sink for heavy metals discharged from the Cochin harbour. The study reveals that there is anthropogenic input of heavy metals to the Cochin estuary. The implementation of a water quality management model for the study area is recommended.

I am thankful to Shri Subrata Sinha, Director, Centre for Earth Science Studies, for the keen interest shown in the above studies and to Dr. M. Baba, Head, Marine Sciences Division, for his encouragement and to late Dr. P. N. K. Nambisan, Director, School of Marine Sciences, Cochin University of Science & Technology for his useful discussions. I am obliged to S/Shri M. N. Muraleedharan Nair and N. R. Prakasan for the assistance given to me in the field and laboratory and to Shri V. Krishnan for typing the manuscript. The technical assistance given by Shri P. P. Simon, Boat Driver is gratefully acknowledged.

Agemian, H. & Chau, A. S. Y. (1976). Evaluation extraction techniques for the determination of metals in aquatic sediments. *Analyst* **101**, 761–767.

Duinker, J. C., Eck, G. T. M., Van & Noting, R. F. (1974). On the behaviour of copper, zinc, iron and manganese in the Dutch Wadden Sea, evidence for mobilisation processes. *Neth. J. Sea Res.* **8**, 214–239.

Etecheber, H. (1979). Repartition et compartment du, Zn, Pb, Cu et Ni dans l'estuarine de La Gironde. *Buil. Institute. Geol. Bassin d'Aquintaine, Bordeaux* 25, 121–147.

Joseph, J. & Kurup, P. G. (1990). Stratification and salinity distribution in Cochin estuary, south west coast of India. *Ind. J. Mar. Sci.* **19**, 27–33.

Malo, B. (1977). Partial extraction of metals from aquatic sediments. *Environ. Sci. Technol.* **11**, 277–282.

Nair, U. N. & Nair, B. K. (1986). Seasonality of trace metals in crassostrea madarasensis (Preston) inhabiting in Cochin backwaters. National Seminar on Mussel Watch, Cochin. Vol. 1, 6–12.

Ouseph, P. P. (1987). Status report on marine pollution along Kerala coast. Proc. of the Inter-departmental Seminar on Status of Marine Pollution in India, Dept. of Ocean Development, New Delhi, 86–105.

Ouseph, P. P. (1988). Heavy metal pollution in the sediments of Cochin estuary. Proc. of the National Seminar on Estuarine Management, Trivandrum (in press).

Paul, A. C. & Pillai, K. C. (1983). Trace metals in a tropical river environment—distribution. *Water, Air Soil Pollut.* **19**, 63–73.

Rajendran, N. & Kurian, C. V. (1986). (*Crassostrea madrasensis*) (Preston)—indicator of metal pollution in Cochin backwaters. National Seminar on Mussel Watch, Cochin, Vol. 1, 121–126.

Remani, K. N., Venugopal, P., Saraladevi, K., Lalitha, S. & Unnithan, R. V. (1980). Sediments of Cochin backwaters in relation to pollution. *Ind. J. Mar. Sci.* 7, 130–131.

Sankaranarayanan, V. N. & Rosamma Stephen (1978). Particulate iron, manganese, copper and zinc in water of the Cochin backwaters. *Ind. J. Mar. Sci.* 7, 201–203.

Sankaranarayanan, V. N., Purushan, K. S. & Rao, T. S. S. (1978).

Concentrations of some of the heavy metals in the Oyster *Crassostrea madrasensis* (Preston) from the Cochin region. *Ind. J. Mar. Sci.* 7, 130–131.

Sen Gupta, R., Singbal, S. Y. S. & Sanzgri, S. (1978). Atomic Absorption Analysis of a few trace metals in Arabian Sea. *Ind. J. Mar. Sci.* 7, 295–299.