CHAPTER 2

MATERIALS AND METHODS

2.1 Description of location

2.2 Analytical techniques

2.2.1 Sampling procedure
2.2.2 Analytical methods

2.3 General hydrography

2.3.1 Salinity
2.3.2 Dissolved oxygen
2.3.3 pH

A brief description of the Cochin estuarine system and an outline of the methods employed are given in this chapter. The Chapter is concluded with general hydrography of the study area.

2.1 Description of location

The Cochin estuary includes a system of interconnected lagoons, bays and swamps penetrating the main land and
enclosing many islands in between, whose total area amounts to approximately 500 square km. The backwater around Cochin is located between Lat. 9°40' - 10°12' N and Long. 76°10' - 76°30' E. The estuary is connected with the Arabian (Lakshadweep) sea by a permanent opening, 450m wide (Fig. 2.1) through which tides act within the estuary. The tides have a maximum range of 1m and the lower reaches of the estuary (barmouth region) are dredged to a depth of 10-15 m. The upper reaches of the estuary are shallower (2-5 m) with little or no tidal influence and have a low salinity. Cochin is the major port on the South west coast of India.

The major sources of fresh water in the estuary are the two rivers, the Periyar in the northern part and Muvattupuzha in the southern part. In addition, several small tributaries, irrigation channels and innumerable drains contribute to the system. A large number of heavy industrial establishments are situated on both sides of the river Periyar and on the southern bank of the river Muvattupuzha. These industrial concerns discharge their wastes into the estuary.

The depth of the estuary varies moderately. Most of the area is about 3m, but the shipping channel in Cochin harbour area is periodically dredged to a depth of about 13m. The estuary provides access to all types of boats, country crafts, ferries etc. including ocean going vessels to the Cochin harbour. The tides in the Cochin estuary are mixed semi-diurnal type with an average range of ≈90cm. During the flood tide, sea water enters the estuary via Cochin barmouth and the
Fig. 2.1 Map of Cochin estuary showing location of stations
flow reverses during the ebb tide. The magnitude of influence of the tide progressively decreases with increasing distance from the barmouth.

The Cochin harbour has attained strategic importance because of its commercial prominence as well as defence potential. It houses a large oil tanker berth, a conveyor belt system for fertilizer transfer and a major ship building yard. Because of the significant influence of land, industries and harbour, the estuary is considerably polluted.

Station locations

The area of investigation and the station locations are depicted in Fig. 2.1. The stations were fixed so as to obtain a fairly good coverage of the prevailing complex environmental conditions. The following is a brief description of the characteristics of the stations where the present study was carried out.

Station 1 is situated in the river Muvattupuzha which drains into the Cochin estuary through the southern side. It is about 20km away from the barmouth. The station represents a purely fresh water riverine system.

Station 2 is the discharge site of a paper pulp mill in the river Muvattupuzha and is always riverine.

Station 3 is 1 km down the discharge site. The characteristics
of the station indicate that settling of most of the waste from the paper mill takes place at this region and has considerable vegetation.

Station 4 is located at the mouth of the river where the Muvattupuzha joins the estuary. During monsoon months, the Station behaves as a fresh water zone.

Station 5 is the mixing zone at the southern part of the estuary. The sediment in the region is always fine and sandy. During monsoon months the station exhibits riverine characteristics and as the season advances to post- and premonsoon, estuarine conditions prevail.

Stations 6 and 7 are located in the same arm of the estuary. These regions are always estuarine and the sediments are characterized by sand, silt, clay or silty clay. Numerous irrigation channels, carrying discharges from various industrial and sewage outfalls drain into these locations. Considerable navigational activities are also present in this region.

Station 8 is located in the northern arm of the estuary where the river Periyar empties its flux into the sea. This station is always typically estuarine. Sewage and waste from oil-mills, food industries etc. are discharged into this area.

Station 9 also represents an estuarine station in the northern arm of the estuary. The retting of coconut-husks is the major activity in this area and huge amounts of plant pith get
accumulated in this region. The sediments of this region contain large quantities of pith and yarns of coconut husk.

Station 10 is a riverine region in the Periyar river. Salinity intrusion occurs during post- and premonsoon seasons. The sediment is always sandy in nature. The station is located about 2 km down the Station 11.

Station 11 is located in the Periyar river near the industrial complex FACT, and it is here that the effluents from the industrial concerns (the fertilizer and the insecticide manufacturing units, the Travancore Cochin Chemicals etc.) are discharged. The sediment of this region always contain oil and grease and when dried has a grey colour.

The stations were broadly grouped into riverine and estuarine ones, based on salinities. Thus, the Stations 1, 2, 3, 4 and 5 in the southern arm and Stations 10 and 11 on the northern arm were classified as riverine. The other four, viz. Stations 6 and 7 in the southern arm and 8 and 9 in the northern arm represented estuarine locations.

The monthly data were pooled and divided into three seasons for getting reliable trends for explaining the features. The monsoon season comprised of the months May, June, July and August. September, October and November were considered as Postmonsoon and December, January, February, March and April as Premonsoon period. The classification was based on rainfall data (Table 2.1).
Table 2:1
Rainfall Data (April '90 - March '91)

<table>
<thead>
<tr>
<th>Months</th>
<th>Rain in mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apr'90</td>
<td>54</td>
</tr>
<tr>
<td>May'90</td>
<td>555</td>
</tr>
<tr>
<td>Jun'90</td>
<td>437</td>
</tr>
<tr>
<td>Jul'90</td>
<td>688</td>
</tr>
<tr>
<td>Aug'90</td>
<td>190</td>
</tr>
<tr>
<td>Sep'90</td>
<td>80</td>
</tr>
<tr>
<td>Oct'90</td>
<td>291</td>
</tr>
<tr>
<td>Nov'90</td>
<td>212</td>
</tr>
<tr>
<td>Dec'90</td>
<td>2</td>
</tr>
<tr>
<td>Jan'91</td>
<td>-</td>
</tr>
<tr>
<td>Feb'91</td>
<td>-</td>
</tr>
<tr>
<td>Mar'91</td>
<td>-</td>
</tr>
</tbody>
</table>
2.2 Analytical techniques

2.2.1 Sampling procedure

Surface and bottom water and surficial sediment samples from the Stations (Fig. 2.1) were collected at monthly intervals from April 1990 to March 1991. Surface water samples were collected using a clean plastic bucket and bottom water was taken by using a modified Hytech water sampler. The surficial sediment samples were collected using a van Veen grab (area 0.032m²). The samples were taken in polythene bags and stored deep frozen until analyses.

2.2.2 Analytical methods

pH measurements were made using a portable Elico pH meter. Salinity was estimated argentometrically by the modified Mohr's method developed by Knudsen. (Grasshoff et al., 1983). The method described by Strickland and Parsons (1977) was adopted for the determination of dissolved oxygen.

Sediment organic carbon content was determined by the chromic acid oxidation method suggested by El Wakeel and Riley (1957). Total phosphorus in the sediments was measured by the modified method of Murphy and Riley (1962) and the total nitrogen by micro-Kjeldahl procedure given by Barnes (1959).

Textural analysis of the sediment was carried out by drying the sample in a hot air oven (90°C) for 6 hours, and subsequent mechanical sieving and pipette analysis as described
by Krumbein and Pettijohn (1938). Shepard’s nomenclature (Shepard, 1954) was used to describe the texture. Strickland and Parsons (1977) method was employed for the determination of pigments. Chlorophyll pigments, carotenoids and pheopigments of the sediments were determined spectrophotometrically in 90% acetone extract using the equation SCOR/UNESCO, 1966. Samples of the sediment which were dried within the folds of filter paper were ground in a mortar for 10 minutes and extracted with 10ml of 90% acetone. 0.1mg MgCO$_3$ having been added immediately before extraction. The samples were kept overnight at 4°C, centrifuged and the absorbance was measured for the total amount of pigments. Pheopigment was measured spectrophotometrically after acidifying the extract with 0.1N HCl.

The protein content was analysed by the method suggested by Herbert et al., (1971). A weighed amount of sample was homogenized in 1N NaOH. The samples were maintained at 80°C for 30 minutes to dissolve the proteins. After cooling, aliquots were transferred to clean test tubes and 5 ml of the copper reagent were added followed by 0.5ml of Folin-Ciocalteu reagent after 10 minutes. Appropriate blank and standards (bovine albumin) were similarly treated.

Lipids were extracted according to the method of Bligh and Dyer (1959). A known amount of the sample was extracted with chloroform- methanol mixture (1:2). Repeated the extraction four times. The extracts were pooled together and extracted with chloroform - water (1:1). The chloroform layer was separated and dried over anhydrous sodium sulphate. The lipid
Carbohydrates were estimated by the phenol-sulphuric acid method (Dubois et al., 1956). Total carbohydrate from the sediment samples were leached by the hydrolysis of the sample with 1N H₂SO₄ at 100°C for 1 hour. Cooled and filtered sample aliquots were taken in clean test tubes. Added 1 ml of 5% phenol and 5 ml of concentrated sulphuric acid. Cooled the test tube at room temperature and measured the optical density. Blank and standards of D-glucose were also treated similarly.

Humic acid in the sediment was analysed by the fluorimetric method. A known quantity of the dried sediment was extracted with 1N NaOH for 24 hrs., filtered and acidified. The precipitated humic acid was redissolved in NaOH and the absorbance measured in a fluorescence spectrophotometer (Hitachi F 3010). Humic acid standard was prepared by dissolving purified humic acid isolated from the aquatic sediments.

Hydroxylated aromatic compounds (tannin and lignin) were estimated by the method detailed in APHA (1981) and modified by Nair et al., (1989). Sediment samples were subjected to 0.05M NaOH leaching for 90 minutes and filtered. 5ml aliquots of the filtrate were pipetted out and 1 ml of citrate solution followed by the tannin-lignin reagent and the carbonate tartarate reagent were added. The optical density was measured at 765nm.

All the chemicals used were of analytical reagent grade.
Milli-Q water was used for the estimations. A Hitachi (150-20) U.V. Visible spectrophotometer was used for the photometric measurements.

2.3 General Hydrography

The study of the hydrographical parameters has great importance in characterising the general features of an estuarine system. They are equally significant for pollution control, harbour design, marine traffic routing etc. The hydrographical conditions in an estuary mainly depend on the intrusion of sea water associated with tides and influx of fresh water from rivers. Precipitation and evaporation processes also contribute to hydrographical changes. In addition, the bottom topography and geographical condition in the estuary exert a profound influence on the hydrographical condition of the estuary. The sedimentary characteristic is more or less governed by the hydrography of the overlying water.

The hydrography of the Cochin estuary has been well documented (Ramamritham and Jayaraman, 1963; George and Kartha, 1963; Qasim and Reddy, 1967; Qasim et al., 1968; Sankaranarayanan and Qasim, 1969; Josanto, 1971; Wellershause, 1971; Haridas et al., 1973; Shynamma and Balakrishnan, 1973; Joseph, 1974; Lakshmanan et al., 1982; Sankaranarayanan et al., 1986). Although the information available pertains to seasonal variation of temperature, salinity, dissolved oxygen, pH, alkalinity and nutrients of the region as a whole, the present
study on hydrography (spatial and seasonal variation of salinity, dissolved oxygen and pH) was conducted as concurrent data are essential for interpretation of the sedimentary behaviour.

2.3.1 Salinity

Salinity has been recognised as an index of the estuarine mixing processes and the tidal effects. The salinity distribution pattern is largely influenced by the mixing and diffusion phenomena occurring in the estuaries. Wide fluctuations in salinity are generally observed in an estuarine system. Except for regions with high evaporation and little rainfall, where the salinity level may exceed $3.5 \times 10^{-3}$, the values would be normally lower than the salinity of sea water.

The monthly data on salinity of surface and bottom waters at Stations 1-11 are given in appendix and the seasonal distribution of salinity is presented in Fig. 2.2.

The Cochin estuary is highly influenced by the influx of fresh water from rivers and by the intrusion of sea water via the bar mouth. In the southern region, except at Stations 1 and 2 during monsoon, low salinity values ranging from 0.00 to $3.42 \times 10^{-3}$ at the surface and 0.00 to $8.85 \times 10^{-3}$ at the bottom were observed. A gradual increase in salinity was encountered as the season progressed to postmonsoon and premonsoon. However, Stations 1, 2 and 3 exhibited fresh water characteristics throughout the period of study. Salinity intrusion occurred at Station 4 during premonsoon only. The highest
Fig. 2.2 Seasonal distribution of salinity
(s) surface  (b) bottom
A value \(35 \times 10^{-3}\) was recorded for surface and bottom waters at Station 7.

In the northern region, at Stations 8 and 9, salinity values ranging between 0.00 to \(0.83 \times 10^{-3}\) at surface and 0.00 to \(0.83 \times 10^{-3}\) at bottom were noticed during the monsoon months. This was brought about by the heavy monsoonal rain causing high fresh water discharge. As the season advanced to post and premonsoon, higher values ranging from \(30.10\) to \(35.86\times 10^{-3}\) and \(4.13\) to \(25.62\times 10^{-3}\) at the bottom and \(12.80\) to \(23.7\times 10^{-3}\) and \(2.37\) to \(5.39\times 10^{-3}\) at surface waters of Station 8 and 9 were observed respectively. This may be the result of the penetration of salt water and low discharge of fresh water into the estuary. A vertical salinity gradient also was observed at these regions during all the seasons. Fresh water conditions were observed at Stations 10 and 11. At Station 10 the salinity increased during the premonsoon period indicating an intrusion of sea water.

2.3.2 Dissolved oxygen

Dissolved oxygen is the most valuable water quality parameter in assessing water pollution. It is also important since the existence of aquatic life is intimately linked with the availability of oxygen for their survival. Though atmospheric oxygen is abundant its solubility in water is low, 9.94 ml \(1^{-1}\) at \(1^\circ\)C and 5.28 ml \(1^{-1}\) at \(30^\circ\)C in fresh water and 7.97 ml \(1^{-1}\) and at \(1^\circ\)C and 4.41 ml \(1^{-1}\) at \(30^\circ\)C in sea water of salinity \(33 \times 10^{-3}\) (Riley and Chester, 1971). The depletion of
oxygen content leads to undesirable obnoxious odours under extreme anaerobic conditions. (Doudoroff Shumway and Peter, 1970; Nelson, 1978).

The concentration and distribution of oxygen in natural waters depend on various factors such as temperature, partial pressure and salinity. Studies on salinity dependent oxygen solubility may help to elucidate the various physical, chemical and biological processes taking place in the estuarine system (Desouza & Sen Gupta, 1986).

Results of dissolved oxygen at surface and bottom waters of all stations are given in appendix and the seasonal distribution in Fig. 2.3. Higher dissolved oxygen content was observed at surface and bottom waters all along the stations during the monsoon period. Dissolved oxygen values ranged from 2.54 to 5.85 ml l\(^{-1}\) at surface and 2.82 to 5.99 ml l\(^{-1}\) at the bottom during monsoon. The values decreased as the season advanced to post- and premonsoon. The lowest value was observed along Stations 4 to 9. This may be explained as the combined effect of low solubility of oxygen due to high salinity and temperature and due to the utilization of oxygen for the biodegradation of organic matter. In general, a spatial and seasonal variation of dissolved oxygen was observed. High dissolved oxygen contents were observed during monsoon due to the greater solubility of oxygen in fresh water and high turbulence.
Fig. 2.3 Seasonal distribution of dissolved oxygen
(a) surface (b) bottom
2.3.3 pH

Many of the life processes are dependent on the hydrogen ion concentration in the surrounding medium. The pH of a medium depends on many factors like photosynthetic activity, rainfall, nature of dissolved materials, discharge of effluents, sewage outfall etc. Variation in pH due to chemical and other industrial discharges renders a stream unsuitable not only for recreational purposes but also for the rearing of fish and other aquatic life (Webb, 1982). Monitoring of pH values is therefore essential for identifying zones of pollution and other quality conditions of water (Clark et al., 1977).

Data on pH of Cochin estuary are given in appendix and seasonal changes in Fig. 2.4. The pH in the entire study area remained around 7 with no significant variations being observed throughout the period of the study. A slightly increased pH was observed during premonsoon except at Station 11. This increased value may be attributed to excessive photosynthetic activity of algae and the near marine condition. The high photosynthetic production during post- and premonsoon in the Cochin backwater was reported by earlier workers also (Silas and Pillai, 1975; Nair et al., 1975). The difference in pH between surface and bottom waters of the estuarine system during post- and premonsoon is not well defined. The discharge of acidic industrial waste and the decrease in flow lead to a successive decrease in pH from monsoon to premonsoon.
Fig. 2.4 Seasonal distribution of pH
(s) surface   (b) bottom