1. INTRODUCTION

An estuary is the place where river meets an inlet of the sea. Pritchard (1967) defined an estuary as a "semi-enclosed coastal body of water which has a free connection with open sea and within which sea water is measurably diluted with fresh water derived from land drainage". Fairbridge (1980), in his review on the definitions of estuaries argues that the tidally affected freshwater region should be considered an integral part of any estuary. The estuaries grouped under these definitions have a salinity significantly lower than the open sea and are termed positive estuaries. Negative estuaries are those where evaporation exceeds river flow plus precipitation and hypersaline condition exists.

Estuaries are divided into three geomorphologically defined categories: the fjord type, the barbuilt type and the coastal plain estuary. Fjords are generally deep with a relatively large body of semi-enclosed seawater below a brackish surface layer. Bar built estuaries are generally associated with depositional coasts and have characteristic bars across their mouths. The coastal plain estuary is a submerged extension of a river valley opening towards the sea.

The majority of estuaries that have been studied fall within the coastal plain category and within this group large differences occur in the circulation patterns, density
stratification and mixing processes. The chemistry of estuaries should be considered in the context of the physical processes of water circulation which occur in them, since the distribution of dissolved and particulate substances are controlled by the circulation and mixing of their waters (Aston, 1978). Consequently, a better classification would be the one based on the salinity distribution and flow characteristics within the estuary. It is the interaction between processes arising from river discharge on one hand and the tidal currents on the other, which leads to the occurrence of a series of types of estuary circulation, described in detail by Dyer (1973), Officer (1976) and Bowden (1980). At one extreme is the salt wedge type estuary, in which the influence of river discharge is dominant and freshwater flows out of the estuary as a surface layer above an intruding wedge of seawater. At the other extreme, when the tidal currents are dominant, the water is almost completely mixed vertically and there is little variation in salinity with depth. The partially mixed type estuary is an intermediate case in which there is a gradual increase of salinity from surface to bottom, with a net seaward flow in the upper layer and an upstream flow below it.

1.1. Estuarine Chemical Reactivity

Estuarine ecological environments are complex and highly variable compared to other marine environments. The dominant feature controlling the distribution, speciation and
reactivity of chemical components within estuaries is the mixing of fresh and saline waters. Differences in the nature of the fresh and saline mixing components produce gradients and transitions of physico-chemical properties within an estuary in response to the circulation and mixing pattern. Estuaries are characterised by complex gradients of salinity, tidal action, current velocity, bottom erosion and sediment accumulation. They are subject to major and often unpredictable variations in response to river flow as well as wind and storm patterns.

In an estuary, mixing occurs between natural waters of very different chemical composition and physico-chemical properties. Although the salinity of sea water is high as compared with the total salt content of river waters, the plant nutrient elements nitrogen, phosphorus and silicon are higher in fresh water than in seawater. Ionic strength and physico chemical parameters such as pH and redox potential may change during estuarine mixing. Estuarine waters also contain suspended solids derived from the inflowing river or seawater or by resuspension of settled sediment as a result of tidal stirring.

Characterization of estuarine samples with respect to salinity is a standard procedure for chemical investigations in estuaries and is known as the 'reactant method' (Morris, 1985). Correlation of the concentration of a dissolved chemical species with salinity for samples collected throughout the salinity range allows an assessment
of gain, loss or conservation of the constituent and an indication of the relative contributions of the species from the separate marine and freshwater sources. One can also deduce the salinity related location of reactivity and the extent to which it has progressed.

1.2. Study of nutrients in estuaries

The term 'nutrients' usually refers to the dissolved inorganic forms of nitrogen, phosphorus and silicon utilised by photosynthetic organisms in the formation of organic matter. Nitrogen and phosphorus are described as being biolimiting elements, which means that the concentration of these elements limits biological growth. The processes that govern the fate of these elements in estuaries differ and consequently the ratios of inorganic nitrogen to phosphorus in estuaries may vary widely with time and space.

Estuaries are generally regarded as one of the most productive of aquatic systems and the nutrient supply from freshwater inputs is important in sustaining their high rates of primary production. Estuaries function as important sinks and transformers of nutrients, thus altering the quantity and quality of nutrients transported from land to the sea (Jordan et al., 1991).

On an areal basis of any class of ecosystems, estuaries receive some of the highest inputs of nutrients because of the local influences from land drainage and often pollution.
A number of estuaries receive nutrient additions (per unit area) over 1000 times the fertilizer loads added to agricultural areas (Nixon et al., 1986). The resulting nitrogen and phosphorus inputs lead to elevated phytoplankton productivity (Ryther and Dunston, 1971; Nixon and Pilson, 1983; Keller, 1988) and can lead to hypoxia and eutrophication. There has been an increase in recent years in the rates of eutrophication of lakes, rivers and estuaries due to the release of nitrates and phosphates from excess fertilizers and sewage effluents (O'Neill, 1985). The great concern over this problem has stimulated much new research in the following areas: the chemistry and biogeochemistry of nutrients in aquatic systems, the quantification of the sources and sinks of nutrients, and the dynamics of nutrient uptake and release.

The distribution and variation of nutrients in estuarine systems are controlled by a variety of physical, geological, chemical and biological processes (Pritchard and Schubel, 1981). Understanding the behaviour of nutrients in estuaries has important implications for global nutrient budgets and for controlling eutrophication of these systems. The study on the hydrographical features and the effect of nutrient enrichment is essential in understanding the water as a useful resource. A discussion of the sources and sinks of nutrients and their distribution with the estuarine system is of great importance. Perhaps one of the most pivotal questions concerning nutrients in estuaries is the degree to
which estuaries behave as traps, retaining and recycling nutrients within the system and the relative contributions of external nutrient supply.

A successful understanding of the role of estuaries as nutrient traps, filters or exporters requires a knowledge of the distribution of dissolved and particulate nutrient species as well as their rates of input, loss, and accumulation in coastal waters. The nutrient budget or mass balance can be a useful tool in describing the fate of nutrients in estuaries. While point source inputs from rivers and sewage treatment plants have been successfully quantified for a number of systems (Loder and Glibert, 1980; Jaworski, 1981; Smith, 1981; Nixon and Pilson, 1983; Childers and Day, 1988), the more spatially variable or sporadic inputs from groundwater seepage, surface runoff, precipitation, and offshore waters are much more difficult to measure. The potentially largest term in most estuarine nutrient budgets is the exchange of nutrients with offshore waters, which is usually determined by difference or ignored due to difficulties involved in measuring small nutrient exchange differences in relatively larger tidal volumes (Kjerfve et al., 1982). In addition, nutrient accumulation rates in estuarine sediments are difficult to measure against the large background of C, N, or P already present, and are complicated by resuspension, bioturbation, and deposition rates that vary widely over time and location (Nowicki and Oviatt, 1990).
The interaction between sediments and overlying water has been recognised as an important factor in the nutrient dynamics of estuarine and marine systems. Highly metabolizable material from autogenic and exogenic sources may be deposited on to the sediment. The subsequent processes that take place at the sediment-water interface are of a complex nature and involve microbial breakdown reactions and adsorption/desorption equilibria between the liquid and solid phase. Due to these diagenetic processes, the interstitial water of the sediment is generally enriched in various nutrients as compared to the overlying water. This concentration difference will lead to an effective transport of nutrients back into the overlying water through diffusion and other mixing processes.

1.3. The Chaliyar River Estuary

The Chaliyar river is one of the major west flowing rivers of the Kerala State. It originates from the Western Ghats and joins the Arabian Sea at Beypore, near Kozhikode in the south-west coast of India. The Chaliyar river estuary is a typical positive estuary. Earlier, a few studies have been conducted in this estuary on salinity intrusion (James and Sreedharan, 1983), and on circulation and mixing (James and Ramanathan, 1983). Distribution of nutrients in the Beypore estuary have been reported by Sarala Devi et al. (1983) and their study was confined to the river mouth only. Premchand et al. (1987) have examined the circulation and flushing characteristics of this estuary during south-
west monsoon season. The salinity distribution pattern and its relationship with dissolved oxygen has been studied by Giridhar Hadnooker et al. (1987). Nirmala et al. (1990) have studied the effect of salinity variation along with other hydrographical parameters on the ecology of this estuary.

Earlier workers were using the name 'Beypore estuary' because most of the studies were confined to the river mouth which is situated at Beypore. The present study area covers 15Km upstream of Chaliyar from the river mouth and will be referred here 'Chaliyar river estuary'.

1.4. Scope Of The Present Work

The present work was undertaken with the main objective of studying the nutrient chemistry of the estuary and to make a sincere attempt in estimating nutrient fluxes. The studies were mainly directed at identifying the sources and sinks of nutrients and defining the important geochemical and biochemical pathways of nutrients in the estuary. The quantity of nutrient salts introduced by the fresh water flow into the estuary is considerable. What happens to the large quantities of nutrients that enter the estuary is not only of ecological interest but also is relevant to water quality management.

Together with other hydrographical parameters, the distribution and seasonal variation of nutrients in the estuary was studied in detail. Large temporal variations of

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nutrient concentrations have been shown to occur within a tidal period at fixed locations. Hence more attention was given to determine the temporal as well as spatial variations of constituents in the estuary.

India has several major estuarine systems distributed all along the east and west coasts. Extensive studies on the hydrographical, biological and physico-chemical aspects of these aquatic systems have been made by many workers. So far no attempt has been made to study the nutrient fluxes in any of the Indian estuaries. In the present work, an attempt has been made to study the fluxes of inorganic nutrients through various cross-sections in the Chaliyar river estuary. The results were analysed to determine the relative influences of riverine and tidal forcing on the fluxes.
CHAPTER 2

MATERIALS AND METHODS
2. MATERIALS AND METHODS

2.1. Description of the study area

The Chaliyar is the third largest river of Kerala state. It originates from the Ilambaliri hills in Gudalur Taluk of Nilgiri district in Tamil Nadu at an elevation of 2066m above mean sea level (Anonymous, 1974). Chaliyar flows towards the west from the Western Ghats and joins the Arabian Sea at Beypore near Kozhikode (Calicut). The river has a length of 169Km and the total drainage area is about 2923 Km² out of which 2535Km² lie in Kerala state and the remaining 388Km² in Tamil Nadu. The Chaliyar river estuary has a port handling cargo and a fishery harbour at Beypore situated at 11° 08'N latitude and 75° 51'E longitude.

The Chaliyar river estuary enters the sea in a south westerly direction and this inlet is situated in a stable region. There is a horse-shoe shaped bar at the entrance and the depths over it vary from 1.5m to 1.9m. The sea bed slope at Beypore is comparatively flat with a 9m contour at a distance of 3.5 Km from the river mouth. The predominant wave heights off the Beypore coast during monsoon and fair weather seasons are 1.2m and 0.6m respectively. The tides at Beypore are of mixed semi-diurnal type with a period of 12 hrs and 40 minutes (Anonymous, 1969).

Maximum river discharge occur during the south-west monsoon months June to August, and during this period, the
tidal limit comes down to a distance of 5 Km from the river mouth. The lowest discharges are found to occur during April-May, and during this period tidal incursion of sea water was observed upto a distance of about 28 Km from the river mouth (James and Sreedharan, 1983). Bottom sediments in the estuary composed of silty sands in shallow areas and clayey silts in deeper areas. Towards upstream of the river, the bottom is mainly sandy with a small percentage of silt.

2.2. Station location

A map of the area of study with location of stations is given in Fig 2.1. Eight stations along four transects across the estuary were occupied. Section 1 is near to the river mouth and the upstream sections are at distances of 5, 10 and 15 Km respectively from the mouth. The two stations selected at each transect were almost equi-distant from the shore, one each on the northern and southern side. Depths along these sections varied with the tide and season, so that mean values and exceptions are stated below.

The physical dimensions of the sections are:
Section 1 (S-1) - Width = 390m; mean depth = 2.45m to 2.95m.
Section 2 (S-2) - Width = 294m; mean depth = 2.99m to 3.50m.
A pocket of deeper water with a mean depth of ~7m occupies the northern side which is localised. Midway and further south along the axis the mean depth is <3m.
Section 3 (S-3) - Width = 200m; mean depth = 4.0m to 4.54m.
Section 4 (S-4) - Width = 243m; mean depth = 2.52m to 3.06m.
Fig. 2.1. Observation sections in Chaliyar river estuary.
2.3. Sampling procedure

Monthly surveys were conducted in the estuary for a period of one year from October 1990 to September 1991. 13-hour tidal observations were made simultaneously at two sections on two consecutive days to get a synoptic picture. Two stations were covered across each section during these surveys. Hourly observations were made for physical parameters such as temperature, salinity and current speed and direction. Current speed and direction measurements were made using an indigenous rotor current meter (accuracy for velocity ±1 cm/sec and direction ±2.68°, designed by NIO, Goa).

Water samples were collected at two hourly intervals from the surface, mid-depth and near bottom of the water column. Surface samples were collected using a clean plastic bucket and Niskin sampler was used for collection of mid and near bottom samples. Sampling was done with the tide and in the least possible time to minimise errors. Samples for dissolved oxygen determination were collected in 125 ml stoppered glass bottles, taking care that no air bubbles are getting trapped in the sample. These samples were fixed immediately with manganous chloride solution (Winkler A) followed by alkaline potassium iodide (Winkler B) solution. Water samples for the analysis of salinity and nutrients were collected in pre-cleaned polythene bottles. Temperature and pH of the water samples were measured in situ and the samples for nutrient analyses were transported to the laboratory.
keeping them in ice boxes. Analysis of ammonia-N, nitrite-N, nitrate-N and inorganic phosphate were conducted immediately at the temporary laboratory set up near the observation site. Other chemical parameters such as salinity, urea-N, total N and total P were measured after bringing the samples to the permanent laboratory.

Sediment samples were collected from all stations at the time of high and low water using a hand operated Van Veen grab. Always the undisturbed middle portion of the grab sample was transferred to wide-mouth polythene bottles using a plastic spatula and kept air tight in ice-boxes for the analysis of interstitial water. The same sediment samples were used for the determination of grain size, nitrogen and phosphorus content.

2.4. ANALYTICAL METHODS

2.4.1. pH, Salinity and Dissolved Oxygen

pH measurements were made using a portable pH meter (PHILIPS, model PP 9046, accuracy ±0.01) and salinity was measured with an electrodeless induction type salinometer (DIGI-AUTO, model 3G, Tsurumi Seiki, Japan, accuracy ±0.01x10^-3) after proper calibration.

Dissolved oxygen was determined by the Winkler's method, in the form recommended by Strickland and Parsons(1972). The principle of the determination and the possible sources of systematic errors are fully discussed by Grasshoff(1983).
2.4.2. Nutrients

(a) Ammonia-N was determined according to the indophenol blue method of Koroleff (1983). In a moderately alkaline medium, ammonia reacts with hypochlorite to form monochloramine which in the presence of phenol, catalytic amount of nitroprusside ions and excess hypochlorite forms indophenol blue. The formation of monochloramine requires a pH between 8 and 11.5. At higher pH, ammonia is incompletely oxidised to nitrite. Both calcium and magnesium ions in sea water precipitate as hydroxide and carbonate at pH higher than 9.6, however their precipitation can be prevented by complexing them with citrate buffer.

Great care was taken to ensure that samples, blanks and standards are not contaminated during the course of analysis. The samples were 'fixed' by the addition of reagents immediately after collection and the absorbance, after the colour development (about 6 hours) was measured at 630 nm. The measured ammonia include both free dissolved ammonia gas and the ammonium ions.

(b) Nitrite was measured by the method of Bendschneider and Robinson (1952). In this method, nitrite in the water sample when treated with sulphanilamide in acid solution results in a diazo compound which reacts with N-1-naphthyl ethylene diamine dihydrochloride to form an azo dye. The absorbance of it is measured at 543 nm.
(c) Nitrate-N in the water sample was quantitatively reduced to nitrite by passing through a reduction column filled with copper coated cadmium granules and measured as nitrite. During the reduction stage, ammonium chloride buffer was added to the sample to maintain a stable pH (Grasshoff et al., 1983). The estuarine samples containing high concentration of nitrate-N were properly diluted before passing through the column.

(d) Urea-N was determined by the diacetyl monoxime method as described by Koroleff (1983). In strongly acidic solutions and in the presence of a weak oxidant, urea forms a condensation product with diacetyl monoxime. This product interacts with semicarbazide and manganous ions to produce a magenta molecular complex, the absorbance of which is measured at 520 nm. Chloride ions are added in excess to increase the sensitivity of the reaction and the presence of phosphate ions enables reasonable reproducibility.

(e) Total N and P were determined by the simultaneous oxidation procedure (Koroleff, 1983). In this method, the water samples were oxidised with the help of a strong oxidising agent such as alkaline persulphate by autoclaving in closed condition. The organic forms of nitrogen and phosphorus and their inorganic forms in lower oxidation states are finally oxidised to nitrate and inorganic phosphate respectively. After cooling, these digested samples were estimated by the previously discussed standard procedures for nitrate and phosphate.
The calibration curve for total-N obtained with standard EDTA solutions is shown in Fig.2.4. For 1cm cell, the calibration factor obtained was 22.5. The percentage recovery of total-N using the above method was estimated with glycine standards within the concentration range of 10 to 50 ugat/l. The results are summarised in Table 2.4.1.

(f) Phosphate: Determination of inorganic phosphate involves the measurement of the concentration of orthophosphate ions by the formation of a reduced phosphomolybdenum blue complex in an acid solution containing molybdic acid, ascorbic acid and trivalent antimony. The most popular of the methods relying on this reaction, which was developed by Murphy and Riley (1962) is that given by Strickland and Parsons (1972). A variation of this method described by Grasshoff et al. (1983) is adopted in the present work. Instead of single solution reagent as in the Murphy and Riley procedure, two stable reagent solutions are used here. 0.5 ml of the mixed reagent containing molybdic acid and antimony tartrate followed by 0.5 ml of ascorbic acid reagent were added to 25 ml aliquots of the samples. The absorbance was measured in 5cm cuvettes at 882 nm within 30 minutes to reduce any possible interference from arsenate. Turbidity corrections were made wherever found necessary.

2.4.3. Interstitial Water

Interstitial water was extracted from wet sediment samples using the Reeburg's squeezer (Reeburg, 1967). The
Fig. 2.4. Calibration curve for total N

Table 2.4.1. Percentage recovery of total-N from glycine standards using the oxidation procedure.

<table>
<thead>
<tr>
<th>Standards used (ugat/l N)</th>
<th>Absorbance</th>
<th>Concentration estimated (ugat/l)</th>
<th>% recovery of total-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>0.210</td>
<td>4.72</td>
<td>94.4</td>
</tr>
<tr>
<td>10.0</td>
<td>0.438</td>
<td>9.90</td>
<td>99.0</td>
</tr>
<tr>
<td>20.0</td>
<td>0.871</td>
<td>19.57</td>
<td>97.8</td>
</tr>
<tr>
<td>30.0</td>
<td>1.280</td>
<td>28.80</td>
<td>96.0</td>
</tr>
<tr>
<td>40.0</td>
<td>1.602</td>
<td>36.00</td>
<td>90.0</td>
</tr>
<tr>
<td>50.0</td>
<td>1.980</td>
<td>44.55</td>
<td>89.1</td>
</tr>
</tbody>
</table>
pore water was carefully collected in specimen tubes and were diluted with distilled water as the quantity obtained were insufficient for various analyses. Ammonia, nitrite, nitrate and inorganic phosphate were estimated for a selected set of samples using the standard procedures as discussed earlier.

2.4.4. Sediment samples

Eh of the sediment samples were determined using a platinum electrode attached to a portable pH meter (PHILIPS, Model pp 9046) after proper calibration.

The sediment samples were dried in a hot air oven around 70°C in glass petri dishes. The dried samples were homogenized and a portion of it was ground to a fine powder in a porcelain mortar. Another portion of the sample was used for grain size determination. Percentage of sand, silt and clay portions was determined by sieving through a net of 64 μ mesh size and pipette analysis as described by Krumbein and Pettijohn (1938).

The powdered samples were analysed for total nitrogen and phosphorus contents. Total nitrogen in the sediment samples were determined by the semi-micro Kjeldahl method (Bremner, 1965). For the determination of total phosphorus, the sediment samples were digested according to Rochford (1951) and the orthophosphate estimated as described earlier (Section 2.4.2.(f)).
2.5. Data Presentation

The data obtained from the field observations and laboratory studies were processed and presented in this thesis under various sections. The methods employed for the presentation of these results are summarised here.

2.5.1. General distribution

The spatial distribution of all the parameters studied are represented by contour lines (vertical profiles) for each month of observation. The contour lines are based on the tidally averaged surface, mid-depth and bottom values of the respective parameter in the water column. Average values of two stations were taken to represent a particular cross-section.

Seasonal changes of salinity and nutrients are represented by integrated mean values in which each value represent 42 data points, i.e., 7 observations at 3 depths in each of the two stations in a cross-section.

The period of study is divided into three seasons: postmonsoon (October to January), premonsoon (February to May) and monsoon (June to September). Tidal variations and inter-relationships of various parameters were analysed, taking a representative month for each season, viz., December for postmonsoon, March for premonsoon and July for monsoon. The same method was followed for describing the distribution of urea-N and nitrogen and phosphorus distribution in
2.5.2. Inter-relationship between various parameters

Inter-relationship between various parameters at all depths, stations and seasons during a tidal cycle were studied using statistical methods. Following analyses were carried out on non transformed data:

i) Karl Pearson's coefficient of correlation between the parameters Ammonia-N, Nitrate-N, Organic-N, Inorganic phosphate, Organic-P and Salinity, and tested using 't' statistics,

\[ t = \frac{|r| \sqrt{n-2}}{\sqrt{1-r^2}} \]

where, \( r \) = correlation coefficient and \( n \) = number of observations.

ii) Three way analysis of variance to test the significance of difference between stations, seasons and depths and their interaction effects.

(Sokal and Rohlf, 1981).

2.5.3. Estimation of nutrient fluxes

Nutrient fluxes were calculated from velocity and nutrient concentration as given in Stern et al.(1986), with some modifications. Instead of the centre point observation in Stern et al.(1986; 1991), sampling was done at two stations in a cross-section and at three depths (surface, mid-depth and bottom) at each station in the present study.
The seaward and landward vectors of riverflow at each sampling depth was multiplied by the respective nutrient concentration and averaged for the water column to get the instantaneous flux. The net fluxes are the algebraic sums of the instantaneous fluxes over the tidal cycle sampled divided by the number of observations in the tidal cycle. Net fluxes for all the stations and their cross-sectional averages for each of the four sections were calculated (using a FORTRAN computer program) and presented as flux per m$^2$ of cross-sectional area per second.

Material transport through a particular cross-section was obtained by multiplying the average of the net fluxes by the mean cross-sectional area. Changing cross-sectional area due to changing water level was also taken into account in the calculations. Fluxes of particulate and dissolved nutrients were not measured separately, so the fluxes discussed here will represent the sums of particulate and dissolved fractions. The positive sign indicates transport towards the sea and the negative sign transport towards the river.