# Some Aspects on the Interrelationships between Nutrients and Plankton in the Estuarine and Nearshore Regions of Goa

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by

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# Contents

**Certificate**

**Declaration**

**Acknowledgements**

**Page No.**

## Chapter 1. Introduction

## Chapter 2. Study Area

## Chapter 3. Methodology

## Chapter 4. Estuarine Environment

## Chapter 5. Nutrients and plankton

# CERTIFICATE

This is to certify that this thesis **“Some Aspects on the Interrelationships between Nutrients and Plankton in the Estuarine and Nearshore Regions of Goa”** is an authentic record of the research work carried out by Shri. M. D. Rajagopal under my supervision at the National Institute of Oceanography, Goa, for the award of the Ph. D. Degree of the Cochin University of Science and Technology and that no part of it has been presented earlier for any Degree in any University

Dona Paula, Goa
2 MAY, 1997

DR. R. SEN GUPTA
RESEARCH GUIDE

# Chapter 1.

# Introduction

# 1.0 Introduction

Estuaries are unique ecosystems because of their continually changing environmental conditions. They form the transition area between the more stable marine and limnetic regions and exhibit wide ranges in hydrographical conditions (Kinne, 1967). There are a variety of definitions for estuaries that have been used in the literature. At the first International Conference on Estuaries held in Georgia in 1964, a confusing array of definitions were proposed and those are to be found in the proceedings of the conference edited by Lauff (1968) under the title "Estuaries".

To most people, estuary is a place where the rivers meet the sea and come under the influence of the tides forming a transition zone between freshwater and sea water. However, many other types of coastal water bodies are estuarine in character and a broad concept is generally adopted by workers on estuarine problems. There is a wide agreement that variable salinity is an essential feature of all estuarine systems and the definition proposed by Pritchard (1967) that "*an estuary is a semi-enclosed coastal body of water which has a free connection with the sea and within which sea water is measurably diluted with freshwater due to land drainage*", has generally been accepted.

There are three definitive characteristics which together distinguish the estuary from all other bodies of water. The first two are geomorphic: the body of water must be semi- enclosed and coastal and with a free connection to the open sea; the third is chemical: there must be a salinity gradient caused by the dilution of sea water with freshwater from upland drainage.

Thus estuaries are complex systems which receive chemical inputs from a variety of different sources. River run off contribute dissolved species derived from chemical weathering of rocks in the water sheds, suspended materials from mechanical weathering of terrigeneous matter and dissolved and particulate material of biogenic origin. The influx of sea water provides a strong electrolyte solution of nearly constant relative composition with respect to major ions. The composition of the river waters that mix with sea water in estuaries varies with the rate of freshwater discharge from the drainage basin and with the geological/geochemical character of each drainage basin. Freshwater and seawater composition of the micronutrients show extreme variations (over several orders of magnitude). In addition, estuarine systems can show strong flow- related (frequently seasonal) variations. As the nutrients pass through the estuary, they undergo various bio-geochemical transformations which affect their distribution in the estuary. In the absence of any bio-geochemical process occurring within an estuary or export to the atmosphere, the composition of a particular element within the estuary will be a linear function of its concentration in the river and the ocean.

If we define the geomorphic characteristics of an estuarine basin and then examine the variation of salinity within the basin as a function of freshwater discharge and tidal velocity, a scheme for classifying estuaries emerges. The classification scheme, first developed by Pritchard (1955), is based on advection - diffusion equation for salt. This salt balance equation states that the time rate of change observed in the salinity at a fixed point in the estuary is caused by two different physical processes, diffusion and advection. Diffusion processes are defined as a flux of salt, advective processes as a flux of salt and a flux of water. Both advective and diffusive processes may occur along the longitudinal, lateral and vertical axis of the estuary. In particular estuaries, under defined freshwater discharge, tidal velocity and wind conditions, these terms may be of the same order of magnitude.

## 1.1 Estuarine studies - Indian scenario

An examination of the literature indicate that estuarine research in Indian ocean regions are mainly focused to India, Australia and South Africa. Notable among the Indian estuaries on which systematic studies have been carried out include Vellar and Ganga estuaries in the East coast, Cochin backwaters and Mandovi - Zuari estuaries on the West coast.

A number of multidisciplinary studies have been carried out on the above estuaries. The physico-chemical and hydrobiological studies of Vellar estuary carried out by Seshadri (1955), Balasubramanyam (1960, 1961), Krishnamurthy (1964, 1971), Ramamurthy (1954), Dyer and Ramamurthy (1969) Venugopalan (1971), Burton et al (1970), Burton (1970), Rajendran (1974), Murty and Muni (1987), Shanmukhappa (1987), Perumal and Subramanyam (1989), Dawabata et al (1993) etc. reveal interesting information on this estuarine system.

Studies on the nutrient distribution in Cochin backwaters have been carried out by Ramamritham and Jayaraman (1963) Qasim and Reddy (1967), Qasim and Gopinathan (1969), Rajagopal (1974), Lakshmanan et al (1987), Qasim et al (1969), Sankaranarayanan et al (1984), Sarladevi et al (1991) etc. Seasonal variability of nutrients and phytoplankton pigments have been studied by Nair et al (1994), Paul and Selvaraj (1993) Mohandas and Ramamritham (1993), Nair et al (1990), Balchand and Nair (1994). Baby and Menon (1987) studied the metal concentration in organisms and Lakshmanaperumalasamy (1987) studied the nitrogen fixing bacteria and Jacob and Menon (1987) studied the effect of organophosphates on organisms. Quantitative ecology of phytoplankton was systematically studied by Gopinathan et al (1984). Distribution of heavy minerals and various enrichment factors have been studied by Mohan (1995). Nair and Azis (1987) studied the hydrobiology and organic pollution in Ashtamudi estuary. Azis and Nair (1986) carried out investigations on the ecology of coconut husk retting grounds in Kerala and Meenakumari and Nair (1993) studied the morphological characteristics of bacteria present in the primary film of Cochin backwaters.

Studies on Mandovi and Zuari estuaries started soon after the setting up of the National Institute of Oceanography at Dona Paula, Goa in 1969. Since then a number of studies have been carried out in this ecosystem on its physical, chemical, biological and geological aspects. The studies which are relevant to the present context include environmental and hydrographic characteristic of the ecosystem carried out by Dehadrai (1970, a & b), Sankaranarayanan and Jayaraman (1971),Cherian et al, (1974, 1975) Varma and Rao (1975), Rao et al (1976), De Sousa et al (1981), De Sousa and Sen Gupta (1986, 1988), Sen Gupta and Naik (1981), Qasim and Sen Gupta (1981) and Rajagopal et al (1981). Determination of heavy metal concentration of the estuarine complex was studied by Zingde et al (1976) George et al (1984), George (1993) and the behavior of some of the major elements was carried out by Shirodkar and Sen Gupta (1985) and Shirodkar and Kamat Dalal (1988). Upadhyay and Sen Gupta (1995) studied the behaviour of aluminium in waters of the Mandovi estuary while Alagarsamy (1991) estimated the organic carbon in the estuarine sediments. Enumeration of the sulphate-reducing bacteria was carried out by Lokabharathi and Chandramohan (1991). Phosphorus retention capacity of the estuarine sediments was studied by Rajagopal

(1984) and Phosphorus availability and Phosphates activity in the sediments of Mandovi estuary was measured by D'silva and Bhosle (1991). The flow characteristics and current studies were carried out by Das et al (1972) Murty and Das (1972), Antony et al (1974), and Murty et al (1976). Recently, Shetye et al (1995) studied the propagation of the tides in the Mandovi-Zuari estuarine network. Studies on the shoreline stability of the Mandovi estuary was carried out by Nayak and Chandramohan (1989).

Studies carried out on biological characteristics outnumber all other disciplines. Phytoplankton studies by Dehadrai and Bhargava (1972), Bhargava (1973), Bhargava and Dwivedi (1974, 1976), Bhattathiri et al (1976), Devassy and Bhargava (1978), Rajagopal (1981), Devassy and Goes (1988, 1989), Zooplankton studies by George and Goswami (1977), Goswami (1982) and Goswami and Devassy (1991), and benthic studies carried out by Parulekar and Dwivedi (1973, 1974) Parulekar et al (1973), Dwivedi et al (1975) Parulekar et al (1975), Parulekar et al (1978) and Ansari and Parulekar (1993) are some of the studies relevant to the present context.

The studies listed above are short-term and restricted to only tidal regions and very few attempts have been made so far to study the estuaries covering the whole salinity range, right from freshwater-end to the salt water (sea) - end. Since the characteristics of this estuarine system is influenced by monsoon rains and tidal currents, it would be very interesting to study the behaviour of chemical constituents through all the seasons and covering the whole range of salinity (0 - 35 PSU). Such studies would help to set background levels for the chemical constituents in different seasons which in turn will help in studies to predict the behaviour and fate of various constituents (both conservative and non conservative) which may eventually find their way into the ecosystem. De Sousa (1983) carried out a comprehensive study of the major and minor ions in relation to their spatial and temporal distribution and the supply and removal mechanisms of some of the minor ions and their fate during estuarine mixing. Similar study on the behaviour of aluminium in the estuarine region was carried out by Upadhyay (1993).

Estuaries receive continuous inputs of nutrients from their freshwater sources, but the fate of these inputs is poorly known. As these nutrients pass through the estuary they undergo various biogeochemical transformations which affect their distribution in the estuary. Assimilation of nutrient ions by phytoplankton, incorporation of nutrient ions onto sediment particles and suspended matter, sorption and desorption processes depending on the estuarine conditions are some of the processes determining the level of nutrients in the estuarine environment.

Since the sediments are the major nutrient pool within the estuary, we need to know more of the processes within the sediments which affect the storage, release and transformation of materials within the sediments. The processes which are taking place in the sediments combined with physical processes are the major factors responsible for the concentrations of the available forms of nutrients for the phytoplankton in the water column.

## 1.2 Work Plan

Until recently there has been very few studies on the distribution of nitrogen and phosphorus in the estuarine sediments. The nitrogenous part of the organic matter deposited in the estuarine environments was found to be partly regenerated as ammonium under reducing conditions and subsequently become oxidised to nitrate in sediment. No information is available on the distribution of various inorganic nitrogen compounds in sediments of this estuarine network. This study presents an account of the exchangeable and non-exchangeable (fixed) ammonium in the sediments in relation with various physico-chemical conditions to describe the mobility of the nitrogen compounds. Similarly, a comprehensive description of the fractionation of the phosphorus compounds in the estuarine sediments are also presented. The above studies explain the transformation processes of this element in the estuarine regions in relation to phytoplankton production. Biological productivity of the estuary was studied in relation to carbon assimilation and chlorophyll concentration. Besides the dominant phytoplankton groups present in the estuaries at different seasons were also identified.

In order to examine the removal of N and P relative to the accumulation of phytoplankton, the nonconservative changes in the concentration of chlorophyll, nitrogen and phosphorus have been determined. Absolute changes were then used to calculate the stoichiometric ratios of concentration changes and compared the findings of this study with similar studies in other regions to examine the potential relationships between nutrient distributions and the phytoplankton community. The ultimate objective of the study is to assess the health of the estuary in the light of the above information.

# Chapter 2.

## Study Area

**Contents** **Page No.**

# 2.0 Study Area

Goa has a coastal stretch of about 100 km and lies between $14^0$ 54'N and $15^0$ 48'N Latitude and between $72^0$ 41'E and $74^0$ 20'E Longitude (Fig. 2.1). Nine rivers rise in the western Ghats and flow towards Arabian Sea through Goa. From north to south these are Tiracol, Chapora, Mandovi, Zuari, Sal, Saleri, Talpona, Loliem and Galgibaga. Of these, the river Mandovi and Zuari are the major and the most important for the economy of the state as they flow through the mining area and grass lands opening up in the Arabian Sea close to Mormugao harbour. These two river basins together cover about 69% of the total geographical area of Goa.

The Mandovi - Zuari estuarine system is located along Latitude $15^0$ 25' to $15^0$ 31'N and Longitude $73^0$ 45' to $73^0$ 59' E. These could geologically be classified as drowned river valley estuaries formed by the Holocene rise in the sea level. Estuaries move in time and space in response to changes in sea level and changes in the rate of sedimentation. Thus a particular estuary, as defined by its location is ephemeral. General characteristics of the drowned river valley estuaries are given in Table 2.1

## 2.1 Mandovi and Zuari estuarine network

These two rivers constitute one of the finest network of water ways and provides cheap and efficient means of transportation. It is through these water ways that over 90% of the territory's mineral ore, chiefly iron and ferromanganese ore is transported to Mormugao harbour by barges. These rivers also provide good fishing ground throughout the year and particularly during the monsoon when the fishing activities in the open sea are suspended due to rough weather.

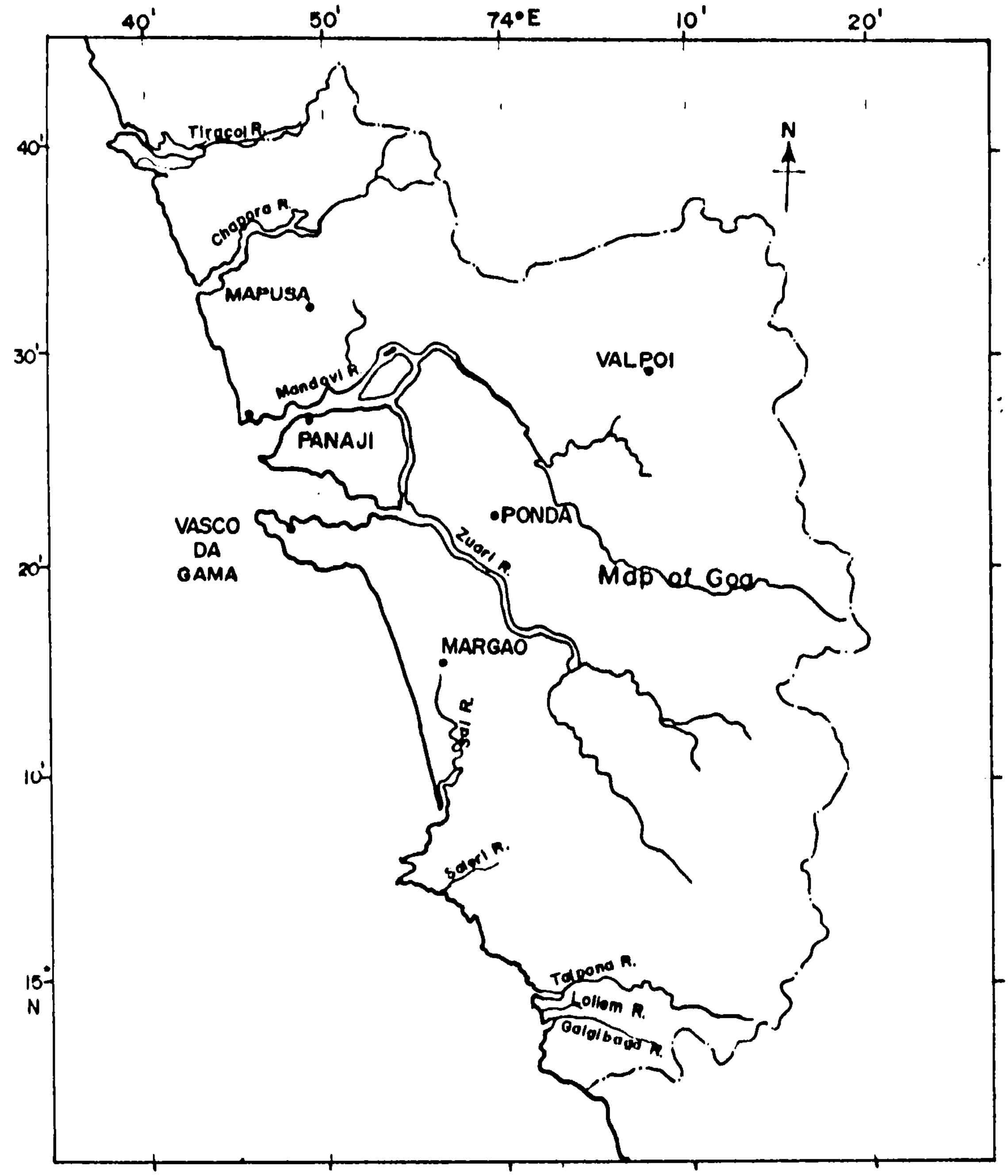


Fig. 2.1 Map showing the rivers in Goa

**Table 2.1 : General characteristics of "Drowned River Valley" estuaries**

| Estuarine type* | Dominant Mixing force | Mixing Energy | Width/depth ratio | Salinity gradient | Mixing $ Index (MI) | Turbidity | Bottom Stability | Biological Productivity |
|---|---|---|---|---|---|---|---|---|
| Type A<br>(Salt wedge) | River flow | Low | Low | Longitudinal, Vertical | $\geq 1$ | Very high | Poor | Low |
| Type B<br>(Partially Mixed) | River flow Tide | Moderate | Moderate | Longitudinal, vertical<br>Lateral | $\langle \frac{1}{10}$ | Moderate | good | Very High |
| Type C<br>(Vertically homogenous) | Tide, wind | High | High | Longitudinal, Lateral | $\langle \frac{1}{20}$ | High | Fair | High |
| Type D<br>(Sectionally homogenous) | Tide, Wind | V.High | V. High | Longitudinal | ? | High | Poor | Moderate |

* Follows Pritchards (1955) advection - diffusion classification scheme.

$ Follows Schubels (1971) definition $M1 = \frac{\text{Vol of fresh water discharge on } 1/2 \text{ tidal period}}{\text{Vol. tidal prism}}$

These two rivers originates from the Sahyadri Hills of the western Ghats and after flowing through a stretch of about 70 km open into the Arabian Sea near the Tiswadi Island and separated by a promontory between them.

River Mandovi is about 3.2 km wide at its mouth while upstream it narrows down to about 0.25 kms. It is fed by monsoon precipitation ( ~ 3000 mm / annum) and from discharges from a catchment area of about 1150 $km^2$. Its basin covers an area of about 1530 $km^2$ and constitute 42 % of the total area of Goa. The flow during the non-monsoon months is governed by semidiurnal tides having a maximum range of about 2.3 m (Murty and Das, 1972). It has a large tributary system and along its course there are a number of islands, narrow bends and shallow depths. River Mandovi carries drainage from 435 $km^2$ of forest land. There are a total of 144 industries (small and medium) located in its basin which discharge 16 x $10^6$ $m^3$ effluents per year to this river and its tributaries. About 2/3 of the mining activities in Goa are located along the Mandovi basin. There are about 20 large mines which generate approximately 7000 - 8000 tonnes of rejects per day per mine and a substantial portion of it is dumped into the river. About 36% of the total area of Goa is used for agriculture, 25% is under forest cover and the remaining is mining and residential area. A large quantity of the synthetic and organic fertilizers used in the agricultural activities eventually find their way into the rivers which are of great significance in determining the water and sediment quality of the rivers.

River Zuari originates from the Dighi Ghat on the Sahyadri hills and meets the Arabian Sea near Mormugao harbour. It is 5.5 km wide at the mouth while upstream it narrows down to less than 0.5 km. it is also fed by the monsoon precipitation and receives discharge from a catchment area of about 550 $km^2$. It's basin covers an area of about 975 $km^2$ and constitutes about 27 % of the total area of Goa (Anonymous, 1979). Like Mandovi it's flow during non-monsoon months is regulated by semidiurnal tides having a maximum range of 2.3 m. It carries drainage from 309 $km^2$ of forest land. There are a total of 141 industries located in it's basin which discharges $8.6 \times 10^6$ $m^3$ of effluents per year into the river and its tributaries. There are 10 large mines in its basin, which generate 1500 - 5000 tonnes of mining rejects per day per mine, of which a substantial amount is expected to reach this river.

The two rivers are connected by a man made canal known as Cumbarjua Canal of about 17 km length and 0.2 to 0.5 km in width and about 14 and 11 km away respectively from the mouths of Mandovi and Zuari. The canal, though not of natural origin, is an interesting example of two estuaries interacting dynamically with one another through a common channel. During the monsoon months when all other traffic out of the river Mandovi gets suspended due to the formation of Sandbar/Shoals popularly known as Aguada bar and Reis Magos bar at the entrance of the Aguada Bay all the barges and boat traffic to Mormugao harbour is diverted via Cumbarjua canal through Zuari river. Therefore, the Mandovi - Zuari estuarine network comprises the two rivers Zuari and Mandovi and the Cumbarjua canal which are influenced by the sea water inflow upto a considerable distance inland and receive a large volume of freshwater during the south west monsoon.

The flow during monsoon and non monsoon months show marked changes. Analysis indicate that the speed of propagation of both diurnal and semidiurnal tides through the main channels of this estuarine network was approximately 6 m/s and amplitude of these tides in the channel remain unchanged over a distance of about 40 km from the mouth and then decayed rapidly upstream over the next 10 km. The undamped propagation was a consequence of the balance between geometric amplification, due to decrease in the cross sectional area in the upstream direction and frictional dissipation and the rapid decay near the upstream end of the channel resulted primarily from freshwater influx (Shetye et al 1995). Both Mandovi and Zuari are coastal plain estuaries of the drowned river valley type. They exhibit semidiurnal tide and are influenced by sea water inflow round the year.

## 2.2 Flow pattern : Mandovi

The formation of the bars / shoals during SW monsoon near the entrance of Mandovi was known for over centuries. Comparing the present conditions prevailing in the bay with those described by Ballard (1927), it appears that those bars have not undergone much change over centuries. This would suggest that some kind of balance exists between the supply and removal of sediment, which maintain the bars, controlled by the interaction of tides, waves, river runoff etc; which determine the circulation pattern in the bay. During premonsoon season when the freshwater discharge is minimum the currents are mainly dominated by the flood and ebb tides. Typical flood and ebb velocities measured upstream of the bar by Murty and Das (1972) are of the order of 160 - 108 cm/s at the surface and 128 - 98 cm/s near the bottom. The formation of a cyclonic gyre in the Caranzalem Bay on the southern bank of the estuary and an ill developed anticyclonic flow in the Sinquerim Bay were noticed by Murty et al (1976). The surface currents in January during ebb ranged from 10 to 74 cm/s (Anonymous 1979), while the bottom currents varied between 8 and 48 cm/s. The corresponding ranges during flood were 11 to 72 cm/s. at the surface and 7 to 37 cm/s at the bottom. During monsoon the speed of the surface currents ranged from 30 to 73 cm/s during ebb and from 30 to 80 cm/s during flood. In post-monsoon the surface currents varied between 11 and 122 cm/s during ebb and between 45 and 105 cm/s during flood. During monsoon the formation of salt wedge extending from the mouth up to about 10 km upstream has been reported by Qasim and Sen Gupta (1981) in the Mandovi estuary.

## 2.3 Flow pattern - Zuari

There is no bar / shoal formation at the mouth of this estuary during monsoon and compared to Mandovi, Zuari receives considerably less freshwater discharge since not many tributaries are opening to Zuari compared to Mandovi. The currents in this estuary also is mainly dominated by the flood and the ebb tides during non-monsoon months while during monsoon the resultant currents are caused by the interaction between the tidal currents and the heavy river discharge. An examination of the data (Anonymous 1979) indicated that during January the average speed of the currents at the surface was 13 cm/s at the mouth of the estuary while at the bottom it ranged between 24 and 69 cm/s. During flood the surface and bottom currents did not show much variations. During monsoon the currents were stronger during ebb compared to those during flood and the surface currents were stronger than the bottom currents during monsoon. The formation of a salt wedge extending up to a distance of 12 km from mouth upstream has been reported by Qasim and Sen Gupta (1981) in Zuari estuary.

## 2.4 River Discharge

Both Mandovi and Zuari rivers are fed by monsoon precipitation and from discharges from a catchment area of about 1150 and 550 $km^2$ respectively. Mandovi basin covers an area 1530 $km^2$ and constitutes 42% of the land area of the territory whereas, Zuari basin covers an area of 973 $km^2$ and constitutes 27% for the total land area of the territory. The average annual discharge has been calculated to be about 16 and 9 $km^3$ respectively for Mandovi and Zuari (Anonymous 1979). It would be pertinent to mention here that the total rainfall in Goa varied from year to year. The bulk of the rainfall in Goa is due to SW monsoon and about 90 % of the total annual rainfall occur during June, July and August. Data indicated that the total annual rainfall in 1981 was 3228 mm compared to 2643 mm in 1980. During 1991 the total annual rainfall was 3081 mm. The northeast monsoon also is felt in Goa though weak and showers are invariably accompanied with lightning and thunders. It may also be noted that the discharge data may be an approximation therefore, use of such information to deduce any particular process should be done with reservation.

# Chapter 3.

## Methodology

# 3.0 Methodology

## 3.1 Sampling :

In order to study the seasonal distribution of various biological and chemical parameters in the estuarine waters, monthly observations have been carried out and samples from Mandovi estuary were collected. Therefore, in the following chapters, characteristics of the Mandovi estuary is discussed in detail and those of the Zuari estuary is compared wherever possible.

Altogether 6 stations (M1 to M6) have been sampled in the area covering sea water dominated (M1 & M2), estuarine (M3 & M4) and freshwater dominated (M5 &M6) regions (Fig. 3.1). Reference stations both at the freshwater end (M7) - free from any effect of salt water, and at sea water end (M0) - free from the influence of freshwater throughout the seasons were also sampled seasonally (pre-monsoon, monsoon and post-monsoon).

Throughout this study the following considerations have been made. The Mandovi river estuary has been divided into three segments (lower, middle and upper estuary) that can be differentiated largely by the salinity distributions in the estuary. The lower estuary extends near to Old Goa (~20 Km) and is dominated by sea water, having surface salinities similar to those found in the adjoining coastal waters. The middle estuary, where most of the freshwater entering the system mixes with the salt water extends from approximately at Old Goa to Amona (~20 Km). The upper estuary, which extends from Amona to Usgao is also tide influenced but with high percentage of freshwater. The boundaries to these segments are transitional and shift with seasonal weather and tidal conditions.

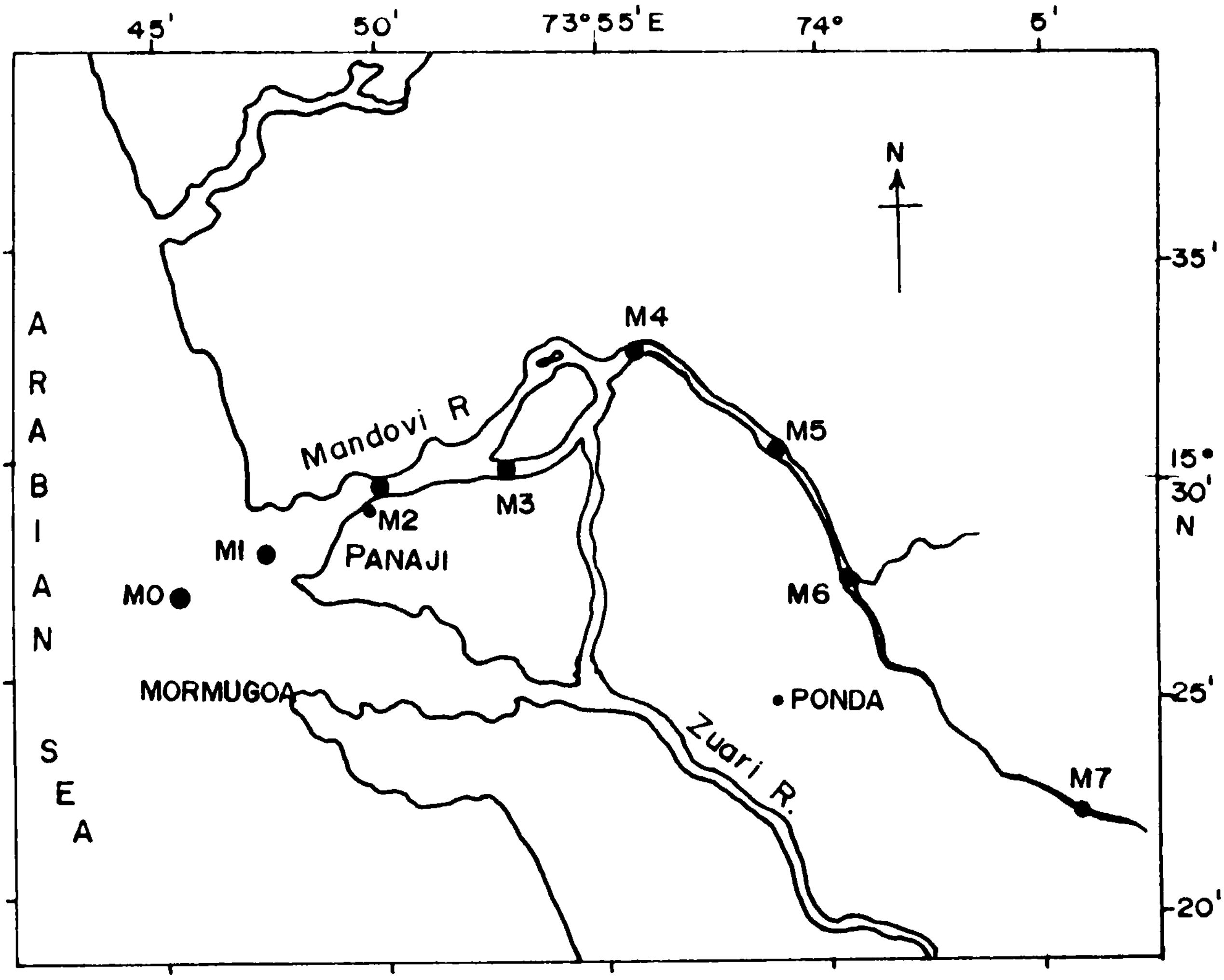


Fig. 3.1 Map showing station locations in Mandovi Estuary

However, sampling stations are at fixed locations irrespective of the above. For convenience the following terminologies with reservation have been used. Lower segment covering station M1 & M2 which is called marine dominated area (**MDA**), middle segment covering M3 & M4 are estuarine area (**EA**) and upper segment covering M5 & M6 are freshwater dominated area (**FDA**).

Samples of water, sediment and phytoplankton were collected for the estimation of various parameters. Details of sampling and analytical methodologies followed are given below.

Observations were carried out at these stations once every month from November 1991 to October 1992. During these observations, water samples were collected using Niskin samplers from near-surface and near - bottom. From those water samples, sub-samples were collected for the estimations of dissolved oxygen (DO), pH, salinity, turbidity, suspended solids, nitrite - N, nitrate - N, ammonia - N, phosphate - P, total nitrogen and total phosphorus. Except for dissolved oxygen and pH the samples for other parameters were pooled together at each station and integrated for different tides. This procedure was adopted to eliminate tidal effect and to have only the residual tidal effect in samples. The samples for DO and pH were analysed separately and averaged.

## 3.2 Sample processing

Dissolved oxygen was fixed immediately after collection and pH was measured on board. Estimation of other parameters were carried out either on board the vessel itself or frozen till analyses in the shore laboratory with- in 24 hours of collection.

## 3.3 Analytical methodology

### 3.3.1 Water samples

Standard analytical procedures were followed for the determination of various chemical parameters. Chlorinity was measured by titration with silver nitrate using Potassium chromate as indicator as per the Mohr-Knudsen titration method and the salinity was computed from chlorinity using Knudsen hydrographic tables.

The pH of the water samples were measured using digital pH meter (Control Dynamics model APX 175/E/C) calibrated with standard pH buffers. Dissolved oxygen (DO) was analysed following the modified Winkler method (Carritt and Carpenter 1966) by fixing a measured volume of sample with Manganous chloride and alkaline potassium iodide and later with standard iodometric titration.

Turbidity was measured by the Nephelometric method which is based on a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of the light scattered by a standard reference suspension under the same conditions. The higher the intensity of the scattered light the higher the turbidity. Standard turbidity suspension for calibration was prepared using hydrazine sulphate and methylene tetramine and the analysis was carried out using a Turbidity meter (HF Instruments, Model No. DRT 100D).

Suspended solids were estimated by filtering a measured volume of waters through pre-weighed 0.45 μ membrane filters and computed from the final weight on dryness on limit basis.

### 3.3.1.1 Nitrogen compounds

The usual procedure to determine nitrate ($NO_3$) in sea water is first to reduce nitrate ($NO_3$) to nitrite ($NO_2$) and then estimate the nitrite colorimetrically by diazotisation and coupling reactions (Bendschneider and Robinson, 1952). In this method the nitrite in the water samples was allowed to react with sulphnilamide (dizotization) and thereafter with N(1-Naphtyl) - ethylene diamine dihydrochloride. The absorbance of the resultant azo dye was measured at 543 nm in a spectophotometer.

The procedure employed for the determination of nitrate in the present study was developed by Morris and Riley (1963) with modification by Grasshoff (1976). Nitrate in the samples was first reduced to nitrite by heterogenous reduction by passing the buffered samples through an amalgamated cadmium column and the resultant nitrite was analysed as above. The measured absorbance was due to the initial nitrite in the sample and $NO_2$ obtained after the reduction of $NO_3$. Necessary correction was therefore made for any nitrite initially present in the sample.

Ammonia nitrogen in sea water samples was determined using the indophenol blue method of Koroleff (1973). 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 form indophenol blue. The formation of monochloramine require a pH between 8 and 11.3. At higher pH ammonia is incompletely oxidised to nitrite. Both calcium and magnesium ions in sea water precipitates as hydroxide and carbonate at pH higher than 9.6. However, their percipitation can be prevented by complexing them with citrate buffer. Care should be taken for the analysis of ammonia nitrogen and the distilled water should be ammonia-free and fresh to avoid any contamination as ammonia is highly soluble in water.

### 3.3.1.2 **Phosphorus compounds**

Dissolved reactive phosphate was measured by the method of Murphy and Riley (1962) in which the samples were made to react with acidified molybdate reagent and reduced using ascorbic acid. The absorbance of the resultant blue complex was measured spectrophotometrically at 880nm. The interference caused by the formation of silico-molybdate complex is suppressed by carrying out the reaction at pH less than 1 using 9N $H_2SO_4$

Total nitrogen and total phosphorus estimations in the samples were carried out by the persulphate oxidation technique in which the nitrogen compounds were converted to nitrates by alkaline persulphate at $115^0C$ (in an autoclave under pressure) and the resultant $NO_3$ was reduced to $NO_2$ by passing through the cadmium amalgam column and finally the $NO_2$ was estimated by diazotisation and coupling with aromatic amines (Koroleff, 1973) Organic phosphorus was converted into inorganic form and estimated using standard method explained above.

### 3.3.1.3 **Phytoplankton, chlorophyll and productivity**

For the estimation of phytoplankton 500 ml of water samples collected from the near-surface and near-bottom were fixed with Lugol's iodine and preserved with buffered formalin. Thereafter, the samples were stored at cool and dark place. After allowing it to settle for a week, the supernatant water was decanted and the cells of phytoplankton were enumerated using Olympus $BH_2$ microscope. The phytoplankton was identified using standard manual up to genera and species level as far as possible. The total number of cells per litre is one of the measures of biomass of phytoplankton in the study area.

The biomass of phytoplankton was also measured by analysing pigments (Chlorophyll a) at surface. Column chlorophyll a was also computed for the study area. Water (500 ml) was filtered through $MgCO_3$ coated GF/F filter paper and Chlorophyll a was extracted in 90% acetone at $4^0$C, after 24 hrs in the dark. The supernatant obtained after centrifugation was measured for fluorescence on Turner fluorometer (sensitivity 0.005 mg) which was calibrated using standard chlorophyll a (Sigma). The measurements were done before and after acidification using one drop of 50% HCl. The chlorophyll a contents were calculated using standard formula. Rates of photosynthesis by phytoplankton is measured by assaying the water samples incubated using $^{14}$C isotope (Sodium carbonate-bicarbonate mixture (5 μCi)) technique and the radio activity was counted using Packard LSS system. Besides this the data base on phytoplankton, chlorophyll and primary productivity for the estuarine region was scanned and used for various computation in the present study.

### 3.3.2 Sediment

Sediment samples were collected using a van Veen grab and the subsamples were removed without disturbing the sediment layers. Fractionation of various nitrogen and phosphorus compounds have been carried out using the sediment samples collected at freshwater dominated sites, estuarine sites and sea water dominated sites.

#### 3.3.2.1 Nitrogen compounds

A significant portion of the nitrogen input is retained in the estuarine sediments and the nitrogenous part of the organic matter deposited in the sediments was found to be partly regenerated as ammonia under reducing conditions which subsequently oxidised to $NO_3$ in sediments of positive Eh (Rittenberg et al, 1975).

Determination of exchangeable $NH_4^+$-N were carried out by the method of Bremner (1965) which involves removal of the ions with 2N KCl followed by steam distillation of the extract. It may be noted that part of the exchangeable ammonium is in soluble form in the sediment. These analysis were carried out on the freeze-dried sediment; exchangeable $NH_4^+$-N , $NO_3^-$-N and $NO_2^-$-N concentrations were found to change when stored wet, presumably due to microbial alteration of the sediment and changes in the equilibrium between free (soluble), exchangeable and non-exchangeable ions.

## 3.4 Pre treatment of sediment

### 3.4.1 Free (soluble) inorganic nitrogen

Pore water containing free inorganic nitrogen was removed from fresh sediment subsamples by centrifugal filtration. Usually a sufficient volume of Pore water (10 to 15 ml) was obtained from one 25g fresh weight subsample. However, if sediment was relatively compact, the filtrates from replicate subsamples were pooled. Filtrates were frozen immediately until analysis.

### 3.4.2 Exchangeable inorganic nitrogen

Other subsamples of fresh sediments were extracted with KCl to estimate total exchangeable inorganic nitrogen (Bremner; 1965, Harris et al 1977). This total exchangeable nitrogen includes both free inorganic nitrogen and inorganic nitrogen that is loosely bound on sediment surface.

For each determination 25g of fresh sediments were placed in a 250 ml polypropylene bottle with 150 ml of 2N KCl and shaken for two hour in a reciprocal shaker. These were centrifuged at 10,000 rpm for 20 min in a refrigerated centrifuge at $5^0$C. The supernatant 2N KCl was drawn off in a polyethylene syringe and were filtered through 0.45 μm pore size Millipore filter that had been flushed previously with de-ionised water to remove traces of nitrogen and phosphorus. Subsamples were filtered and frozen until analysis.

Methods of measuring non-exchangeable ammonium in sediments were evaluated by Mogilevkina (1969) who found method of Silva and Bremner (1965) which is used in this study to be the most satisfactory. It involves the removal of exchangeable $NH_4^+$ -N and Organic -N by alkaline hypobromite followed by treatment with 5N HF- 1N HCl to liberate non-exchangeable $NH_4^+$ -N. However, it is possible that ammonia or organic -N is still trapped in silicate minerals not decomposed by HF (Bremner 1965a). Complex ammonium phosphate minerals are not determined by this method, however, these may not be present in this estuarine sediments. Consistently higher fixed $NH_4^+$ -N values were obtained when freeze-dried sediment was used (Keenay et al 1970), therefore, non-exchangeable $NH_4^+$ -N determinations were made on fresh wet sediments.

**Organic N:** There are no reliable method of measuring total organic -N in sediments. It is estimated as the differences between the total -N and the sum of the exchangeable $NH_4^+$ -N, $NO_3^-$ -N, $NO_2^-$ -N, and the non-exchangeable $NH_4^+$ -N.

## 3.5 Phosphorus Compounds

Phosphorus occurs in sediments in inorganic and organic forms, the relative proportions of which vary with organic matter content but usually the organic forms predominate. The element tends to accumulate in the finer fractions of the sediment and thus increases as the clay content increases.

Three basic methods have been employed to bring the total phosphorus into solution: digestion with strong acids, fusion with alkalis and ignition followed by acid extraction. The acids recommended for digestion are perchloric or hydrofluoric and of the two, perchloric is to be preferred as silica is removed by filtration and methods exist for the determination of the resultant soluble phosphate in which perchloric acid does not interfere. Furthermore, the use of expensive platinum ware also could be avoided.

### 3.5.1 Inorganic phosphorus compounds

An approximation of the total inorganic phosphorus in sediments can be obtained by extraction with strong acid, for example 1 M $H_2SO_4$. Williams et al (1970) suggested that as the solubility of inorganic phosphorus compounds is largely dependent upon pH, the total amount can be brought into solution provided that the pH is made sufficiently low. At pH 1.0 all the inorganic phosphorus, Williams considered, will be mobilised, but not necessarily in solution as some re-sorption of phosphorus will occur.

### 3.5.2 Fractionation of inorganic phosphorus compounds

The individual forms of inorganic phosphorus in sediment are not, as yet, completely identified, Chang and Jackson (1957) postulated three divisions of soil inorganic phosphorus (i.) **Discrete phosphates** precipitated upon surfaces and which are the mostly readily available. These include calcium phosphate precipitated upon calcium carbonate, aluminium phosphate precipitated upon alumino-silicates and iron phosphate precipitated upon iron (III) oxide.

(ii.) **Discrete phosphates** particles which are slightly available and which include calcium phosphates such as apatite and dicalcium phosphate, aluminium phosphate such as variscite, iron phosphates such as strengite and aluminium iron phosphates such as barrandite.

(iii.) **Occluded phosphates** which are but little available and consists of calcium phosphate occluded in calcium carbonate, aluminium phosphate occluded in iron (III) oxides and reductant - soluble iron phosphate also occluded in iron (III) oxides

Two main methods of identifying the inorganic forms of phosphorus have been mainly used : chemical fractionation, depending upon the solubility of different forms in different solvents, and more indirect method based upon the concept of solubility products. If in a system we have a sparingly soluble solid-phase crystalline compound in equilibrium with its ions, the activities of those ions are controlled by the nature of the compound. For example if crystals of $CaHPO_4$ are in equilibrium with $Ca^{2+}$ and $H_2PO_4^{2-}$ ions in solution, then the product of the activities of those ions is constant and characteristic.

In the present method water-soluble, saloid-bound phosphates are first extracted with dilute ammonium chloride ($NH_4Cl$) solution and then the aluminium phosphate is removed with neutral ammonium fluoride ($NH_4F$) solution. Iron phosphate is extracted next with sodium hydroxide (NaOH) and finally, calcium phosphate is dissolved in dilute acid ($H_2SO_4$). The phosphate which are not extracted by these four reagents is completely dissolved by a citrate-dithionate-bicarbonate (CDB) treatment and was called 'reductant-soluble' iron phosphate. This reductant soluble phosphate is explained as being due to an iron oxide precipitate formed on the surface of iron and aluminium phosphate particles during weathering by hydrolysis of iron (III) salts. Some sediments rich in iron oxides contain significant amounts of iron and aluminium phosphate occluded and thus not removed by the dilhionate treatment; the occluded phosphate, however, can be extracted after the dilhionate treatment with fluoride or alkali.

The following inorganic phosphorus fractions have been determined in the estuarine sediments.

(I) **Saloid bound - P** : extracted with dilute $NH_4Cl$ solution

(II) **$NH_4F$-P** : 25 ml of 0.5 M $NH_4F$ adjusted to pH 8.2 (extraction time - 24h). Forms extracted include aluminium phosphate and exchangeable phosphate on clays.

(III) **NaOH-P** : 25ml of 0.1 N NaOH (extraction time 17h). Forms extracted include discrete iron phosphate minerals and some weakly sorbed phosphates.

(IV) **CDB - P** : 25 ml of warm ($60^0$C) citrate-dithionate bicarbonate solution for 15 min. Forms extracted include primarily phosphate sorbed by iron oxyhydroxides.

(V) **$H_2SO_4$ - P** : 25 ml of 0.5 N $H_2SO_4$ for 1h. Forms extracted include varieties of apatite (calcium phosphate).

(VI) **Res. P** : The residual phosphates extractable by digestion with a warmed mixture of $HNO_3$, $HClO_4$ and $H_2SO_4$. Residual organically bound phosphate and resistant or occluded mineral forms of phosphates are extracted.

### 3.5.3 Total Nitrogen and Phosphorus

Total nitrogen (TN) and total Phosphorus (TP) contents of sediments were determined by persulphate digestion method. These estimations include organic nitrogen plus ammonium (but not nitrite and nitrate) and organic phosphorus plus soluble reactive phosphate, but include an unknown, but probably small fraction of nitrogen and phosphorus fixed on clay lattices.

## 3.6 Precision and Reproducibility of Data.

In order to determine the precision of the analytical methods and reproducibility of data, replicate analysis were carried out of a number of subsamples from the same sample and the standard deviation and coefficient of variation were computed. Values were found within the accepted limits. However, periodic calibrations were carried out with reference standards and also for each set of reagents.

# Chapter 4.

# Estuarine Environment

**Contents** **Page No.**

# 4.0 Estuarine Environment

## 4.1 Freshwater inflow and salinity gradients

There is a wide agreement that variable salinity is an essential feature of all estuarine systems. The amount of inflow of freshwater and the rate of exchange with coastal waters regulate the salinity of an estuary, which is important. The freshwater usually enriches the estuary. This may include an organic and inorganic input of nutrients and the organic substance may have a qualitative influence on species composition as well as a generally enriching effect (Lauff 1967). Estuaries with a considerable depth of water and with vertical density gradients at their mouths commonly have a two layered transport system in which a freshened surface layer moving seaward is replaced by an inflow of more saline water at the bottom. If the water is sufficiently deep to develop a negative gradient in nutrients so that a nutrient-poor surface layer drains off and is replaced by inflowing bottom water, that is comparatively rich, the exchange pattern will enrich the estuary.

Seasonal variability of different environmental features in the estuarine system demands an understanding of the freshwater discharge into the system which is chiefly controlled by the spectacular regime of the rainfall during the monsoon, thus making the year divisible into three seasons (1) Pre-monsoon (February-May) (2) Monsoon (June-September) (3) Post-monsoon (October - January).

Seasonal variation in the salinity of the Mandovi estuarine system was very large. From December to May a part of the estuary become an extension of the sea with salinity reaching around 35 PSU. The monthly variation of salinity in the Mandovi at both surface and bottom is shown in Figure 4.1 to 4.3. As discussed earlier the entire study area has been divided into three regions : (a) sea water dominated (M1 and M2), estuarine (M3 and M4) and freshwater dominated (M5 and M6). Salinity variations at the sea water dominated region (M1 and M2) is shown in Fig 4.1. At the mouth of the estuary, the salinity variations were not that much pronounced compared with the other regions of the estuary. It varied between 24.22 and 35.22 PSU for surface waters. With the onset of monsoon in June the salinity of the entire estuarine system decreased sharply. During July and August beyond M3 upstream, only freshwater was observed. In general, the salinity decreased from the mouth towards upstream. The salinity at the surface was lower than that at the bottom in general. Only exception to this was noticed during December at the mouth of the Mandovi estuary (M1). From September onwards, however, the salinity showed sharp rise reaching maximum in premonsoon (May). Salinity in this area would have been affected by the river discharge during monsoon as could be evident from M2 where, the salinity variation was between 7.5 and 34.49 PSU. In both M1 and M2 bottom salinity was slightly higher than that of surface.

The Mandovi estuary has a lower average salinity than that of Zuari because the Mandovi river receives considerable amount of runoff through a large tributary system and along its course it has a number of islands, narrow bends and shallow mangrove swamps. From the predicted tides at Mormugao harbour, the tidal time lag in the Mandovi from M1 to M2 is approximately 75 min. Qasim and Sen Gupta (1981) observed that at any given time of the year, a large horizontal salinity gradient exists from the Zuari-end to the Mandovi-end of the estuarine system via the Cumbarjua canal. De Sousa (1983) observed a mixed condition throughout the estuary during premonsoon months and partially stratified condition during post monsoon. Stratification was observed in the Mondovi-Zuari river mouths during monsoon.

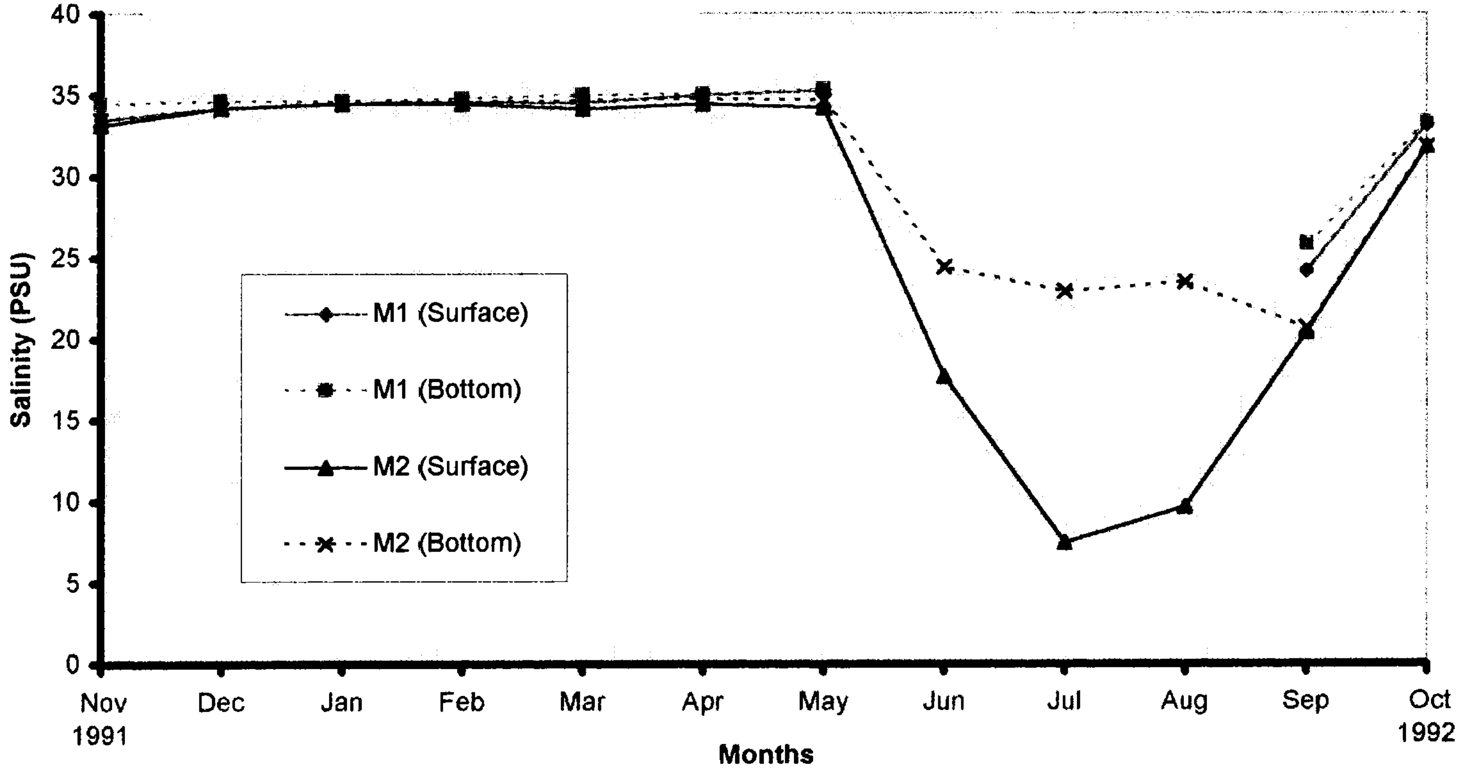


Fig. 4.1 Variations of Salinity at MDA (M1 & M2)

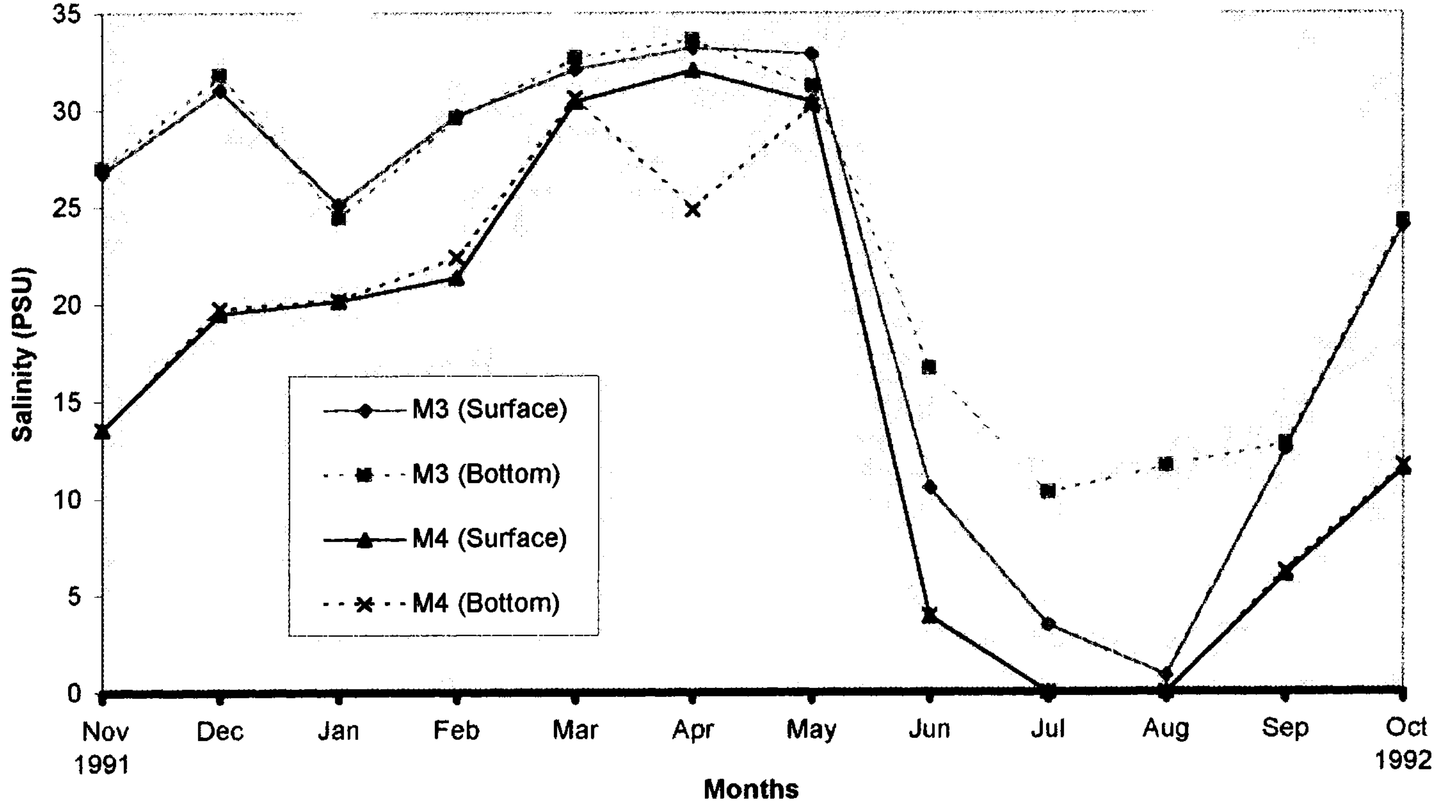


Fig. 4.2 Variations of Salinity at EA (M3 & M4)

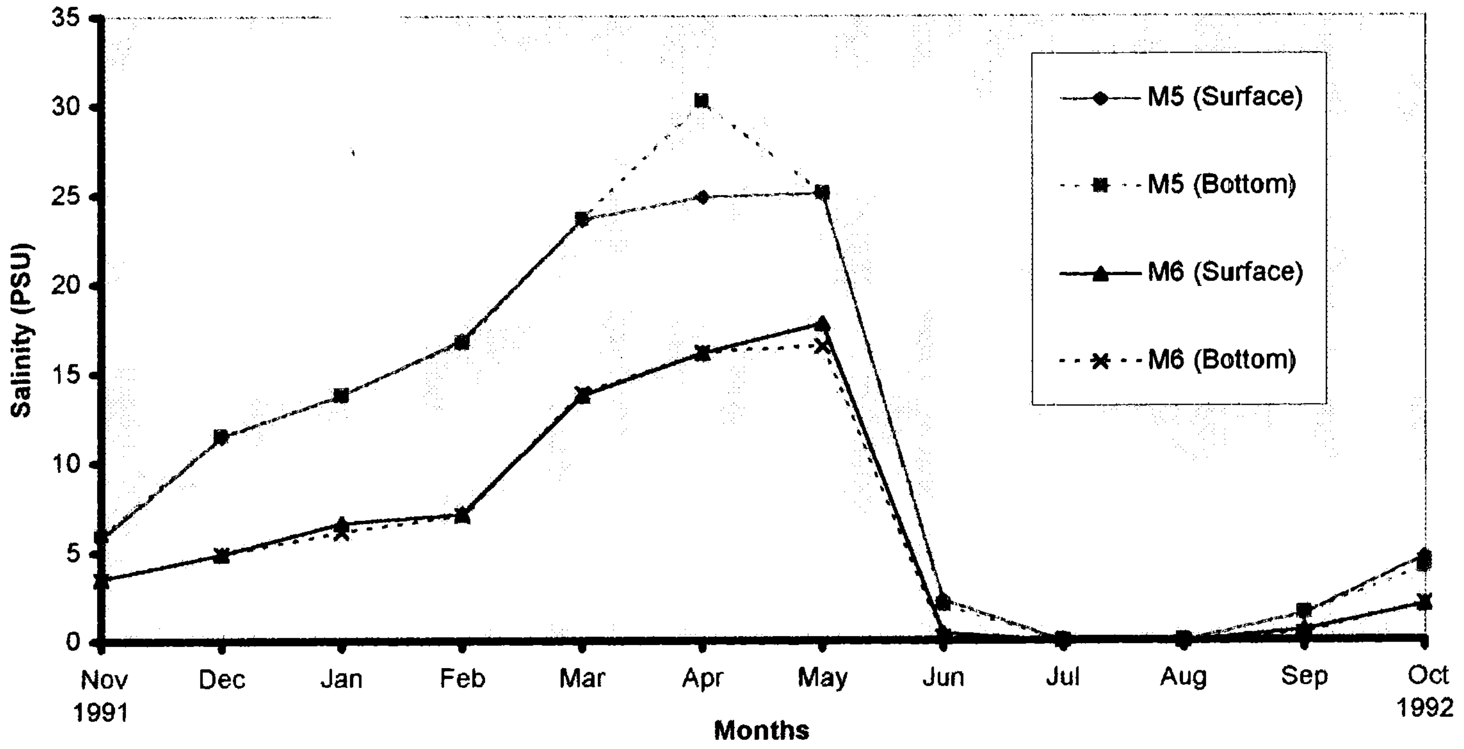


Fig. 4.3 Variations of Salinity at FDA (M5 & M6)

## 4.2 Stratification

Stratification of the Mandovi estuary, as deduced from the salinity data, indicate that the estuary behaves as per the seasons. The stations M1 to M2 near the mouth of the estuary showed mixed conditions during premonsoon months and partially stratified during post monsoon, while during monsoon the estuary showed stratification having double layer with wide salinity differences from surface to bottom. Station M1 could not be sampled due to the rough sea condition during June to August. At stations M2 and M3 the surface salinity during July was 17.72 and 10.59 PSU respectively. The respective bottom (~5m) salinity values were 24.42 and 16.71 PSU.

Measurements of the speed and direction of currents at several places in the estuarine system in different seasons (Murty et al 1976) showed that the maximum current speed during ebb and flood tides was in the middle region of the two estuaries. The average current speed was stronger during the flood tide in the premonsoon and post monsoon periods particularly everywhere in the estuarine system, whereas, during the monsoon months the currents become stronger during the ebb tides as the river runoff accelerates the flow (Varma and Rao 1975). The current velocity in both the rivers during the flood tide is maximum and the currents are directed upstream and largely towards the left side of the rivers looking downstream. The speed of currents varied from station to station and with the state of tides. During the ebb tide the currents are reversed. Thus, to an observer who is travelling seaward during the incoming tide, the seawater would appear to enter the two rivers along their left banks and with the outgoing tides it seems to flow into the sea along the right banks. The water in the estuaries remain well mixed when the freshwater runoff is small. However, during the monsoon, because of the formation of two salt wedges the rivers become stratified 2 - 3 m below the surface depending upon the depth in the estuary (Qasim and Sen Gupta, 1981). Shetye et al (1995) studied the tidal circulation in Mandovi and Zuari estuarine network also confirmed the above findings.

Apart from the distance upto which the salt - wedge formation in the two estuaries occurs (10 km in the Mandovi and 12 km in the Zuari ) during the peak monsoon period, the rest of the estuarine system remain filled with freshwater with practically no salt water incursion anywhere. Immediately after monsoon when the runoff remains still high, partial mixing of salt and freshwater occurs but some stratification continues to remain at a few places in the estuarine system (Murty and Das 1972). In the pre-monsoon season (February to May) there is no stratification anywhere and the water remains well mixed throughout the water column and the entire estuarine system has tidal influence with salt water incursion. Table 4.1: shows the trend of variations of salinity in Mandovi estuary during different seasons.

**Table 4.1 Variation of salinity (PSU) in Mandovi estuary during 1991-1992**

| Station | Pre-monsoon | Monsoon | Post-monsoon |
|---|---|---|---|
| M1 & M2 | 34.58 - 35.68 | 7.5 - 25.86(Sept.) | 31.84 - 34.63 |
| M3 & M4 | 21.42 - 33.67 | 0 to 16.71 | 11.54 - 31.83 |
| M5 & M6 | 7.16 - 25.11 | 0 to 2.33 | 2.11 - 13.82 |
| M7 | 0 | 0 | 0 |
| M0 | 34.8 - 36.5 | 31.8(Sept.) | 33.2 - 36.1 |

Adopting the index of seawater penetration as 1 PSU, the extent of seawater intrusion in the estuarine system was studied by Qasim and Sen Gupta (1981). They observed that the distance upstreams varied from a maximum of about 65 km in May to a minimum of about 11 km in July in the Mandovi and concluded that at any given time of the year there is a much greater amount of salt water in the Zuari than in the Mandovi. De

Sousa (1983) collected a series of surface water samples from the estuaries at low tide from the freshwater end to the marine end at different seasons and analysed salinity and computed the freshwater contents (Officer 1976) and found that the sea water penetration was up to a distance of 43 km in Mandovi and 60 km in Zuari. The present investigation confirm the above studies.

## 4.3 Salt Wedge

Salt Wedge is formed in perennial rivers which are filled with freshwater nearly upto their mouths at the sea during the period of heavy precipitation and runoff. For the rest of the year, the estuarine regions of these rivers become an arm of the adjoining sea with homogenous conditions prevailing vertically. Salt wedge formation in an Indian river has been reported for the first time from the Vellar estuary in the east coast of India (Dyer & Ramamurthy 1969). They observed that the salt wedge formation in this estuary occurs for a period of 2 months during the NE monsoon.

Qasim and Sen Gupta (1981) observed that in Mandovi estuary, during the peak monsoon months while the freshwater dominates the water column, seawater, with varying salinities ranging from 2.5 to 15 PSU was found at the bottom and in the uneven pockets of the sea bed in the form of salt wedge. Although no clear demarcation of the maximum distance of the salt wedge extension in the river Mandovi could be made due to lack of observation during monsoon months, it could be concluded from the salinity data obtained from the bottom that it extends about 10 km upstream. However, salt wedge extending up to 12 km in river Zuari was observed (Qasim and Sen Gupta, 1981).

There are several explanations for the formation of salt wedges. Fox et al (1987) suggested that the geometry of the channels and the discharge from the rivers cause rapid entrapment of seawater within the river mouths. During periods of high freshwater flow, Fox et al (1987) explains that the inertia of freshwater discharge overcomes buoyancy, hence river waters push all salt water out of the channels than overriding it.

It could be summarised that during premonsoon the estuary remained well mixed from surface to bottom almost through their entire length. During monsoon, the estuary becomes freshwater dominated with near-zero salinities at the surface and marginally high salinities at the bottom especially near the mouth showing stratification. Post-monsoon is the recovery period when the estuary changes from stratified to partially stratified to mixed conditions

## 4.4 Dissolved oxygen

The studies of dissolved gases have played a major role in understanding the physical, chemical and biological processes taking place in natural waters. Accurate data on solubility of gases in sea water is of special importance because departures of ocean / sea water from equilibrium with atmospheric gases provide information on many type of processes. Supersaturation by oxygen in waters which are equilibrated with respect to non-reactive gases may suggest photosynthetic production of oxygen, while undersaturation by oxygen may reflect its biological and chemical utilization in respiration and oxidation processes. Considerations, such as these, require reliable solubility data. The solubility data for nitrogen, oxygen and argon have been summarised by Weiss (1970) who developed an expression representing the temperature and salinity dependences of these gas solubilities in water.

Oxygen saturation values were computed using Weiss (1970) equation and oxygen saturation anomaly at varying chlorinities in Mandovi estuary by De Sousa (1983). Accordingly in Mandovi at chlorinities below about 2.35 PSU the water was almost saturated or supersaturated with oxygen. In the chlorinity range between 2.35 and 17.35 PSU the water was invariably undersaturated with respect to DO. In the present case also undersaturation in the above chlorinity range was noticed but the findings were not in conformity in the case of lower chlorinity ranges. The undersaturation of DO recorded in the upper part of the estuary was mainly due to the reduced photosynthetic activity due to high turbidity of water caused due to the discharge of mining rejects from iron ore processing plants or may also be due to high chemical and biological oxidation.

Monthly variations of dissolved oxygen (DO) concentration for surface and bottom waters in the Mandovi estuary are shown in Fig 4.4 to 4.6. DO values ranged in the estuary between 3.02 and 5.78 ml/l. The estuary as a whole showed comparatively higher concentrations at the surface as compared to the bottom waters. There was no definite pattern in the distribution of DO, though, in general it is expected to be slightly higher at the head of the estuary compared to the mouth as decreasing salinity increases the solubility of oxygen in water. Because of the shallow nature of the estuary, the water column gets well mixed showing almost identical values of dissolved oxygen for surface and bottom waters during non-monsoon months. However, during monsoon, the estuary becomes stratified showing differences in the DO concentration between surface and bottom waters.

Barrett (1972) points out that before examining the values of dissolved oxygen concentrations in detail in an estuary, two points needs to be mentioned. Firstly the oxygen content of any water body shows wide

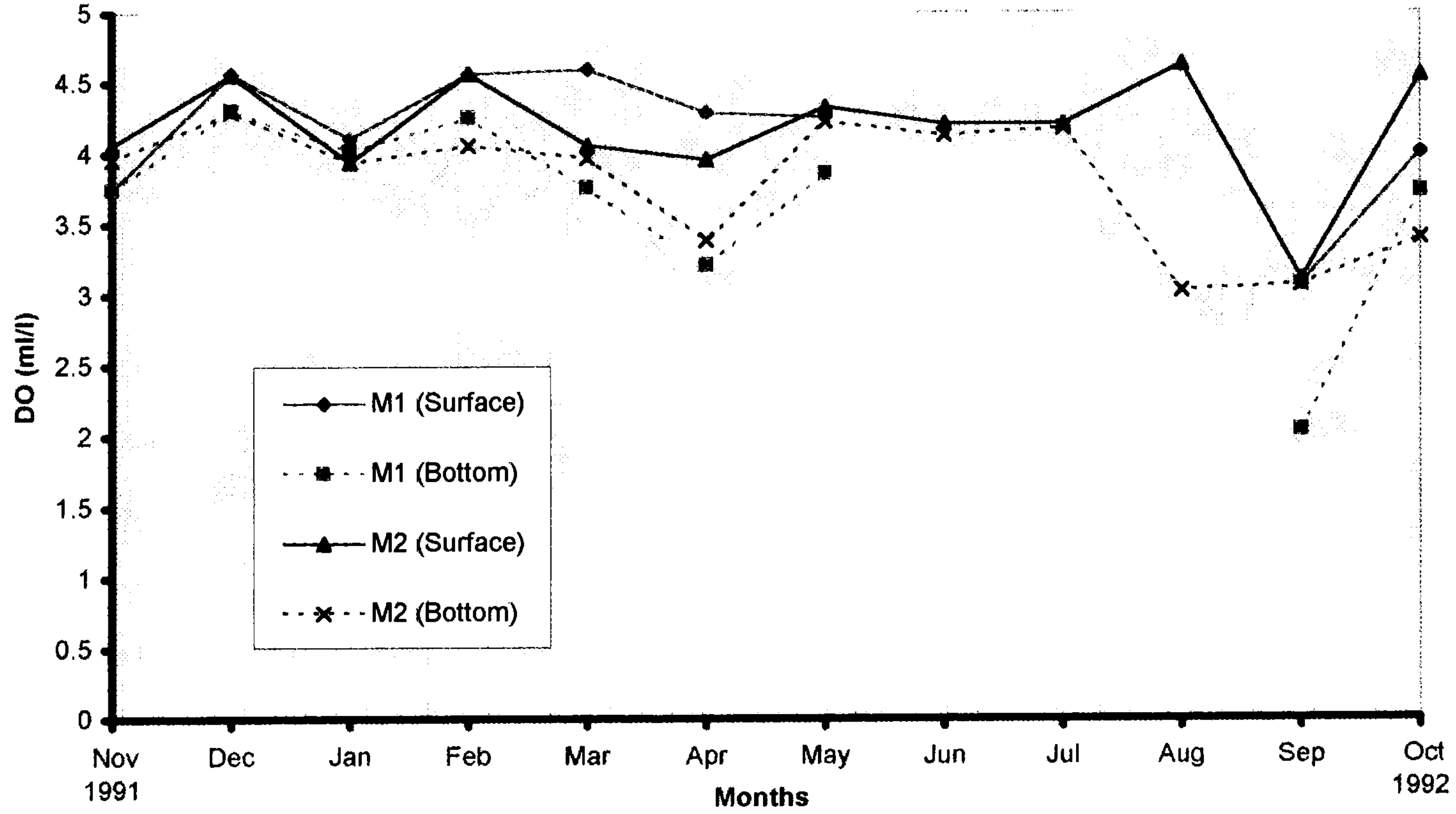


Fig. 4.4 Distribution of DO at MDA (M1 & M2)

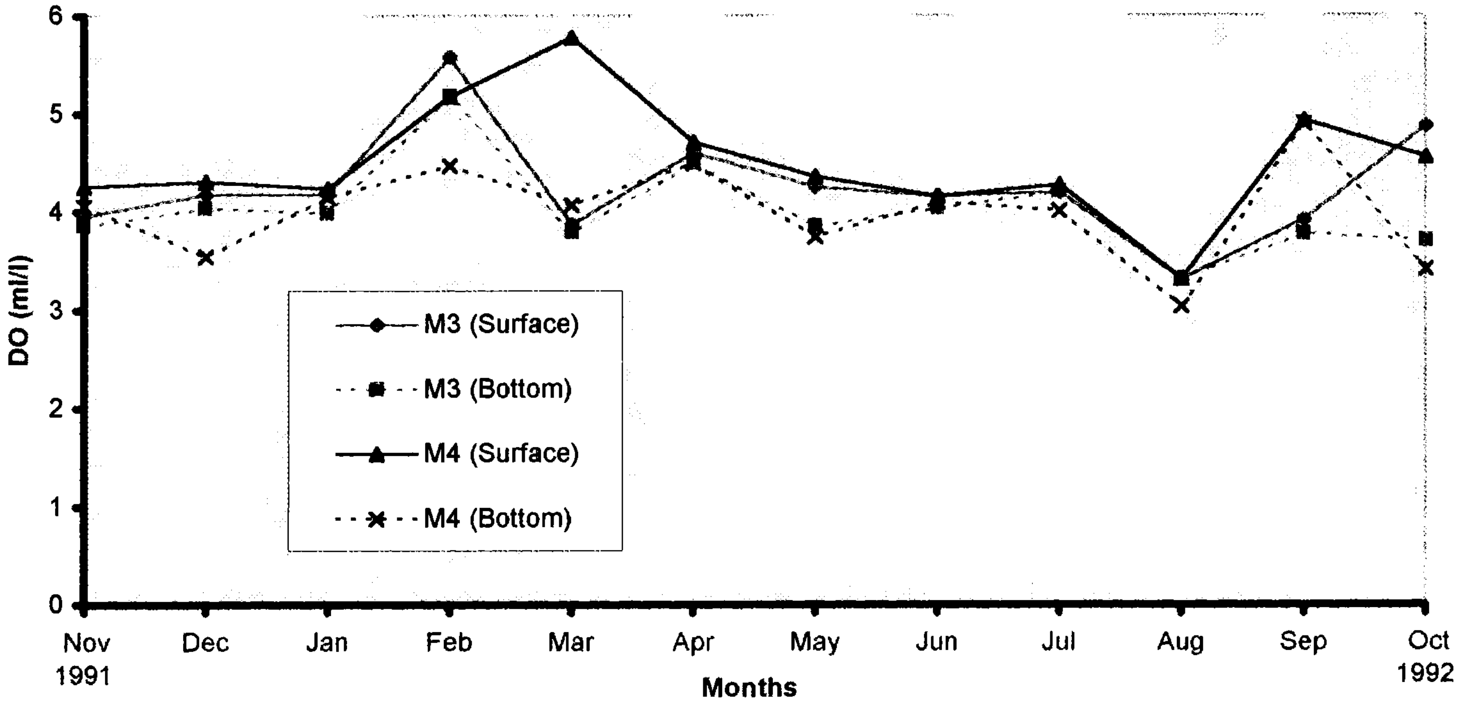


Fig. 4.5 Distribution of DO at EA (M3 & M4)

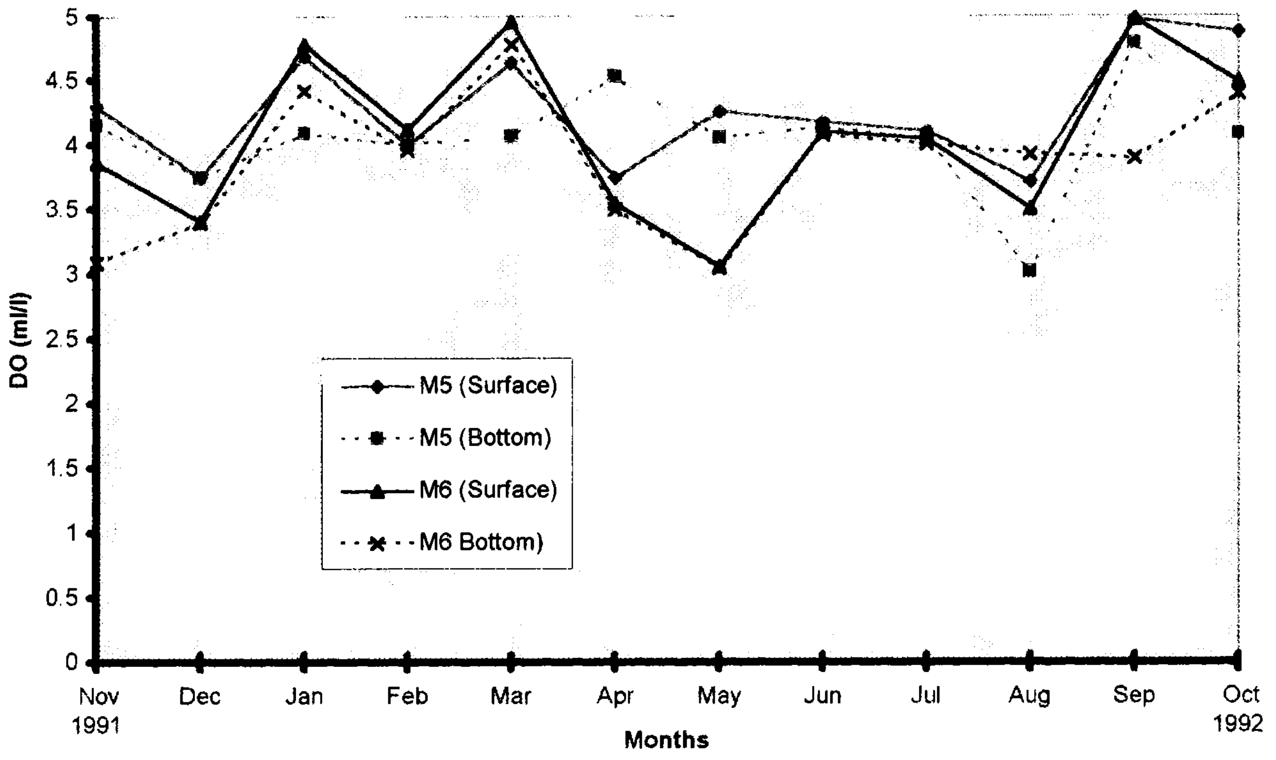


Fig. 4.6 Distribution of DO at FDA (M5 & M6)

fluctuations over each tidal cycle and secondly the concentrations of oxygen varies with the varying flow rates in an estuary.

While studying the dissolved oxygen distribution over tidal cycle Qasim and Sen Gupta (1981) observed that during all the tidal cycles the oxygen concentration decreased with the rising tide and increased with the falling tide. Annual variation ranging from 0.95 to 5.16 ml/l at the river mouth was recorded by Qasim and Sen Gupta (1981). However, such low values were not observed during the present study period. Temporary effect of a local sewage discharge was considered as the reason for low oxygen concentration in the Mandovi estuary. Data indicate that river Mandovi receives 10.7 x $10^6$ $m^3$ of sewage and other effluents every year. Due to the treatment of the effluents to the levels stipulated by the pollution control boards, the quality of the estuarine environment could be maintained to a reasonably healthy level and the concentrations seldom dropped below 3 ml/l except during September at M1. Table 4.2 gives the range of variations of DO in the estuaries during the study period.

**Table 4.2 Variation of dissolved oxygen (ml/l) in Mandovi estuary during 1991-1992**

| Station | Pre-monsoon | Monsoon | Post-monsoon |
|---|---|---|---|
| M1 & M2 | 3.2 - 4.6 | 2.0 - 4.6 (Sept.) | 3.8 - 4.57 |
| M3 & M4 | 3.8 - 5.8 | 3.0 - 4.9 | 3.5 - 4.3 |
| M5 & M6 | 3.0 - 5.0 | 3.0 - 5.0 | 3.0 - 4.8 |
| M7 | 4.08 - 4.55 | 4.07 - 4.11 | 4.01 - 4.14 |
| M0 | 4.00 - 4.8 | 3.0 - Sept. | 3.6 - 4.9 |

An attempt was made to study the relationships between salinity and DO in the estuary by pooling all the DO values against the respective salinity and are shown in Fig. 4.7. No definite relationship could be observed as the scatter was too wide and it could be attributed to the mixing and biogeochemical processes taking place in the estuary in which production and utilization of oxygen takes place as per the intensity of the processes. While studying the chemical variability in Tamar estuary Morris et al (1982) observed that in the lower estuary during winter the oxygen concentration was found at saturation level or approached this condition with increasing salinity and a localised concentration of phytoplankton production has been invoked to explain this situation. In the present case oxygen profiles indicated localised regions of oxygen saturation seaward of the estuary mouth and part of this oxygen consumed was due to the release of significant amounts of industrial and domestic effluents in to the estuary and the rest to respiration of coastal phytoplankton following transport into an inimical lower salinity regime.

According to Odum (1956) there are four main processes affecting the oxygen and carbon dioxide concentrations of flowing waters - (a) release of oxygen into the water by photosynthesis during day by both benthic plants and phytoplankton, (b) uptake of oxygen from water as a result of respiration of benthic organisms, planktonic organisms and sometimes chemical oxidation (c) exchange of oxygen with the atmosphere in the direction depending upon the saturation gradient and (d) influx of oxygen with accrual of ground water and surface drainage along the river.

Quantification of the oxygen involved in various processes in the Norman creek estuary, Brisbane, was carried out by Connel et al (1982) who found that out of 515 kg/day oxygen supplied to the estuary, exchange with air accounted for 45% while photosynthesis accounted for 42% and the rest was found due to accrual. Similarly out of 642 kg/day oxygen lost, plant respiration accounted for 15% while benthic respiration accounted for 52%. This findings reveal that exchange with air and photosynthesis play major role in the supply of oxygen while benthic respiration is the major process for removal of DO from estuaries

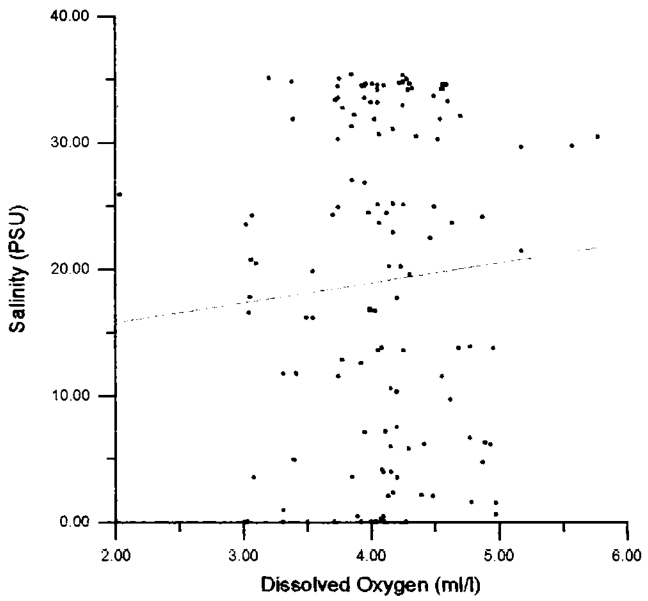


Fig. 4.7 Relationships between DO and Salinity in Mandovi estuary during 1991-92

## 4.5 pH

The study of pH is important in understanding the environmental conditions since pH is a parameter which facilitated the application of thermodynamic data to environmental problems.

In an aqueous solution the species present at equilibrium are controlled by pH and pE; where pE is the negative logarithm of a relative electron activity. The pH of sea water in contact with the air will vary between 8.1 and 8.3 depending upon the temperature and salinity of the water and the partial pressure of carbon dioxide in the atmosphere. Addition of $CO_2$ will cause the pH to decrease as a result of the formation of hydrogen ions by ionisation of carbonic acid, while the removal of carbon dioxide from the system would lead to a rise in pH.

The variation of pH in the Mandovi estuary is shown in Fig. 4.8 to 4.10. At the mouth of the estuary (M1 & M2) pH varied between 7.08 and 8.18. At M3 & M4 the variation was between 6.04 and 8.08, whereas, it was between 6.02 and 7.59 at M5 and M6. During premonsoon pH values were comparatively high and the lowest values were encountered during the monsoon. The values clearly indicated that the pH was higher at the mouth of the estuary which is dominated by sea water. At the freshwater-end (M7) the range of pH observed was between 5.41 (monsoon) and 6.06 (pre-monsoon). The highest pH values observed during premonsoon was probably due to the removal of $CO_2$ from water caused, presumably, by high photosynthetic activity during this season and the low solubility of this gas due to higher water temperature, while the low pH observed during monsoon might have been due to (i) high solubility of carbon dioxide in less saline waters at low temperature observed during this season (ii) due to the low photosynthetic activity caused by cloudy weather and highly turbid waters, (iii) since the estuaries are fed by monsoon precipitation, the rain water during its passage through the catchment area might have passed through industrial and residential areas carrying large amounts of domestic and industrial wastes, the oxidation of which produces carbon dioxide and even the wastes itself may be acidic and (iv) the rain water during its passage through the catchment areas may flow through sulphide bearing mines carrying along with it some sulphide which may eventually be oxidised to sulphuric acid. The surface water invariably showed higher pH near the surface as compared to bottom. The reason being that the bottom is usually the site for oxidation of organic matter with increasing production of $CO_2$. The variation of pH in the estuary indicated that at the mouth of the estuary, where high salinity water dominates, was associated with high pH and it decreased with increasing freshwater content. In order to confirm this salinity - pH, relationships were worked out and are shown in Fig 4.11 Nearing the seaward boundary of the estuary, pH levels approached the values in the range 8.02 - 8.16 except for June (pH 7.7).

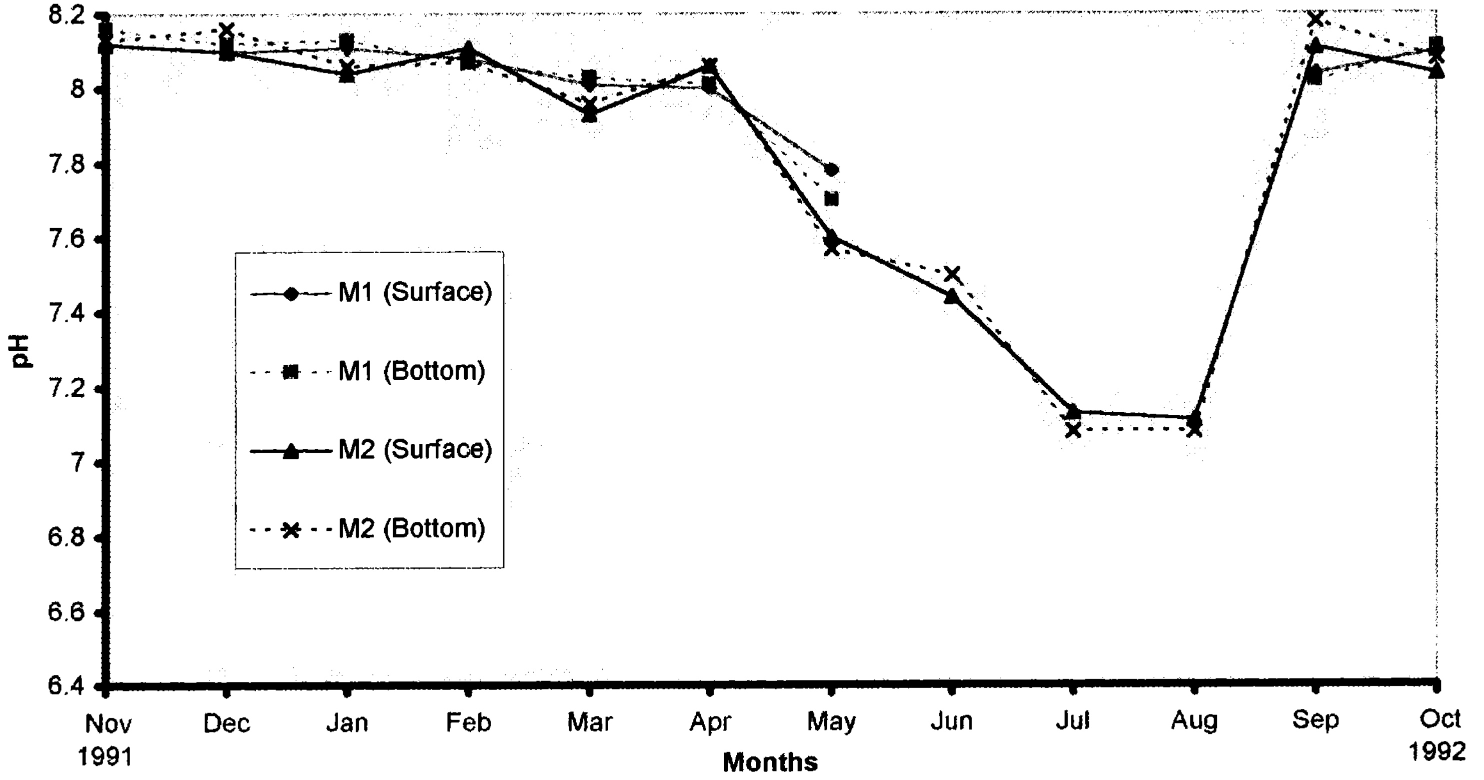


Fig. 4.8 Variation of pH at MDA (M1 & M2)

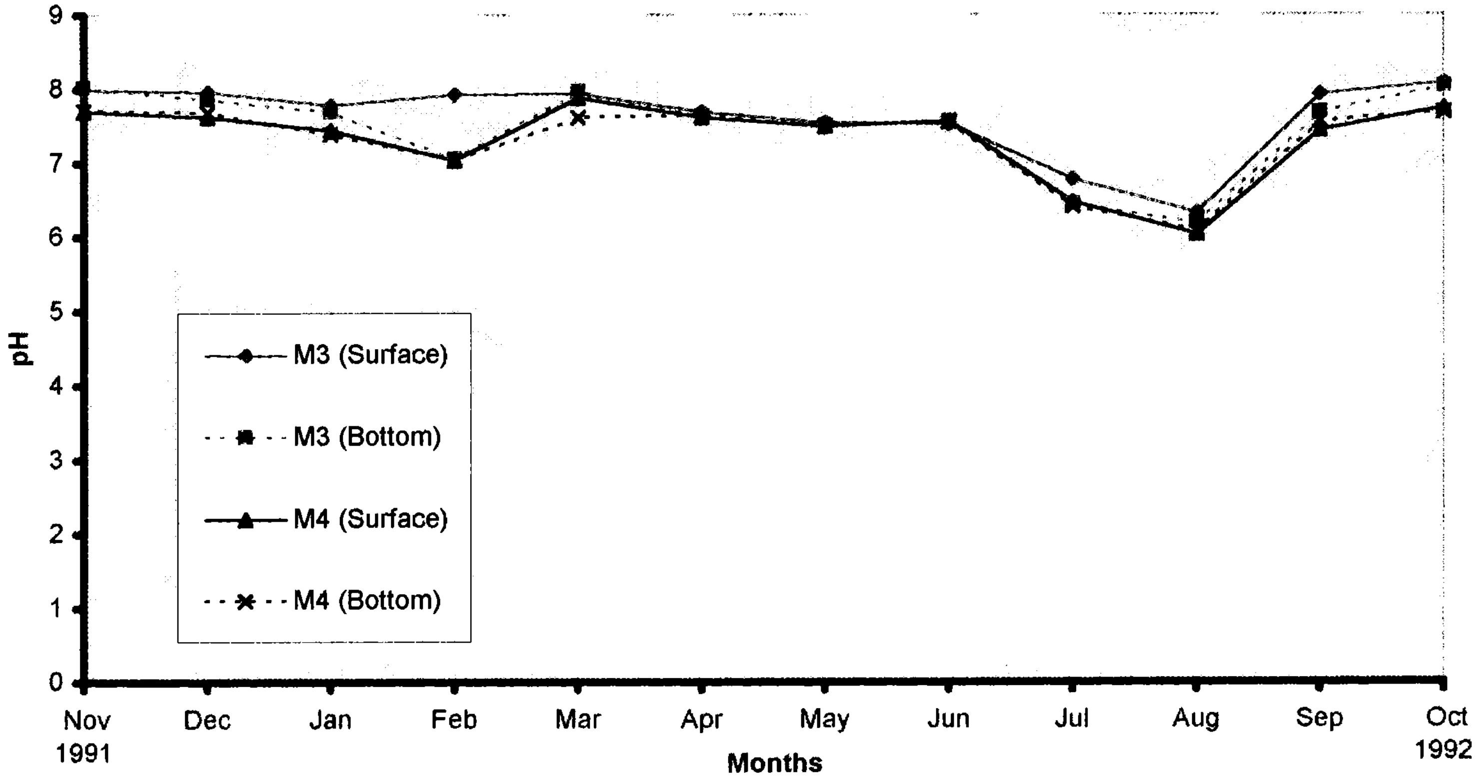


Fig. 4.9 Variation of pH at EA (M3 & M4)

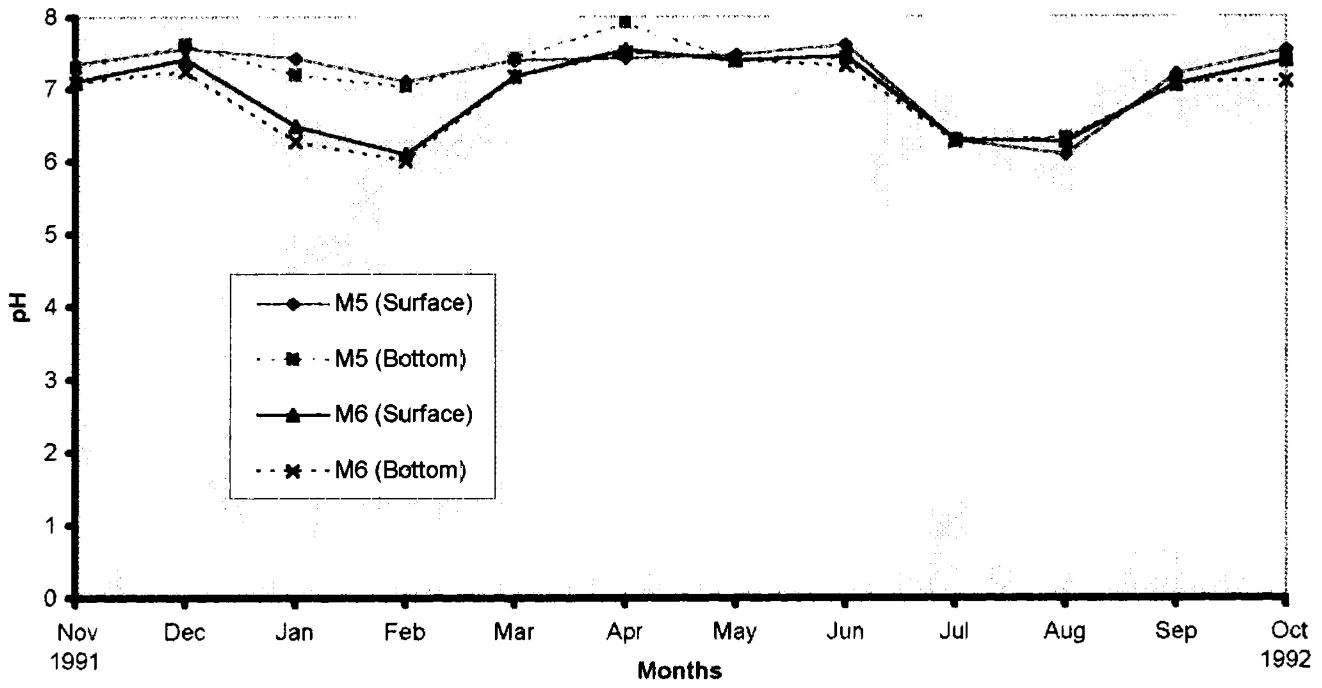


Fig. 4.10 Variation of pH at FDA (M5 & M6)

Freshwater pH values were in general lower (pH range 5.41 - 7.4) and there was generally a pattern of increasing pH with increasing salinity, although not always in a regular manner. Erratic short - term variability in pH relative to salinity could be observed if examined closely. The rate of increase of pH with increasing salinity decreased progressively from 1 to 10 PSU. At salinities higher than 10 PSU, pH changes relative to salinity were less pronounced, although relatively sharp increase in pH occasionally occurred in the more saline range( 25 - 35 PSU). Minor inflections in the pH profiles were invariably found either to covary with minor salinity perturbations in accordance with the general pH - salinity characteristics of the water at the time of sampling or to be associated with localised regions or enchanced primary production. However, these issues will be addressed in the following chapters.

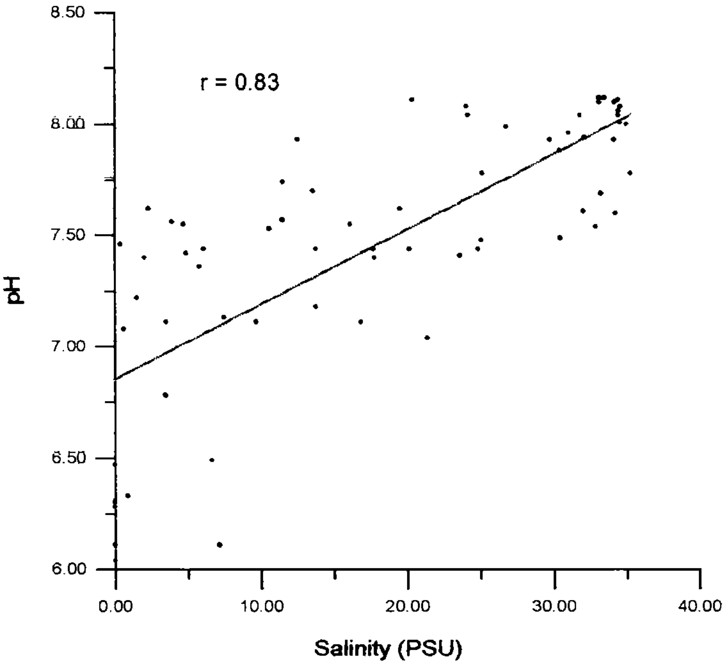


Fig. 4.11 Relationships between Salinity and pH in Mandovi estuary during 1991-92

Mook and Koene (1975) have studied the effect of salinity / chlorinity on the pH during estuarine mixing. According to them both pH and dissolved oxygen at all times showed non-conservative properties and were determined throughout the mixing zone by a variable balance of dynamic factor rather than by attainment of the appropriate thermodynamic equilibrium states or even, consistently , by the production of a time invariant steady state and this situation could be attributed to (a) kinetic limitations to the achievement of equilibrium with in a dynamic open system subject to variable boundary fluxes and (b) transient and localised perturbations produced by *in-situ* chemical and biological processes.

## 4.6 Total suspended solids

The annual input of particulate suspended material to the world ocean, as estimated by different authors, varies from 12.7 x $10^9$ to 51.1 x $10^9$ tonnes. The most part of the average values cited in the literature are within the range of 12-19 x $10^9$ tonnes year$^{-1}$ (Lisitzin 1974, Gordeyev, 1983). According to the above authors the supply of dissolved and particulate organic matter to the world ocean by the rivers total about 600 x $10^6$ tonnes every year. The organic matter contained in particulate material consists of (a) living planktonic algae and other green cells, microzooplankton including eggs and larvae and greater part of aggregated bacterio-plankton (b) the remnants of various organisms and of their faecal pellets, (c) organic mater in skeletal structure and in terrigenous and eolian compounds and (d) organic matter which has been coprecipitated, sorbed from the solution or aggregated. Thus particulate material contains both living and non-living organic matter. The two forms may be present in different proportions and this, affects the composition and properties of particulate material. Owing to its generally high activity it plays an important role in geochemical processes at the sedimentogenesis stage. It is, in effect, an indicator of a basins productivity, its nutrient supply and of the intensity of biochemical processes.

The distribution of suspended particulate material (SPM) in estuarine systems are controlled by a variety of physical, geological, chemical and biological processes (Pritchard and Schubel 1981).

The total suspended particulate materials in Mandovi estuary was estimated and the monthly variations are shown in Fig 4.12. Highest values of SPM was observed during monsoon season (June - September.) with lowest values during premonsoon and intermediate values during post-monsoon period. However, the variations during premonsoon and postmonsoon periods were not very well pronounced. The annual range of variation of SPM in Mandovi estuary was between 0.02 (M7) and 115.8 $mg.kg^{-1}$ (M5). Throughout the monsoon season the suspended material load in the estuary was substantially high and the concentration showed a decreasing trend from the freshwater end to the marine end. SPM concentrations were in general high at the mid regions of the estuary where mixing due to tidal flushings plays a major role in bringing more suspended material in the water column. During monsoon, the rain water washed away the sediment (mainly silt) from the watershed especially from the low lying agricultural lands resulting in high SPM.

Murty and Das (1972) observed that the high sediment load brought in by the seawater gets deposited near the mouth of the estuaries due to the current speed falling below a critical value for different particle sizes and the interaaction of river water with sea water at the confluence. Cherian et al (1974) and De Sousa et al (1981) found that during premonsoon, due to strong wave action, the sediment gets resuspended resulting in higher values near the mouth of the estuaries. In general suspended sediments were comparatively high in the estuary mainly due to strong tidal currents which cause disturbances of the loose bottom sediments and the mud flats. Navigation in the estuary is another significant cause for the higher

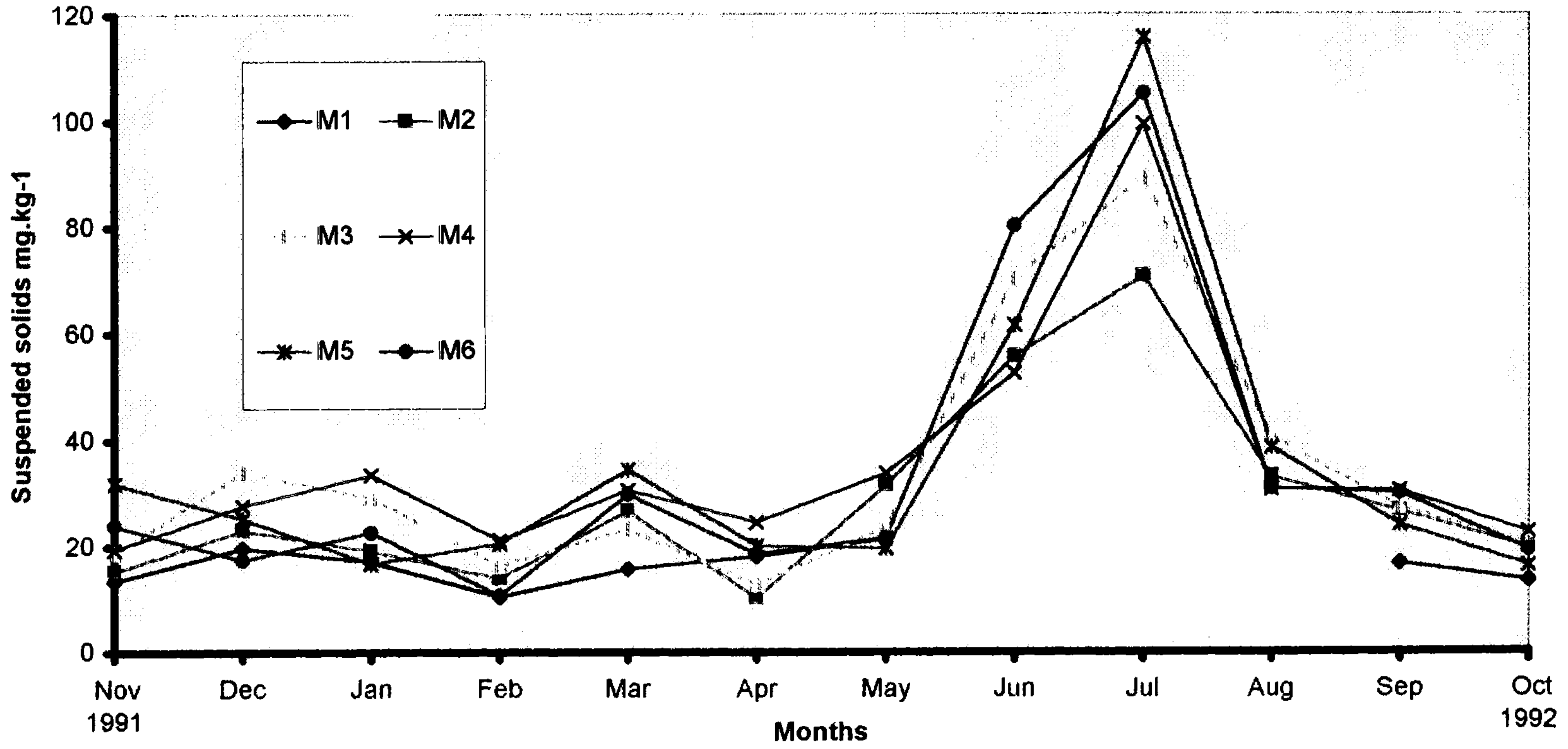


Fig 4.12 Variations of Suspended matter in Mandovi estuary during 1991- 92

suspended load. In order to maintain the navigational channels to accommodate the movement of vessels with higher DWT, the channels are regularly dredged and this also accounts for the suspended load during pre and post-monsoon periods and during these periods the rivers are stable with negligible freshwater discharge and the estuary remain tide dominated. Cherian et al (1975) reported lowest sediment during premonsoon and the load was as high as 214 $mgl^{-1}$ at the mouth and 280 $mgl^{-1}$ at upstream during the monsoon period. They also observed the highest values during premonsoon in the middle and bottom layers during peak flood when the bottom currents were strong. De Sousa et al (1981) observed 136 $mg/l^{-1}$ suspended load during July in the Mondovi estuary. Ward and Twilley (1986) studied the SPM levels in Chesapeake Bay and found that the concentrations varied from 3.3 to 98.6 $mgl^{-1}$ and the increase was noticed towards the landward direction. Highest concentration occurred in the upper estuary, whereas lowest concentrations were found near the mouth throughout the year.

Relationships between salinity and total suspended matter in the estuary was worked out and are presented in Fig 4.13. Though the scatter was too wide to make reasonable relationship between these two parameters. However, the theoretical best fit ($r = 0.65$) shows that the suspended load increased with freshwater content probably explaining the source from the landward side.

Berg (1984) observed low SPM concentration in the Tred Avon a tributary of Choptank river estuary following periods of heavy rains and attributed this reduction to dilution by freshwater runoff from forested areas or from ground water run off which had relatively low SPM concentrations. A possible explanation is that, stronger tidal current in the upper estuary keep fluvial inputs of SPM in suspension and resuspend bottom sediments, maintaining relatively high SPM concentrations. Conversely current velocities decrease where the estuary widens allowing deposition of SPM to occur. Yarbro et al (1981) showed that resuspension of bottom sediments by tidal currents increased SPM concentrations in the middle Choptank river establishing a turbidity maximum. The turbidity variations in the estuary followed the pattern of distribution of suspended particulate material load. Fig 4.14 show the monthly variation of turbidity in the Mandovi estuary. As expected turbidity was

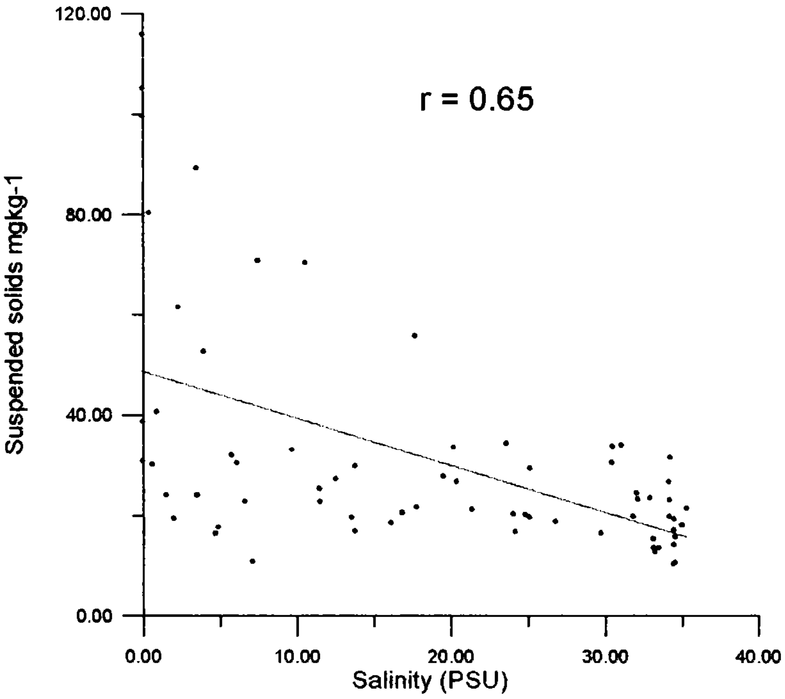


Fig. 4.13 Relationships between Salinity and suspended solids in Mandovi estuary

exceptionally high during monsoon months. However, a moderately good correlation between salinity and turbidity could be observed (Fig. 4.15). Ward and Twilley (1986) observed that freshwater discharge into the Chesapeake Bay was substantially greater, yet concentration of SPM in the upper estuary remained low which indicate that SPM concentration in the estuary may not always increase during high river water exchange. However, the present study did not reveal a definite pattern of distribution of suspended particulate materials in Mandovi estuary.

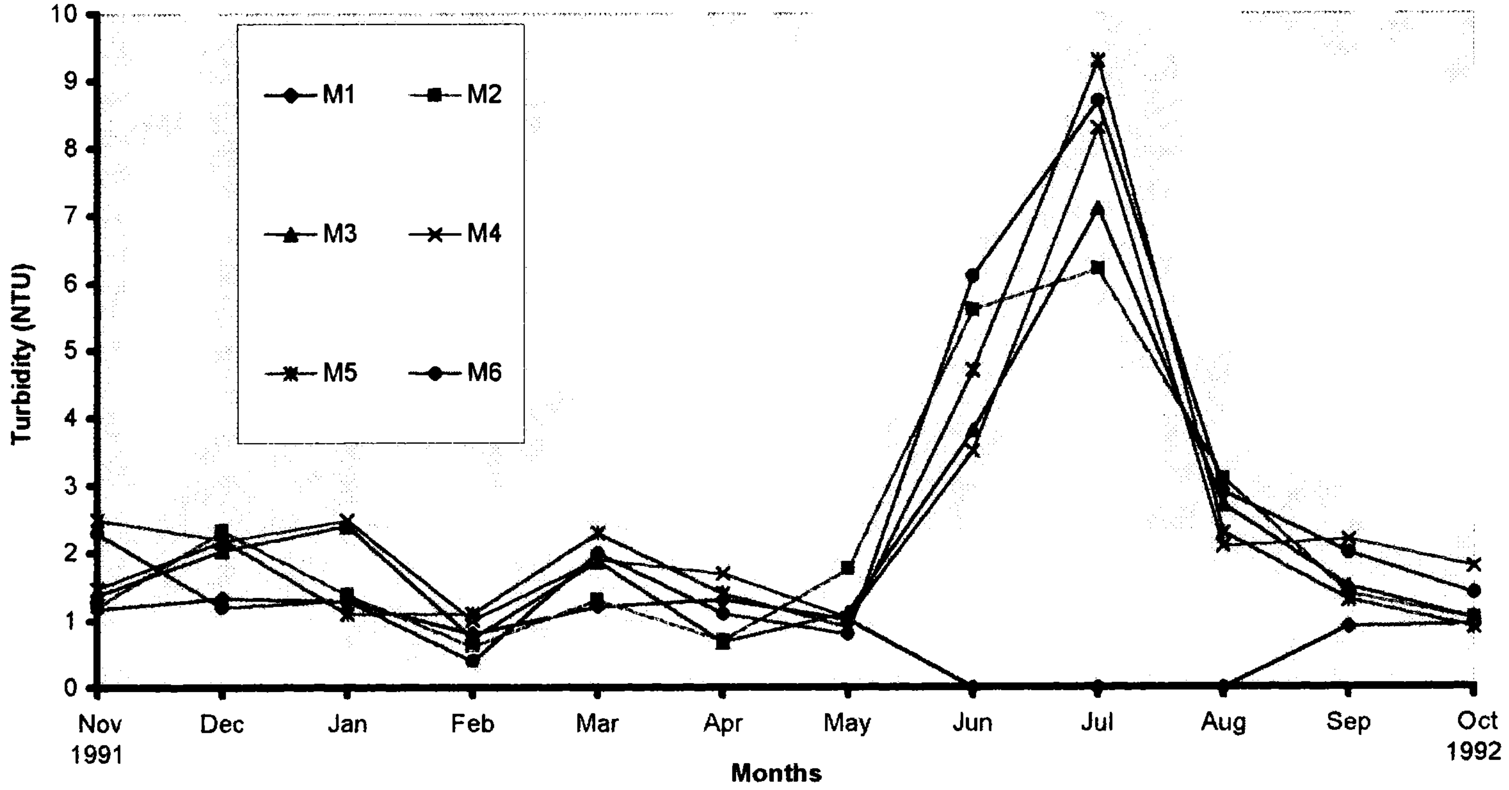


Fig. 4.14 Variations of Turbidity in the waters of Mandovi estuary

Fisher et al (1988) in Chesapeake and Delaware bays observed a turbidity maximum in the oligohaline ( S=1-10 PSU) regions, a chlorophyll maximum in clearer waters sea ward of the turbidity maximum and a nutrient depleted zone at the highest salinities. A feature unique to the Chesapeake Bay was a turbidity minimum at salinities of 15-2 PSU and water was more turbid both towards the river and the shelf. This feature was consistent, but not pronounced and their observations suggest that at higher salinity the loss of suspended particulates from the water column to the sediment which lead to the conclusion that estuaries appear to trap at least part of their particulate loads.

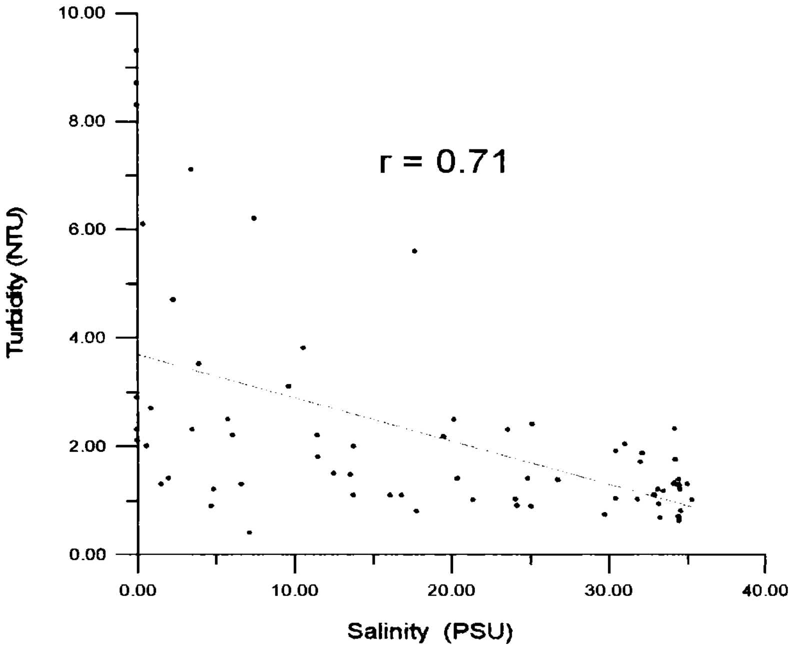


Fig. 4.15 Relationships between Salinity and Turbidity in the waters of Mandovi estuary

It could be summarised that geomorphologically Mandovi estuary has been identified as drowned river valley estuary and classified as a tide-dominated coastal plain estuary. The monsoon brings about changes from typically marine to typically brackish-water conditions. This is followed by a general reduction in the freshwater discharge during the post monsoon period and the restoration of stable marine conditions in the premonsoon months.

The estuary remain homogeneous vertically for about 8 months and gets moderately stratified for about 3 to 4 months in a year. The water in this estuarine system penetrates upto a considerable distance upstream and the semidiurnal type tide occur twice a day rising and lowering the water level by about 2.3cm.

There is strong longitudinal variation in salinity at almost all the depths from mouth to the upstream which gives rise to a range in the longitudinal dispersion coefficients, probably due to advective flux. During monsoon months, due to large influx of freshwater a compensatory salt-water flow occurs below the freshwater in the form of a salt wedge.

# Chapter 5

## NUTRIENTS AND PLANKTON

**Contents** **Page No.**

# 5.0 NUTRIENTS AND PLANKTON

In this chapter an attempt has been made to evaluate the distribution of various nitrogen and phosphorus compounds in different compartments of the estuarine system. The two compartments considered here are the water environment and the sediment environment. Efforts have also been made to estimate various fractions of N and P in both these environments. The third compartment - the phytoplankton is however, dealt with separately to understand its relationships between the other two.

## 5.1 Nutrients in Water Environment

A number of major constituents of seawater together with the trace metals, iron, manganese, copper, zinc, cobalt and molybdenum and the compounds of nitrogen, phosphorus and silicon can be termed as 'nutrients', for, like the terrestrial plants, marine phytoplankton require these elements for their healthy growth. The most important of these elements are nitrogen and phosphorus, which are taken up by phytoplankton from the water to such an extent that at times they may be completely depleted so much so that any further growth of the phytoplankton gets limited. In the foregoing discussions the term 'nutrients' has been applied almost exclusively to the compounds of phosphorus and nitrogen.

The fertility of coastal and estuarine waters is generally high, but the balance of essential elements is not so simply regulated. During most of the time, elements are used as fast as they are returned to the water and the rate of cycling , rather than the potential stock of the elements, become crucial in determining what factor will be the most important in limiting production.

## 5.2 Nutrient inputs to estuaries

Estuaries are interesting and unique aquatic environments in that they have inputs from both terrigenous and oceanic sources as well as from the atmosphere. Freshwater or land inputs such as runoff, point and non-point sources etc, are likely to be in the surface waters of the estuary because of low density. These land derived inputs can also take the indirect routes of ground water seepage through the sediment or wind driven dust from agricultural land. Inputs from the ocean are usually from the deeper waters.

The composition of the river waters that mix with the sea water in estuaries varies with the rate of freshwater discharge from the drainage basin and with the geological / geochemical character of each drainage basin. Within-basin discharge variations approach the between - basin watershed variations for major elements (Carpenter et al, 1969). The major dissolved components (Na, K, Ca, Mg, Al, Cl, $SO_4$) from an estuarine sample can be calculated with knowledge of the concentration of the components in the river and ocean-end members, that is, within accuracies approaching the analytical capability to measure these components, and they behave linearly.

Freshwater and sea water composition of the micronutrient components show extreme variations (over several orders of magnitude). In addition estuarine systems can show strong flow-related (frequently seasonal) variations.

Nutrient concentration in various estuaries are summarised in Table 5.1 to understand the freshwater and sea water composition of some of the micronutrients.

**Table 5.1 Nutrient concentration in various estuaries**

| Estuary Samples | $NO_3^-$-N | $NH_4^+$-N | $Si(OH)_4$ | $PO_4^{3-}$-P | Reference |
|---|---|---|---|---|---|
| | ← | μmol/l | | → | |
| Delaware Estuary | | | | | 1 |
| 0 PSU | 150 | 50 | 110 | 2.0 | |
| 30 PSU | 1 | 1 | 7 | 0.3 | |
| Susquehanna-Chesapeake | | | | | 2 |
| 0 PSU | 100 | 10 | - | - | |
| 30 PSU | 1 | 1 | - | - | |
| Zaire (Africa) | | | | | 3 |
| 0 PSU | 8 | 0.5 | 160 | 1.2 | |
| 30 PSU | 0 | 0 | 0 | 0 | |
| Magdalena (S.Africa) | | | | | 4 |
| 0 PSU | 17 | - | 225 | 3.0 | |
| 30 PSU | 0 | - | 0 | 0.2 | |
| Scheldt (Belgium) | | | | | 5,6 |
| 0 PSU | 0 | 600 | 230 | 40 | |
| 30 PSU | 30 | 40 | 10 | 20 | |
| Potomac - Chesapeake | | | | | 7 |
| 0 PSU | 110 | 200 | - | 32 | |
| 30 PSU | 1 | 1 | - | 0.2 | |
| Hudson | | | | | 8,9 |
| 0 PSU | 40 | 30 | 100 | 5 | |
| 30 PSU | 5 | 5 | 40 | 1.5 | |

Reference
(1) Carpenter et al (1969)
(2) McCarthy et al (1975)
(3) Van Bennekan et al (1978)
(4) Fanning and Maynard (1978)
(5) Wollast and Debroen (1971)
(6) Van Bennekan et al (1975)
(7) Jaworski et al (1972)
(8) Garside et al (1976)
(9) Simpson et al (1975)

One of the more spectacular increase of nutrients to a major estuarine system has been reported by Vander Eijk (1979) for the Rhine river - Wadden Sea - North Sea system. In a ten year period (1959 - 1968) the annual phosphate load of the Rhine increased from 4,000 to 15,000 tonnes of phosphorus and ammonia plus nitrate increased from 190,000 to 340,000 tonnes as nitrogen.

Webb (1981) prepared a conceptual model which is largely a theoretical construction containing the essential attributes of the system - by diagrams of boxes representing components and arrows between boxes representing relationships or transfer of materials or energy. This conceptual model is reproduced in Fig 5.1. This model is of one compartment size, representing the entire estuary and contains bi-directional arrow indicating the possible fluxes of nutrients between the estuary and other systems. This estuary Webb (1981) studied was considered as a moderately stratified estuary as contrasted to highly stratified or vertically homogenous. This simple box model becomes a mass balance if all inputs and outputs of a given substance are added up. This one compartment model becomes inadequate when we consider processes and transfers within the compartment. Process which affects nutrients can be either biological, chemical or physical. The circles indicating nutrient cycles within the box are meant to show that transformations of carbon and nitrogen in those estuaries are biological, while those of phosphorus and silica may be both biological and chemical. Silica uptake and incorporation by diatoms is considered biological, while its regeneration is largely chemical through dissolution. Phosphorus cycles biologically, but its exchange with sediments is probably chemical and possibly controlled by oxygen concentration (Mortimer 1971, Patrick and Khalid (1974) and Webb and Elia (1980). The rate of mixing indicated by the centre circle varies greatly within estuaries and can affect the rates of biological and chemical transformations of the nutrients. Thus in an estuary in which light does not reach the bottom, sediment-released phosphate is unlikely to be incorporated to the phytoplankton until it reaches the lighted surface zone.

Numerous attempts have been made to depict conceptual models of inorganic and organic nutrient cycles in the aquatic environments.

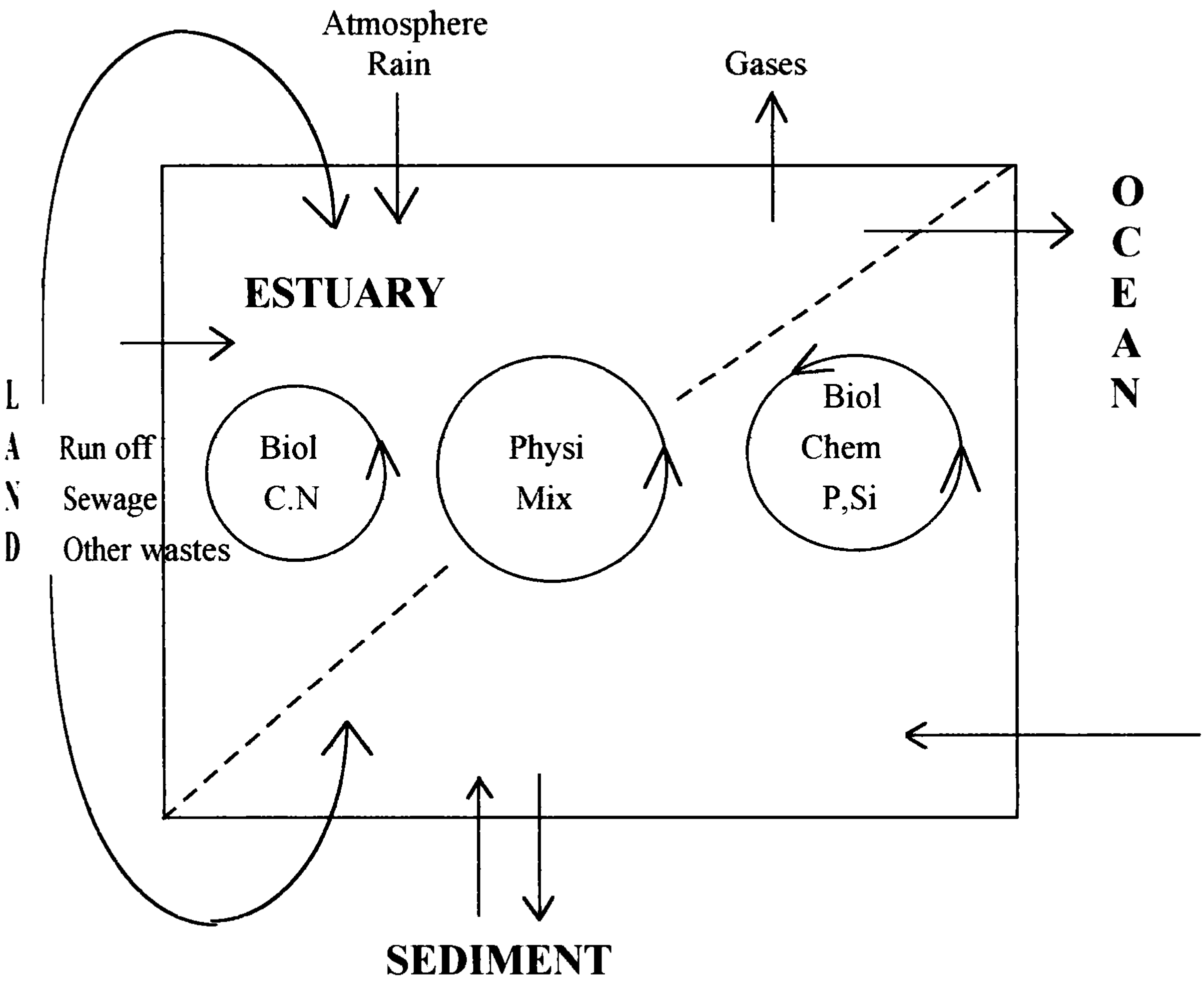


Fig : 5.1 Model of moderately stratified estuary indicating major routes of input and outputs of nutrients and the kinds of cycles and processes considered.
( Kenneth L. Webb, 1981)

However, this type of conceptual models tend to be inadequate when dealing with short-term phenomena. Therefore, there is a need to appreciate the appropriateness of time scales of sampling related to the time scale of the process being studied. Nixon (1981) presented a conceptual model incorporating both trophic and nutrient concepts and the same has been widely accepted. In the present study conceptual models were not attempted. On the other hand mixing diagrams(property-property plots) are used to infer the importance of processes such as phytoplankton accumulation and nutrient removal. This approach has been quantitatively described by Boyle et al (1974) and several others discussed interpretation and limitation of this method (Burton, 1976; Loader & Reichart, 1981; Sharp et al 1982).

## 5.3 Nutrient sources.

Estuaries are important pathways of the plant nutrients, nitrogen and phosphorus, from the land to the ocean. As the nutrients pass through the estuary, they undergo various biogeochemical transformations which affects their distributions in the estuary. To quantitatively understand these processes, it is important to characterise the sources of these nutrients to the estuary, their spatial and temporal variations, and the degree to which they are affected by human activities. Some estuaries, for example the Umpqua river estuary in Oregon (Peterson et al 1988) receive most nutrients from their watersheds, while others for example the Hudson River Estuary (Jaworski, 1981) are dominated by anthropogenic waste inputs. Hager and Schemel (1992) studied the sources of some nutrients to San Francisco Bay and their effects on the distributions of these nutrients in the bay. They observed that agricultural return flow, drains and municipal waste water treatment plants were the largest sources of nutrients to the river during low river flow. Nitrogen and phosphorus mass balances were estimated for the portion of the Potomac river basin watershed located above Washington (Jaworski et al 1992) they observed that the major sources of nitrogen were animal waste and atmospheric deposition whereas, animal wastes and fertilizers were the main sources for phosphorus. River runoff is considered as the most important source of nutrients in to the estuaries and once within the estuary, the distribution of concentration of any given chemical species of a particular nutrient depends upon various physical, chemical, biological and geological processes. (Vollenweider 1975). Phosphorus and nitrogen sources of some of the estuaries are summarised in Table 5.2.

**Table 5.2 Largest phosphorus and nitrogen sources for some estuarine systems**

| Estuary | Ecosystem watershed description | Largest phosphorus sources | Largest nitrogen sources |
|---|---|---|---|
| Hudson | Forested/Industrial/Urban | Waste water discharges (73%) | Waste water discharges (63%) |
| San Francisco | Agricultural/Industrial /urban | waste water discharges (60%) | Waste water discharges (47%) |
| Lake Superior | Forested/Rural | Land run off (60%) | Air (59%) |
| Potomac | Forested/Urban | Waste water discharges (84%) | Waste water / land runoff (50%/50%) |
| Chesapeake Bay | Forested/Industrial /Urban | Waste water discharges (69%) | Land runoff (68%) |

As can be seen from the tabulation; the major source of phosphorus or nitrogen can vary from ecosystem to ecosystem. Likewise, the relative percent contribution of a given source can also vary significantly depending on the geographical location, industrial/urban development, and agricultural practices. The sources of nutrients therefore include the surface freshwater drainage from land, groundwater inflow, direct waste discharge from land, rainfall and fallout of particulates from the atmosphere. In some cases the nutrients are supplied to the estuary from adjacent coastal waters, though more often nutrients are exported from the estuary to these coastal waters. Fixation of gaseous nitrogen from the atmosphere also contributes an input of nitrogen-based nutrients to some parts (generally lower salinity regions) of some estuaries. Within the estuary there are proximate sources of nutrients, such as regeneration from bottom sediments and oxidation of organic matter within the water column.

## 5.4 Nitrogen species

The most abundant form of nitrogen in seawater is the molecular nitrogen. In addition to this, the seawater contains low, but extremely important concentrations of inorganic and organic compounds in which nitrogen occurs in many of the **nine** oxidation states from -3 to +5 which are biologically active. Organic nitrogen is in the reduced (-3) state in both cell protoplasm and in such compounds as urea, uric acid and amino acids which may occur in the marine environment. Ammonia (which is the sum of free $NH_3$ and ammonium $NH_4^+$ ions) a major input to estuaries both from sewage and from release by the sediments is the most reduced form of nitrogen and can be used directly by phytoplankton and other micro-organisms in assimilatory processes without further reduction. Nitrate ions ($NO_3^-$) and nitrite ions ($NO_2^-$) are the other important inorganic forms of nitrogen. Nitrous oxide and some other short lived species like hydroxylamine and hyponitrite are also inorganic forms of nitrogen present in low concentrations. Table 5.3 shows the different N compounds at its oxidation states.

| Oxidation Level | Possible Intermediate | | Processes | | | |
|---|---|---|---|---|---|---|
| | | | Anaerobic | | Aerobic | |
| +5 | $HNO_3$ | Nitrate | | → | → | ← |
| +4 | $NO_2$ | Nitrogen dioxide | | | → | |
| +3 | $HNO_2$ | Nitrite | | → | ⇆ | ⇆ |
| +2 | NO | Nitric oxide | | | | |
| +1 | $N_2O$ | Nitrous oxide | | | ⇆ | ⇆ |
| +0 | $N_2$ | Nitrogen | → | ← | | |
| -1 | $NH_2OH$ | Hydroxyl amine | | | ⇄ | ⇄ |
| -2 | $N_2H_4$ | Hydrazine | | | | |
| -3 | $NH_3$ | Ammonia | ← | ← | ← | → |
| | | | A | B | C | D |

In the above chart the processes A, B, & C are reductions and move down, D is an oxidation process and move up. Arrows to the right indicate where material is known to enter the process and arrows to the left indicate where material is known to leave the process.

In well oxygenated seawater, nitrate-nitrogen is the thermodynamically most stable form of combined inorganic nitrogen.

The main source of nitrate in estuaries is from land drainage mainly in river water which carries the products of rock weathering and of the decay of the organic material, together with discarded wastes both industrial and domestic. There are also contributions from atmospheric transport and rain water which carries nitrate resulted from atmospheric oxidation of ammonia. Contribution from submarine weathering , glacial actions at the poles and volcanic and other geothermal activity also are recorded. (Fetch, 1966, Hager and Schemel 1992)

## 5.5 Phosphorus

Phosphorus is one of the most important nutrients and required for the zooplankton and phytoplankton growth. It is a dynamic variable in all natural systems and depending on the specific situation it may be concentrated temporarily or permanently in one or more of the following regions: the biosphere, the hydrosphere or the lithosphere. (McCarthy, 1970, Magnein et al 1992)

In most hydrologic conditions, phosphorus and other nutrients are constantly being incorporated in organisms and being depleted in water. Simultaneously (through excretion and decay) these are being released to the system. To account for phosphorus in natural waters one must be able to explain the quantitative mechanisms for the uptake and release of nutrients.

The main source of phosphorus in estuaries and sea is river runoff. The decomposition of organic matter results in the liberation of phosphorus compounds which are carried to the estuaries by land drainage. Similarly during weathering, phosphorus is liberated as alkali phosphates and dissolved or colloidal calcium phosphate. Use of super phosphates in agriculture results in large unutilized quantities of it reaching the estuaries. A large quantity of detergents is in use in present days in washing and cleaning. Most of these detergents contain polyphosphates which finally end up in the estuaries and sea. (Kemp and Boynton, 1984, Simon, 1988).

### 5.5.1 Phosphorus species

In natural waters, phosphorus exists as soluble fraction or insoluble particulate fraction. In soluble fraction a portion may be reactive to molybdate and which constitutes the soluble reactive phosphate (mostly orthophosphates) and a portion which becomes reactive only after oxidation, which constitutes the soluble organic fraction. The particulate phosphorus can also be divided into particulate inorganic and organically bound phosphorus.

The species of inorganic phosphorus in seawater are orthophosphate ions, represented by phosphoric acid ($H_3PO_4$) and its dissociation products, $H_2PO_4^-$, $HPO_4^{2-}$ and $PO_4^{3-}$ and ion complexes of these ions with the other constituents of seawater.

Phosphoric acid is a triprotic acid which dissociates in water as follows.

$$H_3PO_4 \rightleftharpoons H^- + H_2PO_4^-$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$$

$$HPO_4^{2-} \leftrightharpoons H^+ + PO_4^{3-}$$

Reactive phosphorus in solution exists mostly as ions of orthophosphoric acid $H_3PO_4$. In river water when pH is low (around 7) phosphate is present mostly as $H_2PO_4^-$ with small fractions being present as $HPO_4^{2-}$ and $PO_4^{3-}$. In seawater when the pH is around 8 phosphate is present mostly as $HPO_4^{2-}$ (87%) while 12% of it is present as $PO_4^{3-}$ and 1% as $H_2PO_4^-$ (Kester and Pytkowicz, 1967). According to them about 96% of $PO_4^{3-}$ and 44% of $HPO_4^{2-}$ are present in association with calcium and magnesium as their ion pairs.

## 5.6 Distribution of Nitrogen compounds

Since nitrogen is a principal nutrient involved in the biological activity, its distribution in seawater is controlled by biological processes.; this results in the removal of this element from water in the upper euphotic layer. In some cases the nitrogen compounds are completely removed from the surface waters and this results in **'limiting'** the further growth of primary producers. Below the euphotic layer, however, the sinking dead cells and the fecal pellets of living organisms start decomposing, thereby, liberating nitrogen compounds first as ammonia which is oxidised to nitrate via nitrite as intermediate product. The decomposition of organic matter is accompanied by the utilization of dissolved oxygen present in water. The mineralisation of organic matter under oxidising condition can be reported by the relation proposed by Richards(1965)

$$(CH_2O)_{106}(NH_3)_{16}\,H_3PO_4 + 138O_2 \rightleftharpoons 106\,CO_2 + 122\,H_2O + 16HNO_3 + H_3PO_4$$

According to the above relation, organic matter on mineralisation will liberate carbon, nitrogen and phosphorus in the atomic ratio

$$C : N : P = 106 : 16 : 1$$

Since the major source of nitrogen compounds in estuaries is runoff, their concentration in river water is expected to be high decreasing towards the sea-end. However, biological activity will play an important role in controlling the concentrations of nitrogen compounds in surface waters.

If we assume that the major elements in phytoplankton and zooplankton growth are C, N, P, H, and O we may write the following symbolic equation for the up-take.

$$a\,HPO_4^{2-} + bHCO_3^- + cNO_3^- + d\,H_2O + eH^+ \rightleftharpoons C_bN_cP_aH_qO_r + sO_2$$

Where a,b,c are constants or variables.

Redfield et al (1963 ) analysed the rate of change of nutrients with respect to one another and, assuming that the change is due entirely to organism uptake and that there was a fixed organism composition. Thus they have defined an organism stoichiometry of $C_{106}\ N_{16}\ P_1\ H_{263}\ O_{110}$ with 138 atoms $O_2$ for oceans. Actual analysis of organisms do not always agree with this composition, although many of the analysis compiled were for culture studies that involved nutrient concentration many orders of magnitude greater than those found in natural waters (Buttler et al 1970). On the other hand, there are analysis of net hauls which deviate significantly from the foregoing average formulation (Fisher, et al 1988). Nitrogen compounds are present as cellular constituents, as non-living particulate matter, as soluble organic compounds and as inorganic ions in solution. All these forms are interrelated by a series of reactions collectively known as “nitrogen cycle”, which portrays the flow of nitrogen from inorganic forms in soil, air and water into living systems and then back again into inorganic forms. Fig 5.2 presents a simplified reaction sequence of the interconversions between organic nitrogen and the main inorganic forms, the principal reactions are labeled.

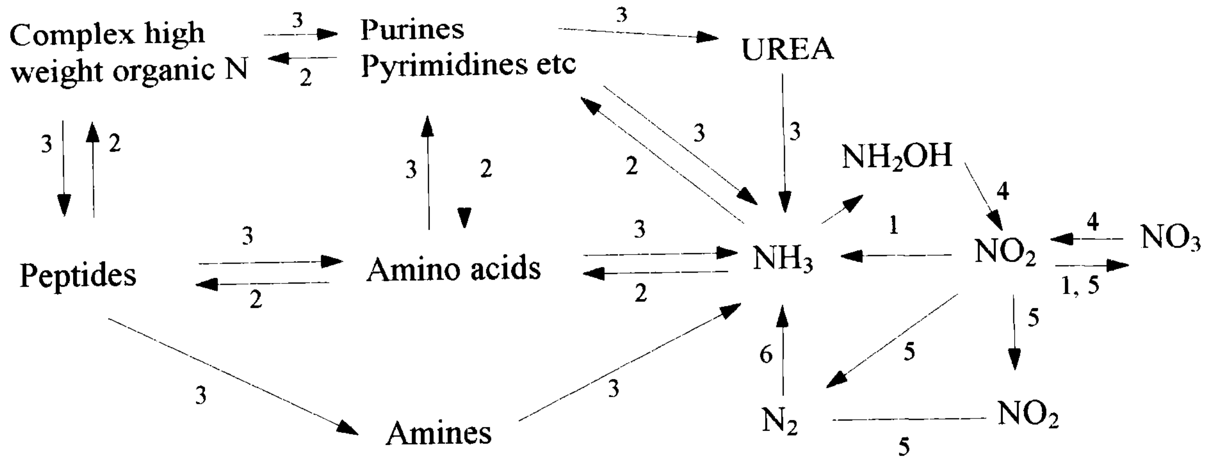


Fig. 5.2 Simplified nitrogen cycle showing molecular transformations:
1) Nitrate assimilation 2) Ammonia assimilation 3) Ammonification
4) Nitrification 5) Denitrification 6) Nitrogen fixation

(Brezonik L. Patrick, 1972)

By far the greatest influx of inorganic nitrogen into organisms results from ammonia and nitrate assimilation. These reactions predominate in surface waters and are mediated primarily by phytoplankton. Nitrate tends to be the predominant inorganic nitrogen compound in surface waters but there is considerable evidence that ammonia is the preferred form for planktonic assimilation, since it is already at the reduction level. Thus the concentration of nitrate in the open sea will generally be very low (~1 $\mu mol.l^{-1}$) in the euphotic zone while below this layer it shows increasing trend reaching 35 to 45 $\mu mol.l^{-1}$ in deep oceans. In certain areas of restricted circulation and where the productivity in the surface layer is high such as in northern Arabian Sea, the Eastern Tropical North Pacific the Baltic and the Black Seas and in the Cariaco Trench in the Caribbean Sea the oxidation of organic matter proceeds at such a rate that oxygen is completely depleted resulting in anoxic conditions (Sen Gupta, 1973). Under these conditions the mineralisation of organic matter proceeds via denitrification in which bacteria utilize the energy from nitrate to break the organic matter while nitrate itself is reduced to ammonia and / or molecular nitrogen with nitrite as intermediate product. According to Mckinney and Conway (1957) the oxygen required for the oxidation of organic matter is removed selectively in the order of precedence:

$O_2 > NO_3^- > SO_4^{2-} > CO_3^{2-}$.

Since the major source of nitrogen compounds in estuaries is runoff, their concentration in river water is expected to be high decreasing towards the sea-end. However, biological activity will play important role in controlling the concentrations of nitrogen compounds in surface waters.

Distribution of the various nitrogen compounds in the estuarine system was estimated for an understanding of the variations with respect to seasons and location of the estuary. For this purpose, the nitrogen compounds determined were $NH_3$-N, $NO_3$-N, $NO_2$-N and Total N. From the total N concentration total organic N was computed by subtracting the total inorganic fractions ($NH_3$ + $NO_2$ + $NO_3$). As discussed earlier, the temporal variations have been presented for marine dominated area (M1 & M2), estuarine area (M3 & M4) and freshwater dominated area (M5 & M6) and for reference purpose M0 and M7 values have been compared.

Distribution of $NH_3$ in M1 and M2 (Fig 5.3) showed that the concentration of this nitrogen compound varied between 0.43 (April) - 3.56 $\mu$mol.$l^{-1}$ (September) along the marine dominated area (MDA), 0.40 (December) to 3.86 $\mu$mol.$l^{-1}$ (September) in the estuarine area (EA) (Fig 5.4) while fresh water dominated areas (FDA) showed the concentration between 0.51 (December) and 3.93 $\mu$mol.$l^{-1}$ (September) (Fig 5.5). The seasonwise variation of concentrations indicated that during premonsoon it was low between 0.43 and 1.73 $\mu$mol.$l^{-1}$, during monsoon it varied between 1.04 and 2.76 $\mu$mol.$l^{-1}$ whereas, post monsoon season the concentration was comparatively high ( up to 3.93 $\mu$mol.$l^{-1}$).

$NO_2$-N concentration varied between zero and 2.9 $\mu$mol.$l^{-1}$ during May and January respectively for MDA (Fig 5.6) whereas, it was 0.07 (August) - 2.9 $\mu$mol.$l^{-1}$ (January) and Zero (July) - 2.95 $\mu$mol.$l^{-1}$ (January) at EA (Fig. 5.7) and FDA (Fig 5.8) respectively. Seasonal variability of $NO_2$ indicated that it was between zero and 1.31 $\mu$mol.$l^{-1}$ during premonsoon. During monsoon the concentration of $NO_2$ varied between Zero to 2.88 $\mu$mol.$l^{-1}$ and it was 0.03 and 2.9 $\mu$mol.$l^{-1}$ during the post monsoon season. $NO_2$ concentration were considerably low throughout the estuary during February (0.02-0.04 $\mu mol.l^{-1}$) whereas, in the preceding month it was high (0.55 - 2.9 $\mu mol.l^{-1}$). An interesting aspect noticed during monsoon was that during the beginning of monsoon the concentration increased in the estuary (0.73 - 2.88 $\mu mol.l^{-1}$) and during the following months the concentration in the upper reaches (upstream) of the estuary was low compared to the mouth and coastal regions.

Examination of the $NO_2$ data indicated that the distribution of this nitrogen compound in the estuarine region was closely related to the biogeochemical processes taking place in the estuaries rather than the general input into the estuaries. If the river runoff was the major source of input of $NO_2$ into the estuaries, $NO_2$ values should have shown the peak through out the estuary during monsoon season. At MDA and FDA the peak of the values were observed during post-monsoon periods (January) whereas, in the EA besides the peak observed in January the predominant peak was noticed during monsoon. This clearly shows that the $NO_2$ concentrations noticed in the estuary was a product of transformations taking place in the estuarine region presumably from the nitrogenous organic matter brought into the region during monsoon flows. Ammonia ($NH_3$ + $NH_4$) concentrations also support this view that high ammonium concentrations estimated during post-monsoon throughout the estuary in the water column was mainly due to the ammonification processes of the organic matter brought into the estuary during runoff and subsequent nitrification processes would have been responsible for the high $NO_2$ content. Since this process is reversible and simultaneous metabolic and geochemical processes taking place in this region would have altered the concentration subsequently.

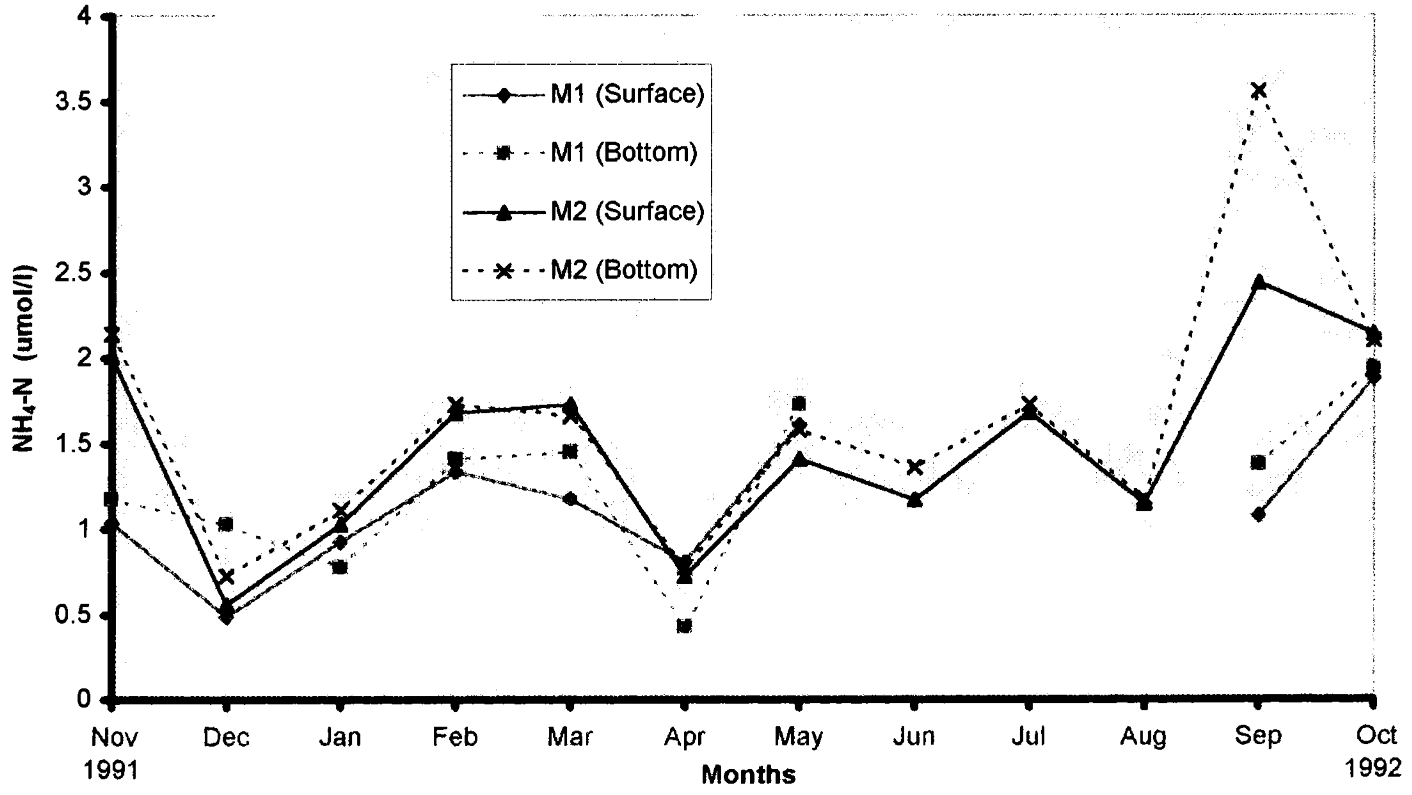


Fig. 5.3 Distribution of $NH_4$-N in the water of M1 & M2

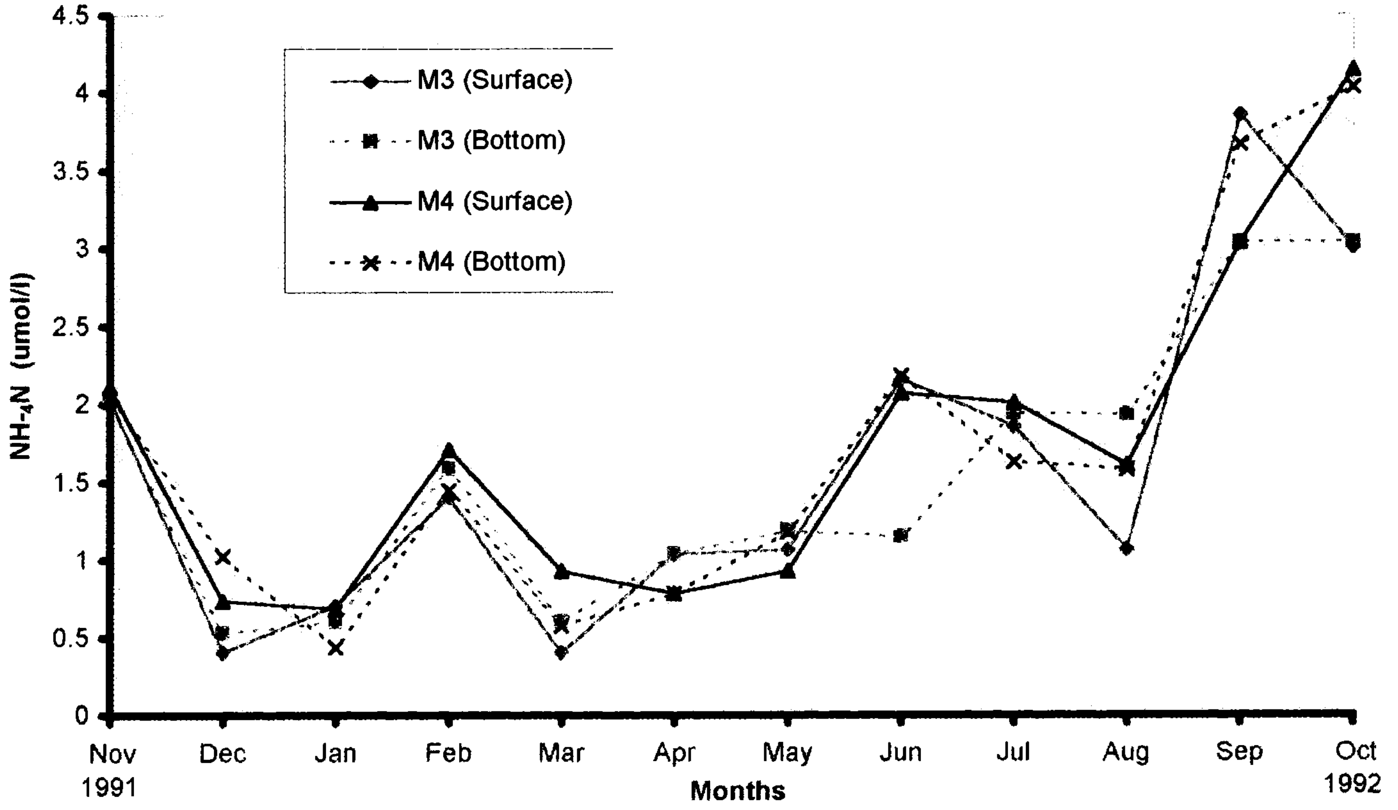


Fig. 5.4 Distribution of $NH_4$-N in the water of M3 & M4

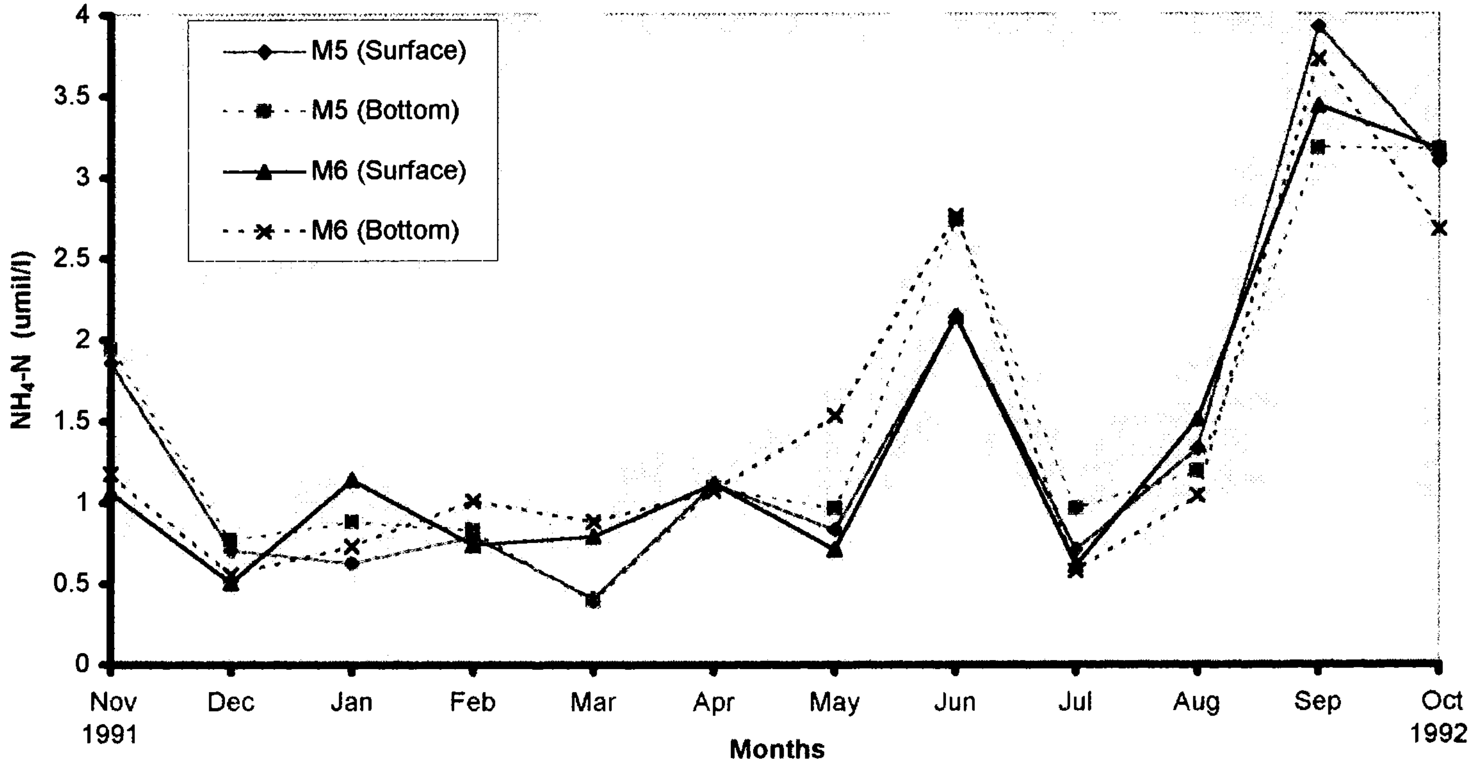


Fig. 5.5 Distribution of $NH_4$-N in the waters of M5 & M6

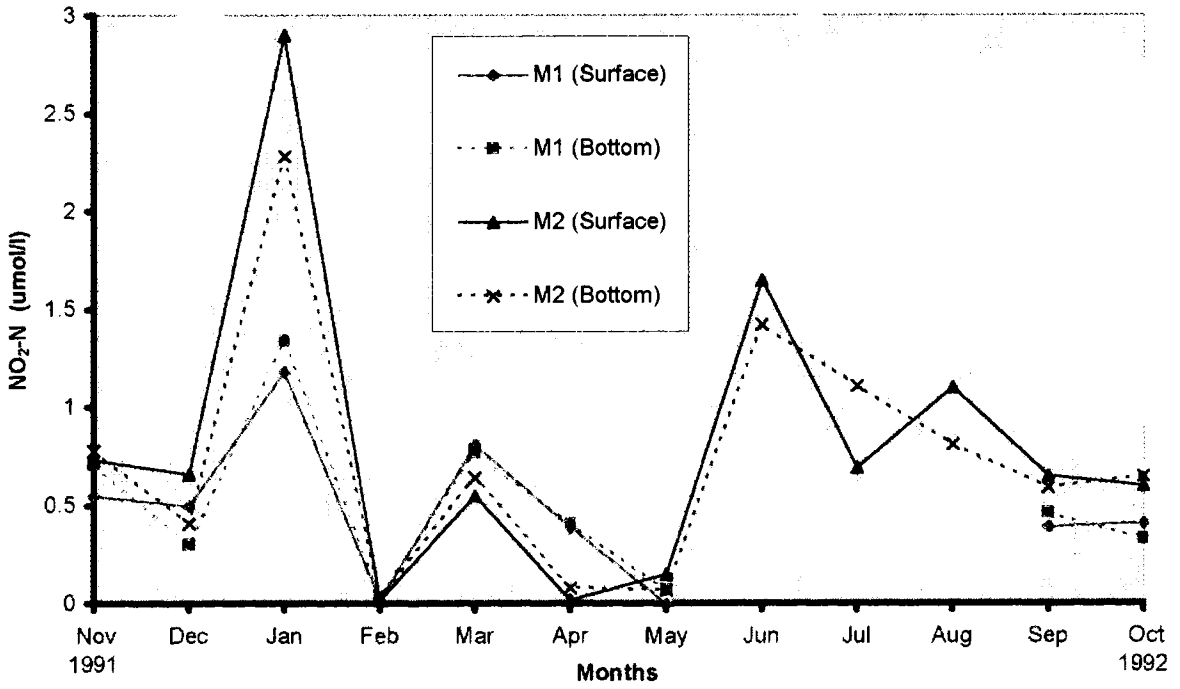


Fig 5.6 Distribution of $NO_2$-N in the waters at M1 & M2

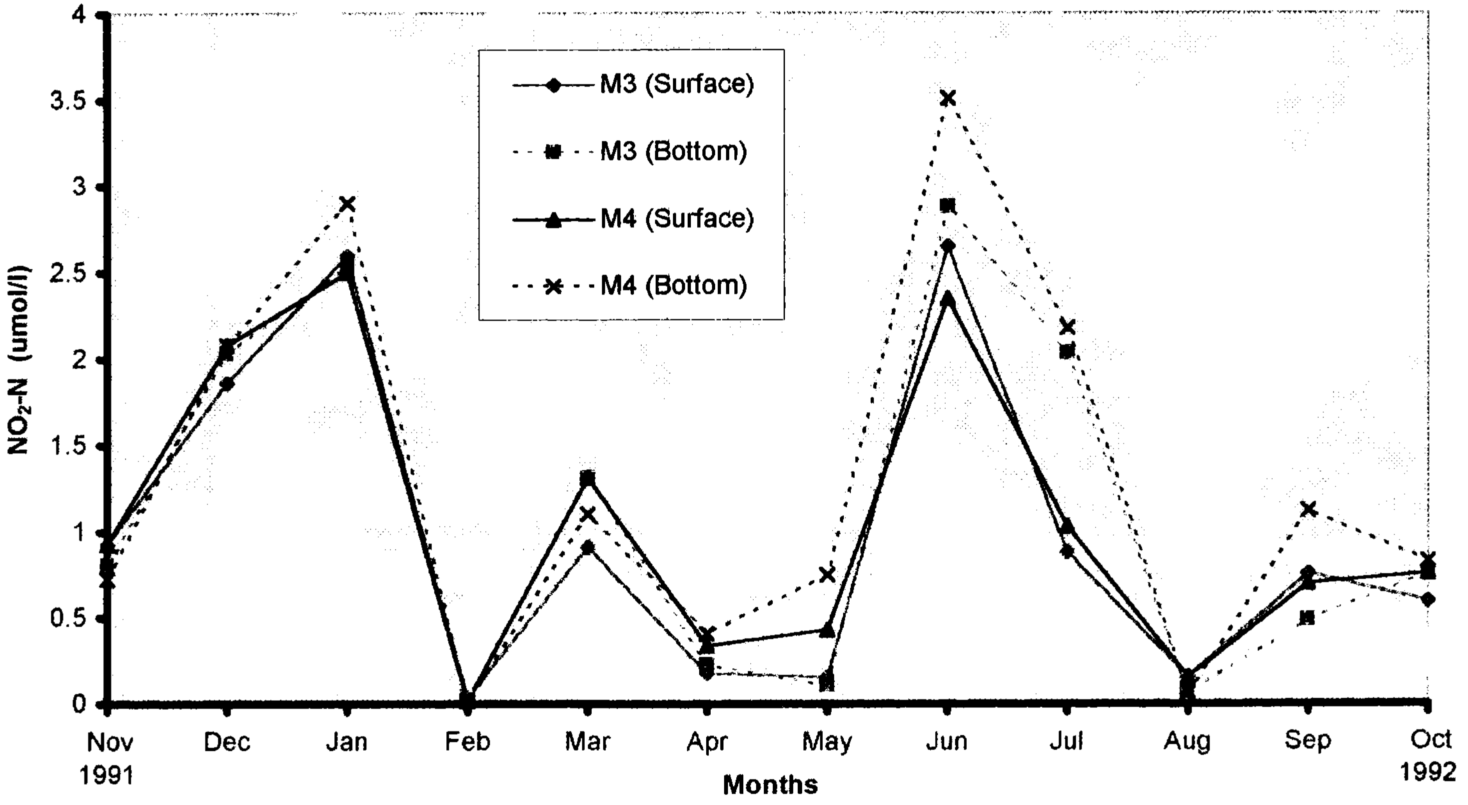


Fig. 5.7 Distribution of $NO_2$-N in the waters at M3 & M4

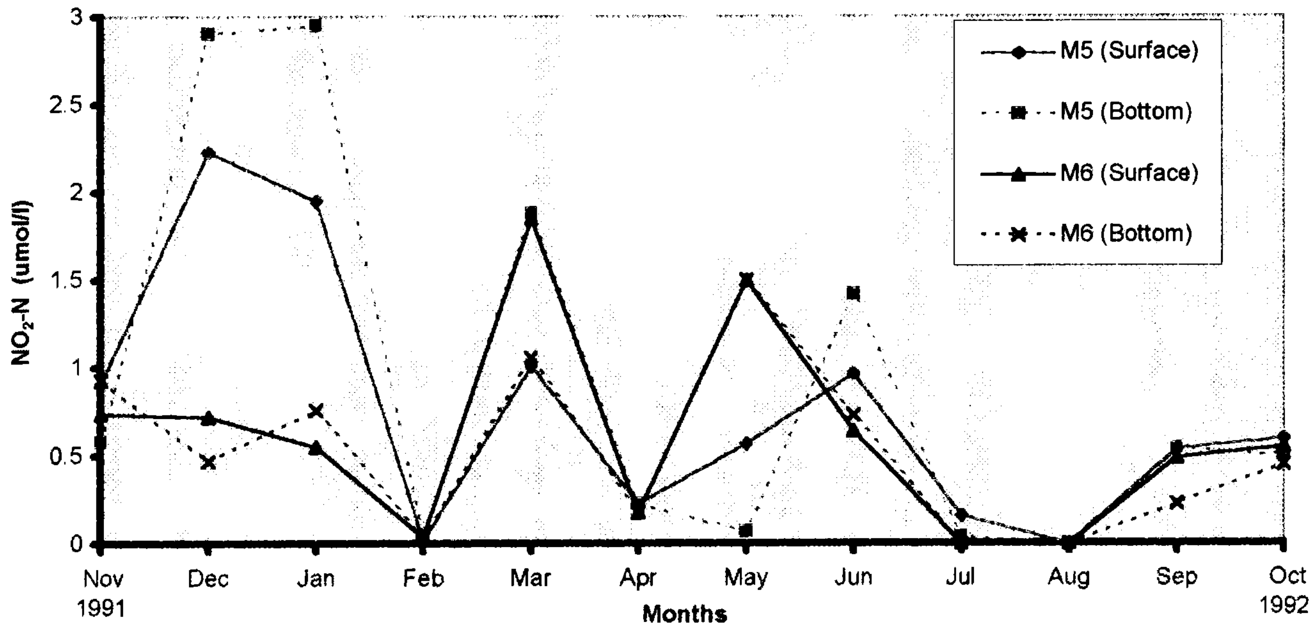


Fig. 5.8 Distribution of $NO_2$-N in the waters at M5 & M6

Nitrate-nitrogen concentration showed a significant relationship with the freshwater flow condition and therefore, its concentration was following a more or less seasonal trend. Concentration in the MDA (Fig 5.9) varied between 0.07(May) -11.88 µmol.l$^{-1}$(July). The distribution of $NO_3$ in this area clearly showed two peaks (January and July) and during premonsoon season it showed minimum concentration. In general, bottom waters showed higher concentrations compared to the surface except in one or two occasions (August and September).

Concentration in the region closer to the sea (M1) was less as compared to the inner stations(M2) Estuarine Area(M3 & M4) also showed (Fig 5.10) more or less the same trend of variations as that of MDA. In this area, the concentration varied hetween 0.41 (May) to 11.7 µmol.l$^{-1}$ (July). However, as in the case of MDA the main peak could be observed during July and a secondary peak which also was well pronounced, could be seen during December. As expected the minimum could be observed during May in EA also due to the uptake by organisms. Distribution of $NO_3$-N in the FDA (Fig 5.11) also showed seasonal variations as in other areas with maximum observed during monsoon months. Two more maxima observed during December and March indicated that this fraction of nitrogen has the same input sources at the upstream region of the estuary other than river runoff.

Premonsoon concentrations of $NO_3$-N varied between 0.04 and 12.17 µmol.l$^{-1}$ in the Mandovi estuary. It was between 2.06 and 12.54 µmol.l$^{-1}$ during monsoon, whereas, 0.44 to 12.2 µmol.l$^{-1}$ was the range of concentrations during the post monsoon period. Therefore, the general trend of variation of $NO_3$-N exhibited an interesting seasonal relationship. In general, concentration of $NO_3$-N in bottom waters were comparatively higher than surface waters and except during December at M3 and M4 and M5, the range of variation in surface and bottom waters were not very significant. The estuary in general showed fairly high concentration of $NO_3$-N indicating the intensity of various N-transformation processes taking places in this environment. As in the case of $NH_3$ and $NO_2$ the concentration of $NO_3$ also showed peaks during post monsoon period. It could be presumed that during this period the transformations of organic nitrogen brought into the estuary get transformed into $NO_3$ via $NH_3$ and $NO_2$ through ammonification and nitrification processes. Considering the importance of inorganic forms of nitrogen in the process of assimilation by phytoplankton an attempt has been made to compute the total inorganic forms of nitrogen which is the sum of ($NH_3$+$NH_4$)-N + $NO_2$-N and $NO_3$-N. Total inorganic nitrogen in the MDA (Fig 5.12) varied between 0.01 (April) and 14.72 $\mu$mol/$l^{-1}$(July). Not much variations could be observed in the EA (Fig 5.13) and in this region the concentration varied between 1.64 (May) and 15.67 $\mu$mol.$l^{-1}$ (July). Whereas, the range of concentrations in the FDA (Fig. 5.14) were between 1.76 (April) and 15.85 $\mu$mol.$l^{-1}$ (December). The distribution in MDA showed two maxima - a well pronounced one during July and a less pronounced one during January - and a single minimum during April. EA also showed a similar trend as that of MDA showing the maxima during July and December with the minimum during May. Concentration in the FDA showed a fluctuating trend with maxima during December, March and July. In general, bottom waters showed higher concentrations of combined inorganic nitrogen compared to the surface waters. A close examination of the data indicate that the total inorganic nitrogen showed more or less similar trend of distribution as that of $NO_3$-N as this fraction of inorganic -N was the principal form throughout the estuary.

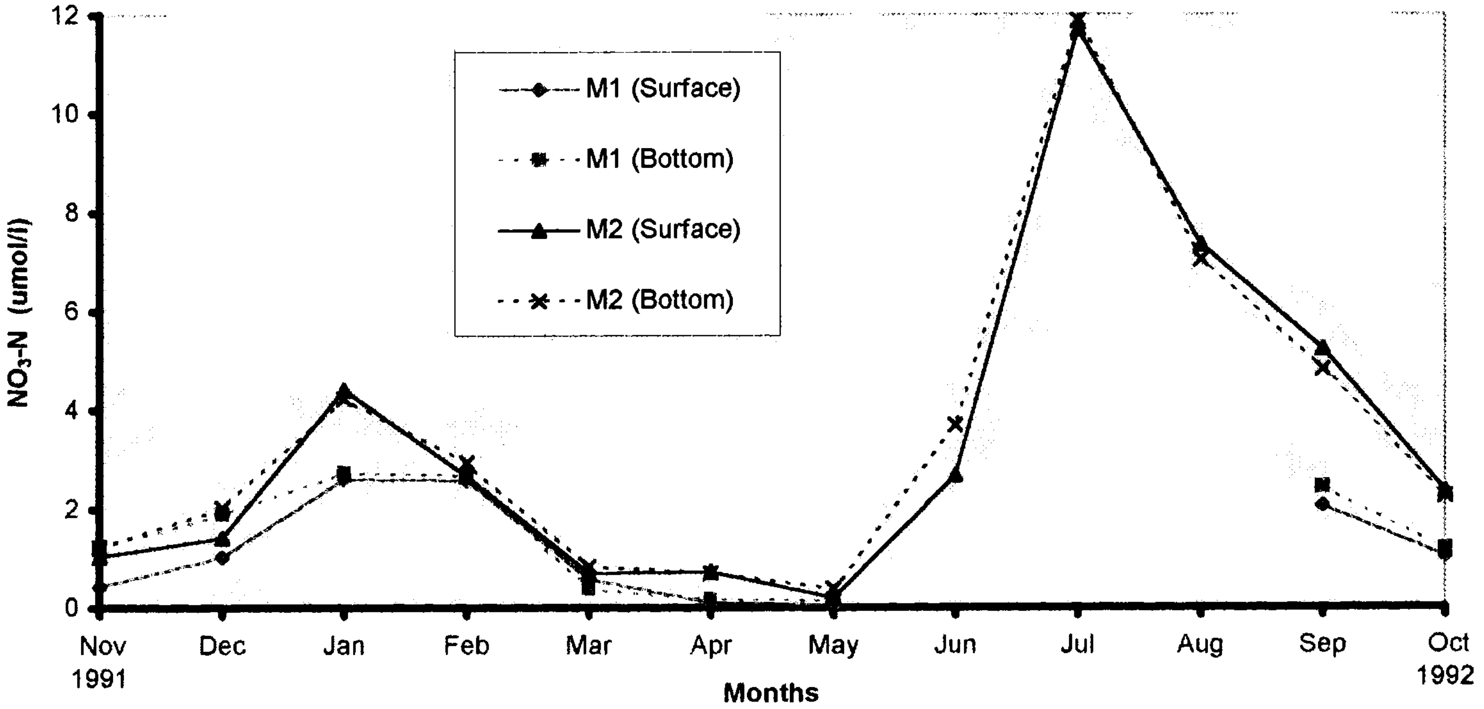


Fig. 5.9 Distribution of $NO_3$-N in the waters at MDA (M! & M2)

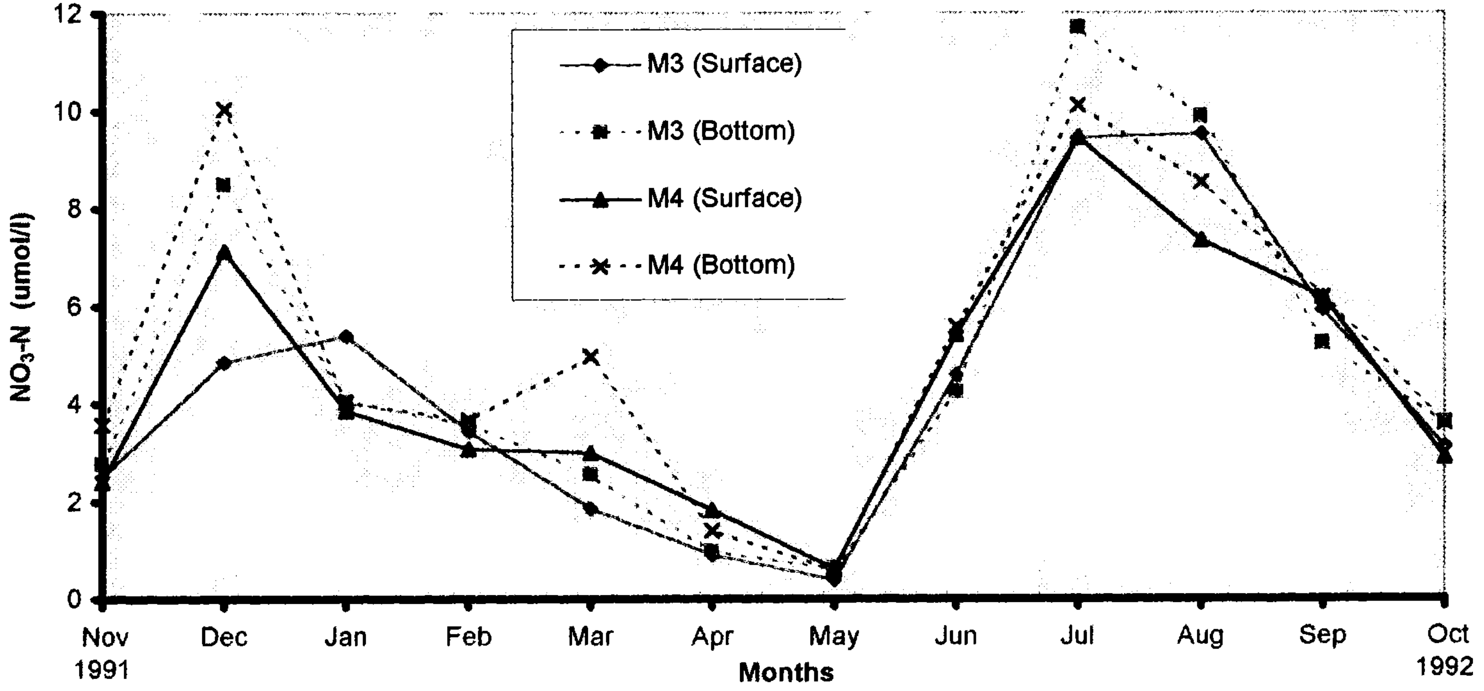


Fig. 5.10 Distribution of $NO_3$-N at EA (M3 & M4)

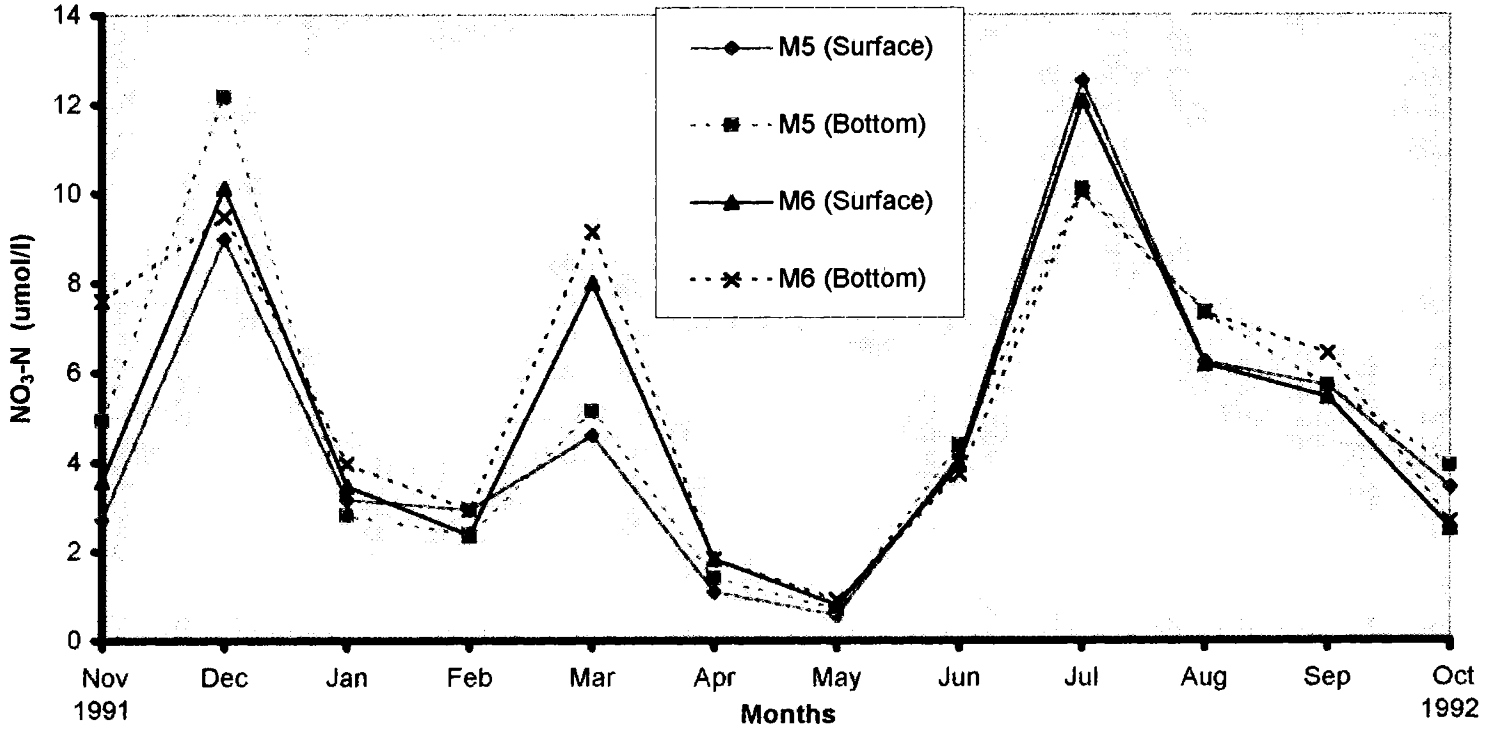


Fig. 5.11 Distribution of $NO_3$-N for FDA (M5 & M6)

Estimation of the total nitrogen in the estuarine waters indicated that the variation of concentration in MDA (Fig 5.15) was between 4.19 (April) and 22.06 $\mu mol.l^{-1}$ (July). It varied between 4.9 (May) and 24.71 $\mu mol.l^{-1}$ in the EA (Fig. 5.16) whereas, in the FDA (Fig 5.17) Total nitrogen ranged between 2.87 (May) and 23.53 $\mu mol.l^{-1}$. Seasonal variation also has been worked out for total nitrogen in this estuarine system. Premonsoon concentrations varied between 4.19 and 15.01$\mu mol.l^{-1}$ and monsoon and post monsoon variations were between 8.11 and 25.71 and 5.17 and 23.53 $\mu mol.l^{-1}$ respectively. Distribution of Total N in the estuarine region in general do not follow a definite pattern although it exhibited relationship with freshwater inflow. Considerable amount of nitrogen is brought into the estuary during the river runoff and atmospheric precipitation. However, compared to MDA and FDA estuarine area (M3 & M4) showed higher concentrations of TN during the study period.

There is no analytical methodology as such for the estimation of organic nitrogen from water. Therefore, this fraction of nitrogen was computed from total nitrogen and total inorganic nitrogen by difference. Concentration of organic nitrogen in the estuarine region is shown in Fig 5.18 - 5.20. At MDA the concentration of organic nitrogen varied from 2.41 (October) to 11.94 $\mu mol.l^{-1}$ (January). In the estuarine area it was between 3.07 (October) and 14.11 $\mu mol.l^{-1}$(September) whereas, in the FDA the range of concentration was between 1.11 (May) and 8.52$\mu mol.l^{-1}$ (December). During premonsoon the variation in the estuary was between 1.11 and 8.91 $\mu mol.l^{-1}$. Variations in the concentrations noticed during Monsoon (2.18 - 14.11 $\mu mol.l^{-1}$) and post monsoon (2.41 and 11.94 $\mu mol.l^{-1}$) were more or less similar.

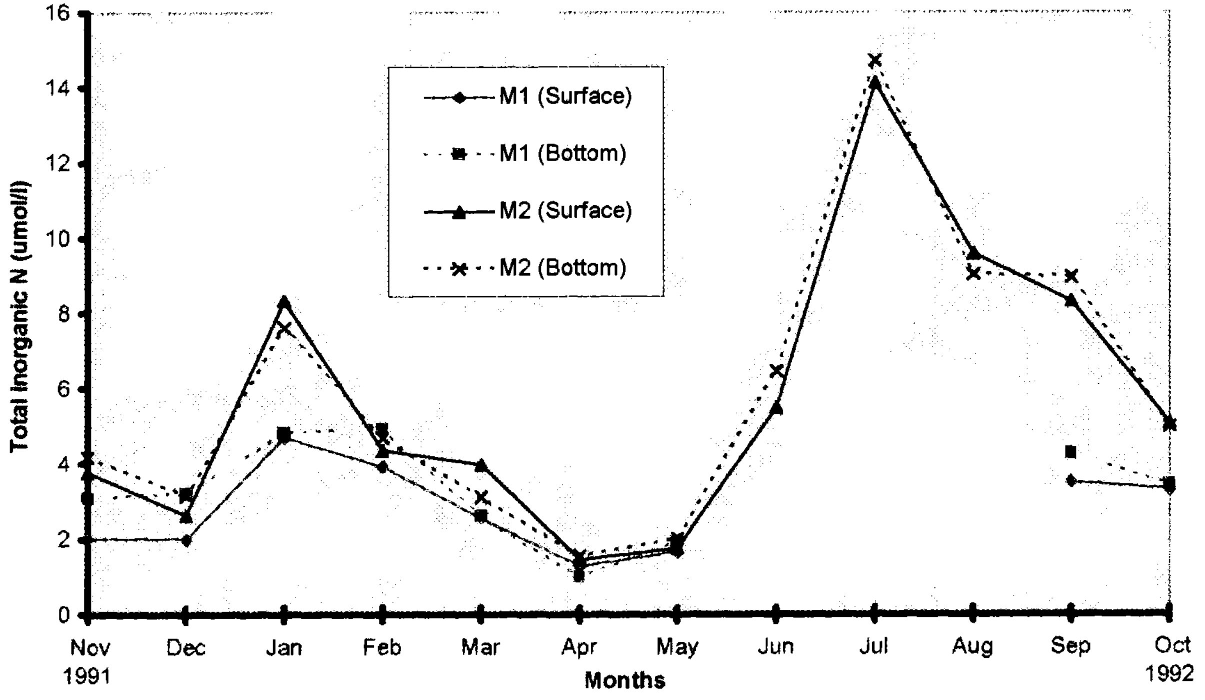


Fig. 5.12 Distribution of Total inorganic N in the MDA (M1 & M2)

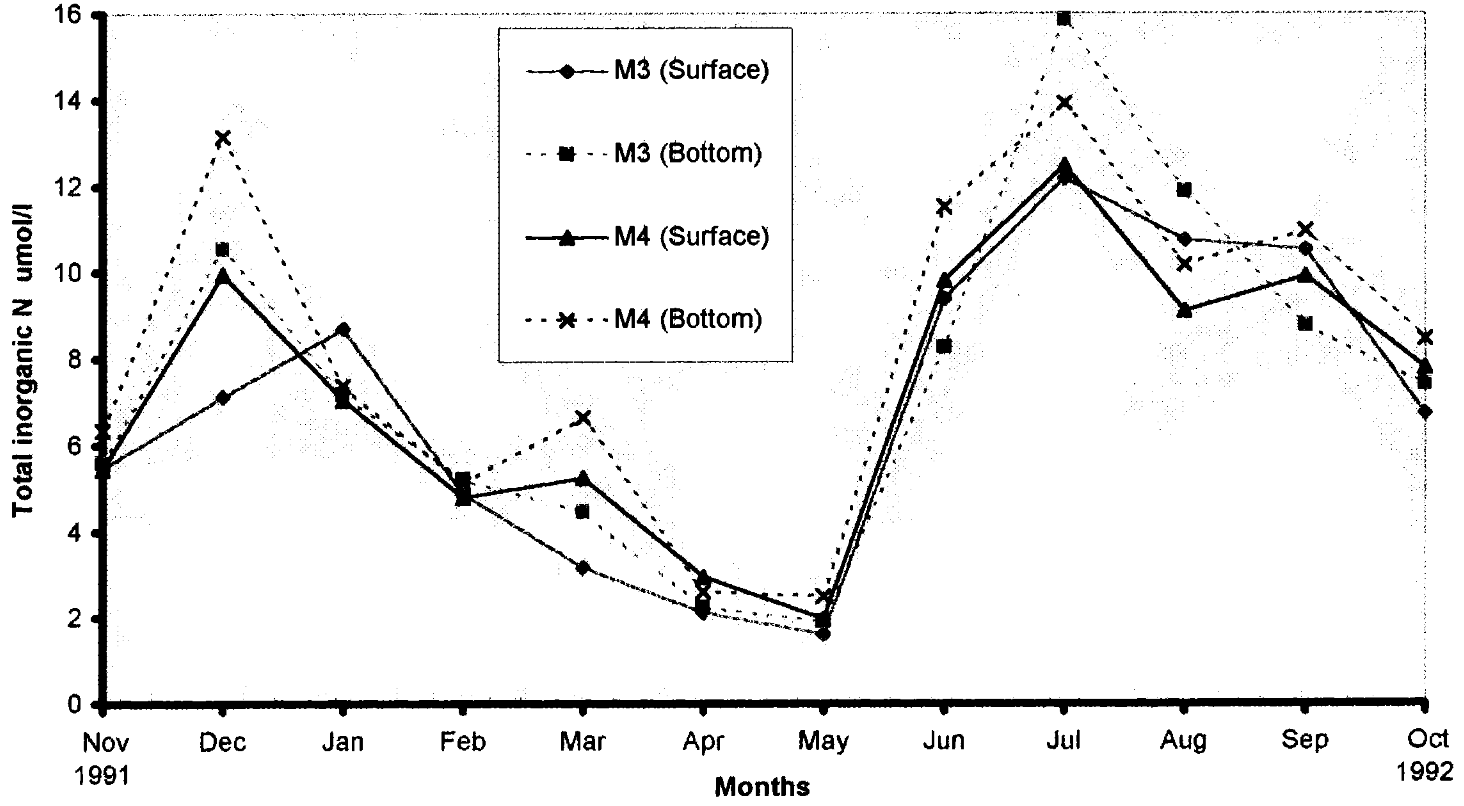


Fig. 5.13 Total inorganic N for M3 & M4

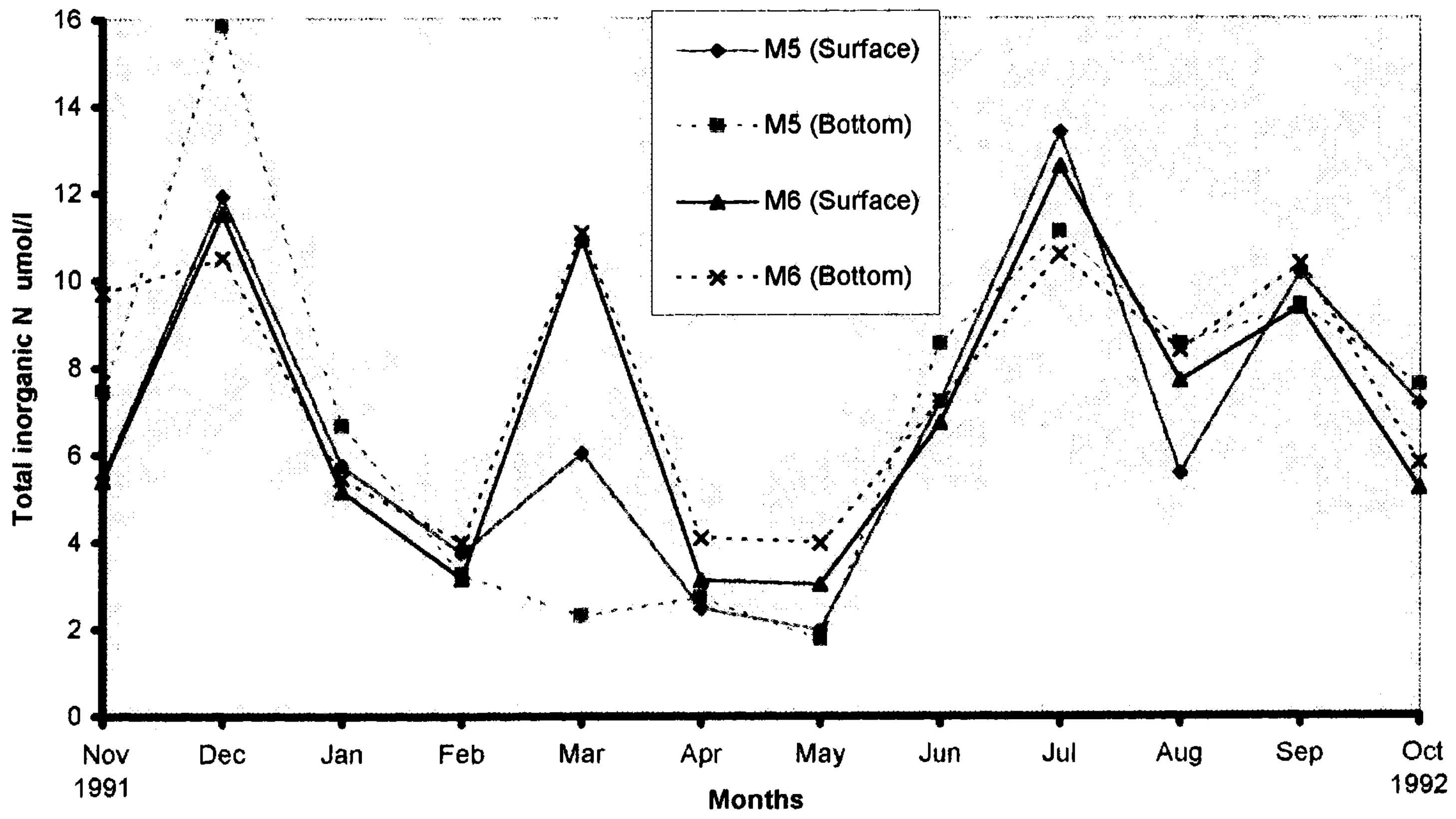


Fig. 5.14 Total inorganic N for M5 & M6

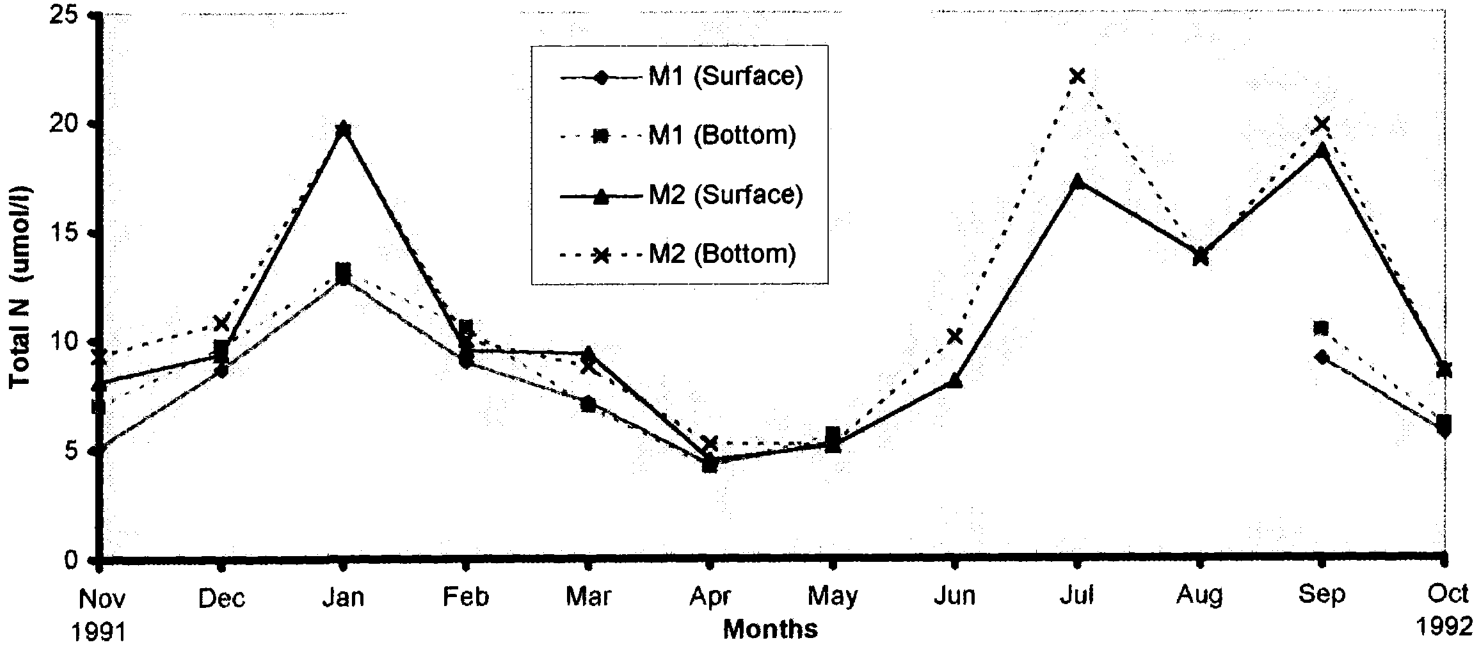


Fig. 5.15 Distribution of Total N in MDA

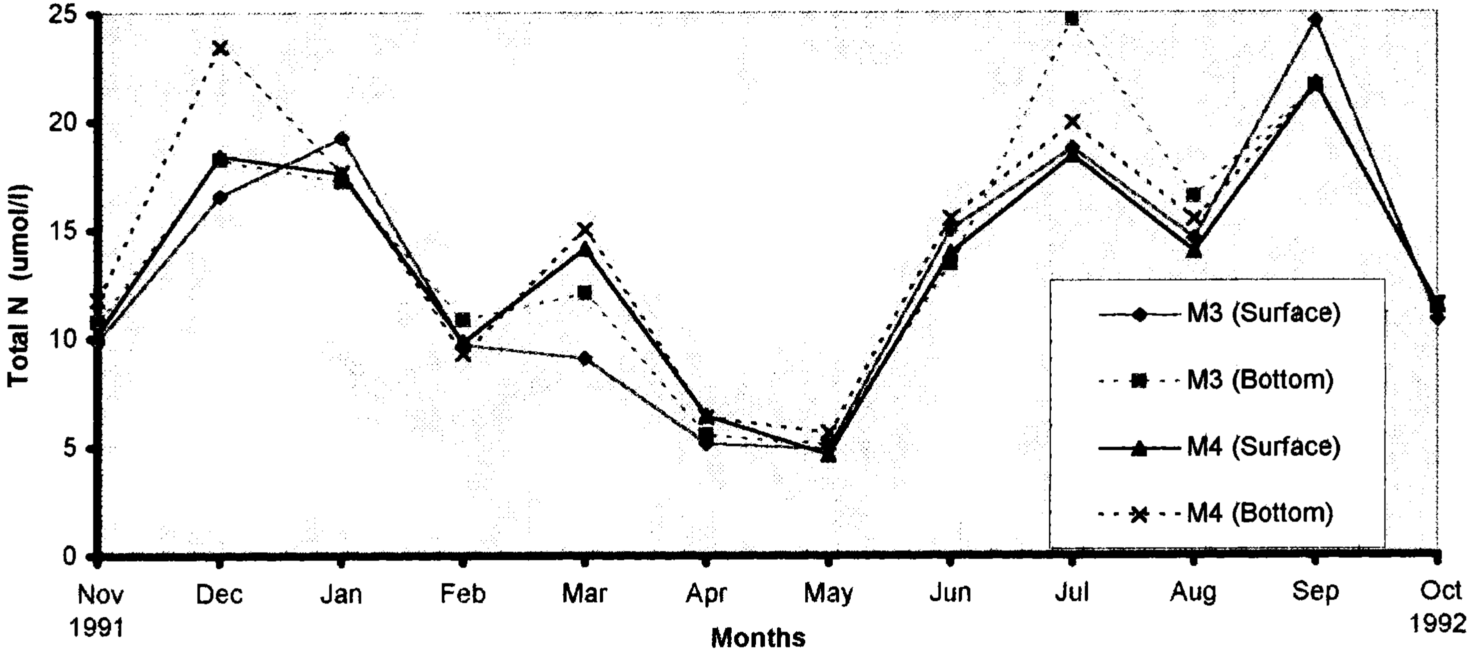


Fig. 5.16 Distribution of Total N in EA

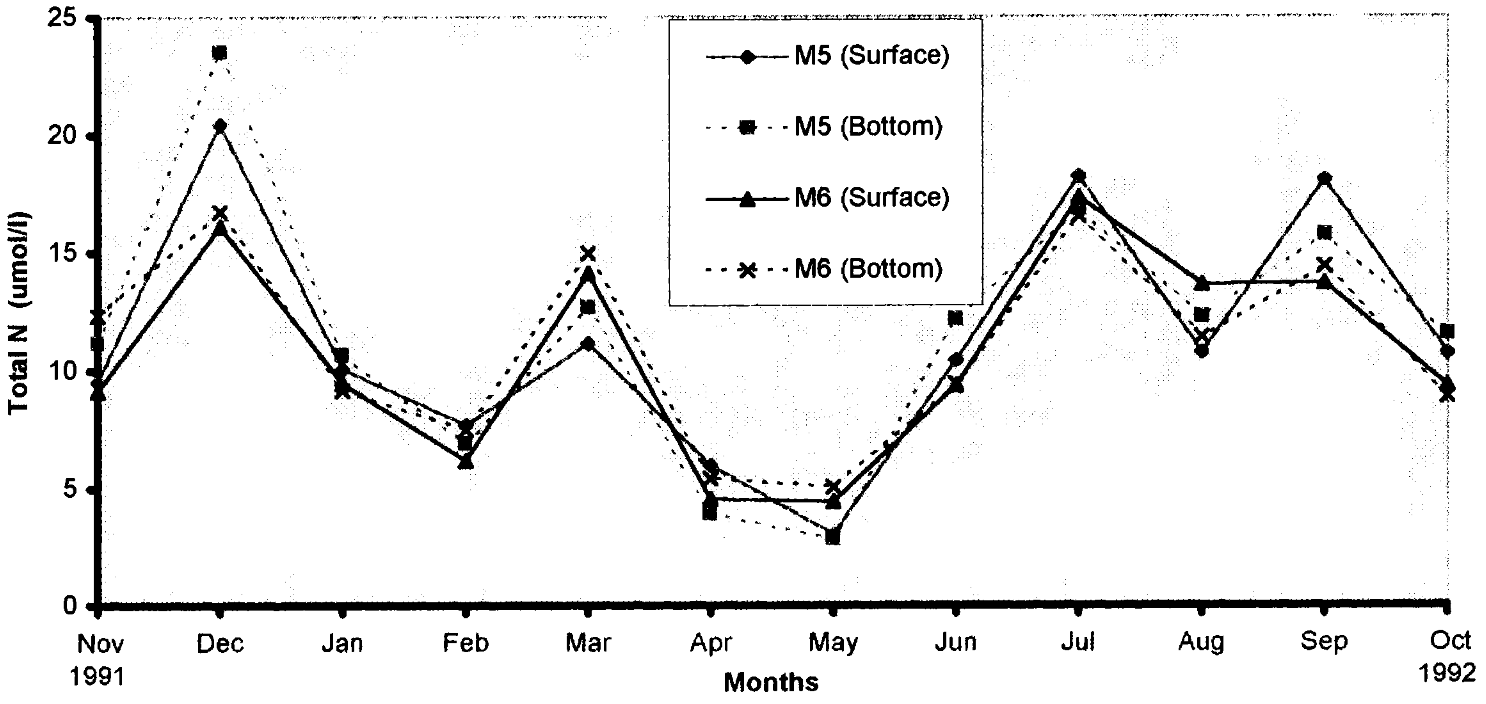


Fig. 5.17 Distribution of Total N in FDA

Percentage of inorganic-N with respect to total-N also was estimated for the estuary and the same is shown in Fig 5.21 to 5.23. The marine dominated area of the estuary exhibited generally low percentage of inorganic nitrogen except for the monsoon season. Estuarine and freshwater dominated area showed a reverse trend where inorganic-N concentrations, showed higher concentrations than organic-N. Table 5.3 shows the monthly variation of the percentage organic N in the Mandovi estuary.

**Table 5.3 Percentage of organic N in Mandovi estuary**

| Stations | Nov | Dec | Jan | Feb | Mar | Apr | May | June | July | Aug | Sep | Oct |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| M1 | 60.7 | 76.6 | 63.3 | 56.1 | 64.1 | 69.1 | 68.3 | | | | 63.1 | 41.9 |
| M2 | 53.5 | 71.7 | 57.8 | 54.2 | 57.5 | 67.2 | 65.6 | 36.1 | 18.0 | 30.1 | 55.3 | 40.8 |
| M3 | 45.0 | 58.9 | 54.8 | 49.7 | 65.1 | 58.8 | 66.5 | 37.3 | 35.1 | 26.4 | 57.2 | 34.7 |
| M4 | 46.5 | 45.9 | 60.0 | 51.0 | 62.9 | 53.8 | 57.1 | 29.4 | 32.3 | 34.9 | 54.4 | 32.1 |
| M5 | 42.7 | 41.6 | 42.8 | 51.2 | 45.8 | 58.4 | 35.1 | 30.7 | 26.8 | 29.8 | 41.5 | 33.3 |
| M6 | 40.7 | 28.4 | 45.3 | 48.9 | 22.5 | 31.1 | 32.0 | 28.0 | 27.3 | 31.5 | 31.3 | 44.1 |

Freshwater and seawater composition of the micronutrient show extreme variations. Anthropogenic inputs of nutrients to estuarine systems are a cause of over-enrichment. The input from these sources can dominate the sum of all the inputs of nutrients to estuarine systems. Liss (1976), and Carpenter et al (1969) found that a particular nutrient form may be gained or lost by chemical reactions, biological uptake or metabolic activity and/or adsorption on or desorption from suspended matter. In the absence of biogeochemical processes occurring within an estuary or export to the atmosphere, the composition of a particular element within that estuary will be a linear function of its concentration in the river and the ocean. Chloride (salinity) is the usual reference or conservative property upon which variations of other elements are measured. Therefore, hypothetical behaviour of substance in the estuarine environment plotted against salinity exhibit deviations from linearity which indicate non conservative behaviour, from which 'net loss' or 'net gain' of that particular element in the estuary could be estimated.

Salinity dilution plots (or mixing diagrams) are useful for identifying net sources and sinks of various constituents as they mix along the estuarine salinity gradient (Liss 1976). Salinity is assumed to be mixed conservatively and other constituents are compared to it as salinity increases from a freshwater 'end-member' to a saline 'end member'. freshwater 'end-member' to a saline 'end member'. There are many potentially complicating factors in the interpretation of such plots therefore this must be used with caution (Sharp et al 1982). Additionally the "net" characteristics in these plots may obscure or distort the characteristics of simultaneously occurring sources and sinks in a region.

In order to study the behaviour of nitrogen compounds during mixing in Mandovi estuary the relationships of these compounds with salinity has been worked out. $NH_3$-N and $NO_2$-N did not show any regular pattern of variation in its concentration. However, no linear relationships between these compounds and salinity could be noticed. Fig. 5.24 shows the relationships with $NH_3$-N and salinity. There was a decreasing trend in the concentration of $NH_3$-N with respect to salinity. Concentrations of the $NH_3$-N at the freshwater end of the estuary was comparatively high indicating that the breakdown of nitrogenous (mainly organic) material takes place in the upper regions of the estuary. No linear relationship between $NO_2$-N and salinity could be noticed (Fig 5.25) as the scatter was too wide.

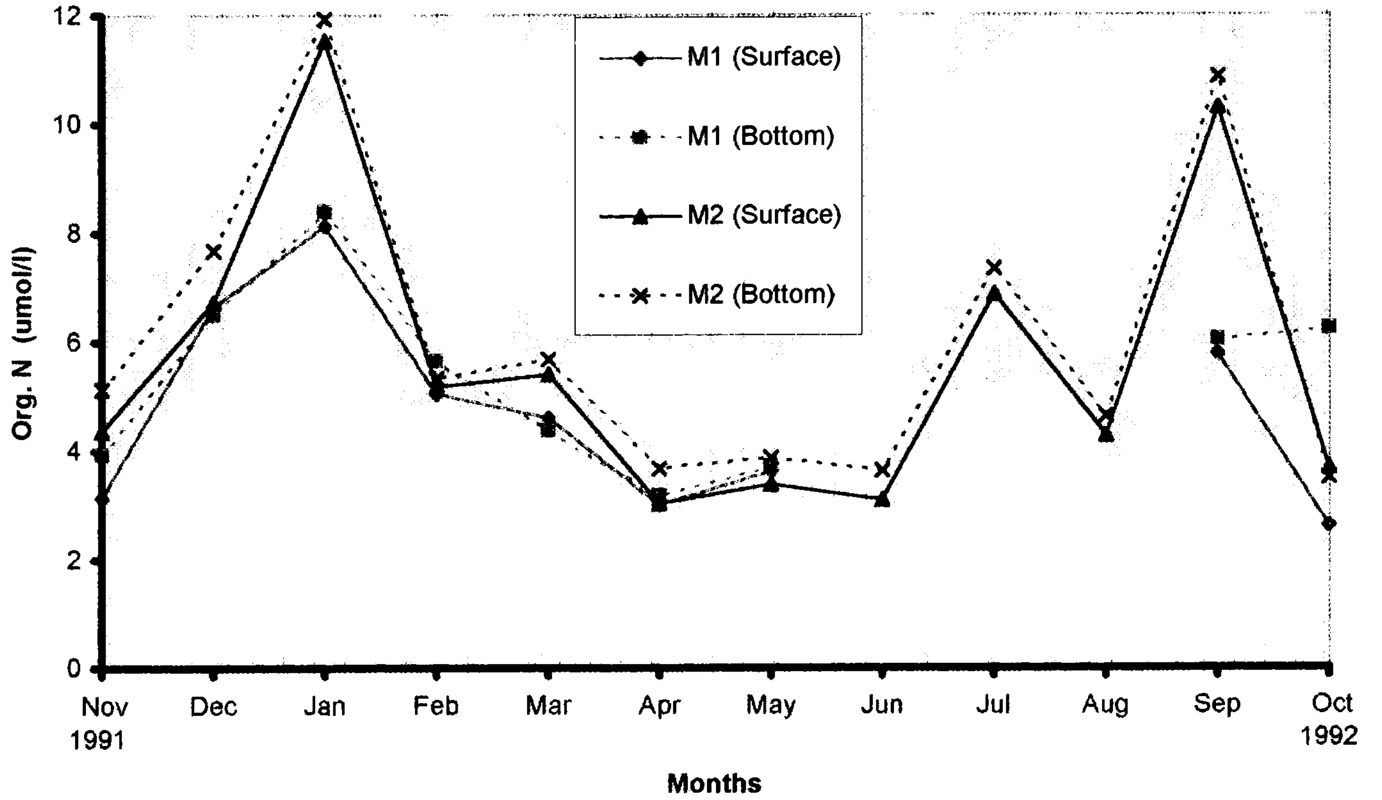


Fig. 5.18 Distribution of Organic Nitrogen in MDA

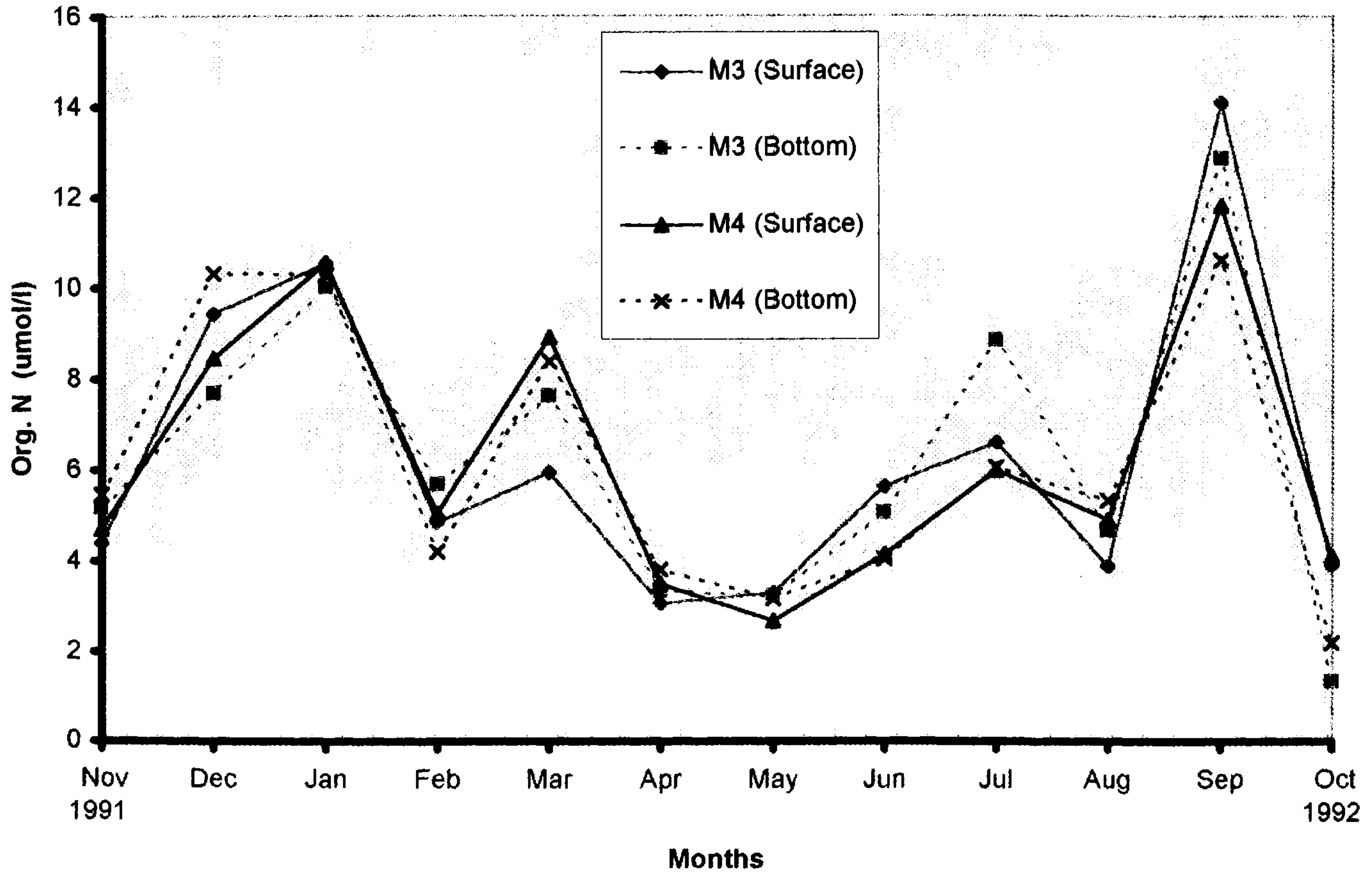


Fig. 5.19 Distribution of Organic Nitrogen in EA

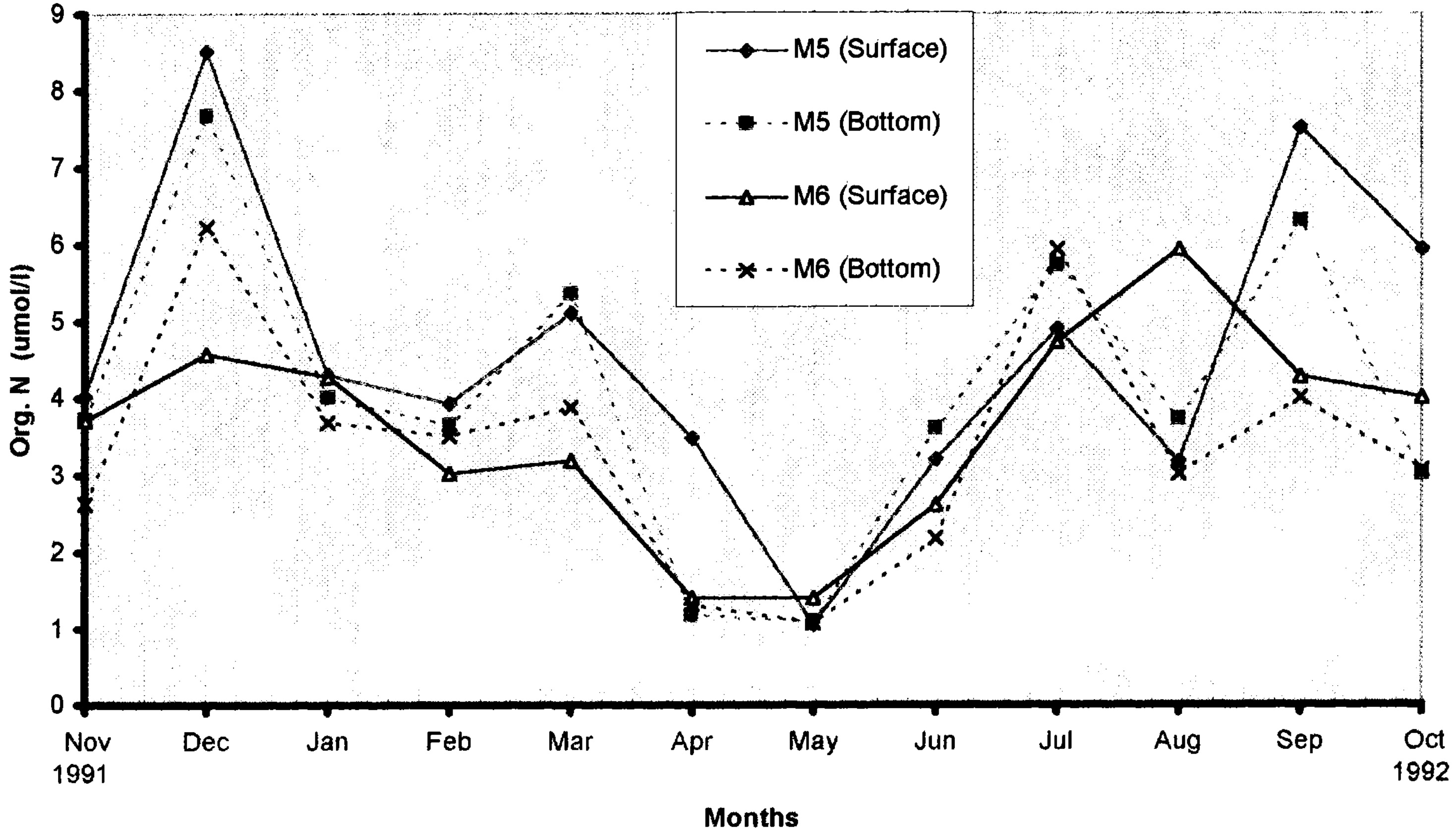


Fig. 5.20 Distribution of Organic Nitrogen in FDA

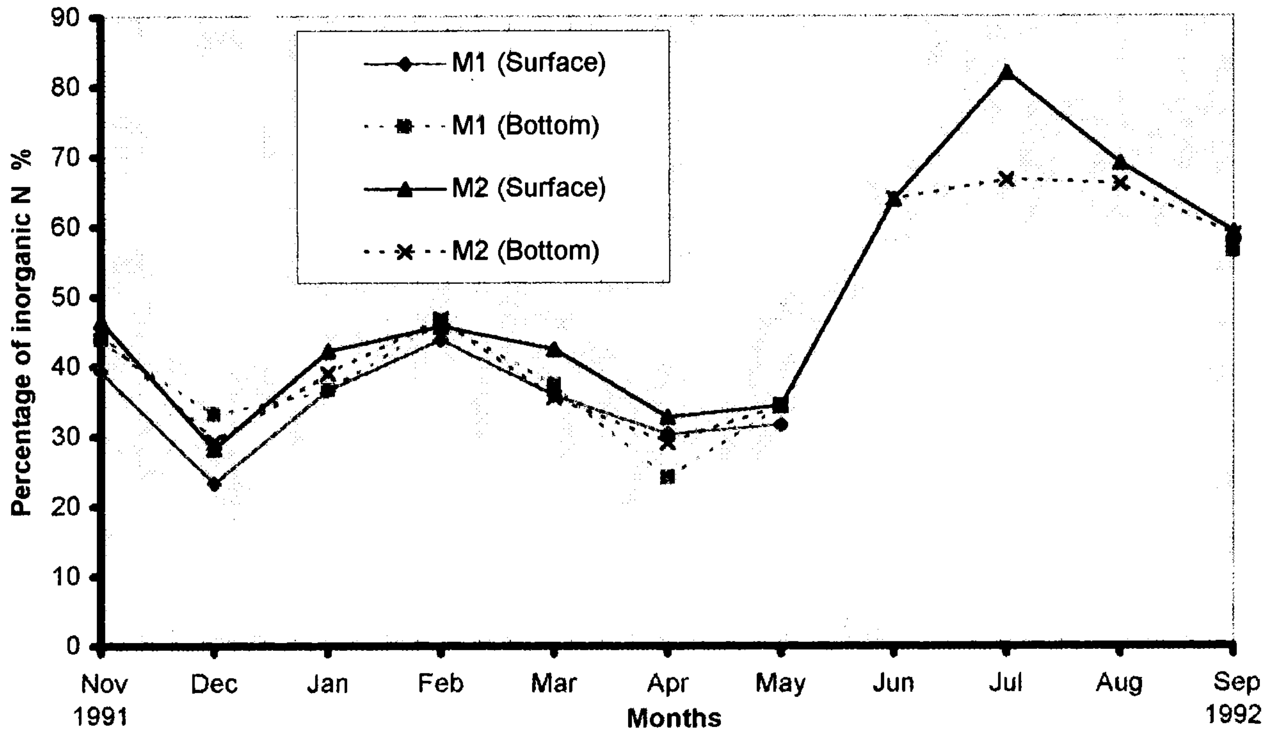


Fig. 5.21 Percentage of Inorganic Nitrogen in MDA

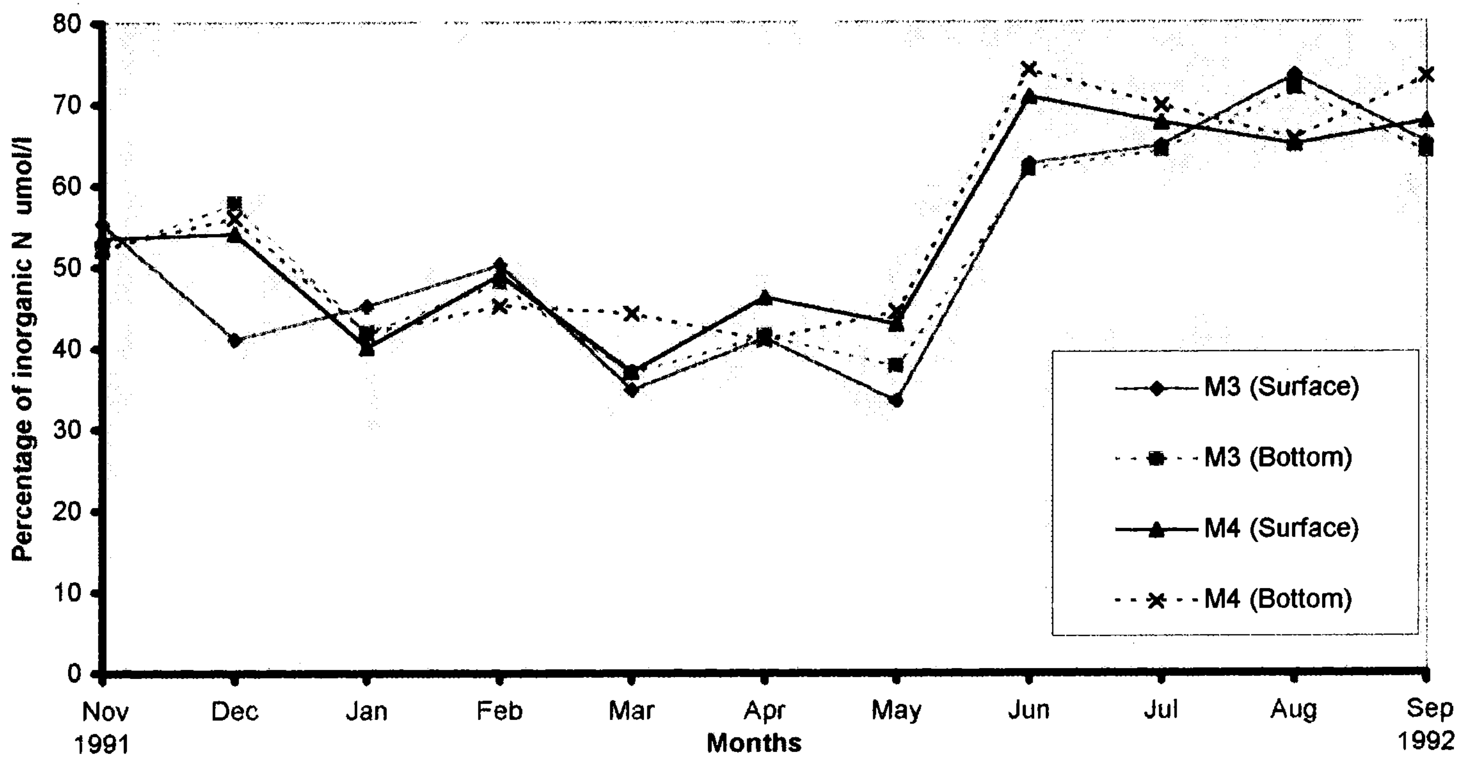


Fig. 5.22 Percentage of Inorganic Nitrogen for M3 & M4

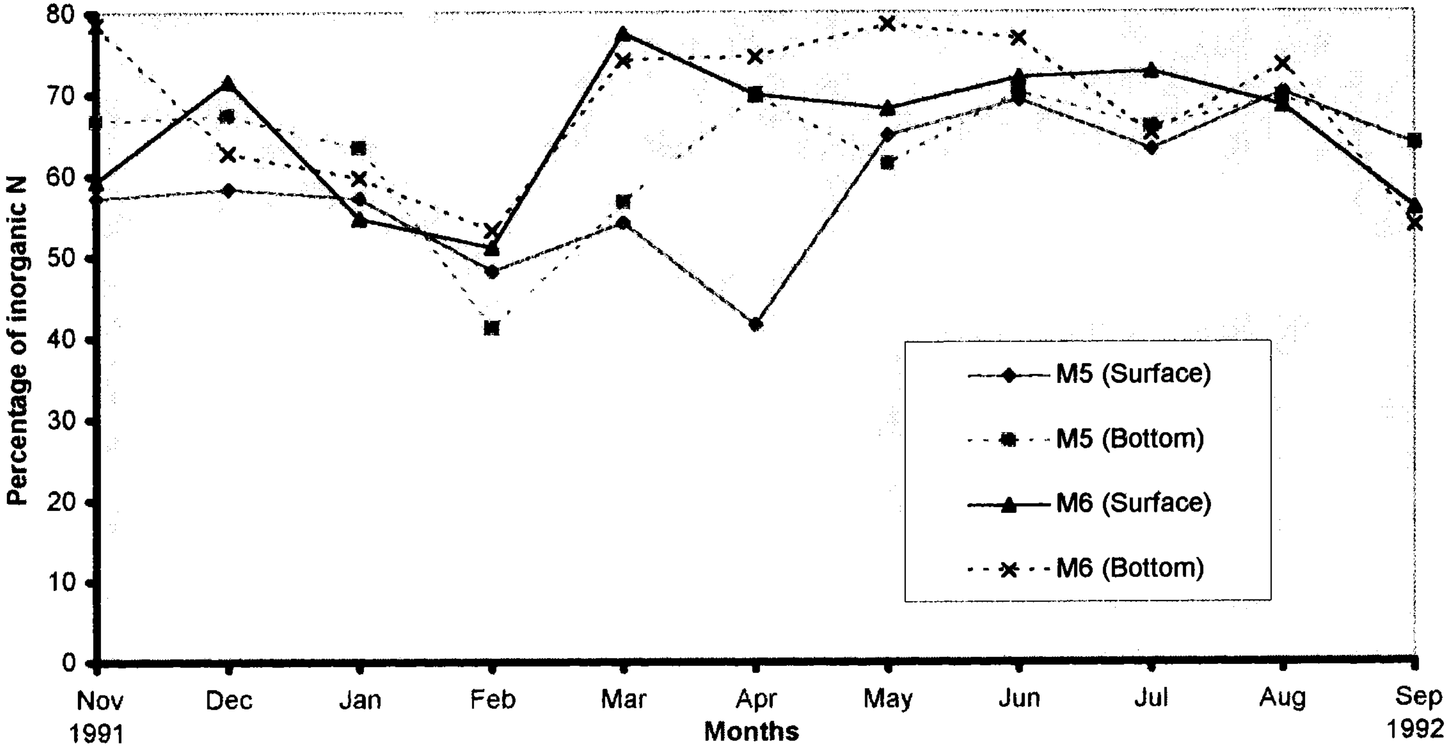


Fig. 23 Percentage of Inorganic Nitrogen in FDA

Average observed and expected concentrations of nitrate in Mandovi estuary during estuarine mixing have been worked out and shown in Table 5.4. In order to compute the nitrate concentration, the observed concentrations of nitrate at station M7 (Freshwater) are averaged over three seasons for average $NO_3$ in "source river water". Similarly, the observed nitrate concentrations at M0 also are averaged for the three seasons to get the average $NO_3$ concentrations in "source seawater". The expected concentration for different seasons, are calculated by using the mixing relationship of Carpenter et al (1975).

$$X_{sample} = X_{river} + \frac{X\,sw - X_r}{Cl\,sw}\, Cl_{sample}$$

From the average observed nitrate concentrations ($NO_{3OBS}$) and those calculated from mixing and dilution relations ($NO_{3CAL}$), the nitrate gained or lost during mixing in estuaries were determined by difference.

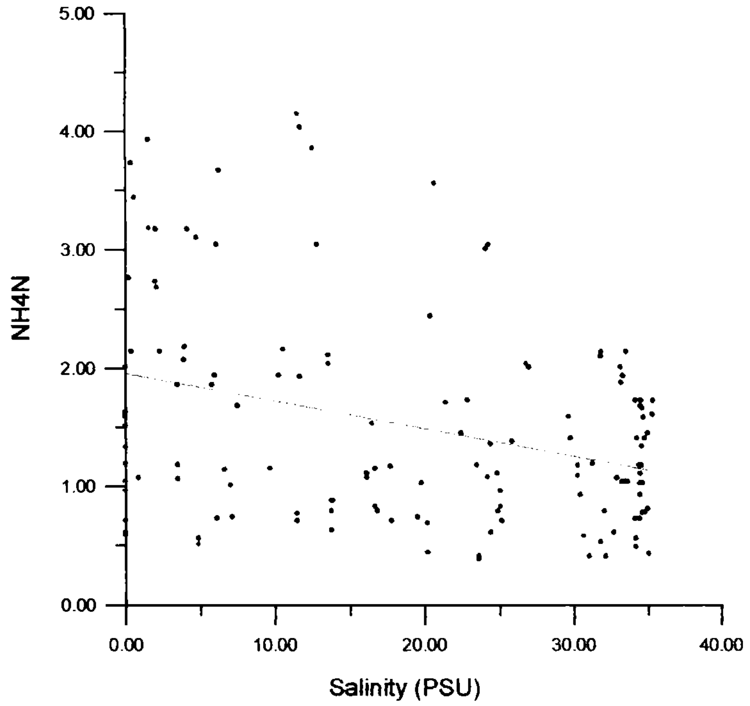


Fig. 5.24. Relationships between salinity and $NH_4$-N in the waters of Mandovi estuary during 1991-92

**Table 5.4 Observed and expected concentrations of $NO_3$-N during estuarine mixing.**

| Seasons. | NO3-N ($\mu mol/l^{-1}$) | | | $N_{cal}$ ($\mu mol/l^{-1}$) | | $N_{obs}$-$N_{cal}$ (%) | |
|---|---|---|---|---|---|---|---|
| | Sea $N_{obs}$ | Estuarine $N_{obs}$. | Riverine $N_{obs}$. | Mixing | Dilution | Mixing | Dilution |
| Pre-monsoon | 3.4 | 3.0 | 3.1 | 3.4 | 3.4 | -21 | -21 |
| Monsoon | 1.6 | 5.2 | 8.1 | 6.1 | 6.1 | +13 | +13 |
| Post-monsoon | 3.2 | 5.7 | 3.4 | 3.7 | 3.7 | +42 | +42 |

Nitrate showed a negative relationship in the estuary indicating the source at the freshwater end (Fig 5.26). This relationships was worked out by pooling the data for all the seasons together. Perhaps there would have been a some-what better linear relationships between nitrate and salinity if it was worked out seasonwise. De Sousa et al (1981) while studying the characteristics of the Mandovi estuary noticed that during premonsoon 14% nitrate was lost. The loss during monsoon was 8% which was followed by a substantial gain of 39% during premonsoon. In the present study 21% loss was estimated during premonsoon season while monsoon and post monsoon recorded 13 and 42% gains respectively. Possibility of substantial input of nitrogen from river runoff has long been established in

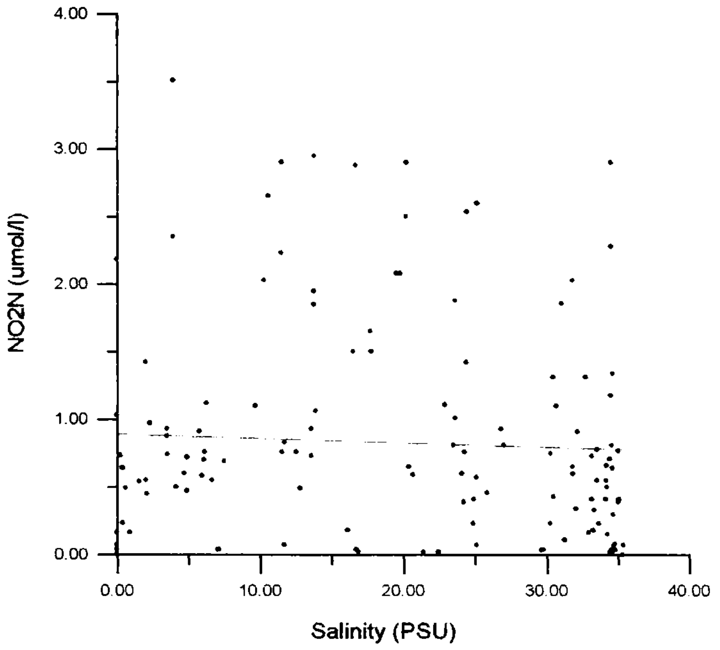


Fig. 5.25. Relationships between Salinity and NO2-N in the waters of Mandovi estuary during 1991-92

this estuarine system. De Sousa (1981) observed that explosives used in mining as another source of $NO_3$-N in these estuarine waters. Besides this large amounts of synthetic fertilizers used in agricultural lands in the basins of Mandovi also finds their way into the estuaries. All these contribute to the nitrogen content of the estuaries leading to its high concentrations during monsoon. During monsoon the turbidity of the water increases due to heavy load of suspended matter throughout the estuary. Besides this the availability of the sunlight also will considerably get reduced which ultimately be responsible for low primary productivity during this season (Dehadrai and Bhargava, 1972, Dehadrai, 1970 a). Therefore, uptake due to biological utilization during monsoon will be minimium resulting in discharging of a substantial portion of the $NO_3$-N into the sea.

Fig 5.24 indicated that $NH_3$-N concentrations in the estuary did not show any linearity in its distribution. Concentration at the high saline (marine end- member) region did not show wide fluctuations and the values ranged between 0.5 and 2.2 $\mu mol.l^{-1}$. An interesting aspect noticed in the salinity -$NH_3$ plot is that the concentration of $NH_3$-N was the highest in the salinity range between zero and 15 PSU. Probably this means that $NH_3$ production takes place in this region possibly through the breakdown of the nitrogenous organic material brought into the estuary from landward sources.

Scatter plots of $NO_2$-N and salinity (Fig. 5.25) revealed that the $NO_2$-N distribution was uniform throughout the estuary irrespective of the freshwater source. Being an intermediate product between ammonia and nitrate this nitrogen compound undergoes rapid transformation within the water column besides being assimilated by the phytoplankton.

The most abundant form of nitrogen in the major riverine inputs was nitrate. Freshwater nitrate concentrations are positively correlated with runoff and at the freshwater-end $NO_3$-N concentrations as high as 13 $\mu mol.l^{-1}$ was noticed.

At higher salinities, nitrate decreased to less than 0.5 $\mu mol.l^{-1}$ near the seaward edge. A close examination of the $NO_3$-salinity plot (Fig 5.28) indicate that the scatter was wide at upstream region of the estuary. Total inorganic nitrogen concentration also showed a more or less similar trend of distribution as that of $NO_3$-N (Fig 5.28) showing clearly the landward source of input. However, total nitrogen did not show a close relationship with salinity (Fig 5.27).

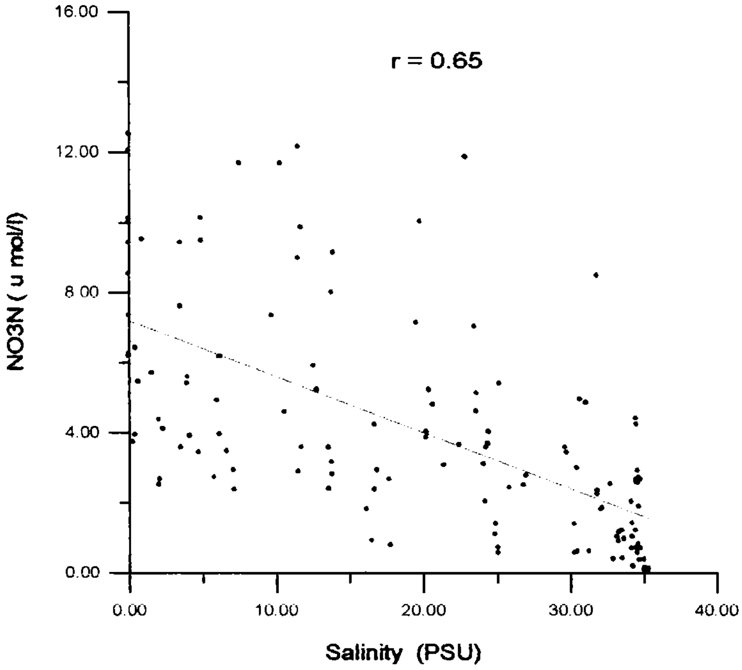


Fig. 5.26. Relationships between salinity and $NO_3$-N in the waters of Mandovi estuary during 1991-92

An attempt was made to calculate the percentage of various inorganic nitrogen compounds in total inorganic nitrogen and are given in Table 5.5. Percentage of $NO_3$-N dominated during the monsoon period reaching a percentage as high as 81.2 % of the total inorganic nitrogen. This is the period during which the estuary experienced a low rate of biological assimilation due to high turbidity and varying salinity conditions. Considerable amount of organic matter is supplied to the estuary during this period as evidenced from the suspended sediment data. As the season progressed the added $NO_3$-N was either used up or incorporated into the sediment compartment. Ammonia nitrogen which showed considerably low percentage during monsoon maintained an increasing trend during post-monsoon due to the breakdown of organic-N (Ammonification). As this process continued throughout the post-monsoon period, transformations of the released ammonium into $NO_2$-N took place during premonsoon period which either got oxidized to the stable product $NO_3$-N

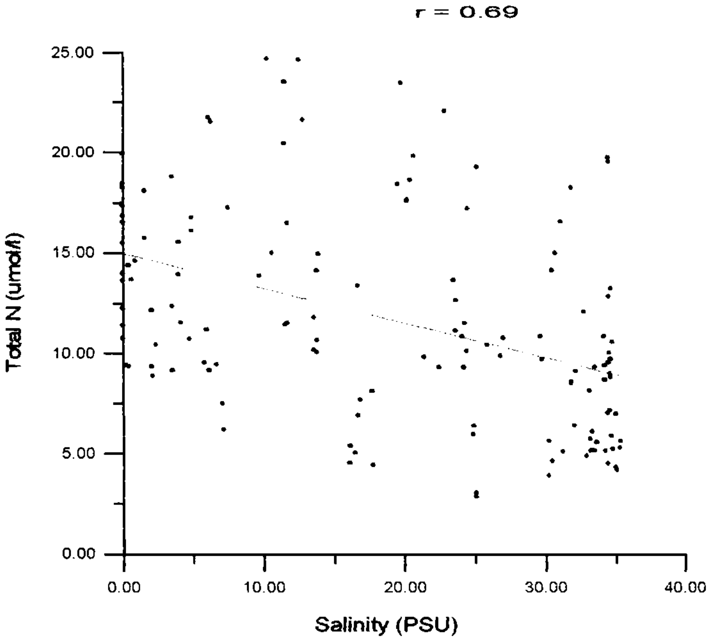


Fig. 5.27. Relationships between Salinity and Total N in the waters of Mandovi estuary during 1991-92

or partially used up by the phytoplankton. It is important to realise that the concentration changes observed are the net results of competing or opposing processes (eg. Ammonium production, uptake and oxidation to nitrate). Ammonium and nitrite always appeared to be influenced strongly by regeneration and nitrification therefore, the percentage losses or gains of these two species of nitrogen should not be correlated with the biological activity. While studying the fate of nutrients in estuaries Fisher et al (1988) suggested that $NO_3$-N was the form of TN most influenced by phytoplankton uptake in Chesapeake Bay, whereas, ammonium was more influenced in Delaware Bay. Their observation also suggested that in Chesapeake Bay about one half of the N inputs are lost from the water column, principally via nitrate consumption. Fisher et al (1988) and Magnein (1992) found that the ammonium maximum at salinities approximating 5 PSU was a regular phenomenon in some estuaries (Delaware and Chesapeake) and the large source of ammonium in the oligohaline to upper mesohaline region was most likely due to the mineralisation of nitrogen within the estuary and / or anthropogenic inputs in the region. Kemp et al (1990) observed that the oligohaline to upper mesolaline region was also an area of active vertical mixing where ammonium is regenerated from sediments in that region or transported from the mid-mesohaline region.

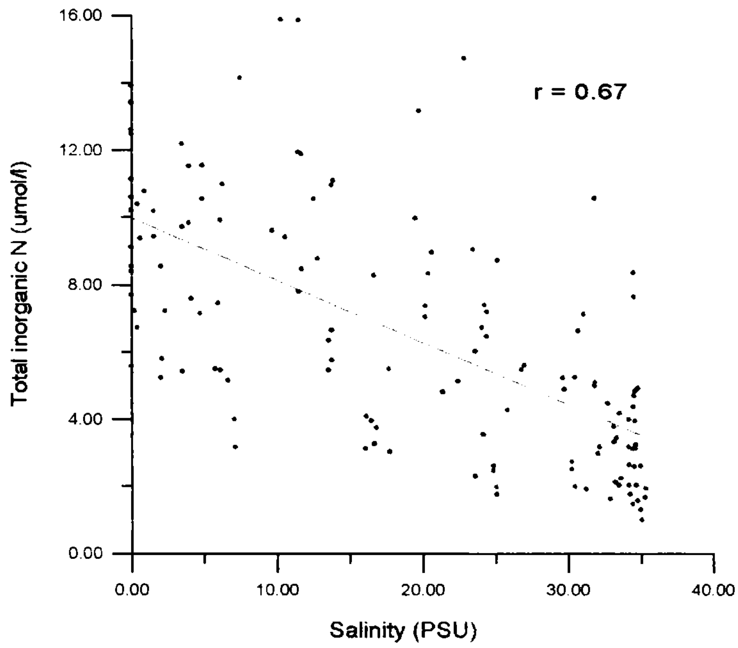


Fig. 5.28. Relationships between Salinity and Total Inorganic -N in the waters of Mandovi estuary during 1991-92.

Proliferation of phytoplankton takes place during premonsoon with the increased intensity and duration of day light and low suspended sediment load. This leads to rapid removal of dissolved inorganic nitrogen species. Therefore, the loss of $NO_3$ noticed during this period could be attributed to biological utilisation. Perhaps nitrogen will be lost due to denitrification also. However, this estuary is shallow and well oxygenated throughout, therefore nitrate loss due to denitrification is ruled out.

A net gain of 42% was noticed during post monsoon period. De Sousa (1983) also noticed similar condition in Mandovi estuary and suggested that inflowing subsurface sea water rich in $NO_3$ could be a possible reason for the gain during this period. Decomposition of organic matter taking place in the sediments and the resultant products such as ammonium, on subsequent oxidation steps form $NO_2$ and $NO_3$ which finds their way into the overlying waters, due to physical process, could be considered as one of the reasons for the substantial gain during this period.

**Table 5.5. Percentage of various inorganic fractions in Total inorganic N in the waters of Mandovi estuary.**

| | M1 & M2 | | | M3 & M4 | | | M5 & M6 | | |
|---|---|---|---|---|---|---|---|---|---|
| | $NO_3$ | $NO_2$ | $NH_3$ | $NO_3$ | $NO_2$ | $NH_3$ | $NO_3$ | $NO_2$ | $NH_3$ |
| Nov | 33.0 | 20.1 | 46.9 | 49.3 | 14.8 | 35.9 | 65.3 | 11.3 | 23.4 |
| Dec | 57.7 | 16.8 | 25.5 | 70.8 | 19.7 | 10.5 | 82.2 | 26.7 | 5.1 |
| Jan | 54.8 | 30.1 | 15.1 | 57.2 | 34.7 | 7.8 | 58.3 | 26.9 | 14.8 |
| Feb | 60.0 | 7.1 | 32.9 | 68.7 | 5.9 | 25.4 | 68.2 | 9.8 | 22.0 |
| Mar | 20.5 | 22.4 | 57.3 | 63.3 | 23.7 | 13.0 | 76.6 | 16.4 | 8.0 |
| Apr | 32.0 | 16.8 | 51.2 | 51.6 | 11.7 | 36.7 | 49.8 | 6.6 | 43.6 |
| May | 10.7 | 3.9 | 85.4 | 25.5 | 17.9 | 56.6 | 28.4 | 43.6 | 28.0 |
| Jun | 58.2 | 25.6 | 21.2 | 50.8 | 29.1 | 20.1 | 54.4 | 12.3 | 33.3 |
| Jul | 81.2 | 6.2 | 12.6 | 74.7 | 11.3 | 14.0 | 83.7 | 4.9 | 11.4 |
| Aug | 77.2 | 10.2 | 12.6 | 84.1 | 2.0 | 14.9 | 84.2 | 0.0 | 15.8 |
| Sep | 58.2 | 7.5 | 34.3 | 58.5 | 7.6 | 33.9 | 60.7 | 5.0 | 34.3 |
| Oct | 40.4 | 6.5 | 53.1 | 43.4 | 6.7 | 49.9 | 48.7 | 8.2 | 43.1 |

Studies of Mackay and Leatherland (1976) in Clyde estuary, Fanning and Maynard (1978) in Magdalena river plane, Sharp et al (1982) in Delaware estuary, Fanning and Pilson (1973) in the Mississipi estuary and Van Bennekom etc (1978) in Zaire estuary reveal interesting information on the behaviour of nitrate in estuaries.

Relationships between total-N and total inorganic-N with salinity have been worked out and are shown in Fig. 5.27 and 5.28 respectively. Though there was no linear relationship between $NO_2$ and $NH_3$ with salinity when plotted separately, total inorganic nitrogen ($NH_3$+$NH_4$+$NO_2$+$NO_3$) showed a good correlation (negative). However, total-N with salinity did not show linear relationship as expected.

## 5.7 Distribution of Phosphorus compounds

Spatial and temporal variation of phosphorus compounds in the Mandovi estuary has been studied in detail. Generally, in the open sea the concentration of dissolved inorganic phosphorus in surface waters is low due to its utilization by phytoplakton. Its concentration may range from 0.1 to about 0.2 $\mu mol.l^{-1}$ in tropical areas, where very little seasonal variations in its concentration occur. However, in temperate waters, higher phosphate concentrations are observed in surface waters in the range 0.5 to 1.0 $\mu mol.l^{-1}$ (Spencer, 1975) where significant seasonal variations occur with high concentrations in winter and low in summer.

Pomeroy et al (1972) have analysed the factors controlling phosphorus distribution in shallow turbid well mixed estuaries. They note that in such estuaries the concentration of dissolved phosphorus is far higher than it is in either or the adjacent sea. Furthermore, the sediments typically contain large reservoirs of phosphorus. Normal cycling of phosphorus involves its passage from open estuary sediments to the marsh. Through adsorption onto suspended sediment particles and sinking of phytoplankton, it returns to the sediments to complete the cycle. They found that any concentration of phosphate in the water greater than 1 μ $mol.m^3$ shifts the equilibrium towards sorption onto sediment particles. In such estuaries, physical and biological processes combine towards sorption onto sediment particles. In such estuaries, physical and biological processes combine to regulate the phosphorus levels of the water column and to determine the seasonal distribution of phosphorus between the various habitat types of the estuary. In this type there is a high receiving capacity for excess phosphorus and high tolerance for phosphorus enrichment.

The vertical distribution of phosphate in open ocean generally show a gradual increase from low concentrations at the surface to a maximum at depths between 500 to 2000m. In general, the regular increase with depth starts significantly from about 100 m to 150 m i.e. below the thermocline where the bacterial decomposition of organic matter release the phosphate into the water. High concentrations, > 3.5 $\mu mol.l^{-1}$, have been observed in the Northern Arabian Sea (Sen Gupta et al 1976). The phosphate concentrations in surface waters can be significantly high in areas of upwelling, where the cold, nutrient-rich water from deeper layer is brought up by the process of upwelling.

In coastal and estuarine waters, phosphate is normally high in surface waters and this is due to the enrichment by land drainage in the rivers and coastal waters. Therefore, in an estuary phosphate concentration is expected to be high towards the freshwater end and decreases towards the sea-end. Phosphate concentration rarely gets completely depleted at the surface waters and in most cases it is not a limiting factor for productivity and this property is attributed to the buffering activity of suspended sediments in water, especially in estuarine waters, which maintain a minimum concentration of phosphate. Dissolved inorganic phosphate ($PO_4$-P) concentrations in the estuary ranged between 0.09 (May) and 3.20 $\mu mol.l^{-1}$ (June). Variation of concentration in MDA (Fig 5.29 ) was between 0.09 (May) to 2.25 $\mu mol.l^{-1}$ (October). In the estuarine area (Fig 5.30) it varied between 0.15 (May) and 3.04 $\mu mol.l^{-1}$ (October) whereas at FDA (Fig 5.31) the concentration varied between 0.1 (May) and 3.20 $\mu mol.l^{-1}$.

Seasonal variation of phosphorus compound indicates that during premonsoon the concentration varied between 0.09 and 1.79 $\mu mol.l^{-1}$ while it was 1.47 and 3.2 $\mu mol.l^{-1}$ and 0.24 and 3.04 $\mu mol.l^{-1}$ during monsoon and post monsoon respectively with very few exception. Bottom waters showed higher concentrations than surface waters.

Almost throughout the estuary bottom water showed higher concentrations of $PO_4$-P as compared to the surface waters. At MDA the lowest concentration was noticed during the pre-monsoon (May) season. During monsoon as well as post-monsoon concentration of $PO_4$-P was comparatively high. The peak obtained during monsoon (June) at the mouth and coastal area is due to river runoff whereas, intrusion of nutrient-rich upwelled water might be the reason for high values of $PO_4$-P during post-monsoon season. A near-similar feature was noticed at the estuarine and freshwater dominated area also. Though considerable input of phosphorus during river runoff takes place at the freshwater end of the estuary besides lateral entries through anthropogenic inputs, the concentration of $PO_4$-P and other fractions within the estuary did not exhibit wide fluctuations. The processes affecting the transformations (both biological and non-biological) of the various fractions of phosphorus and nitrogen in the estuary is discussed in the following sections.

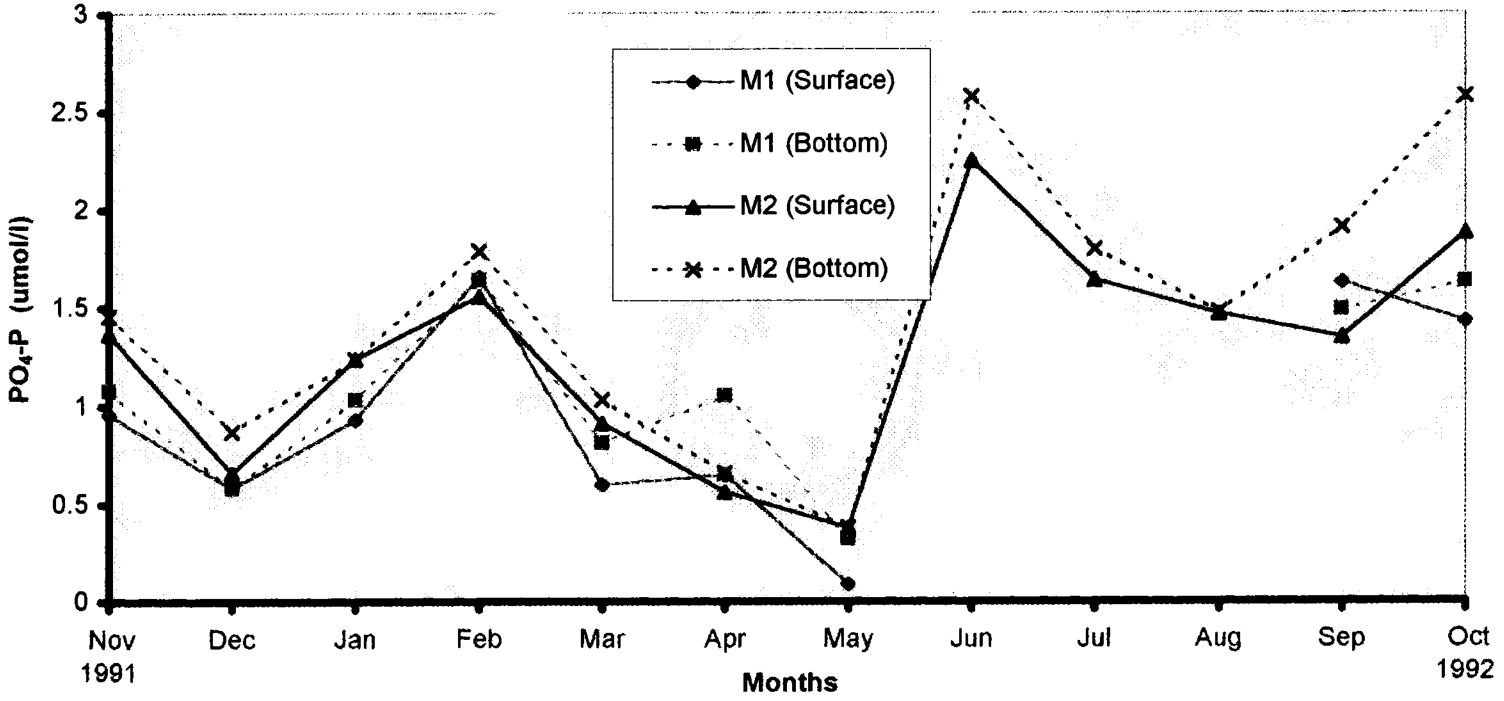


Fig. 5.29 Distribution of PO4-P in MDA

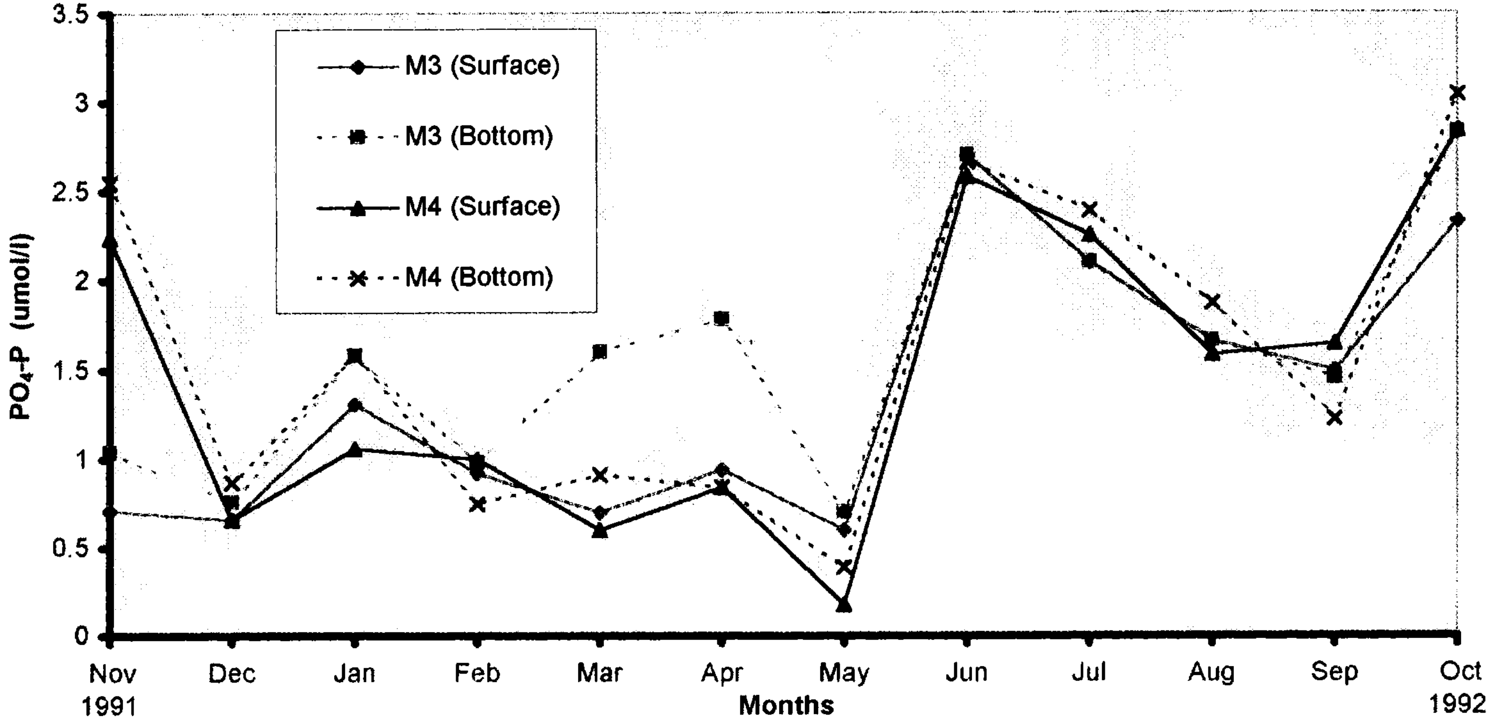


Fig. 5.30 Distribution of PO4-P in EA

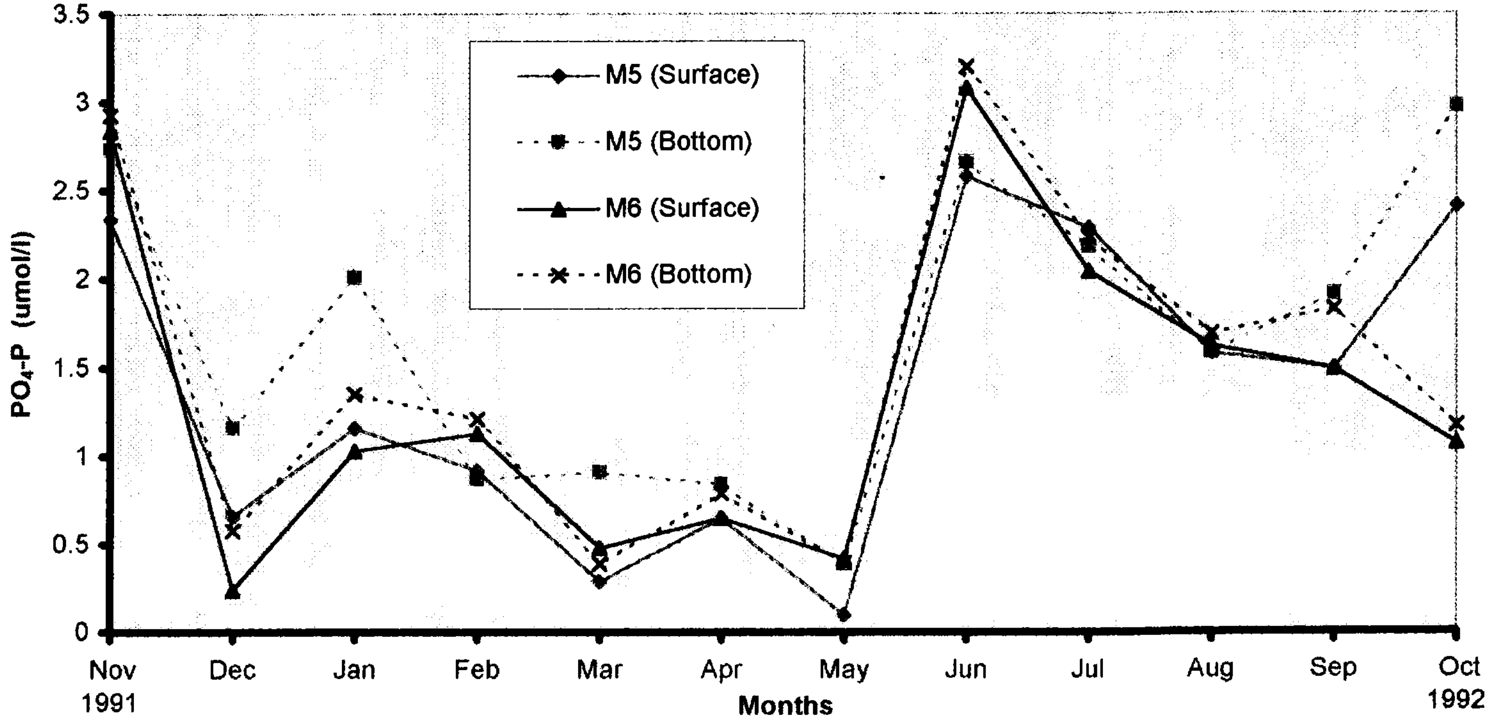


Fig. 5.31 Distribution of PO4-P in FDA

Total phosphorus concentration showed two maxima, a less pronounced one during February and a more pronounced one during June in the lower reaches of the estuary (M1 & M2) and a minimum could be observed during May (Fig 5.32). In the estuarine area the minimum was observed during May and during June and October the concentrations were considerably high compared to other months. (Fig 5.33). Freshwater dominated areas of the estuary did not show any definite pattern of variations (Fig 5.34) and this clearly indicated that variation of total phosphorus in the water column was influenced by some other sources other than river runoff. However, sediment phosphorus data, which is discussed elsewhere in this document will reveal more details on the fate of phosphorus in this estuarine system. The distribution of the total phosphorus also showed more or less the similar trend as that of $PO_4$-P. Both FDA and MDA showed two peaks, one during pre-monsoon and the other in monsoon. However, EA showed only one peak during monsoon.

The vertical distribution of phosphate in open ocean generally show a gradual increase from low concentration at the surface to a maximum at depths between 500 to 2000 m. In coastal areas and in estuarine waters, the phosphate content normally is high in surface waters due to enrichment by land drainage by the rivers and coastal waters. Thus in an estuary, the phosphate content is expected to be high towards the freshwater end and decreases towards the sea-end. One important observation regarding phosphate distribution in surface water is that it is very rarely completely depleted and in most cases it is not a limiting factor for productivity and this property is attributed to the buffering activity of suspended sediments in water, especially in estuarine waters, which maintain a minimum concentration of phosphate.

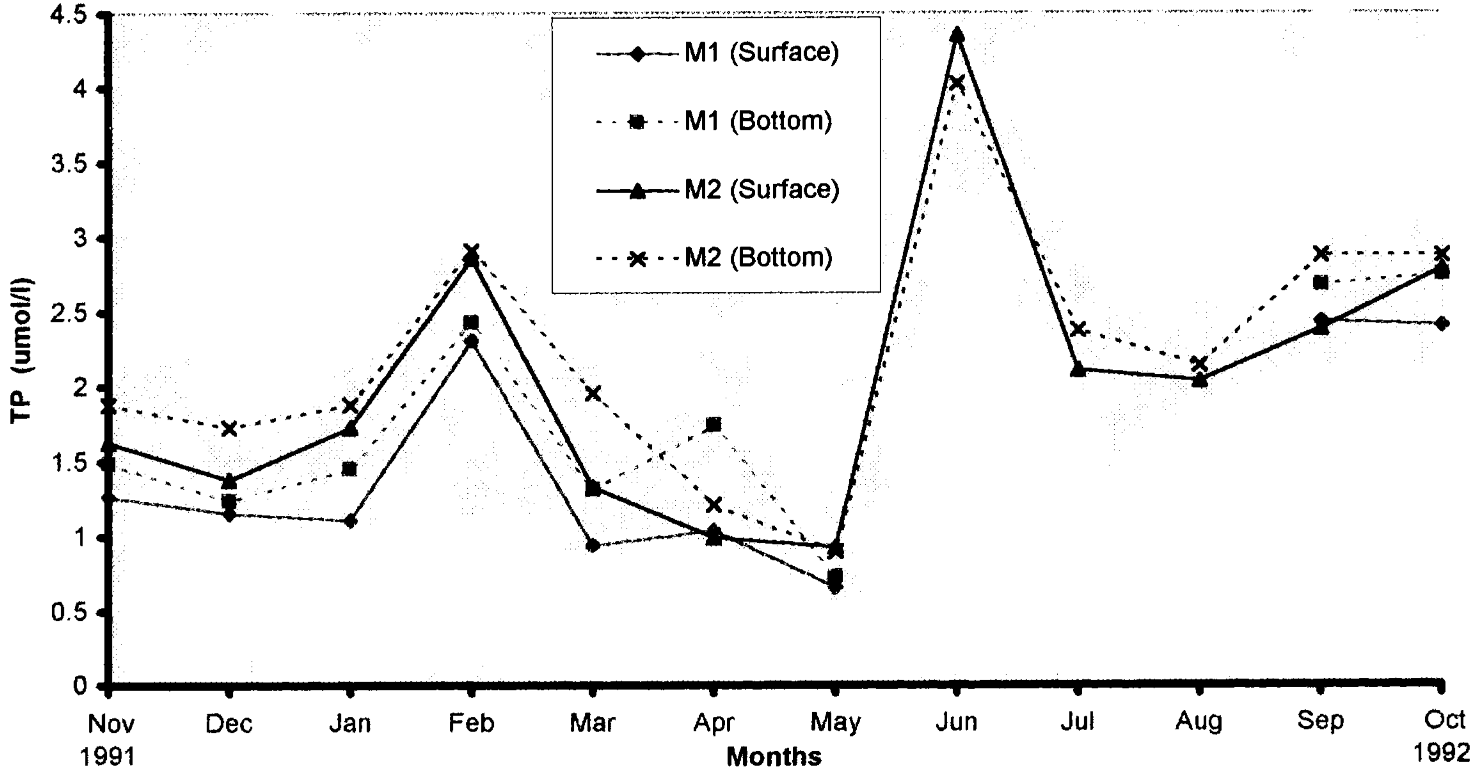


Fig. 5.32 Distribution of Total Phosphorus MDA

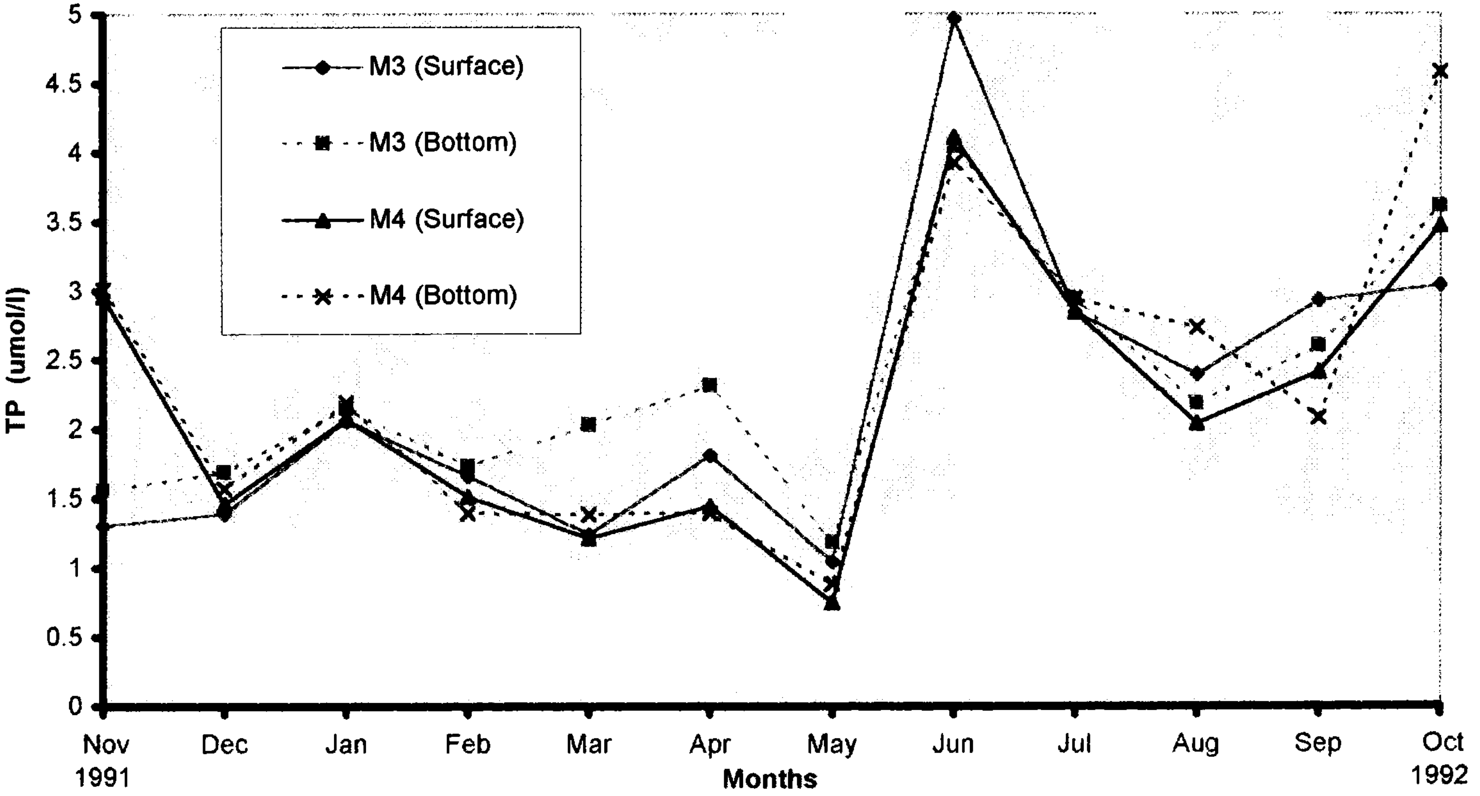


Fig. 5.33 Distribution of Total Phosphorus in EA

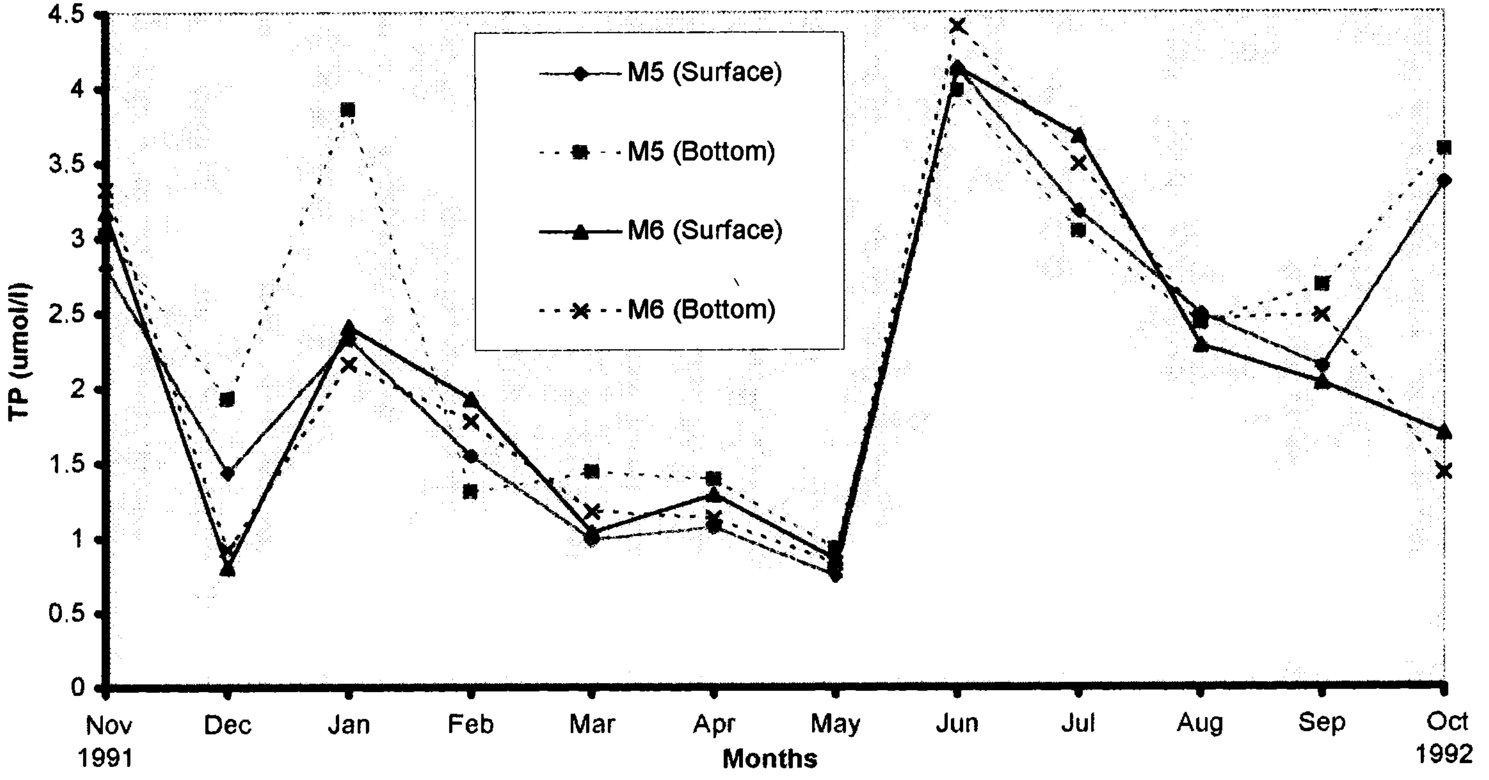


Fig. 5.34 Distribution of Total Phosphorus in FDA

De Sousa (1983) observed that in Mandovi estuary during premonsoon and monsoon, phosphate is removed to the tune of 17 % and 16 % respectively. However, he noticed a gain of 91 % during post-monsoon. An attempt has been made, in the present case, to study the behaviour of phosphate in the estuaries and it is estimated that during premonsoon a net loss of 23 % and during other seasons a net gain of 18 and 53 % respectively for monsoon and post-monsoon take place. The above results are obtained by considering the system as a whole and averaging the concentrations at different stations over the seasons.

Phosphorus is one of the essential micronutrients required by the living organisms. In surface waters the primary producers utilizes phosphates dissolved in waters. Therefore, due to the uptake of the phytoplankton large amounts of phosphates are removed from water. The loss of $PO_4$-P in the estuarine waters observed during premonsoon could largely be attributed to its utilization by primary producers. Another mechanism by which phosphate is removed from the water is by inorganic adsorption onto the sediment particles. However during premonsoon this process may not be very active because the inorganic removal usually occurs when the water has low salinity and high sediment load. This non-biological removal of phosphate may be important during monsoon season because the conditions such as low salinity of waters, high sediment load, high iron content and high oxygen content etc will favour its adsorption by sediments. (Jitts, 1959, Pomeroy et al 1965 and Liss 1976). Though substantial quantity of $PO_4$ is removed during this season, the quantity of input into the estuaries through river runoff compensated the loss and finally a marginal gain of 18 % could be registered during monsoon.

During post monsoon the phosphate showed 53 % gain. Possible sources of this gain are (I) some outfall discharging sewage (domestic and/or industrial) into the estuarine system which is rich in phosphate; (II) desorption of phosphate adsorbed earlier at low salinities is released when the salinity increased; (III) phosphate supplied by subsurface sea water either through entrainment or as intrusion of upwelled water. The most probable factor which contribute to the phosphate gain during post-monsoon is the desorption and release of phosphate which is held by sediment in adsorbed form in low salinity region.

Many workers have pointed out that the estuarine sediments act as 'buffer' for phosphate concentration in water. Pomeroy et al (1965) have shown by laboratory experiments that sediment act as buffer of phosphate maintaining its concentration in water between 0.7 and 0.9 $\mu$mol.$l^{-1}$ and according to them, this concentration of phosphate is sufficient for phytoplankton growth and if the concentration is maintained at this level by contact with sediment, phosphate will never be a limiting factor.

Phosphate salinity relationships for the Mandovi estuary has been worked out to evaluate the behaviour of phosphorus during estuarine mixing. Pooling $PO_4$-P plot, concentration for the entire estuarine region for various seasons, a salinity -$PO_4$-P plot has been constructed. (Fig 5.35) A study of the scatter diagram indicated that a poor linear relationship between salinity and $PO_4$-P exist in the estuary. More or less the same relationship could be noticed for salinity -total P concentrations (Fig 5.36) while no relationship could be noticed for salinity -org-P concentrations (Fig 5.37).

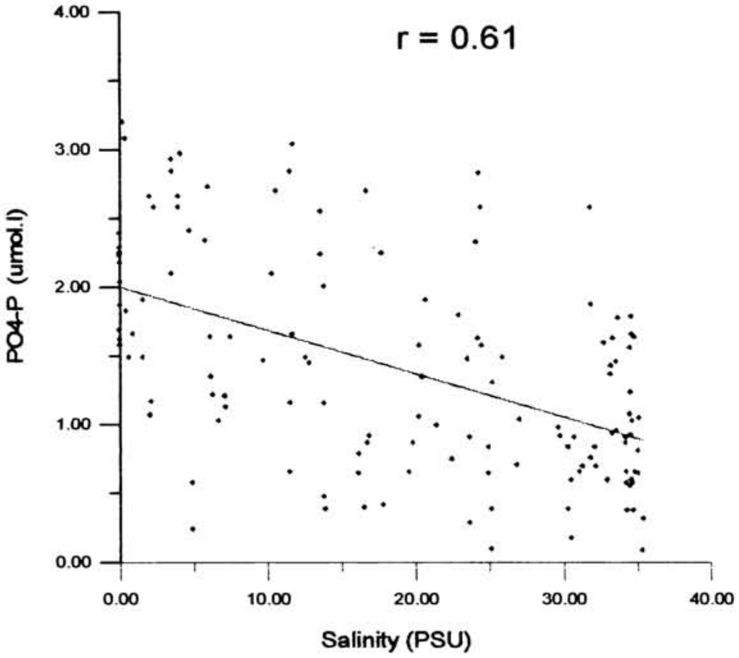


Fig. 5.35. Relationships between salinity and $PO_4$-P in the waters of Mandovi estuary during 1991-92.

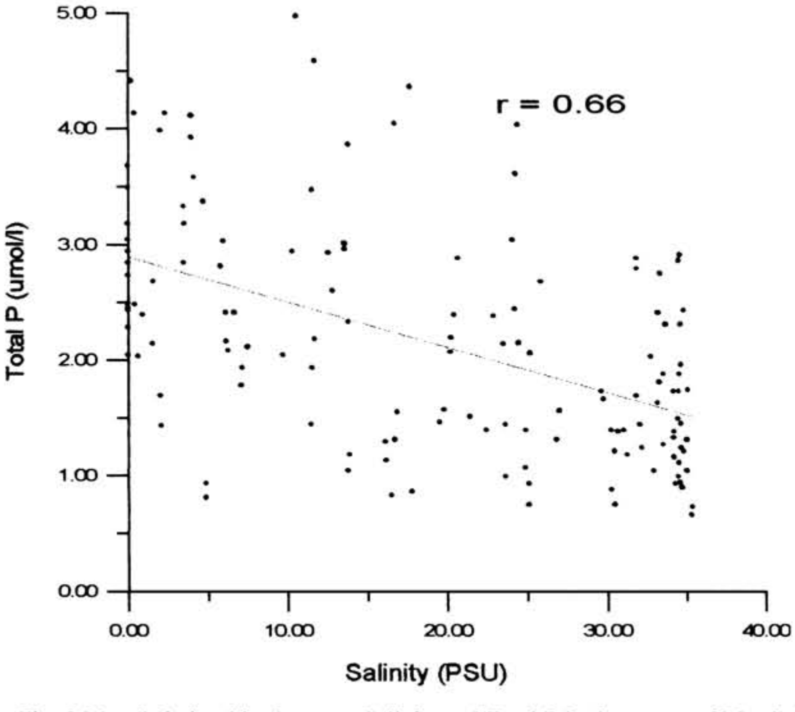


Fig. 5.36. Relationships between Salinity and Total-P in the waters of Mandovi estuary during 1991-92.

Sharp et al. (1982) observed apparent estuarine source of phosphate in their plot of phosphate versus salinity in Delaware estuary and have explained it as due to an exchange of phosphate between particulate and dissolved phases. The studies of Simpson et al (1975) in Hudson river estuary showed an increase in phosphate with salinity and have attributed it to the river and sewage discharges both of which contained high phosphate. The laboratory experiments of Jitts (1959) also have shown that the mechanism of phosphate removal by estuarine sediments is similar to that found in soil in which iron is directly involved, and had shown that at pH 3 and 7 almost complete removal of phosphate occurred while at pH 11 only slight adsorption took place. Froelich, (1988) and Chambers and Odum (1990) have shown by laboratory experiments that phosphate removal by sediments is greatly affected by salinity and that 99 % adsorption occurred at salinity around 2 PSU. They also observed that lowering the pH of the solution enhanced the adsorption; this is probably because of the presence of phosphate as $H_2PO_4^-$ at low pH rather than $HPO_4^{2-}$ ions at higher pH (Kester and Pytkowicz 1967).This suggests that in estuaries where river water with low pH mixes with sea water of pH around 8, the efficiency of phosphate removal will be greater in freshwater than in saline water part of the estuary. Therefore, the

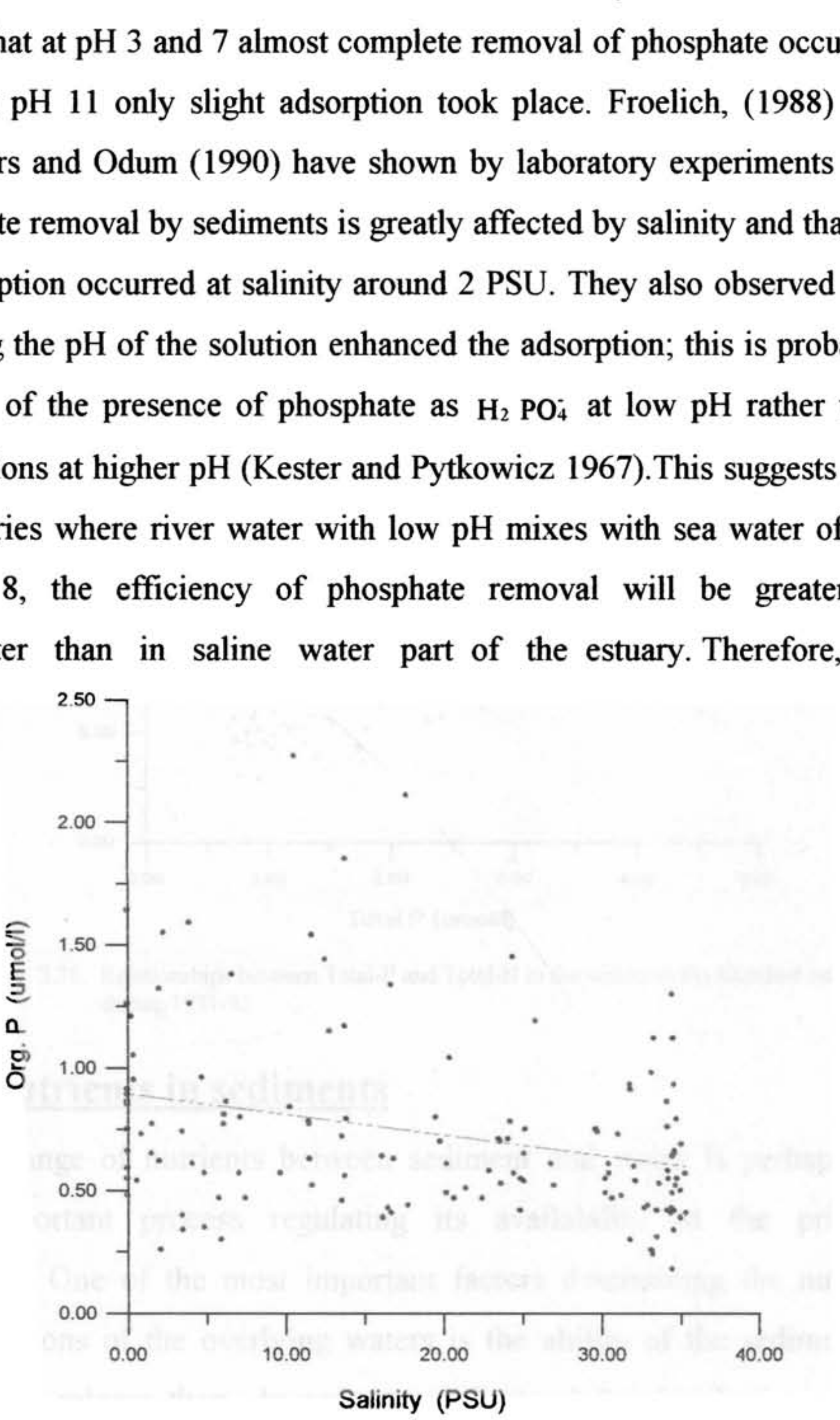


Fig. 5.37. Relationships between Salinity and organic-P in the waters in the Mandovi estuary during 1991-92

phosphate buffering capacity of the estuarine sediments and the rapid exchange of phosphate between sediments and water will be important both at times of flushing by heavy rainfall when highly oxygenated waters with low salinity are bringing down large quantities of terrestrial phosphate and silt and at times of heavy demand by phytoplankton.

The scatter showing total-N and total-P plots are given in Fig 5.38. Though the scatter was wide, positive correlation between this two parameters could be noticed.

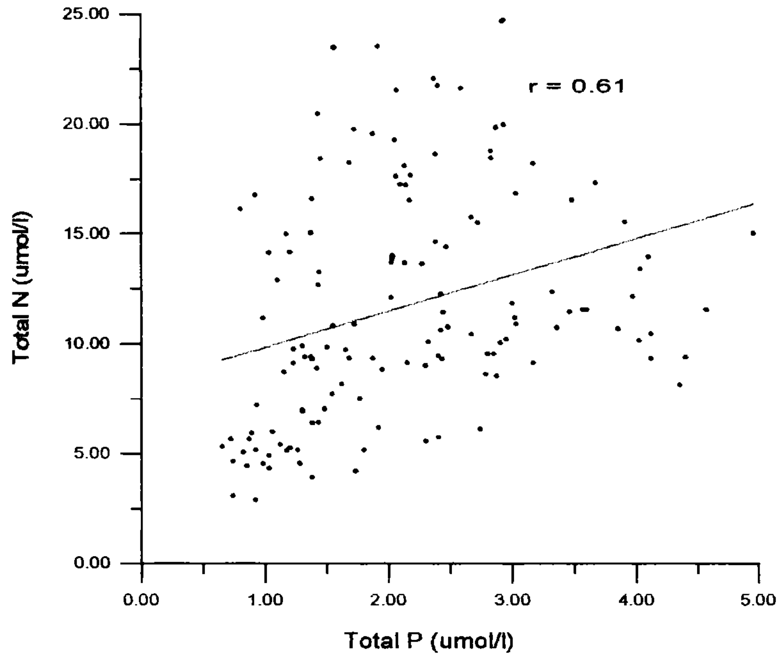


Fig. 3.38. Relationships between Total-P and Total-N in the waters in the Mandovi estuary during 1991-92.

## 5.8 Nutrients in sediments

The exchange of nutrients between sediment and water is perhaps the most important process regulating its availability to the primary producers. One of the most important factors determining the nutrient concentrations of the overlying waters is the ability of the sediment to adsorb and release them. In order to understand the distribution of the various fractions of nitrogen and phosphorus compounds in the estuarine sediments, samples collected during premonsoon, monsoon and post monsoon seasons have been analysed.

### 5.8.1 Phosphorus distribution in sediments.

In the previous section the distribution of the various phosphorus and nitrogen compounds in water have been discussed. It was observed that the distribution of phosphorus and nitrogen compounds in the water column in the estuary were not homogenous. The dissolved phosphates, of course, tend to reach uniform concentrations but this tendency is counteracted by other compounds either organic (biochemical) or inorganic. The organic forms are formed by the phosphates being taken up metabolically by the phytoplankton, so that these cellular phosphate molecules must inevitably follow the active migration processes of the phytoplankton and the sinking rate of the dead cells. Both processes will therefore, lead to local differences in the particulate phosphate concentration. But there are other features that work against this due to the rapid mineralization of most organic matter of algal cells in estuaries and also due to the geochemiclly loose binding of the phosphate molecules to the organic mater of the algal cells (P - O - C bonds which hydrolyze easily), the phosphate molecules escape easily from sedimentation with dead phytoplankton.

The forms and amounts of P in estuarine systems are a function of P input (external P), the P output (internal P) and the interchange (Chemical, biochemical and physical processes of P) among the various sediment and water P compartments. A Schematic presentation of the dynamics of sediment P is given in Fig 5.39.

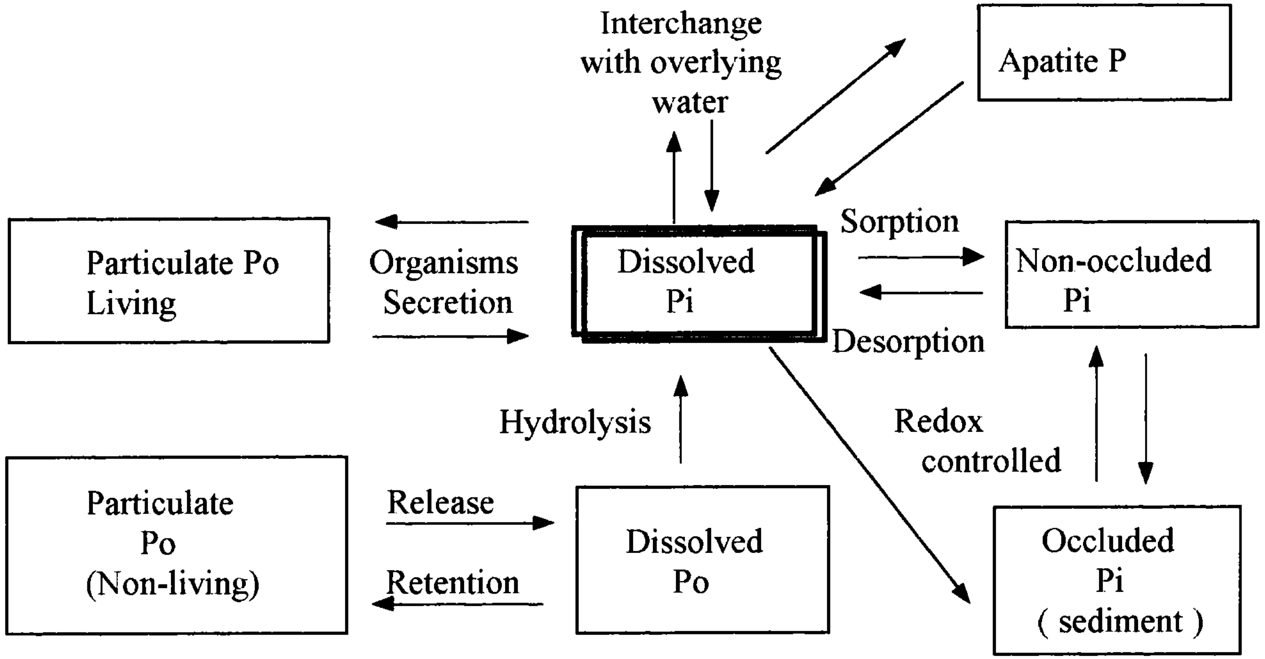


Fig : 5.39 Dynamics of sediment P (Pi = inorganic P, Po= organic P)

Release of sediment P to the overlying waters occur through suspension of particulate forms or transport of dissolved forms through turbulent mixing and diffusion. Although sediment act as a 'sink' for P (Olsen 1966) as evidenced by the appreciable amounts of P in sediments which greatly exceed that in the overlying water column, release to the overlying water of dissolved inorganic P can occur if the concentration of interstitial dissolved inorganic P exceeds that in the estuarine water. (Stum & Leckie 1971).

The approach of evaluating the forms of sediment inorganic P through P relationships to sediment elemental composition through selective removal of certain forms of elements provides useful information on the association of inorganic P in estuarine sediments. Although organic forms of phosphorus are not themselves directly available for phytoplankton nutrition, they do form the main source of available phosphorus. On the other hand, mineralisation of organic matter does not necessarily result in release of available phosphorus and in some cases the reverse is true and immobilisation of soluble inorganic phosphorus already present will occur.

Large quantities of phosphorus are consistently found deposited in estuarine sediments, but often the quantities of soluble phosphorus found in the waters are very small. If a mechanism could be discovered to increase the release of the phosphorus from the bottom sediments so that it could contribute to the production of algae it would be a valuable contribution. It has been found that total productivity in some aquatic biological communities is directly limited by the concentration of available phosphorus and that several biogeochemical processes are involved in regulating the availability of phosphorus in the nutrient cycle. Of the possible mechanisms returning phosphorus to the $PO_4$-P pool in the water column, the following have been considered to be important : (a) direct release of phosphorus by the ultraplankton, (b) excretion of phosphorus by zooplankton; and (c) enzymatic hydrolysis of organic phosphorus excreted by organisms or produced by autolysis or decomposition of dead plankton.

Pomeroy et al (1965) found that the most important factors determining the phosphorus concentrations of the overlying waters is the ability of the sediment to adsorb and release phosphorus. Sediment-water phosphorus exchange reactions are governed by various factors such as mixing processes, sediment type and particle size, oxidation-reduction potential, sediment microbial population and pH. Strom and Biggs ( 1982) carried out extensive studies in the Delaware river estuary on the distribution of phosphorus in sediments and observed that one of the important processes in the estuarine environment is the incorporation of phosphorus into the sediment phase, either by sorption mechanisms or by the formation of insoluble inorganic phosphate minerals.

It is therefore, interesting to ascertain the relative importance of the above factors and others in determining the phosphorus concentrations in the estuarine sediment along the estuarine gradient in relation with its concentration in water column to have an assessment of the health of the ecosystem.

Several distinct phases of sedimentary phosphorus in the estuary have been identified (Hesse, 1973). Association of phosphorus with colloidal iron has been demonstrated in freshwater, estuarine and deep-sea sediments (Mortimer 1941, 1942, Jitts, 1959, Berner, 1973 and Harter, 1969). Authegenic ferrous phosphate minerals, vivianite and ludlamite have been identified in freshwater reducing environments (Nriagu and

Dell, 1974) and vivianite has been detected in estuarine sediments (Bray et al 1973). The formation of an insoluble aluminium phosphate mineral variscite has been suggested by Lindsay and Moreno (1960). Authegenesis of calcium phosphate minerals of the apatite variety was observed in the ocean bed (Manheim et al 1975). Several authors have suggested that calcium phosphate minerals are the major phosphorus sinks in freshwater (Stum and Morgan 1970).

In addition to these discrete forms identifiable in sediments, weakly bonded, labile phosphorus associations have also been estimated (Atkinson 1987). Anion exchange on clays (Pomeroy et al 1963) has been identified as an important mechanism whereby phosphorus is sorbed into the sedimentary phase. Investigations of estuarine sediments have attempted to relate the capacity of the sediments to sorb and fix phosphorus into soluble phases to such factors as clay content (Pomeroy et at 1965), metal colloids (Jitts, 1959), organic content and variables such as pH, salinity and calcium activity (Nelson, 1967).

### 5.8.2 Available phosphorus

Sediment phosphorus can be considered as non-available, potentially available and immediately available. Immediately available phosphorus is the inorganic form occurring in soil solution and which is almost orthophosphate. Phytoplankton do directly take up orthophosphate from solution and quantitative estimations of the uptake have been carried out by several workers (Goldman and Ryther, 1975, McCarthy et al, 1975, and Taft et al 1975). The most important form of potentially available phosphorus is the organic; inorganic forms other than orthophosphate is largely unavailable. Relatively available inorganic phosphorus tends to accumulate in its stable state under prevailing conditions, thus in calcareous sediments the available inorganic phosphorus would be acid soluble whereas in acidic sediments the adsorbed phosphorus would be more available. In sediments with low oxidation potentials certain forms of phosphorus are normally considered as unavailable. (Hesse, 1973).

In most sediments the main source of orthophosphate is the organic matter (decomposition product) unless, of course direct fertilization with soluble phosphate has been made. Birch (1964) found that the organic phosphorus in sediment was of significant value in predicting phosphorus availability. Williams (1976) precisely stated that the significance of organic phosphorus availability was valid only if pH exceeded 5.5 as more acid conditions adversely affected mineralisation.

The measurement of total-P in sediments is of less significance in determining available phosphorus except that a very low total-P content will indicate probable phosphorus deficiency.

The amount of phosphorus in a sediment sample that is available to phytoplankton (in water column by diffusion and other physical processes) could be determined by one of the two methods: biological or chemical, but for the most reliable results both methods should be employed in conjunction. The chemical techniques that has received and is still receiving attention is that of extraction with one or more solutions. Many attempts have been made to formulate a 'universal' extractant for available phosphorus but with no success and it is difficult to envisage such a solution ever being made.

Available phosphorus determined by chemical extraction procedure include all forms of phosphorus, but predominantly that associated with iron, aluminium and calcium, the relative amounts brought into solution will depend partly upon the amount present in the sediment and partly on the solubilities in various solvents.

Two main methods of identifying inorganic forms of phosphorus are (a) chemical fractionation depending upon the solubility of different forms in different solvents and a more indirect method based upon the concept of solubility products. A modified Chang and Jackson (1957) procedure for serial extraction of sediment phosphorus was based on the latter concept used to separate the sediment phosphorus in 0.5g portions of the composite samples into the following fractions.

(I) **Saloid-bound phosphorus** : Water soluble which is the first fraction removed with dilute $NH_4Cl$ solution.

(II) **$NH_4F$-P** : Forms extracted include aluminium phosphate and exchangeable phosphate on clays.

(III) **NaOH-P** : Forms extracted include discrete iron phosphate minerals and some weakly bonded phosphates.

(IV) **CDB-P** : Forms extracted include primarily phosphate sorbed by iron oxyhydroxides.

(V) **$H_2SO_4$-P** : Forms extracted include varieties of apatite-calcium phosphate.

(VI) **Res-P** : Residual phosphates extractable by digestion with a warmed mixture of $HNO_3$, $HClO_4$ and $H_2SO_4$-commonly called occluded phosphates.

In spite of modifications to the serial extraction procedure of Chang and Jackson (1957), Fife (1963), Williams et al (1967, 1970a and 1970) and Strǫm (1976), the specificity of the procedures are only moderate. Some labile organic phosphorus in sediments is hydrolysed by even mild treatment or solubilised by mild bases (Anderson, 1960). Some phosphates extracted by fluoride reagent may be resorbed and later recovered in subsequent extraction steps (Williams et al 1970a). The extraction procedure followed here would be inappropriate for calcareous sediments as side reactions to form Ca-F phosphate complexes would distort the proportions of the phosphate fraction relative to acid soluble phosphate. Therefore the absolute values for phosphorus fractions must be interpreted with some caution. The sum of the fraction will be the total inorganic phosphorus in sediments ($\Sigma P_i$). Organic phosphate are estimated as the difference between the total P ($\Sigma P$) and the sum of inorganic P($\Sigma P_i$).

Estimations have been carried out on sediment samples collected at different salinity gradients of the estuary during pre-monsoon (April), monsoon (July), and post-monsoon (October). The percentage of different fractions of inorganic phosphorus in the sediments are shown in Fig. 5.40-42. During pre-monsoon season, high salinity conditions prevailed over the estuary and the pH variations in the water column were not very significant. Inorganic P variations in the water column during this period indicated that the concentration varied between 0.66 (M2) and 1.78 $\mu mol.l^{-1}$(M3). The total-P ($\Sigma P$) during pre-monsoon ranged between 1.13 (M6) and 2.31$\mu mol.l^{-1}$

Sediment $\Sigma P$ distribution showed that it ranged between 302 and 435 ppm and the percentage of total inorganic P($\Sigma Pi$) was between 55 and 77% [the concentration ranged between 210 (M6) and 310 ppm (M2)]. Concentrations of various fractions of inorganic-P ($\Sigma Pi$) in the sediment during premonsoon is given in Table 5.6. Saloid bound fraction was very low 5.2 (M5) to 10.4 ppm (M2) during this season compared to other fractions. Percentage variations of different fractions during April is shown in Fig. 5.40. It indicated that CDB-P form was most significant and its concentrations showed a decreasing trend from the mouth to the freshwater end and the Fe-P showed a reverse trend. Aluminium fraction, though considerably low as compared to Fe and CDB showed more or less a distribution pattern with increasing values towards the upper

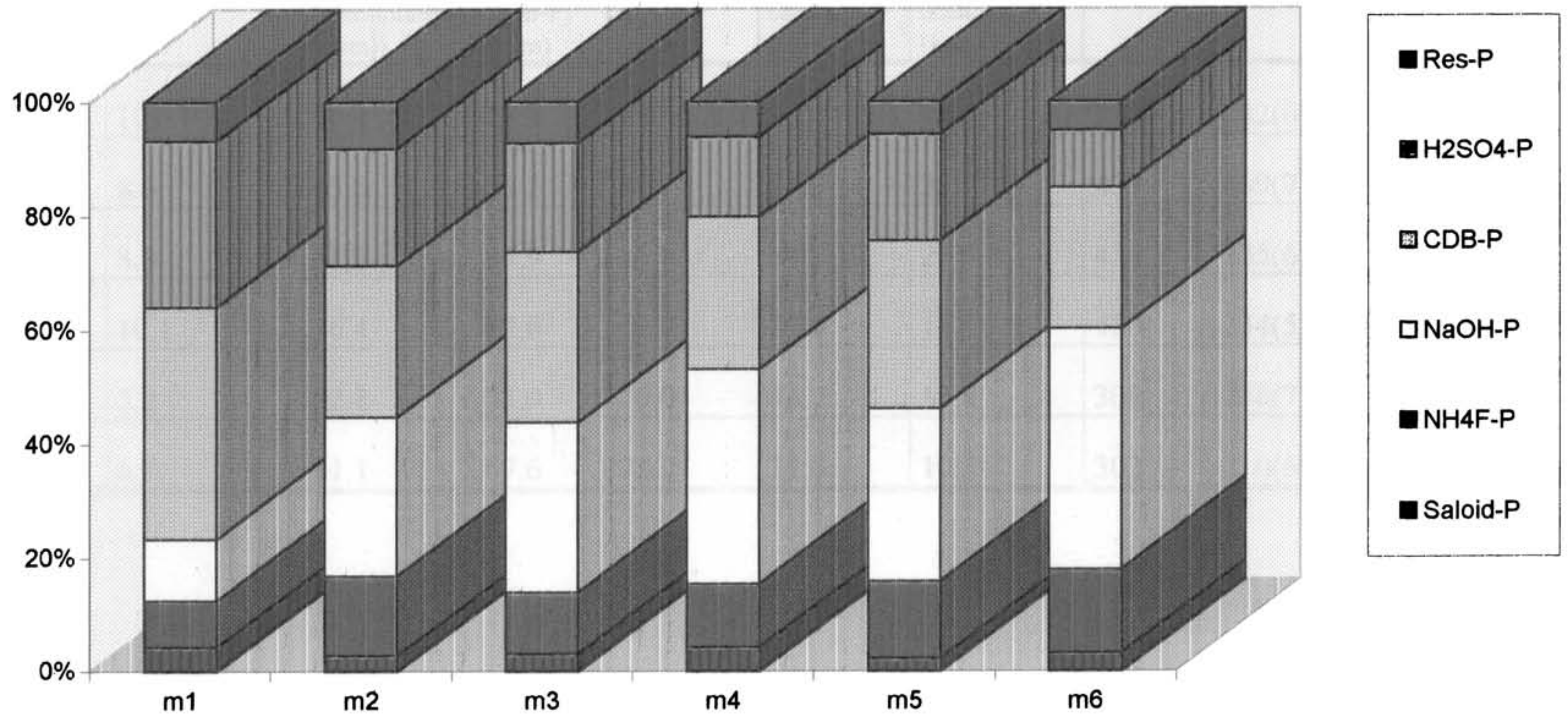


Fig. 5.40 Distribution of various fractions of inorganic phosphorus in sediments during premonsoon (April)

**Table 5.6 Concentrations of various phosphorus fractions in the Mandovi estuary during pre-monsoon**

| Station | Saloid-bound-P (ppm) | $NH_4F$-P (aluminium-P (ppm)) | NaOH-P (Iron-P) (ppm) | CDB-P Fe-oxy-P (ppm) | $H_2SO_4$ calcium-P (ppm) | RES-P occluded-P (ppm) | ΣP (ppm) | ΣPi (ppm) | ΣPorg (ppm) |
|---|---|---|---|---|---|---|---|---|---|
| M1 | 10.4 | 20.1 | 26.1 | 98.5 | 70.4 | 16.5 | 348 | 242(69%) | 106(31%) |
| M2 | 8.6 | 43.5 | 86.2 | 81.1 | 63.3 | 25.3 | 432 | 309(71%) | 123(29%) |
| M3 | 8.8 | 31.3 | 84.9 | 85.0 | 54.2 | 20.8 | 435 | 285(65%) | 150(35%) |
| M4 | 10.1 | 26.4 | 87.8 | 62.7 | 32.5 | 14.5 | 420 | 234(55%) | 196(45%) |
| M5 | 5.2 | 32.8 | 72.0 | 70.0 | 44.2 | 13.8 | 308 | 238(77%) | 70(23%) |
| M6 | 6.7 | 31.1 | 67.6 | 72.9 | 21.0 | 10.7 | 302 | 210(69%) | 92(31%) |

reaches of the estuary and the calcium bound phosphorus showed a reversing trend. Probably the distribution of these fractions followed the source of the respective elements in the estuaries.

Concentration of various fractions of phosphorus during post-monsoon season is given in Table 5.7. $\sum P$ in the sediment varied between 189 (M6) and 366 ppm (M4) and the concentration of $\sum Pi$ ranged between 154 (M6) and 291 ppm (M4) which indicated that 71-86% of the $\sum P$ was $\sum Pi$ and the rest (14-29 %) was $\sum P_{org}$. Percentage variations of different phosphorus fractions in the estuarine sediments during post-monsoon(October) is shown in Fig 5.41. Aluminium-P varied between 10.2% (M1) and 32.6 % (M6) and calcium-P ranged between 44.6% (M1) and 12.6%. Occluded and Saloid bound P were considerably low during this period. Compared to the premonsoon season the percentage of CDB-P during post-monsoon was considerably low and it varied between 13.8 % (M1) and 21.8 % (M6).

Variations of different fractions during monsoon did not show any definite trend. During monsoon the estuary exhibited freshwater predominance and the pH also dropped considerably due to the freshwater discharge. $\sum P$ in sediments varied between 316 (M3) and 340 ppm (M6) and 81 to 88 % of it was inorganic ($\sum Pi$). Variation of concentration of different P forms in sediments during monsoon is given in Table. 5.8 and the percentage variations are shown in Fig. 5.42. Compared to other seasons Saloid-bound forms showed an increasing trend from the mouth to the upstream. An examination of the data indicate that the percentage variation of all other forms except calcium-P showed a similar trend. Phosphorus distribution in the sediments of the Delaware river estuary was studied by Strom and Biggs (1982) Who found that the total inorganic phosphorus fraction decreased by a factor of two along the axis

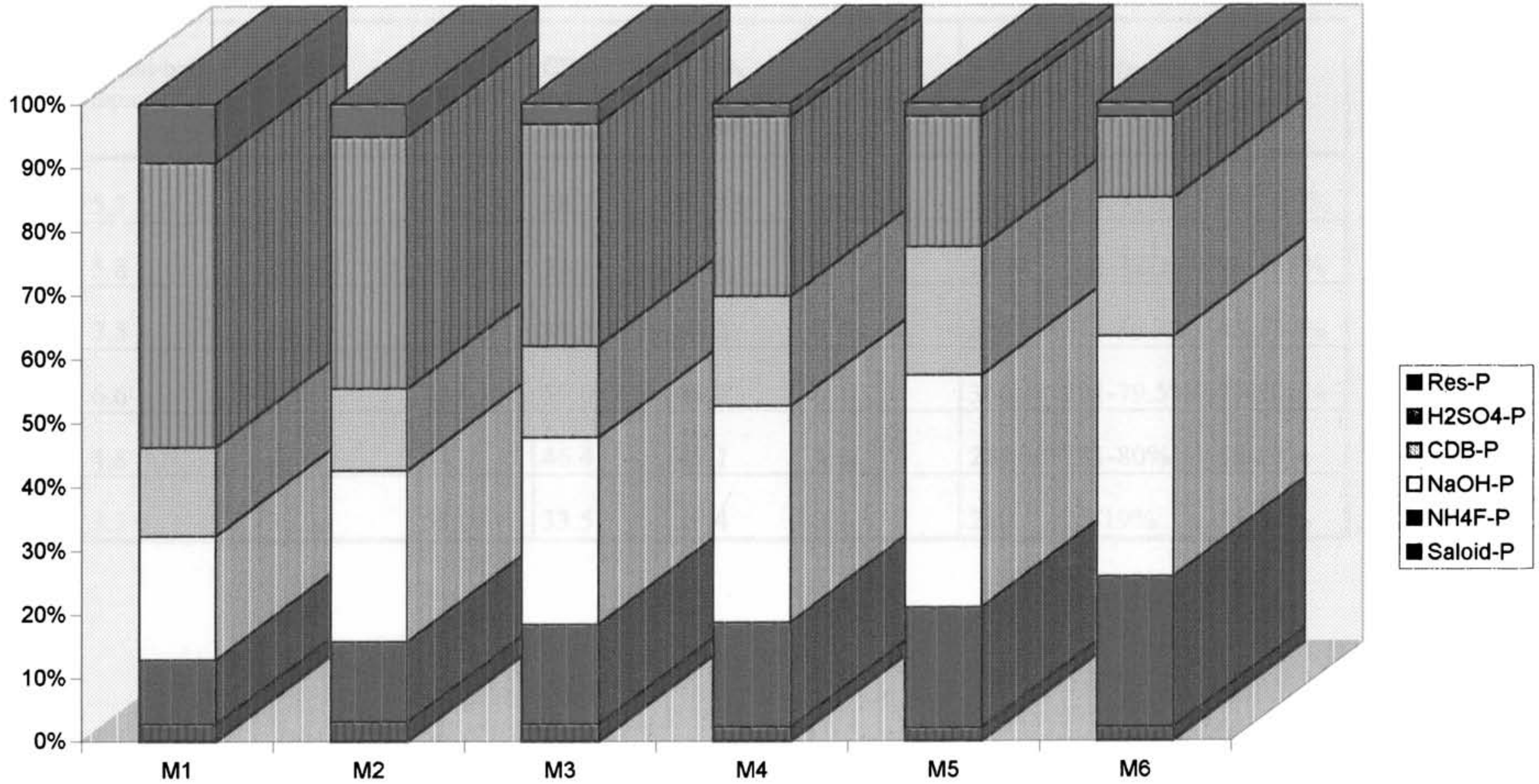


**Fig. 4.41** Percentage of various fractions of inorganic phosphorus in sediments during postmonsoon (October)

**Table 5.7 Concentrations of various phosphorus fractions in the Mandovi estuary during post-monsoon**

| Station | Saloid-bound-P (ppm) | $NH_4F$-P (aluminium-P (ppm)) | NaOH-P(Iron-P) (ppm) | CDB-P Fe-oxy-P (ppm) | $H_2SO_4$ calcium-P (ppm) | REs-P occluded-P (ppm) | $\sum$P (ppm) | $\sum$Pi (ppm) | $\sum$Porg (ppm) |
|---|---|---|---|---|---|---|---|---|---|
| M1 | 5.7 | 20.9 | 39.8 | 28.3 | 91.43 | 18.9 | 228 | 205-71.1% | 83.28.9% |
| M2 | 5.8 | 23.8 | 50.4 | 24.1 | 74.1 | 9.7 | 226 | 188-32.2% | 38-168% |
| M3 | 7.5 | 42.2 | 79.4 | 38.7 | 94.3 | 8.0 | 314 | 271.86.35 | 43-137% |
| M4 | 6.6 | 47.7 | 98.6 | 50.0 | 81.7 | 6.1 | 366 | 291-79.5% | 75-205% |
| M5 | 4.8 | 43.6 | 84.1 | 46.4 | 47.1 | 4.8 | 289 | 231-80% | 58-20% |
| M6 | 3.3 | 36.3 | 58.0 | 33.5 | 19.4 | 3.4 | 289 | 25-19% | 35-19% |

of the bay in a downstream direction and it was largely due to a substantial decrease in the CDB-P and NaOH-P. Acid soluble-phosphorus ($H_2SO_4$-P) and $NH_4F$-P did not vary substantially as a function of distance along the axis of the estuary.

Studies dealing with the distribution of phosphorus in estuarine and marine sediments have found numerous factors which influence the concentration of phosphorus in sediment and sediments capacity to sorb added phosphate. Williams (1976) found that phosphorus exists in sediments in different forms according to pH, Eh, organic matter content and inorganic phosphorus is typically combined with iron, aluminium and calcium and is adsorbed as the anion onto clay minerals and organic complexes. Upchurch et al (1974) found that in acid sediments phosphorus is combined largely with iron and aluminium and in neutral or alkaline sediments calcium phosphate predominates. Aluminium and iron phosphates were associated with the finer sediment particles and were thus carried by water movement to the deeper parts of the estuary before settling. Calcium phosphate was associated with the coarse particles and so was deposited in the shallow water. In the present study aluminium phosphate and calcium phosphate concentrations followed the finding of Upchurch (1972) and the variation of phosphorus content of the sediments was most closely associated with variation of reductant soluble iron oxyhydroxides.

Studies on the non-conservative behaviour of iron during estuarine mixing (Sholokovitz 1976, Boyle et al 1977), Moore et al (1979) suggest that iron is transported in freshwater primarily as organically stabilized colloids that are destabilized and flocculated in the low salinity range within estuaries. CDB-P, the form of phosphorus presumed in the extraction procedure to be reacted to reductant soluble metals especially Fe, showed

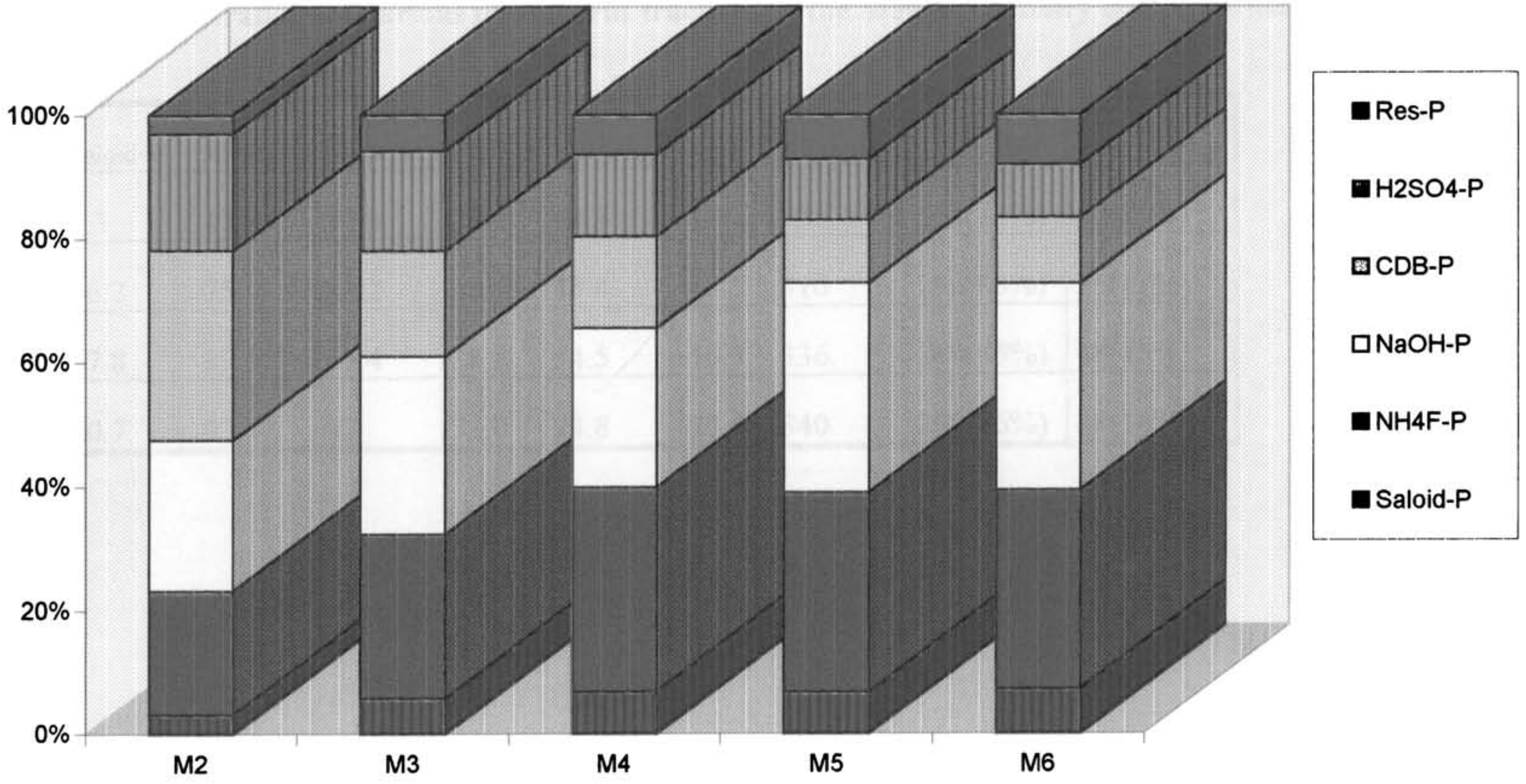


**Fig. 5.42 Percentage of various fractions of inorganic phosphorus in sediments during monsoon (July)**

**Table 5.8 Concentrations of various phosphorus fractions in the Mandovi estuary during monsoon**

| Station | Saloid-P | NH4F-P | NaOH-P | CDB-P | H2SO4-P | Res-P | ∑P (ppm) | ∑Pi (ppm) | ∑Porg (ppm) |
|---|---|---|---|---|---|---|---|---|---|
| M2 | 8.3 | 47.8 | 57.8 | 73.1 | 44.7 | 7.1 | 328 | 268(84%) | 60(16%) |
| M3 | 16.2 | 75.0 | 81.2 | 48.4 | 45.4 | 16.5 | 316 | 280(88%) | 36(12%) |
| M4 | 17.8 | 89.5 | 67.4 | 38.8 | 34.5 | 16.7 | 336 | 288(85%) | 48(15%) |
| M5 | 20.7 | 93.4 | 97 | 31.0 | 24.8 | 23.4 | 340 | 292(86%) | 48(14%) |

a strong positive correlation with Fe, Likewise with NaOH-P the phosphorus form presumed to be associated with discrete iron phosphate. Those mechanisms that lead to the deposition of dissolved iron or suspended colloidal iron oxyhydroxides from the water column would immobilise phosphorus as well, and concentrate it in the sediments of the upper reaches of the estuarine system (Serruya 1971). Ku and Feng (1978) studied the factors affecting phosphate adsorption equilibrium in lake sediments and found that both Al and Fe are important binding materials.

A difference in phosphate binding was also seen by difference in pH dependency of adsorption (Ku and Feng 1978) by two different sediments and adsorption isotherm at $11^0$C and $20^0$C also indicated a significant decrease in the exothermicity of the reactions at lower pH which may suggest that more than one mechanism is operative in the pH range of 5.5 - 7.0.

Stumm and Leckie(1971) considered the equilibria between solid phase and interstitial water of the sediment in combination with mass transport and found that decreasing the loading can cause release due to re-equilibration of the sediment to a lower solid phase concentration; increasing the loading produce the opposite effect and this relationship can vary seasonally as a result of shifts in redox potential, pH and temperature. The pH of the overlying water and sediment is a dominating factor because it controls the concentration of available iron, aluminium and calcium as well as affecting sorption-desorption reactions, precipitation-solubilisation reactions and oxidation-reduction reactions. Because of its direct and indirect effects on all aquatic biological and chemical reactions, pH ultimately become a major controlling factor in the availability of sediment-bound phosphorus for algae utilization. Nur and Bates (1979) studied the effect of pH on the aluminium iron and calcium phosphate fractions of lake sediments and found that the pH at which fixation is at minimum is well within the range of pH values for natural waters.

The ability of sediments to sorb inorganic P added in the laboratory has been studied (Rajagopal and Reddy 1984) with a view to understand the role of sediments in the removal of dissolved P from or the release of dissolved P to interstitial water and it was found that the process of adsorption and desorption of P were pH dependent. Williams et al (1970) studied the adsorption and desorption of inorganic phosphorus by lake sediments in 0.1M NaCl system and observed that the reaction involved in the adsorption and desorption of added P were not always completely reversible.

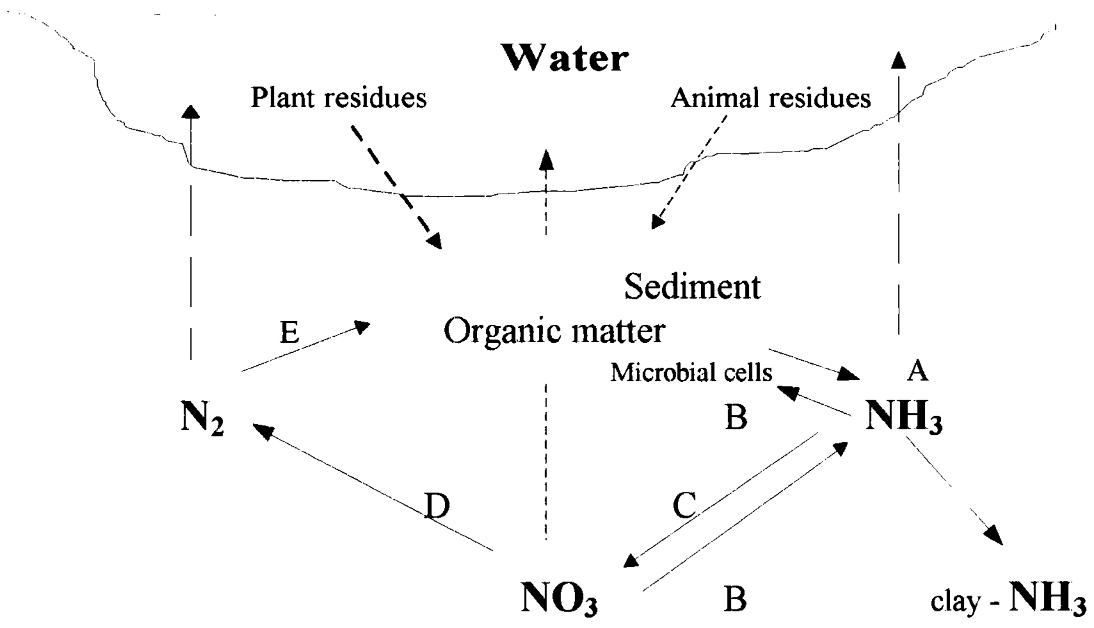
Laboratory experiments carried out under controlled conditions to study phosphorus retention capacity of sediments from Mandovi estuary (Rajagopal and Reddy, 1984) indicated that the process of adsorption and desorption of phosphorus were pH dependent. Adsorption of P was maximum (58-98 % of added P) at pH 4. Both exchangeable P and ratio (desorbed P / adsorbed P) were significant at higher pH (pH 10) than at pH 4 and 7. No direct correlation between the quantity of organic matter and the P retention capacity could be obtained in the estuarine sediments. Harter (1969) observed a direct relationship between acid-extractable aluminium, organic matter and to a lesser extent acid-extractable iron content of the sediment and their ability to sorb and retain P. Rehm (1985) observed that a chemical bonding is rather responsible than the physical bonding for the exchange of P between water and sediments as the reaction rate increases with temperature and the phase change appears to be controlled by the formation of the chemical bonds with Fe, Al and Ca ions that are either on mineral surface or in solution.

Higher exchange capacity of sediments and the rapid exchange rate of P between sediments and water will be important in an estuary both at times of flushing by heavy rainfall and river outflow and at times of heavy phosphate demand by phytoplankton. Low salinity and pH and high turbidity at freshwater-end of the estuary favour the formation of the sorption complex. In the estuary mixing of this water with sea water present an environment of higher salinity and pH thus favouring regeneration. Therefore, coupling the properties of P sorption complex with change in the environmental properties associated with water as it flows from rivers through estuaries into the sea, the enhanced fertility of estuaries compared with adjoining freshwater and marine region appears as a natural consequence. In Mandovi estuary, pH of the water varied between 6.4 and 8.2. Therefore, it could be presumed that this pH will favour the desorption of the sorption complex, the formation of which is assumed to be in the freshwater-end where the pH is relatively low. Usually, a part of the phosphate carried by the solids as sorption complex is immediately available for regeneration. Another part which has incorporated in to the solids is available only after much longer contact with the changed environment.

### 5.8.3 Distribution and forms of nitrogen in estuarine sediments

The largest pool of nitrogen in the estuarine environment can be the organic nitrogen brought into the estuaries by river runoff. This organic-N undergo transformations. The most important among these processes are ammonification and nitrification. The ammonium produced by the decomposition diffuse out of the sediment into the overlying water column or be adsorbed onto the sediments. It is therefore, interesting to know how important ammonium adsorption was relative to its production by organic matter decomposition by determining the relationship between the amount of dissolved $NH_4$-N in pore water and the amount adsorbed on the sediments. Until recently there have been very few studies of the distribution of nitrogen in estuarine sediments. Keenay (1970) and Konard et al (1970) reported the sediment organic nitrogen distribution of Wisconsin lakes and Konard et al (1970) estimated various fractions of nitrogen compounds in sediments and found that fixed ammonium-N and amino acid-N accounted for about 50 % of the total nitrogen in these sediments. The nitrogen part of the organic matter deposited in marine basins was found to be partly regenerated as ammonia under reducing conditions and become oxidised to nitrate in sediment of positive Eh (Rittenberg et al, 1975). Campbell and Lee (1965), Bremner (1965), Degens (1965), Craft et al (1988). Bowden (1984) studied the distribution of nitrogen compounds in sediments and have made comprehensive reviews.

The concentration of various nitrogen species in water is the net result of the rates of N immobilisation, mineralisation, nitrification and denitrification. Observations of Hutchinson (1957) revealed that many lakes exhibited a dichotomic $NO_3$-N distribution pattern; maximum $NO_3$-N at intermediate depth: low $NO_3$-N in the surface waters due to immobilisation and low $NO_3$-N in the bottom waters due to denitrification. Serruya and Berman (1969) observed that the concentration of $NH_4$-N in surface waters is a critical parameter and high levels of $NH_4$-N in deep waters of stratified estuaries arise from a combination of $NH_4$-N from sediments and decomposition of settling sestonic material. A schematic presentation of the N transformations in sediments is shown in Fig 5.44.



A ) ammonification
B ) immobilization
C ) nitrification
D ) denitrification
E ) $N_2$ fixation

Fig No. 5.44. Schematic presentation of major transformations processes of nitrogen in sediments ( Kemp & Mundrochova - 1972 )

The forms and amounts of N in grab samples of three Wisconsin lake sediments were determined by Keeney et al (1970). In most sediments the bulk of nitrogen is in organic forms and usually present near the surface. The inorganic forms of nitrogen include nitrate which is soluble and easily leached or taken up; nitrite which is usually a transitional stage between nitrate and ammonium; ammonium which occurs as the easily removable exchangeable ion and also in more unavailable fixed (non exchangeable) forms and traces of gaseous forms such as dinitrogen and nitrogen monoxides and elemental nitrogen.

The principal source of plant-available nitrogen in sediments is organic nitrogen which is microbiologically converted via ammonium and nitrite to nitrate and the rate of production of nitrate is controlled by the rate of the breakdown of organic nitrogen to ammonium. This ammonium has the tendency to get adsorbed onto the sediment particles which may either be lost as fixed ammonium or get released to the water column as exchangeable ammonium. Byrnes et al (1972) have investigated $^{15}NH_4$-N transformations and migration in sediments *in-situ*. They found that some $NH_4$-N added to sediments is rapidly incorporated into organic-N. It has been established that microbial activity produces free ammonium in organic waterlogged sediment with C:N ratios less than 30:1 by atoms (Envezor, 1976)

In the present study dried sediment samples were ground after removal of calcareous particles and bottom fauna and estimation of Total-N, nitrate, nitrite and exchangeable $NH_4$-N was carried out as per the method of Bremner (1965). This involved removal of the ions with 2N KCl followed by steam distillation of the extract. Non-exchangeable (fixed) ammonium in sediments were evaluated by Mogilvkina (1969) who found the method of Silva and Bremner (1966) which is used here to be the most satisfactory. It involved the removal of exchangeable $NH_4$-N and organic-N by alkaline hypobromite followed by treatment with 5N HF - 1N HCl to liberate fixed $NH_4$-N. However, it is possible that ammonia or organic-N is still trapped in silicate minerals not decomposed by HF. Complex ammonium phosphate minerals are not determined by this method and these also may be present in small quantities in estuarine sediments.

Ammonium produced by the decomposition of organic nitrogen compounds in sediments can accumulate in pore waters, diffuse out of the sediments into the overlying water column or be adsorbed onto the sediments. The study was aimed to determine how important ammonium adsorption was, relative to its production by organic matter decomposition, by determining the relationships between the amount dissolved in the pore water and the amount adsorbed on the sediments in both sediment samples and laboratory experiments. The mechanism of ammonium adsorption in terms of whether exchangeable or non-exchangeable adsorption was more important, whether adsorption was reversible and whether the ammonium was being adsorbed preferentially onto the clay minerals in the sediments or onto the associated organic matter.

Ammonium adsorption on clay minerals as reported in soil science literature are (a) exchangeable ammonium, an ion-exchange reaction occurring on the surface of the clays and (b) non-exchangeable (fixed) ammonium, adsorption in the interlayers of the clay from the geochemical point of view. The earliest work on ammonium adsorption was done by Stevenson (1962) who found that fixed ammonium was the predominant form of nitrogen in some shales and igneous rocks. The importance of fixed ammonium in marine sediments was first shown by Stevenson and

Tilo (1970). It has been thought that almost all of the nitrogen found in sediment was organically bound, but they determined that fixed ammonium was 10-20 % of the total nitrogen. Other studies showing the importance of fixed ammonium in both marine and lake sediments include those of Keeney et al (1970) and Kemp and Mundrochova (1972). Hartman et al (1976) and Muller (1977) showed that the amount of fixed ammonium was linearly related to the potassium content of the deep-sea sediments and concluded that the ammonium is mainly fixed within illite.

Samples of sediments were collected using van Veen Grab. For the estimation of ammonium two sub-samples (I) up to 5cm and (ii) below 5 cm were collected and homogenised. Therefore, the results are expressed accordingly.

Adsorption and desorption isotherms for ammonium were determined by measuring the exchangeable and non-exchangeable ammonium of sediments that had been equilibrated in the laboratory with estuarine water having varying concentrations of dissolved ammonium. Sediments were homogenised before being used in the adsorption experiments. Filtered estuarine water was used in all the experiments. The ammonium concentrations were adjusted with ammonium chloride ($NH_4Cl$).

After initial experiments which showed that adsorption and desorption were rapid, ammoniated sea water and wet sediments in a 5:1 ratio were shaken for 2 days. The mixture was filtered and dissolved ammonium in the sea water and exchangeable and fixed ammonium in the sediments were measured. To determine if ammonium adsorption by organic matter was important, I treated the same sediments with 30 % $H_2O_2$ before adding the ammoniated water.

Standard analytical procedure (Bremner 1965) was used to determine various nitrogen forms in sediments. The ammonium dissolved in the pore water was determined by micro Kjeldahl method. Exchangeable ammonium is defined as the amount of ammonium released by shaking wet sediment with an unbuffered 2N KCl solution. The released ammonium includes both that dissolved in the pore water and that adsorbed on the sediment, because the amount of dissolved ammonium was subtracted from the total exchangeable ammonium. Exchangeable ammonium is used here as that fraction only which adsorbed on the sediment. Exchangeable and dissolved ammonium were measured in alternate samples.

The only method which release fixed ammonium from sediments is total destruction of the clay minerals. Organic-N compounds were first eliminated by a potassium hypobromite oxidation of the organic matter. The exchangeable ammonium was removed with potassium chloride and finally the clay structure was destroyed with a hydrofluoric-hydrochloric acid solution. The fixed ammonium released during the last step was measured by micro Kjeldahl method.

Pore water containing free inorganic nitrogen was removed from fresh sediment subsamples by centrifugal filtration. Tubes containing fresh sediments were spun at 5000 rpm for 20 min in a refrigerated centrifuge ($5^0$C). Details of the estimations are given in the chapter dealing with analytical methodology.

### 5.8.3.1 **Exchangeable ammonium** ($NH_4$-N exh)

Percentages of dissolved ($NH_4$-$N_{dis}$) and exchangeable ($NH_4$-$N_{exh}$), fixed ammonium ($NH_4$-$N_{fix}$) and organic-N concentrations in the sediments samples are give in Table 5.9.

**Table 5.9. Percentage of various fractions of nitrogen compounds and other characteristics of Mandovi estuarine sediments.**

| Station | Type of sediment | sediment pH | Org. N % | Fixed $NH_4$-N % | Exchangeable + Dissolved $NH_4$-N % |
|---|---|---|---|---|---|
| M1 | Silty clay | 8.0 | 78 | 14 | 8 |
| M2 | Silty clay | 7.8 | 86 | 11 | 3 |
| M3 | Silty clay | 7.2 | 76 | 19 | 5 |
| M4 | Sandy silt | 7.0 | 61 | 24 | 15 |
| M5 | Sandy silt | 6.4 | 63 | 19 | 18 |
| M6 | Silty sand | 6.4 | 56 | 19 | 25 |

I have worked out the relationships between exchangeable and dissolved ammonium in the estuarine sediments. It is found that both are linearly related with a correlation coefficient of 0.94 (Fig 5.45). Similarly the relationship between dissolved ammonium and non-exchangeable (fixed) ammonium also showed a positive correlation of 0.93 (Fig 5.46) which indicate that an equilibrium exist between these nitrogen compounds in the estuarine sediments. It is important to know the conditions responsible for the alteration of this equilibrium so that the sediment inorganic nitrogen availability in the estuarine sediment could be predicted.

Rosenfield (1979) reported dimensionless linear adsorption constants (K) of about 1-2 for ammonium in subtidal sediments for Long Island Sound. The constant K, is the ratio of sediment sorbed ammonium to free porewater ammonium in a given volume of fresh sediments. Similar measurements for Norths River sediments yield K constants that range from 0.80 to 3.31 depending on the sediment type. That is on a fresh volume basis sorbed ammonium is about 1 to 3 times more abundant than free pore water ammonium in these sediments.

The vertical profile of ammonium in sediments is established and maintained by a dynamic balance between production, consumption and physical transport of ammonium at each depth. Production of ammonium by microbial mineralisation of organic nitrogen is great in surface sediments, in part because the quantity and quality of organic nitrogen inputs is the highest (Bowden 1984). Ammonium removal from a given depth zone is attributable to both biological processes (e.g. plant uptake, microbial immobilization, nitrification etc.) and physical processes (e.g. tidal and groundwater flushing, diffusion along concentration gradients). In Mandovi estuary the balance of these processes normally favours the accumulation of ammonium in surface sediments with consistently lower values deeper down the sediment profile.

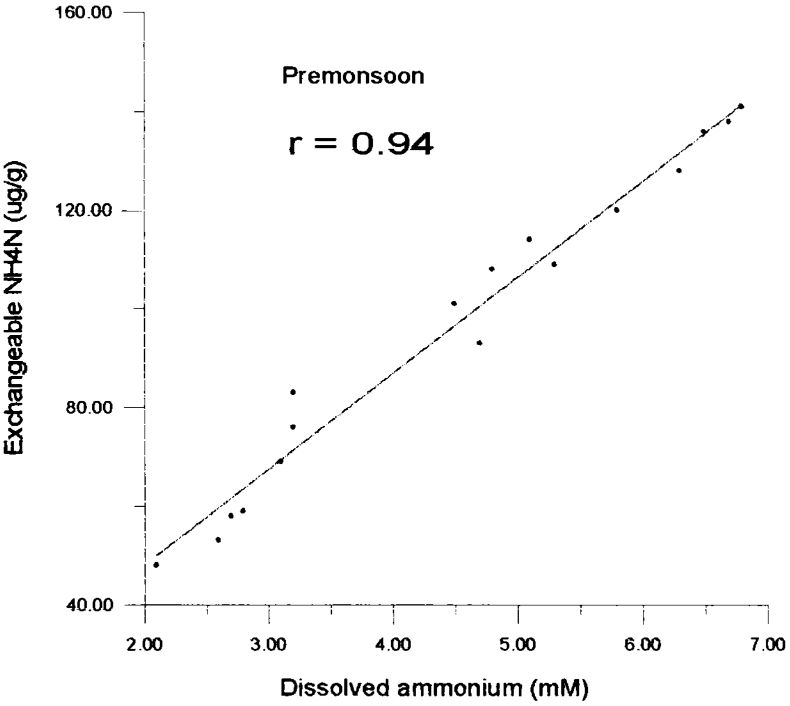


Fig. 5.45. Relationship between Dissolved ammonium and Exchangeable ammonium in estuarine sediments.

Exchangeable ammonium adsorption by sediment appears to be linear, reversible and predominantly associated with the organic matter rather than clay content. Fixed ammonium was also measured in samples and laboratory experiments. A linear relationship between fixed ammonium and dissolved ammonium was observed with a correlation coefficient of 0.87. The fixed ammonium appears to increase with increasing concentrations of dissolved ammonium but not as much as with exchangeable ammonium in the laboratory condition.

This suggests that a sort of dynamic equilibrium between dissolved, exchangeable and fixed ammonium in sediments exists. However, in the estuaries various other factors controlling the sorption-desorption processes and transformation processes of the nitrogen compounds may be responsible for maintaining this equilibrium.

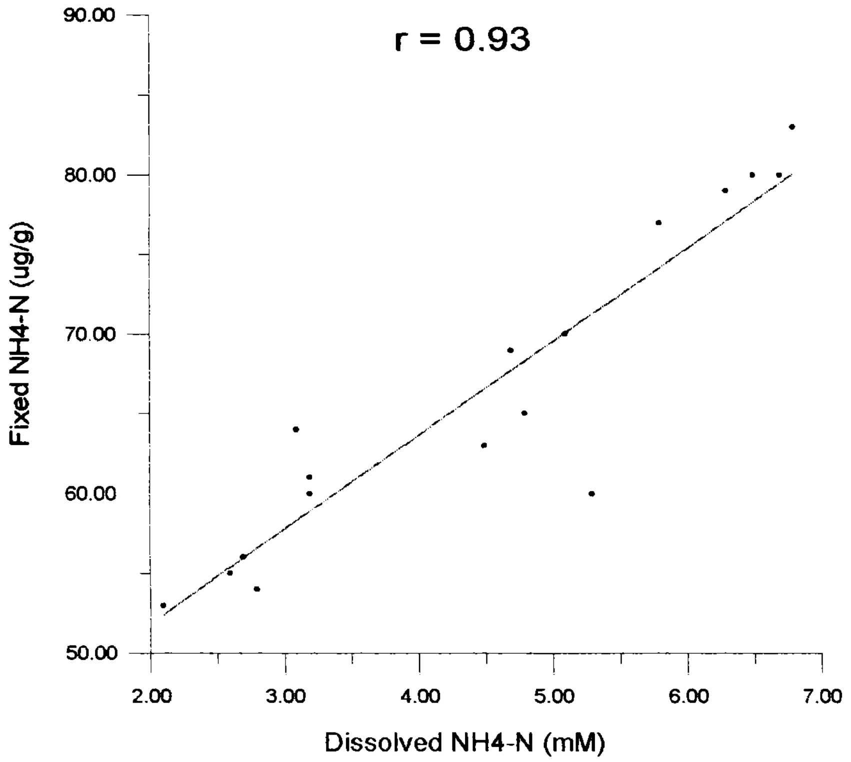


Fig. 5.46. Relationship between dissolved ammonium and fixed ammonium in estuarine sediments.

The above results indicate that apparently a dynamic "equilibrium" exists between dissolved, exchangeable and fixed ammonium in the sediments. The concentrations of exchangeable ammonium increased linearly with increasing concentrations of dissolved ammonium; exchangeable ammonium adsorption was rapid and reversible and predominantly associated with the organic matter rather than the type of sediments. The concentrations of fixed ammonium also increased with increasing concentrations of dissolved ammonium. This pool of nitrogen is very important in regulating the nitrogen supply to the overlying water column during non-monsoon months.

## 5.9 Phytoplankton

In the previous section, the distribution of nutrients (N & P) in the major compartments of the estuarine ecosystem *viz.* the water environment and the sediment environment has been discussed. The third major compartment - the phytoplankton - which mainly depend on the other two compartments for their metabolic requirements need special attention. Therefore, attempt has been made in this section to study the spatial and temporal variations of phytoplankton population, primary production, chlorophyll *a* content and species diversity indices to evaluate its relationships with other major compartments.

Generally estuaries are more productive both at primary and secondary levels as compared to adjoining sea or rivers. The continually changing environmental characteristics of the estuaries make them unique ecosystems. The kind of organisms most often thought of as being the first processors of added nutrients to the estuarine environment are the photoautotrophs : phytoplankton and macrophytes. Although little is known about the relative importance of their role, the autotrophic and heterotrophic bacteria also may utilize these materials. Until 1970's phytoplankton were often thought of as being diatoms large enough to be collected in nets. Subsequent observations revealed that plankton net could retain only a small portion of the total plankton algae. For nutrient utilization as well as primary productivity, the large sized group of phytoplankton may be of trivial importance (McCarthy et al 1977, Goering and Dugdale 1966). However, in the present study, phytoplankton was enumerated in the samples of water collected at different stations which was fixed with Lugol's iodine and preserved in 3 % formaldehyde. Identification of the phytoplankter was made as per the method of Vollenweider (1969) and Sournia (1978). A large volume of data base generated from the estuarine regions in the past by different workers (Thanks to Drs. V. P. Devassy and P. M. A. Bhattathiri) has also been used in this study.

### 5.9.1 Chlorophyll

Results indicated that the chlorophyll *a* concentrations in the estuary fluctuated widely and the values showed peaks during premonsoon season, and a sharp decline was noticed in the monsoon months throughout the estuary. A close look at the chlorophyll *a* (Chl *a*) data show that in the marine dominated area ( M1 & M2) the surface water concentration of Chl *a* ranged (Fig. 5.47) between 0.4 (June) and 4.9 $mg/m^3$ (may). The column Chl *a* concentration in this area showed variations between 1.6 (June) and 9.7 $mg/m^2$. In the estuarine area the surface Chl *a* concentration showed considerable increase as compared to MDA and ranged between (Fig. 5.48) 0.2 (August) and 5.9 $mg/m^3$ (May). As in the case of MDA the concentration showed an increasing trend from January to May and a sudden decline during the monsoon months.

Data from the FDA (M5) showed that the Chl *a* concentration was low in this area as compared to other areas. The concentration varied between 0.2 (June) and 2.0 $mg/m^3$ (May). The column Chl *a* concentration in the EA and FDA varied considerably. It was between 0.3 (July) and 13.8 $mg/m^2$ (May) for the EA (Fig 5.49) and in the FDA it showed a variation between 0.2 (July) and 2.2 $mg/m^2$.

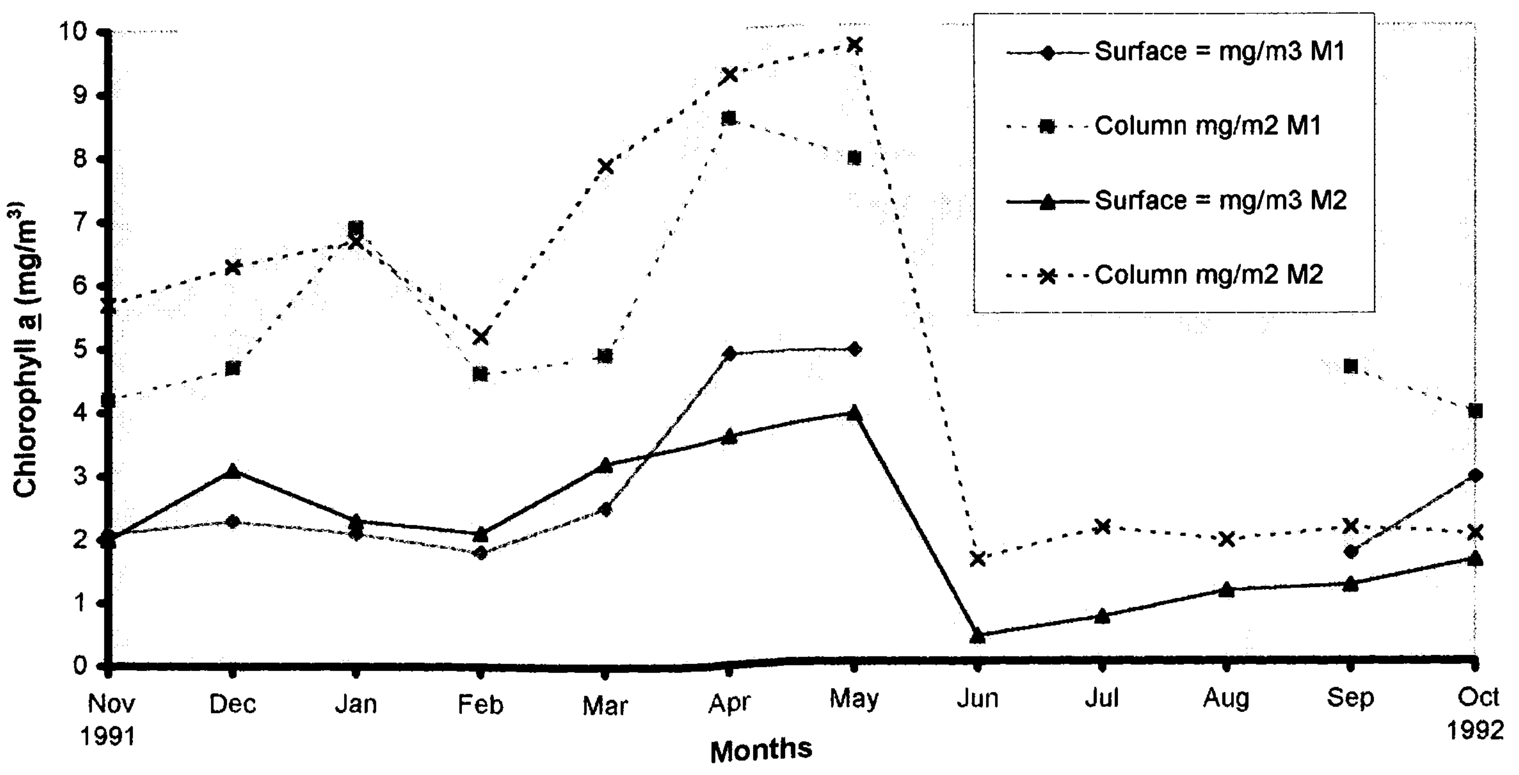


Fig. 5.47 Distribution of Chlorophyll a in MDA

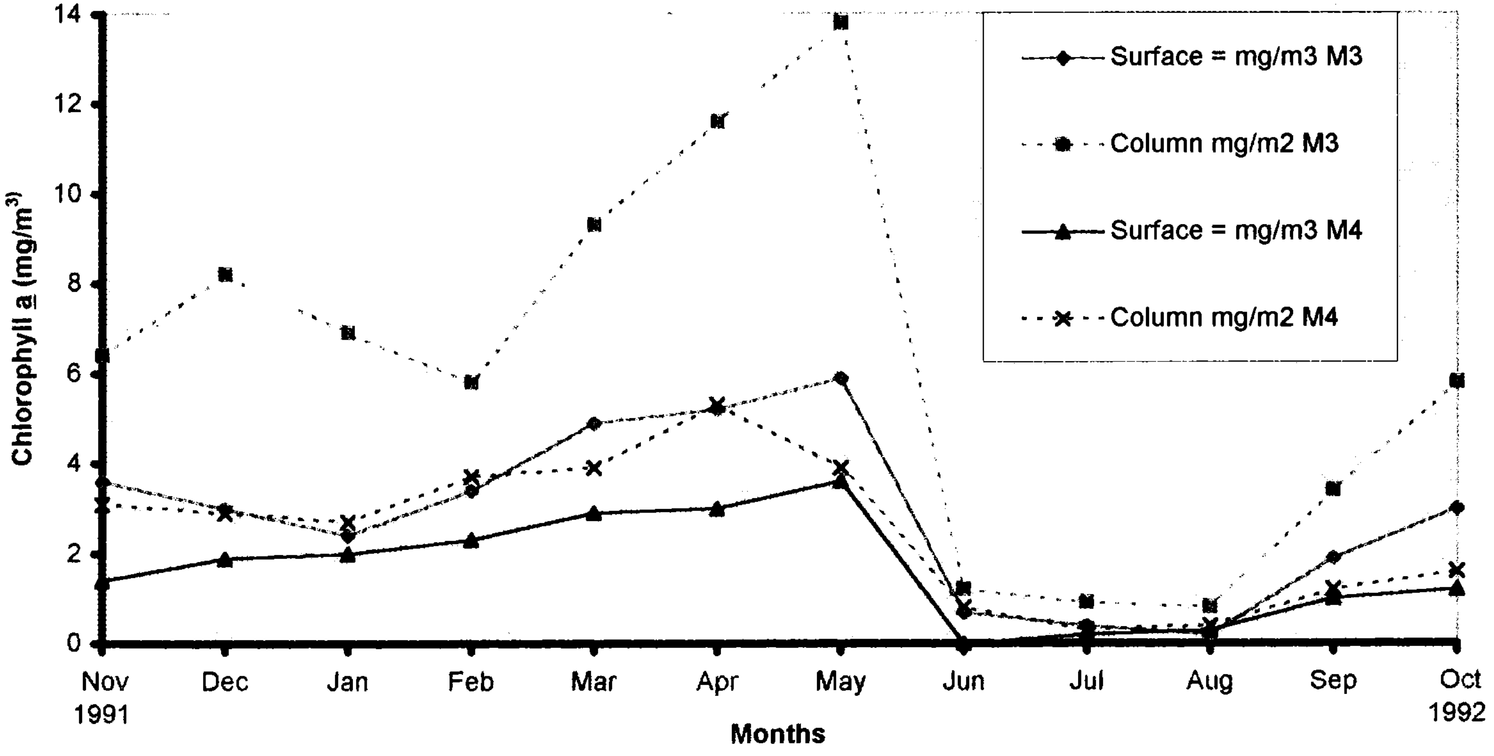


Fig. 5.48 Distribution of Chlorophyll a in EA

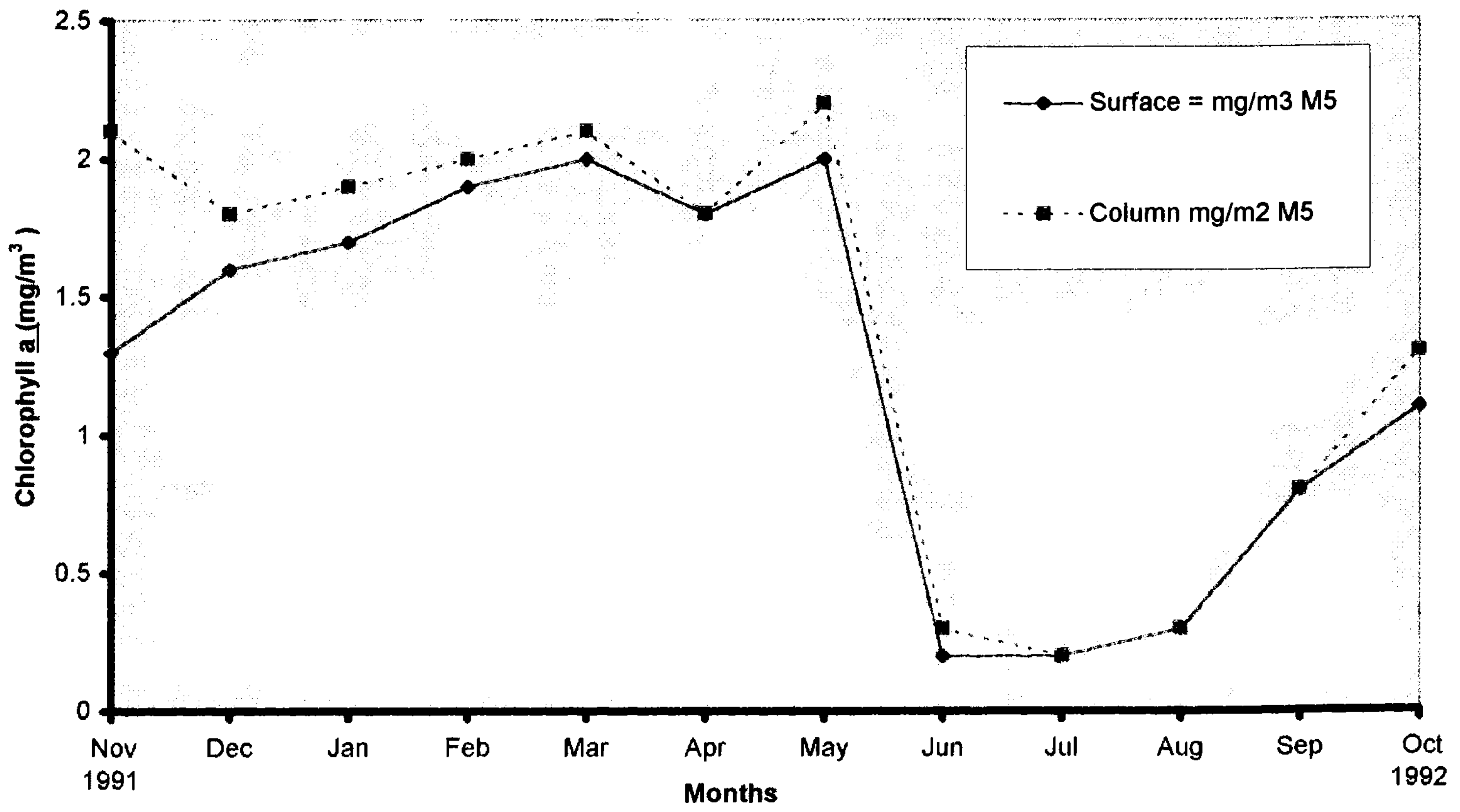


**Fig. 5.49 Distribution of Chlorophyll a in FDA**

Variations of concentrations with respect to seasons showed some interesting results. Concentrations of Chl *a* (both surface and column) were considerably low during monsoon throughout the estuary (0.2 to 1.9 $mg/m^3$ for surface Chl *a* and 0.2 to 3.4 $mg/m^2$ for column Chl *a*). A recovery is noticed during the post monsoon season. During this period the concentration varied between 1.10 and 3.6 $mg/m^3$ for surface Chl *a* and between 1.3 and 8.2 $mg.m^2$ (column Chl *a*). During premonsoon, the estuary exhibited the highest concentration of Chl *a* (1.8 to 5.9 $mg/m^3$)and column Chl *a* (1.8 to 13.8 $mg/m^2$).

Chlorophyll *a* values in the estuary generally follow changing environmental conditions in the estuaries. During monsoon when the water was turbid and the estuary become freshwater dominated, Chl *a* concentration dropped considerably. Though, during monsoon the supply of inorganic nutrients in to the estuary was maximum, the Chl *a* concentration remained considerably low. But, during the rest of the periods nutrient concentrations and Chl *a* showed significant correlations.

Chlorophyll *a* concentrations in the Zuari and Mandovi estuaries were studied by Devassy & Bhattathiri (1974), Bhattathiri et al (1976), Devassy & Bhargava (1978), Dwivedi et al (1974). In general the observations showed that the surface water chlorophyll *a* concentrations were higher than bottom waters, and majority of the stations showed seasonal variations with higher concentrations during pre-monsoon and post-monsoon months. Bhattathiri et al (1976) recorded variations in the column Chl *a* concentrations from 1.6 to 12.7 $mg/m^2$ during pre-monsoon period in Mandovi estuary. Bhargava and Dwivedi (1976) showed Chl *a* variations from 0.56 to 11.86 $mg/m^3$ during post-monsoon months.

From the Figure(5.47-5.49) it is clear that the Chl *a* maxima was during May throughout the estuarine region. A secondary maxima also could be observed during the post monsoon period (October). It is interesting to note that the concentration during the Chl *a* maxima in MDA and EA was almost similar. (5.9 mg/m3). Whereas, the Chl *a* maxima was obtained at FDA at a Chl *a* concentration around 2 mg/m$^3$.

In Cochin Backwaters Qasim and Reddy (1967) recorded Chl *a* variation between 2.96 and 7.34 mg/m$^3$ at the surface waters. Nair et al (1975) recorded Chl *a* concentration as high as 206 mg/m$^3$ for the Vembanad Lake (Kerala). However, Joseph & Pillai (1975) obtained highest Chl *a* values of 21.2 mg/m$^3$ during post-monsoon season for Cochin Backwaters. In the Vellar estuary Chl *a* concentrations varied from 2.05 to 21.56 mg/m$^3$ (Krishnamurthy and Sundararaj 1973). In Killai Backwaters Chl *a* variatios have been found to be between 1.55 and 12.7 mg/m$^3$ (Bhatnagar 1971). Devassy (1983) observed that abnormally high Chl *a* concentrations normally synchronized with bloom situations in Mandovi and Zuari estuaries. Annual average column Chl *a* concentration between 5.1, 6.2 and 8.2 mg/m$^2$ were recorded for Zuari, Cumbarjua canal and Mandovi estuary respectively (Devassy, 1983). Bhargava and Dwivedi (1976) reported the annual mean concentrations of surface chlorophyll *a* as 4.12, 4.42. and 3.05 mg/m$^3$ in Zuari, Cumbarjua and Mandovi estuary respectively.

Fisher et al (1988) studied the chlorophyll *a* distribution in the Chesapeake Bay which was found positively correlated with temperature and the position (in terms of salinity) of the chlorophyll maxima was inversely correlated with temperature. This means that in the Chesapeake Bay the Chl *a* maxima was both large and closer to the freshwater at higher temperature.

## 5.9.2 Phytoplankton population

Variations in the surface phytoplankton (diatoms, dinoflagellates and other algae) counts indicated that 45 diatom species belonging to 26 genera, 8 dinoflagellates species belonging to 6 genera and 3 species of blue green algae and 2 green algae were encountered in the estuaries during the post-monsoon.

The cell concentrations at the surface fluctuated from 12.2 x $10^3$/l (July) to 1203 x $10^3$/l (May) in the estuarine region. The species composition indicated that diatoms were the predominant organisms and the maximum cell concentration were reached during the premonsoon period. Even when the diatom numbers were minimum, they contributed about 60 % of the total phytoplankton in the estuary. The distribution of dinoflagellates were erratic and no definite pattern could be observed during the study period.

### 5.9.2.1 Seasonal variations

Phytoplankton exhibited a bimodal peak in Mandovi showing a prominent peak during May and an occasional peak in October. The most frequently occurring phytoplankton group recorded during premonsoon is given in Table 5.10.

In Mandovi estuary the blue green algae *Richelia intracellularis* and the diatom *Fragilaria oceanic* dominated the population during pre-monsoon in the mouth area. Other dominant forms were *Rhizosolenia stolterforthii*, *Coscinodiscus* sp; *Nitzschia* sp; *Melosira sulcata*, *Chaetoceros* sp; *Thalassiosira* sp, *Thalassiothrix* and *Skeletonema costatum*. During pre-monsoon blooms of *Trichodesmium erythreaum* was noticed near the mouth (M1) and a quantitative estimation showed that this species alone contributed over 90 % of the total phytoplankton in the sample and the rest were mainly *Chaetoceros*, *Coscinodiscus* sp. *Nitzschia* sp. and *Pleurosigma* sp. By the onset of monsoon heavy diatom bloom of *Fragilaria oceanica* was noticed near the mouth (M1). As the monsoon advanced the phytoplankton composition both qualitatively and quantitatively was found to be poor. Phytoplankton species composition during post-monsoon season is given in Table 5.11.

**Table 5.10. Dominant phytoplankton species expressd as Nos x $10^4$/litre during premonsoon.**

| | FDA | | EA | | MDA | |
|---|---|---|---|---|---|---|
| | HT | LT | HT | LT | HT | LT |
| Station. No. | 1 | 2 | 3 | 4 | 5 | 6 |
| *Nitzschia sp* | 2.6 | 9.4 | 0.4 | 2.4 | 2.2 | 4.0 |
| *N.migrans* | 0.4 | 0.1 | 0.2 | 0.2 | 1.4 | 1.3 |
| *N.closterium* | - | - | - | - | 0.2 | 0.2 |
| *N.seriata* | 3.6 | 12.2 | 7.2 | 0.04 | 10.4 | 3.4 |
| *N.longissima* | - | - | 1.1 | 0.2 | 6.4 | 1.8 |
| *N.bilobata* | 0.01 | 0.01 | | 0.04 | 1.3 | 0.6 |
| *N.panduriforms* | - | - | 0.6 | 0.1 | 1.7 | 0.2 |
| *Pleurosigma sp.* | 0.01 | 0.4 | 0.6 | 0.06 | 0.4 | 0.03 |
| *Diploneis sp.* | - | 0.2 | 0.6 | 0.4 | 0.3 | 0.01 |
| *Leptocylindrus sp* | 2.2 | 13.0 | 5.2 | 2.6 | 2.0 | 1.2 |
| *Chaetoceros sp.* | 4.4 | 22.0 | 1.0 | 2.1 | 3.8 | 1.6 |
| *C.lorenzianus* | - | - | 1.2 | 1.0 | 1.8 | 2.1 |
| *C.decipiens* | - | - | - | - | 0.1 | 0.2 |
| *C.peruvianus* | - | - | - | | 0.01 | |
| *Melosira sp.* | 1.0 | 6.0 | 0.04 | 0.8 | 0.13 | 0.03 |
| *M.sulcatta* | - | - | 0.2 | 0.6 | 1.11 | 0.2 |
| *Navicula sp.* | 2.4 | 2.4 | 1.0 | 2.4 | 1.2 | 2.4 |
| *Rhizosolenia sp.* | 0.4 | 1.0 | 0.4 | 0.8 | 0.2 | 0.4 |
| *R.setigera* | - | - | - | 0.12 | 0.6 | 0.01 |
| *R.alata* | - | - | 0.6 | 0.04 | 0.05 | 0.02 |
| *R.stolterforthi* | 0.07 | - | 0.8 | 0.8 | 0.04 | 0.06 |
| *R.shrubsolei* | - | - | 0.2 | 0.2 | 0.3 | 0.10 |
| *Thalassiosira sp.* | 3.8 | 43.2 | 5.6 | 0.7 | 2.03 | 1.11 |
| *Thalassiothrix sp.* | 4.0 | 3.2 | 5.6 | 2.9 | 2.03 | 1.07 |
| *T.longissima* | - | - | 1.7 | 0.02 | 4.11 | 2.03 |
| *Thallssionema* | - | 0.06 | 0.2 | 0.2 | 1.7 | 1.4 |
| *T.nitzschoides* | - | - | 0.4 | 0.2 | 0.14 | 0.7 |
| *Coscinodiscus sp.* | 0.2 | 0.2 | 0.4 | 2.4 | 0.02 | 0.2 |
| *Coscinosira sp.* | - | - | 0.7 | 0.1 | 0.10 | 0.2 |
| *Biddulphia sp.* | 0.02 | 0.4 | 0.2 | 0.06 | 1.1 | 0.6 |
| *Asterionella japonica* | | 0.08 | 1.0 | 1.1 | 2.0 | 1.7 |
| *Licmophora sp.* | | | 0.8 | 0.6 | 0.01 | 0.2 |
| *Fragiaria sp.* | | 0.4 | 0.11 | 6.4 | 0.03 | 0.4 |
| *Dinnophyxis sp.* | - | 0.2 | 0.1 | 0.2 | 0.2 | 0.2 |
| *Cerataulina sp.* | - | 1.2 | 0.05 | 0.16 | 0.01 | 0.01 |
| *Skeletonema costatum* | 3.4 | 3.4 | 1.6 | 1.2 | 1.2 | 1.6 |
| *Streptotheca* | | - | 0.02 | 0.8 | 1.7 | 0.8 |
| *Climacosphaenia* | 0.4 | 0.4 | 0.8 | 0.8 | 1.4 | 0.12 |
| *Planktoniella* | 0.01 | - | 0.6 | 0.2 | 1.0 | 0.8 |
| *Ditylum* | - | - | 0.4 | 0.2 | 0.8 | 0.4 |
| *Silicoflagellate* | 0.2 | 0.01 | | | 0.4 | 0.2 |
| *Ceratium sp.* | - | - | 0.2 | 0.10 | 0.10 | 0.60 |
| *Peridinium sp.* | 0.2 | 0.2 | 0.8 | 0.2 | 0.2 | 0.2 |

**Table 5.11. Phytoplankton species composition during post monsoon in Mandovi estuary**

**DIATOMS**

*Amphiprora gigantea*
*Asterionella japonica*
*Aulacodiscus sp.*
*Bacillaria paradoxa*
*Bacteriastrum hyalinum*
*Bellerochia malleus*
*Biddulphia mobilensis*
*B. sinensis*
*Chaetoceros curvisetus*
*C. laciniosus*
*C. lorenzianus*
*Coscinodiscus excentricus*
*C. centralis*
*C. marginatus*
*C. radiatus*
*Coscinodiscus sp.*
*C. oculus iridis*
*Cyclotella striata*
*Ditylum sol*
*D. brightwell*
*Eucampia zodiacus*
*Fragilaria oceanica*
*Hemiaulus sinensis*
*Leptocylindrus danicus*
*L. minimus*
*Liconophora abbreviata*
*Melosira sulcata*
*Nitzschia closterium*
*N. bilobata*
*N. longissima*
*N. seriata*
*N. sigma*
*Navicula membraneae*
*Pinnularia alpina*
*P. angulatum*
*Pleurosigma elongatum*
*Rhizosolenia alata*
*R. robusta*
*R. stoterfothii*
*R. styliformis*
*Schroederella delicatula*
*Stephanopyxis palmeriana*
*Thalassionema nitzschioides*
*Triceratium favus*
*Tetraselmis gracilis*

**DINOFLAGELLATES**

*Ceratium macroceros*
*C.furca*
*Dinophysis caudata*
*Exuviella marina*
*Gonyaulax sp.*
*Peridinium divergence*
*P. depressum.*
*Prorocentrum micans*

**OTHER ALGAE**

*Flagellates*
*Tetraselmis gracilis*

Post-monsoon period was very conducive for maximum proliferation of both diatoms and dinoflagellates. During this season bloom of *Nitzschia closeterium* occurred (October) near the mouth and the coastal regions and that alone contributed 66% of the total population. Other species dominated during this period was *Pleurosigma*. *Tetraselmis gracilis* and *Chaetoceros* sp.

### 5.9.2.2 Species diversity

One of the most important information pertinent to ecological studies is the number of species present in an environment and the distribution of these within the population. It gives a measure of the way in which individuals in an ecological community are distributed among species. According to McArthur (1965). Shannon-Weaver theory of information function is the most useful measure of diversity index. It gives the relation of the diversity index to the population as

$$D = \sum_{n=1}^{S} P_n l_{n2}(1 / P_n)$$

Where $P_n$ is the proportion of the sample belonging to n^th^ species and S is the total number of species in the sample. Species diversity index varied between 0.38 (May) to 4.6 (June) during pre-monsoon.

In the Zuari and Mandovi estuaries the species diversity indices of phytoplankton varied from 0.49 to 4.2 during pre-monsoon (Devassy 1983) and when the bloom occurred it was between 0.49 and 3.2. In Cochin backwaters the indices were found to vary between 1.59 and 4.5 (Devassy and Bhattathiri 1974) and during the bloom period, the values were still lower. In the case of Vellar estuary the indices varied from 0.1 to 1.63 for diatoms and from 1.59 to 4.5 for dinoflagellates. Platt and Subba Rao (1970) measured the diversity index as the diatom bloom progressed and observed that the values varied between 0.57 and 3.3. Edden (1971) showed that for phytoplankton from the Indian Ocean, the diversity index ranged from 2.23 to 4.54. During massive *Trichodesmium* bloom in the Goa coast the indices were found to vary from 0.05 to 0.96. whenever the bloom declined the values rose as high as 2. (Devassy et al 1978, Devassy and Goes 1988).

It is known that plankton of the tropical waters has higher species diversity than the plankton of the temperate latitude (Mullin, 1967). In the Mandovi and Zuari estuaries diverse phytoplakton species composition was observed when the diversity index was low. An inverse correlation between diversity and productivity has been observed (Grindley 1979). Greater species diversity occurred in waters of high salinity and low phosphate (Raymont 1980). Lack of nutrients or spatial heterogenity do not seem to be factors affecting species diversity in the estuaries. Anologous situations where diversity tend to decrease with higher standing stock have been reported (Deevey 1971).

### 5.9.3 Primary Productivity

Primary production, estimated as $^{14}C$ assimilation, was observed fluctuating from season to season and from station to station and showed seasonal and spatial heterogenity as was observed with Chl *a* concentration and phytoplankton cell counts.

As in the case of Chl *a*, primary production values were higher in the estuarine regions compared to MDA and FDA. Surface primary production at the marine dominated area (M1 & M2) varied between 4.0 (July)and 63 mgC/m$^3$/h (May) (Fig. 5.50) and the column concentration ranged 6.0 (July) and 104 mgC/m2/h (May). Estuarine area exhibited slightly higher concentrations as compared to the MDA and the range of surface primary production concentration was between 2 (June) and 91 mgC/m$^3$/h (May) (Fig. 5.51). Column production showed a similar pattern as in the case of MDA. It varied between 2 (June) and 104 mgC/m$^2$/h (May). In general primary production in the freshwater dominated area was low as compared to MDA an EA. The surface production ranged between 2 (June) and 40 mgC/m$^3$/h (October) and the column production varied (Fig 5.52) between 2 (June) and 57 mgC/m$^2$/h (October).

Observations carried out in the Mandovi estuary (Devassy 1983, Bhattathiri & Devassy 1979, Bhargava and Dwivedi 1976) show that in Mandovi the productivity values as high as 81.83 mgC/m$^3$/h at the surface and 135.38 mgC/m$^2$/h in the column was recorded during October. Devassy (1983) observed that the dominant phytoplankton contributing to higher production were *Leptocylindrus danicus* in December (33.9%; *Skeletonema costatum* 98.9%) and *Leptoclindrus minimum* (31.%) in October and *Richelia intracellularis* (90.3%) in May. However, in this study such details were not worked out. Bhattathiri &

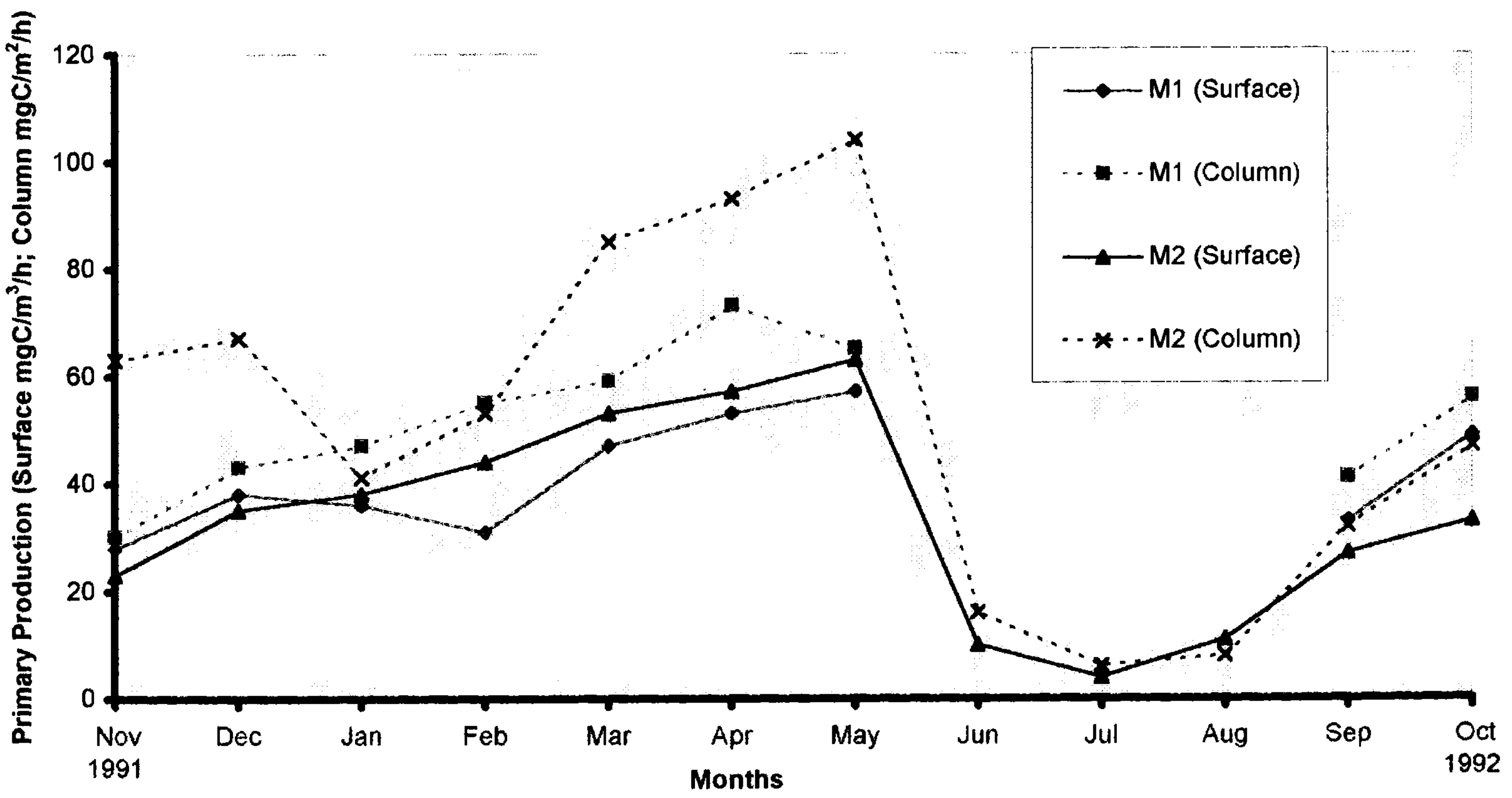


Fig 5.50 Primary Productivity in the waters of MDA

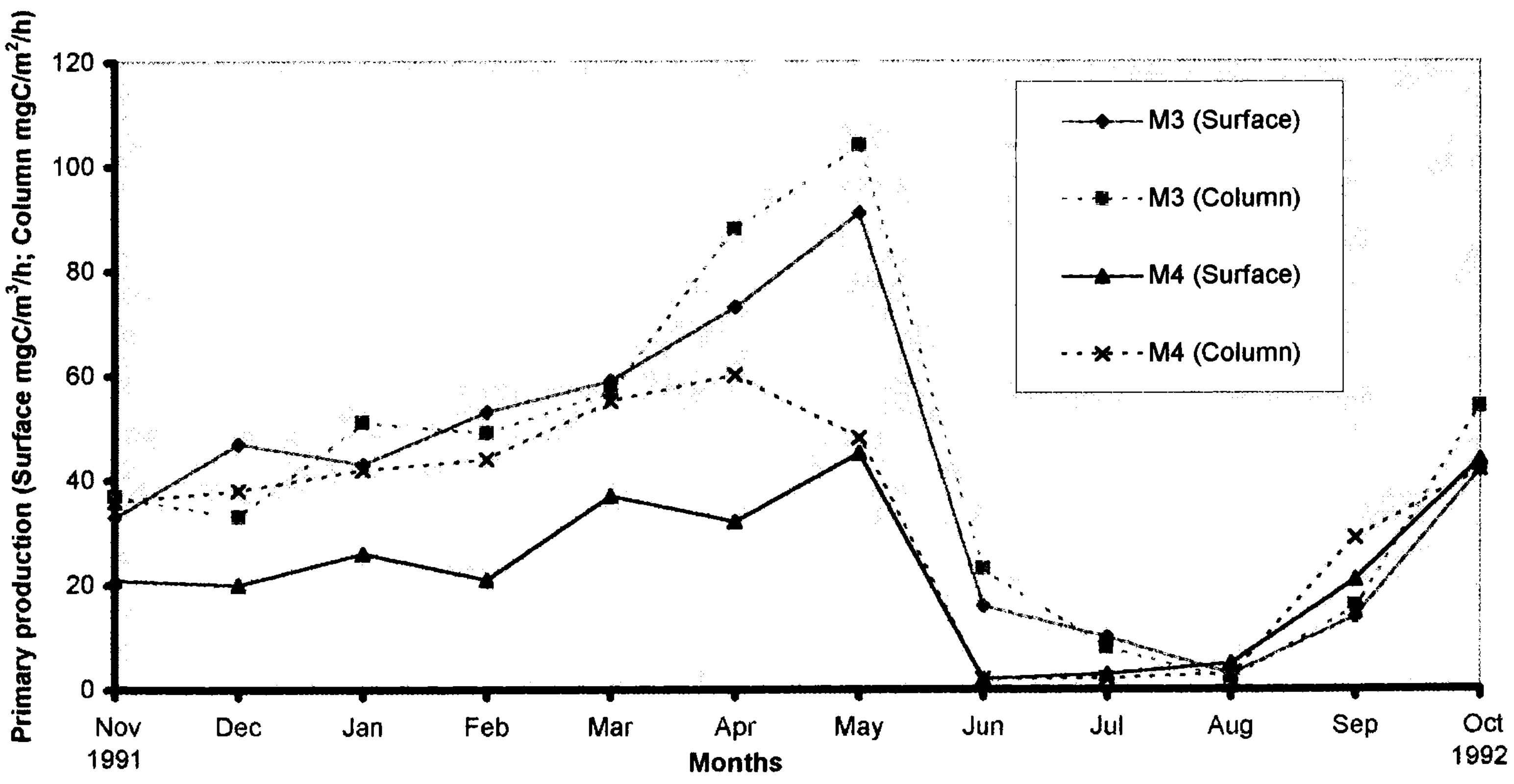


Fig. 5.51 Primary Productivity in the waters of EA

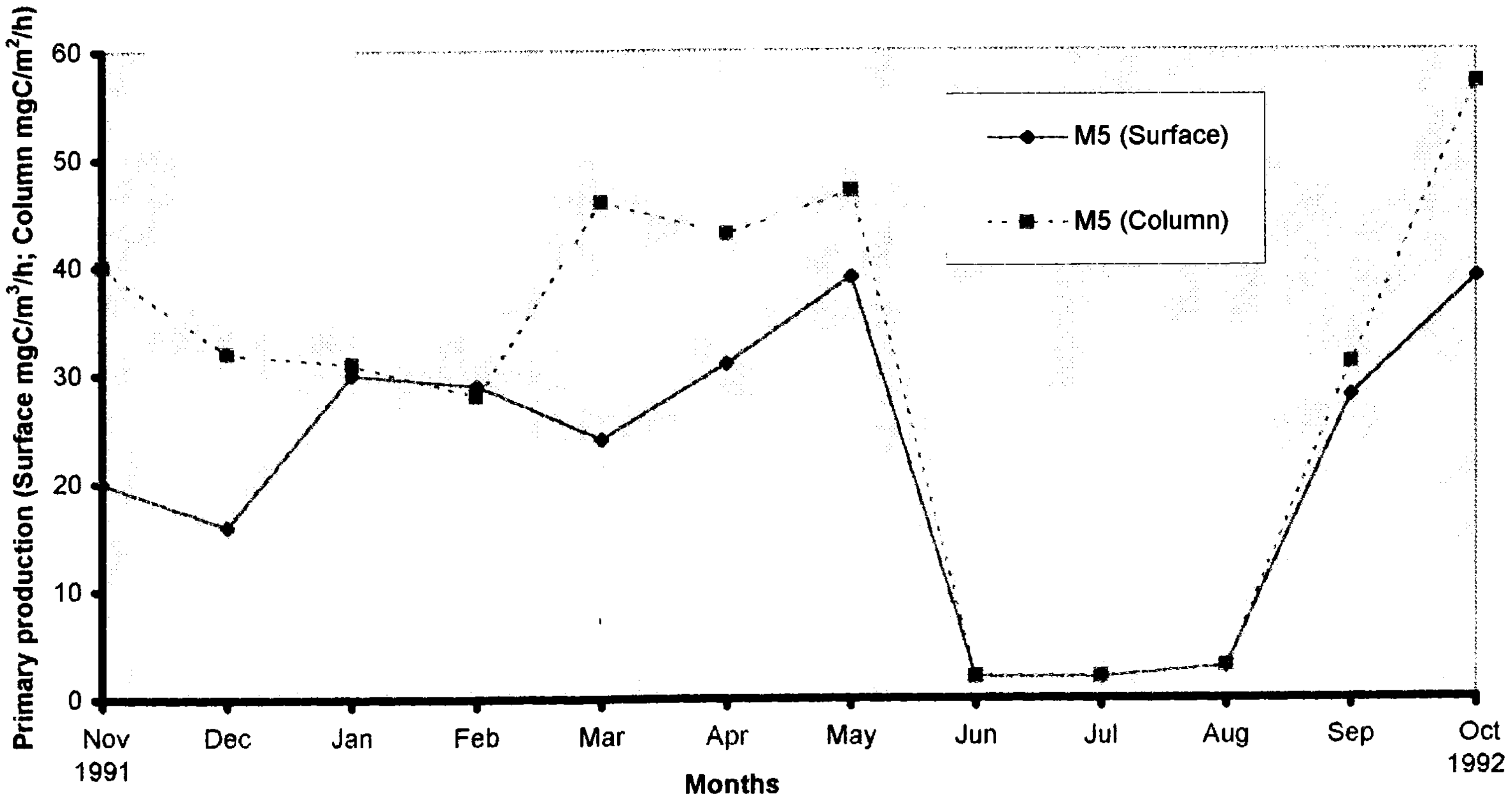


Fig. 5.52 Primary Productivity in the waters of FDA

Devassy (1979) observed that productivity peaks were observed during February, May and October and the highest surface production was obtained during October. The highest column production was recorded during September (104.32 mgC/$m^2$/h) at the mouth of Mandovi and coastal regions and the same was attributed to the nutrient rich cold water entering the estuarine mouth and coastal regions due to upwelling. Devassy, while studying the ecology of Mandovi river in relation to the upwelling of the area, found that primary production was high during October. Species dominance with respect to production showed that Coscinodiscus marginatus (34.3%) dominated in February, Richelia intercellularis (65.4%) in May Nitzschia closterium in June (49.9%) and October (54.6%).

Seasonal variations of observed primary production, chlorophyll *a* and phytoplankton cell count in Mandovi estuary (Devassy, 1983) is given in Table 5.12.

**Table 5.12. Seasonal variations of biological characteristics of Mandovi, Zuari estuarine system.**

| | | Pre-monsoon | Monsoon | Postmonsoon |
|---|---|---|---|---|
| Primary production (mgC / $m^2$ / h) | Zuari | 43.83 | 21.31 | 64.48 |
| | Cumbarjua canal | 72.49 | 11.97 | 71.49 |
| | Mandovi | 65.75 | 10.20 | 99.11 |
| Chl *a* (mg/$m^3$) | Zuari | 5.97 | 1.28 | 7.76 |
| | Cumbarjua canal | 7.51 | 2.51 | 8.73 |
| | Mandovi | 6.62 | 4.25 | 13.64 |
| Phytoplankton cell count x $10^3$/$m^2$ | Zuari | 201.56 | 106.17 | 477.75 |
| | Cumbarjua canal | 415.61 | 90.27 | 184.22 |
| | Mandovi | 364.82 | 146.02 | 655.30 |

During post monsoon period the following major groups were identified in the estuarine and marine dominated regions (Table 5.13).

Table 5.11. **Dominant groups of phytoplankton identified during monsoon period from the estuarine regions.**

| | Marine dominated area | Estuarine area |
|---|---|---|
| *Coscinodiscus marginatus* | 11% | 15% |
| *C. radiatus* | 4.8 % | 4 % |
| *Coscinodiscus sp.* | 16.2 % | 18 % |
| *Cyclotella striata* | 6.4 % | 5.6 % |
| *Leptoclindrus damicus* | 3.8 % | 28.6 % |
| *Navicula longissima* | 16 % | 13 % |
| *Nitschia longissima* | 12 % | 2.7 % |
| *N. serata* | 14 % | 8 % |
| *N. bilobata* | 17 % | 25 % |
| *Rhizosolenia alala* | 19 % | 7 % |
| *Chaetoceros borenzianus* | 23 % | 18 % |

The above species dominated the total phytoplankton population and the percentage indicate that some species proliferated more than 25 % of the total bulk of the phytoplankton.

Distribution of various phytoplankton species collected during post-monsoon period from the nearshore regions are given in Table 5.12. In general, it was noticed that phytoplankton population was considerably high in this area as compared to the estuarine regions. Probably physico-chemical conditions in the nearshore region is more conducive for the proliferation of the species observed, which is the reason for higher phytoplankton population. However, such details will be discussed in the following sections.

Variations of phytoplankton population during the post-monsoon period in the nearshore regions is given in Table 5.14. A comparison of the data indicate that compared to pre-monsoon period phytoplankton counts at the sub-surface was considerably low. However, surface phytoplankton population during post-monsoon was higher as compared to pre-monsoon season (Table 5.15).

**Table 5.14 Variations of phytoplankton abundance ($10^4 l^{-1}$) in post-monsoon at the nearshore region (Station M0)**

| Species | Surface | Depth 5(m) | Depth (15m) |
|---|---|---|---|
| *Nitzschia seriata* | 1.8 | 1.0 | 0.8 |
| *Nitzschia closterium* | 3.0 | 2.0 | 1.2 |
| *Nitzschia sp.* | 2.0 | 2.0 | 1.2 |
| *Chaetoceros sp.* | 22.2 | 15.8 | 10.6 |
| *Schroderella sp.* | 0.4 | 0.4 | 1.6 |
| *Biddulphia sp.* | 1.1 | 0.2 | 0 |
| *Planktoniella sp.* | 0.8 | 0.2 | 0.2 |
| *Pleurosigma sp.* | 0.6 | 0.1 | 0.4 |
| *Ditylum brightwellii* | 0.2 | 0.8 | 0.4 |
| *Coscinodiscus sp.* | 1.1 | 1.0 | 1.0 |
| *Ceratulina sp.* | 0.8 | 0.2 | 0.4 |
| *Navicula sp.* | 28.8 | 70.0 | 8.2 |
| *Leptocylindrus sp.* | 2.0 | 4.2 | 1.2 |
| *Rhizosolenia sp.* | 1.6 | 1.0 | 0 |
| *Skeletonema costatum* | 80.8 | 71.8 | 36.8 |
| *Thalassiosira sp.* | 0.2 | 0.2 | 0.4 |
| *Thalassiothrix sp.* | 2.8 | 1.6 | 1.8 |
| *Melosira sp.* | 2.8 | 4.2 | 2.2 |
| *Eucampia zoodialus* | 0.1 | 0.2 | 0.8 |
| *Fragilaria sp.* | 1.0 | 1.1 | 0.2 |
| *Silicoflagellates* | 0.2 | 0 | 0 |
| *Oscillatoria sp.* | 0.2 | 0.8 | 0 |
| *Ceratium sp.* | 1.1 | 0.4 | 0.8 |
| *Prorocentrum micans* | 0.2 | 0.1 | 0 |
| *Peridinian sp.* | 0.8 | 0.2 | 0.6 |
| *Dinophysis* | 0.8 | 0.2 | 0.2 |
| Total | 157.4 | 179.7 | 71 |

**Table 5.15 Spatial variation phytoplankton abundance ($10^4 l^{-1}$) in pre-monsoon at the near shore region.**

| Species | Surface | Depth(5m) | Depth(15m) |
|---|---|---|---|
| *Nitzschia seriata* | 8.2 | 2.6 | 0.4 |
| *Nitzschia closterum* | 0.3 | 1.0 | 0.4 |
| *Nitzschia sp.* | 0.2 | 1.0 | 1.2 |
| *Chaetoceros sp.* | 81.0 | 60.6 | 10.4 |
| *Biddulphia sp.* | 1.9 | 0.2 | 0.8 |
| *Planktoniella sp.* | 7.2 | 5.6 | 3.2 |
| *Pleurosigma sp.* | 7.8 | 3.2 | 0.2 |
| *Ditylum brightwellii* | 1.9 | 0.2 | 0 |
| *Coscinodiscus sp.* | 19.3 | 7.8 | 6.2 |
| *Ceratulina sp.* | 1.8 | 0.2 | 0 |
| *Navicula sp.* | 16.8 | 12.6 | 5.3 |
| *Surirella sp.* | 0.8 | 0.2 | 0.2 |
| *Leptocylindrus sp.* | 11.8 | 13.2 | 8.6 |
| *Rhizosolenia sp.* | 3.7 | 1.8 | 0.3 |
| *Skeletonema costatum* | 1.2 | 1.3 | 0 |
| *Thalassiosira sp.* | 2.9 | 1.1 | 1.3 |
| *Thalassiothrix sp.* | 3.8 | 3.2 | 0.9 |
| *Melosira sp.* | 9.2 | 1.3 | 1.0 |
| *Asterionella japonica* | 7.3 | 1.4 | 1.8 |
| *Eucampia zoodialus* | 0.2 | 0.2 | 0 |
| *Fragilaria sp.* | 2.1 | 1.2 | 1.2 |
| *Silicoflagillates* | 0.8 | 0.2 | 0 |
| *Noctiluca sp.* | 1.9 | 1.8 | 0.3 |
| *Oscillatoria sp.* | 3.1 | 2.8 | 1.1 |
| *Ceratium sp.* | 2.2 | 2.1 | 1.8 |
| *Prorocentrum micans* | 0.6 | 0.2 | 0.2 |
| *Peridinian sp.* | 0.8 | 0.7 | 0.2 |
| *Dinophysis* | 1.1 | 1.8 | 0.3 |
| Total | 199.9 | 129.5 | 47.3 |

## 5.10 Interrelationships between plankton and nutrients

The exchange of chemical elements between sea water and the biomass is a cyclic process. The cycle may be broken down in to two phases: synthesis and regeneration. Elements are withdrawn from the water during the synthetic phase by photosynthesis in the proportions required for the growth of the primary producers, which are predominantly the phytoplankton. These elements are ultimately returned to the water in the regenerative phase as the decomposition products and excretions of both the primary producers and the subsequent members of the food chain, which prey upon them, including the microorganisms which complete the decomposition of organic matter. In other words, the ratio of change of the nutrients in water is equivalent to the ratio of their concentration in phytoplankton.(Redfield et al 1963).

Under natural conditions photosynthesis of phytoplankton is regulated spatially and temporally by several environmental factors. It should obtain a range of substances from their environment in order to sustain growth and division. Some of the universally required constituents are available in abundance relative to what is needed such as $CO_2$, $Na^{-}$, $K^{-}$, $Mg^{2-}$, $Ca^{-}{}_{1}$ and $SO_4^{2-}$, a variety of elements such as N, P, Fe, Mn, Zn, Cu, Co etc present in very low concentrations. The latter group of elements are therefore, considered as micronutrients, among them nitrogen and phosphorus which are essential for the organism are called the essential micronutrients.

In this section the relationships between various forms of nitrogen and phosphorus present in the Mandovi estuary and the phytoplankton activities have been worked out through statistical analysis.

## 5.10.1 NITROGEN COMPOUNDS

Nitrogen is notable for a wide range of dissolved inorganic forms in which it can occur in natural waters, reflecting the complexity of the chemistry of the elements and of the nitrogen cycle in the environment. The forms which have been detected are the dissolved gases - molecular nitrogen ($N_2$) and nitrous oxide ($N_2O$) and the ionic forms of nitrate ($NO_3^-$) and ammonium ($NH_4^+$) which is in equilibrium with a small fraction of unassociated ammonia ($NH_3$). Nitric oxide (NO) has been detected as a product in experimental studies of biological interconversions of nitrogen species and other intermediates such as hydoxyl amines ($NH_2OH$) also occur in traces. (Richards, 1965, Sen Gupta, 1973). Urea and a range of organic nitrogen compounds such as amino acids and biologically refractory material of organic nitrogen compounds also occur in solution.

Significant rates of fixation of molecular nitrogen are found in freshwater environments. It is now known that molecular nitrogen is utilized by some marine organisms, particularly by colonies of the blue green algae- *Trichodesmium* (= *Oscillatoria*). Biological fixation may, nevertheless, be significant in relation to the oceanic budget of combined nitrogen (Delwiche, 1970). Free nitrogen is produced by denitrification in anoxic waters, and under some conditions in sub-oxic waters, and this process may lead to its concentrations significantly above the 100% saturation values in isolated water masses.

The dominant form of combined nitrogen which show variations in concentrations in the ocean is the nitrate ion. However, other forms which are detectable in the euphotic zone include the reduced species which are the end-products of biological activity viz. organic nitrogen compounds,

$NO_2$ and ammonium. Ammonia is released in the decomposition of organic nitrogen compounds, but is also a major excretory product of many invertebrates including zooplankton. Nitrite is often detected in the mixed layer and in certain sub-surface waters. It is formed as an intermediate in the interconversions of nitrate and ammonium.

The reduction of $NO_3^-$ to $NH_4^+$ and the reverse oxidative reactions are of particular importance. These processes occur in two stages with $NO_2^-$ and other forms as intermediates. The oxidative processes, described as nitrification, can be shown as.

$$NH_4^+ + OH^- + 1.5O_2 \rightleftharpoons H^+ + NO_2^+ + 2H_2O \quad \text{and}$$

$$NO_2^- + 0.5O_2 \rightleftharpoons NO_3^-$$

A major role in the regeneration of nitrate is played by two main groups of autotrophic nitrifying bacteria, the ammonium oxidizers (*Nitrosomonas*) and the nitrite oxidizers (*Nitrobacter*). The ammonium - oxidising species (*Nitrocystis*) an obligate species and two nitrite oxidising bacteria also have been identified (Watson and Waterbury 1971).

Phytoplankton organisms are able to utilize various forms of combined nitrogen so that considerable recycling may occur without the completion of the sequence of oxidative reactions which regenerate $NO_3$. When nitrate is utilized, it must be reduced in the cell to ammonia for the synthesis of organic nitrogen compounds. This cellular reductive pathway to organic nitrogen (assimilatory nitrate reduction) involves the initial reduction of nitrate by nitrate *reductase* with cofactor NADPH or NADH as an electron donor. Further reduction to ammonia is carried out by nitrite *reductase*. Under certain circumstances considerable leakage of nitrite from cells may occur due to extracellular reduction and are important in the marine transformation of nitrogen species. Therefore, observed concentration of a particular species of nitrogen in the estuarine environment is the result of various processes described above and are dependent on the mass balance of the above reactions.

### 5.10.2 Phosphorus compounds

Phosphorus is an indispensable element, invariably present in all living organisms. It is essential in the structure of nucleic acids, phospholipids, and ATP. Certain proteins actively participate in a wide spectrum of biochemical reactions, involving energy transfer to the living tissues and the exchange between organism and their surrounding environment.

The chemistry of phosphorus in seawater is considerably simpler than that of nitrogen. The principal form of dissolved phosphorus in the ocean is inorganic orthophosphate. In the pH range characteristic of sea water orthophosphate ions ($PO_4^{3-}$) are largely associated as $HPO_4^{2-}$. Organic compounds of phosphorus produced by biological processes form a significant, and in some cases a dominant part of the total dissolved phosphorus under certain conditions, notably in water bodies sustaining a high level of productivity. There is little detailed information on the rates of conversion of dissolved organic phosphorus to inorganic phosphate and that there is however, no evidence that significant amounts of organic phosphorus occur in the long-term refractory pool of dissolved organic material.

## 5.11 Interrelationships

Concentrations of various fractions of nitrogen and phosphorus compounds present in the estuarine region has been discussed in the previous sections. An examination of the data indicated that in the Mandovi estuary, the concentrations of any of the essential nutrients seldom fall below certain limits. Therefore, the environment maintained a reasonable level of these nutrients for the sustainable growth of the plankton organism. Ranges of variations of different chemical parameters observed in the Mandovi estuary are given in Table 5.16. The lowest concentration of $PO_4$-P observed in the estuary was during pre-monsoon period (0.09 μmol/l). During post-monsoon period the concentration ranged between 0.3 and 2.9 μmol/l whereas, during monsoon it varied between 1.22 and 3.2 μmol/l.

Inorganic nitrogen compounds also showed seasonal variations. Ammonia ($NH_3$+$NH_4$) concentration varied between 0.41 and 3.93 μmol/l. The annual variation of $NO_2$-N was zero to 2.9 μmol/$l^{-1}$ whereas $NO_3$ varied between 0.04 and 12.54 μmol/$l^{-1}$.

In order to understand the relationships between the observed concentrations of various nutrient fractions and the phytoplankton (as Chl *a*) their absolute concentrations in the water column have been correlated.

Linear regression analysis to study the relation between Chl *a* and primary productivity has been worked out and presented. A linear positive correlation between Chl *a* and primary productivity could be obtained for Mandovi estuary with a correlation coefficient r = 0.90 (Fig 5.53). Carbon assimilation expressed as mgC/$m^3$/h has been considered as an indirect measure for the concentration of phytoplankton. Column Chl *a* and column carbon assimilation relationships indicated that these are also linearly related with a correlation coefficient r = 0.83 (Fig. 5.54);

**Table 5.16 : Seasonwise ranges of various environmental parameters in the Mandovi estuary during**

| Season | Salinity | pH | Turbidity | Suspended solids | $NH_3$+$NH_4$ | $NO_2$ | $NO_3$ | $PO_4$ | TN | TP |
|---|---|---|---|---|---|---|---|---|---|---|
| | (PSU) | | (NTU) | mg/kg$^{-1}$ | ← µmol/l$^{-1}$ → | | | | | |
| Premonsoon | 7.09-35.68 | 6.02-8.21 | 0.4-2.3 | 10.6-33.8 | 0.43-1.73 | 0.00-1.31 | 0.04-12.17 | 0.09-3.04 | 10.1-15.1 | 0.66-2.91 |
| Monsoon | 0-25.86 | 5.41-8.18 | 0.91-9.3 | 16.8-115.8 | 1.04-2.76 | 0.00-2.88 | 2.66-12.54 | 1.22-3.20 | 8.1-24.7 | 2.03-4.07 |
| Postmonsoon | 2.04-34.63 | 7.11-8.16 | 0.9-2.5 | 13.6-33.6 | 0.41-3.93 | 0.03-2.9 | 0.4-12.2 | 0.3-2.9 | 0.81-4.58 | 5.2-23.6 |

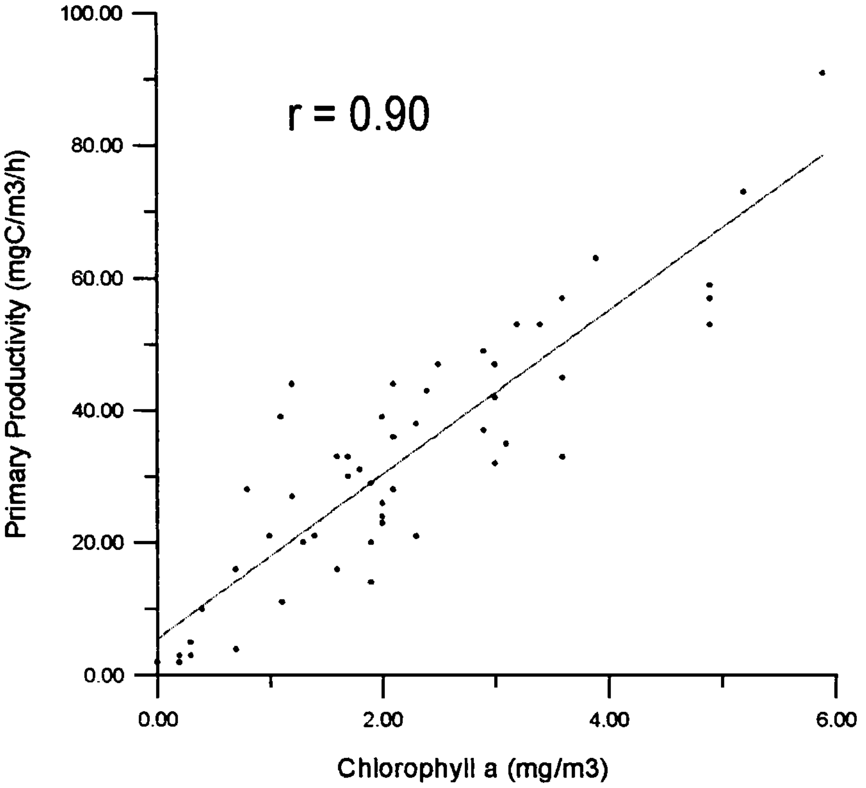


Fig. 5.53. Relationships between chlorophyll and carbon production in Mandovi estuary

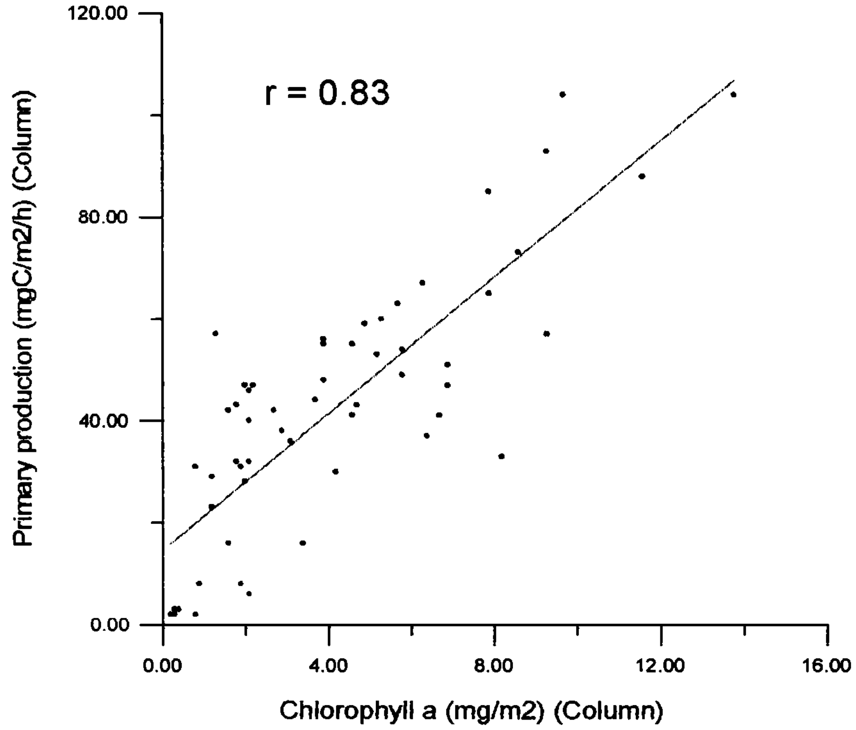


Fig. 5.54. Relationships between Chlorophyll (Column) and Carbon production (Column)

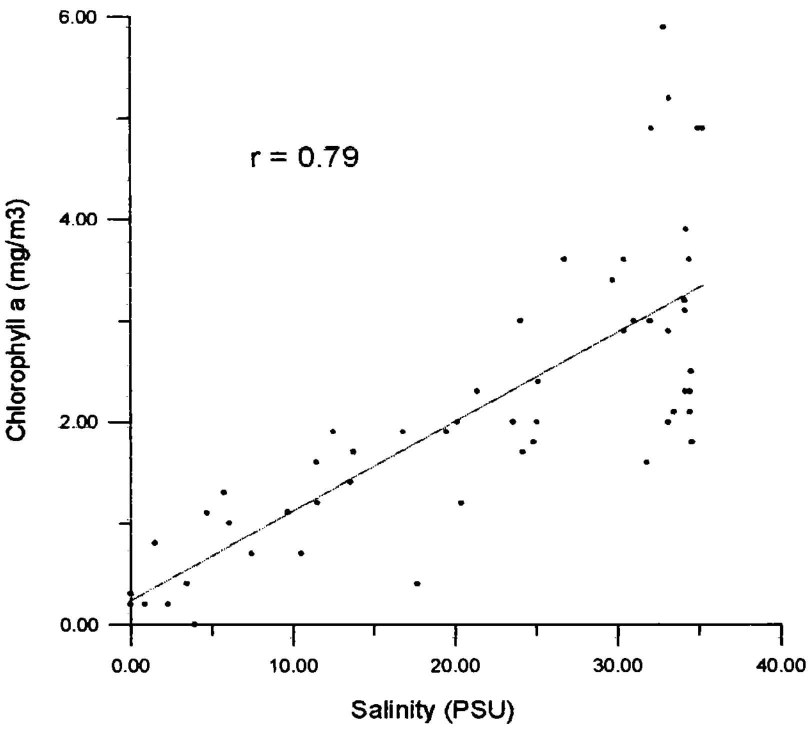


Fig. 5.55. Relationships between salinity and chlorophyll a (Linear fit)

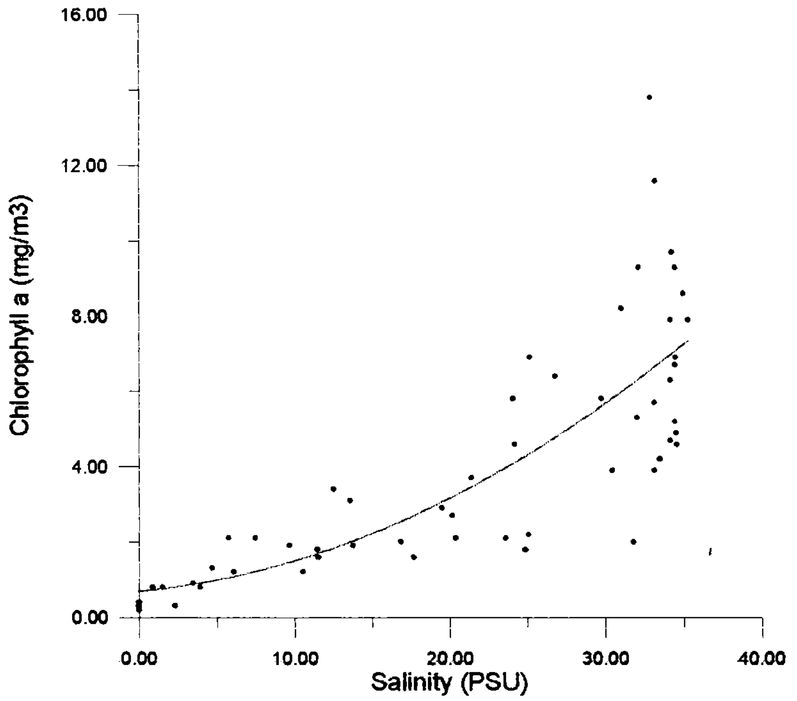


Fig. 5.56. Relationalship between Chlorophyll a and salinity (Polynomial fit)

Salinity - Chlorophyll *a* relation also has been worked out since the estuary is subjected to considerable salinity variations due to the freshwater discharge. The salinity-Chl *a* relationship showed interesting features. A positive correlation with $r = 0.79$ could be obtained when attempted for straight line fit (Fig. 5.55). However, it could be inferred from the graph that better relationship would be possible as the scatter was too wide. Therefore, polynomial equations were applied and the graph thus obtained showed that upto salinity 10 PSU the relationship was more or less linear and above salinity 10 PSU it was parabolic (Fig 5.56). The relationship explains that considerable variations in the concentrations of Chl a due to mixing and nutrient dynamics takes place at the transient zone, estuarine zone and the marine dominated zone. Many of the tropical phytoplankton organisms seem to be well adjusted with changes in salinity. Qasim et al (1972) observed abundance of many phytoplankton organisms at low salinities in Cochin backwaters. However, the reverse is true for Mandovi estuary.

The role of suspended sediments in nutrient dynamics and productivity in the estuarine regions is well documented. Heavy river runoff is responsible for the high suspended sediment load in the estuarine region. Relationships between salinity and suspended sediment load has been worked out using linear regression analysis (Fig. 4.13) and also using polynomial equations and are given in Fig 5.57.

In general, three environments with respect to total suspended sediment load could be identified. They are : (a) a region of high concentration of suspended load (40-120 $mg.kg^{-1}$) in the upper estuary and landward portions of the middle estuary,(b) a transition zone where concentration decreased rapidly and (c) a region of slightly higher concentration compared to (b) but diminishes seaward. The differences between these regions were almost pronounced due to high river discharge. Large amounts of suspended load were introduced into the upper estuary through runoff. During low freshwater discharge periods boundaries between segments, were less discernible. In the upper estuary (which is narrow) the fluvial inputs of suspended sediments will remain in suspension and resuspend bottom sediments maintaining relatively high suspended sediment concentrations. Conversely current velocities decrease where the estuary widens, allowing deposition of suspended sediments. Yabro et al (1981) showed that resuspension of bottom sediments by tidal currents increased suspended sediment load in the middle Choptank River estuary which was partially responsible for establishing turbidity maximum.

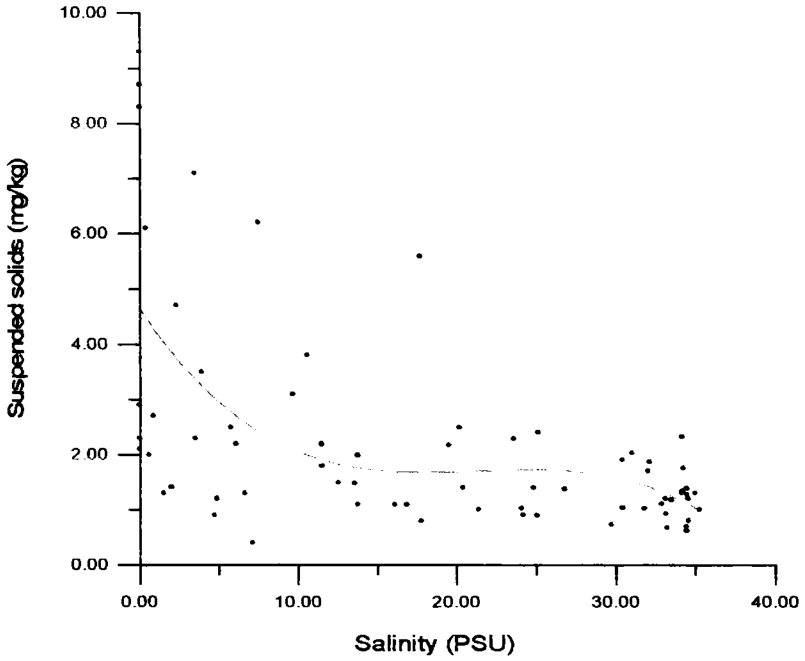


Fig. 5.57. Relationship between Suspended solids and Salinity (Polynomial fit)

This suspended sediment concentration has very high significance in the estuarine nutrient loadings. Dissolved phosphate concentration in many estuaries are maintained within a narrow range by adsorption/ desorption reactions involving particles (Pomeroy et al, 1965, Butler and Tibbits 1972, Sharp et al 1982 and Fox et al 1985,1986). Carritt and Goodgal (1954) found that phosphates were removed from solution in turbid freshwaters, transported on particles into estuaries and released back to solution with increasing salinity. Since that early work the adsorption of phosphate on the particle surface has been examined extensively in the laboratory. In mixing studies, many mineral phases including aluminium oxides (Chen at al 1973), iron oxides (Lijklema, 1980, Bowden et al 1980, Carpenter and Smith 1984, Crosby et al 1984) and 'clays'. (Chen et al 1973) have been shown to adsorb phosphate. Natural estuarine particles, also have shown a large capacity to remove (Pomeroy et al 1965; Pierce 1982) and release (Pomeroy et al 1965, Fox et al 1986) phosphate.

The general mechanism of phosphate buffering involves the equilibration of the dissolved phosphate pool with a reservoir of particle-bound phosphorus (Froelich 1988). When the ambient phosphate concentration differs from the equilibrium concentration, phosphate is either released or adsorbed until equilibrium is achieved. Fox (1989) suggested that this apparent equilibrium between the concentration of phosphate and particle-bound phosphorus results from the association of phosphorus with iron oxides.

The associations of particle-bound phosphorus with natural solid phases have been examined mainly through sequential chemical extractants. In estuarine suspended and bottom sediments, particle bound-phosphorus is associated with organic matter and phases of iron, aluminium and calcium (Upchurch et al 1974, Seralathan and Seelaramaswamy 1977). Factors responsible for incorporation of phosphate ions onto particles have been discussed in earlier sections. The most important environmental factor regulating the adsorption - desorption process in the estuarine region is pH.

In Mandovi estuary pH increased with increasing salinity. Therefore, changes in both salinity and pH during estuarine mixing favoured the release of phosphorus from AI-P and Fe-P. In such cases the overlying water column will have higher phosphate concentrations due to the supply from sediments.

Since phosphate concentrations are usually higher in rivers, phosphate is adsorbed in freshwater-end and released downstream within the salinity gradients as $PO_4$ concentrations decreases through mixing. The central component of any phosphate buffering mechanism is the reactive phase in which $PO_4$ can be stored. Based on laboratory studies and field measurements, Fox (1989) proposed that iron oxides control the concentration of dissolved $PO_4$ in freshwaters through sorption reactions.

Adsorption studies on the sediments of Delaware estuary with aluminium oxides (Lobo, 1991) suggests that $PO_4$ also can be buffered through Al-oxides. Normal estuarine gradients in pH and salinity promote the buffering of $PO_4$ concentrations. Since the adsorption of phosphate onto iron and aluminium oxides is the greatest at lower pH and in freshwaters, particles rich in these oxides will strongly adsorb phosphate in freshwaters. When those phosphorus rich particles are transported into the salinity gradient, phosphate will be released from the particles back into solution. The capacity of the system to buffer phosphate concentrations within the salinity gradient appear to be limited. The release of phosphate from suspended particles is probably supplemented by release from bottom sediments in the lower salinity region of the estuary < 15 PSU. Sediments below the sediment-water interface may become anoxic; have high iron content and have low carbonate content. These characteristics favour the release of phosphate from iron complexes. (Krom and Berner, 1981, Marshall 1982);

If the above explanations are correct then lower reaches of the estuarine region should be supplied with phosphorus which was released from sorption complexes transported from the upper reaches of the estuary. While studying the nutrient - plankton relationship the recurrence of a blue-green algal bloom (*Macrocystis aeruginosa*) in the freshwater tidal portions of the Potomac estuary, Seitzimger (1991) related it with the enhanced release of phosphorus from benthic sediments. It was observed that phosphate released under aerobic conditions increased as a function of overlying water pH between pH 8 and 9, the sediment-water phosphate flux was found low and beginning with an overlying water pH of 9.5, the phosphate flux markedly increased. The increased release of $PO_4$ at high pH was probably the result of solubilisation of iron and Al-$PO_4$ complexes.

Stumm and Morgan (1981) observed that some lakes have shown a correlation between high pH and high P concentration in water column, but have not related to this to measurement of P release rates from the sediments as function of pH.

Phosphate-chlorophyll *a* relationships confirms the above mechanisms and explains that phosphate is inversely correlated with chlorophyll *a* in the estuary. Linear regression relationships for chlorophyll *a* and phosphate has been attempted and are given in Fig 5.58. a negative relationships with correlation coefficient r = 0.76 could be obtained. However, the scatter diagram indicated the possibility of a second order relationship (non-linear) and thus the polynomial equations were computed. Fig 5.59 gives the non-linear best fit for phosphate and chlorophyll *a* relationship in the Mandovi estuary. This relationship explains that at the middle reaches of the estuary, consumption of the $PO_4$-P by the phytoplankton was high and chances of lateral input of

$PO_4$-P through the treated effluents from the municipal treatment plant and the domestic sewage account for maintaining the observed concentrations. Qasim and Sen Gupta (1981) observed higher concentrations of inorganic nutrients at the mouth of the rivers and coastal regions and attributed to the upwelled nutrient rich and cold waters from the Arabian Sea.

Relationships between productivity and nitrate and phosphate concentrations in the photic layer in different parts of the Baltic Sea was studied by Sen Gupta (1972) and observed an inverse relationship between productivity and nutrients. Nixon (1981) observed that factors other than nutrient availability influence the amount of phytoplankton biomass produced. One of these factors is the river discharge at the head of the estuary which influence the amount of dissolved and particulate nutrients supplied from the upstream watershed; the amount of dilution of nutrients from sewage treatment plant effluents, the turbulence level and state of stratification of the water column, light penetration by virtue of the amount of suspended sediment supplied and the residence time of algal cells in the various tidal reaches. An attempt has been made to study the correlation between the concentration of $PO_4$-P in surface water and the carbon production (Fig 5.60). A linear relationship (inverse) could be obtained with correlation coefficient $r = 0.64$. In an estuarine environment this correlation looks very significant compared to oceanic conditions due to the fluctuating environmental conditions prevailing in estuarine regions.

The factors controlling the regeneration of phosphorus are manifold. It's regeneration is promoted by the increase in the density of phytoplankton and bacteria populations, increases in temperature and decrease in phosphorus content of waters. Experiments carried out on algal cultures(Grill and Richards, 1964) established the fact that after the death

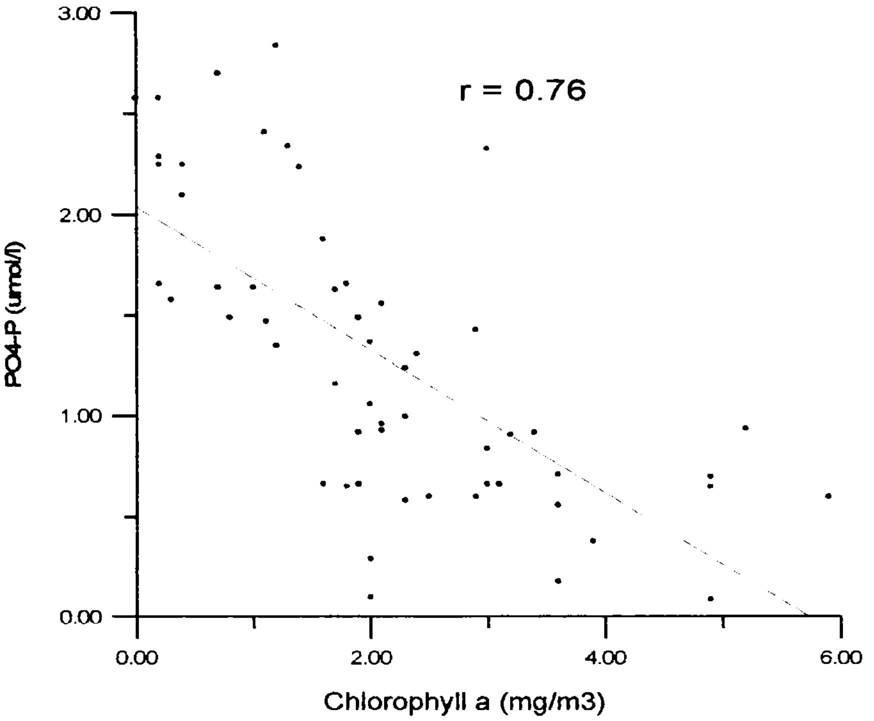


Fig. 5.58. Relationship between Chlorophyll a and $PO_4$-P (Linear fit)

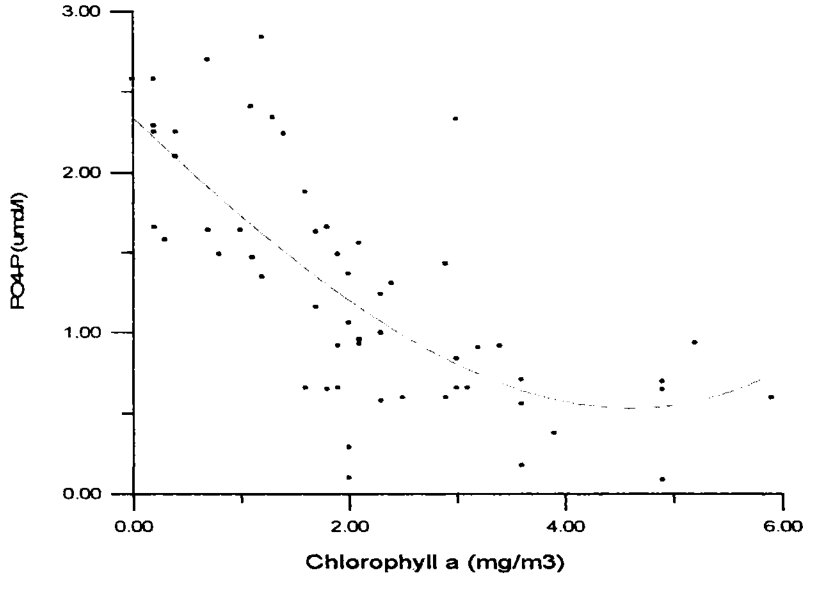


Fig. 5.59. Relation between PO4-P and Chlorophyll a (Polynomial fit)

of living organisms autolysis and microbial activities attain intensive development, that in the course of a few days 80% of the phosphorus is regenerated; most of which is released into solution in the form of phosphate. This pelagic regeneration, biological process of phosphorus has been dealt in detail by several workers. (Grill & Richards, 1964; Rowe, 1978). However, the non-biological release of phosphorus (Benthic regeneration) discussed earlier may be considered as the most significant processes regulating the availability of phosphorus in the estuarine environments.

Phytoplankton normally satisfy their requirements for this element by direct assimilation of dissolved inorganic phosphate (orthophosphate ion) and some times by utilizing dissolved organic phosphorus (Fisher et al, 1992). In polluted waters polyphosphate, which is inorganic and organic soluble phosphorus detected as orthophosphate after acid hydrolysis, may be present in appreciable amount. Some coastal algae such as *Skeletonema costatum* and *Amphidinium carteri* can use polyphosphate as a phosphate source in the presence of excess nitrate. These species appear to be able to hyrolyze an external supply of polyphosphate more rapidly than it is utilized by the cells with the result that orthophosphate may accumulate in the surrounding water (Solorzano and Sharp 1980). Phytoplankton are generally unable to directly take up even simple dissolved phosphate esters. Instead they obtain the phosphate from these compounds by producing a membrane-bound or extracellular enzyme, the alkaline phosphates. This enzyme cleaves off the phosphate group on the compound and then the free phosphate ion can be taken in by regular phosphate transport system. Alkaline phosphates may be induced in some phytoplankton at orthophosphate concentration $< 0.1\ \mu mol.l^{-1}$ particularly when the organic phosphate concentration is appreciably higher than the inorganic. This enzyme has been detected in Mandovi estuary (D'Silva and Bhosle 1991) who found that the activity was inversely related to salinity. Potential phosphatase activity was found to be indicative of the extent and rate of decomposition of organic phosphorus in sediment in this estuary.

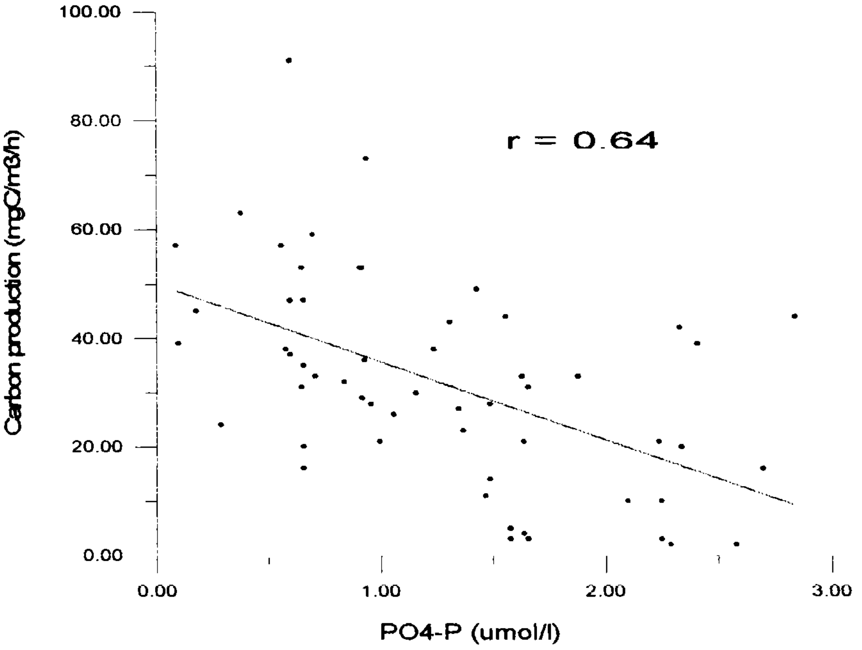


Fig. 5.60. Relationships between Carbon production and $PO_4$-P (Linear fit)

The process involved in the assimilation of $NO_3$ by phytoplankton appear to involve two steps: The first step is the uptake of nitrate from outside the cell, and the second involves the utilization, of $NO_3$ within the cell. These two processes involve different enzyme system. The first involve active uptake of $NO_3$ from the water and the translocation across the cell membrane. Falkowski (1975) showed that in the marine diatom *Skeletonema costatum* an enzyme (a nitrate-chloride activated *ATPase*) is found for the $NO_3$ uptake. Within the cell; the enzyme, *Nitrate reductase*, reduces the nitrate to nitrite- a process which also requires energy in the form of a photo-synthetic reductant NADPH. The synthesis of $NO_3^-$ *reductase* is inhibited by the presence of ammonium at a concentration above 0.5 μM. (Eppley et al 1969). Thus Conway (1977) reported that ammonium is preferentially taken up by phytoplankton approximately twice as fast as $NO_2$ or $NO_3$ depending on the nutrients past history of the cell. In the presence of $NO_2$ only *nitrite reductase* is synthesized while in the presence of $NO_3$ both *nitrite* and *nitrate reductase* are synthesized (Eppley et al 1969, 1977).

Molecular nitrogen is fixed by certain blue-green algae eg. *Callothrix sp.* and *Trichodesmium sp.* yeasts and bacteria (Dugdale and Goering 1964). *Trichodesmium* can also actively utilize both ammonium and $NO_3$. Nitrogen fixation together with ammonia utilization are probably the most important source of algal nitrogen in tropical environments. (Goering, 1966). Algae generally show a preferential utilization for $NO_3$, $NO_2$ and ammonia (Guillard 1963), some exceptions are found among the green algae and few flagellates. Of those different forms of nitrogen compounds, ammonium is generally utilized in preference to $NO_3$ (McCarthy and Eppley 1972) in different species of phytoplankton cultures in natural phytoplankton population.

Ammonium like $NO_3$ and $NO_2$ appears to be transported across the cell membranes by an active process, although no specific enzyme(s) has been associated with this process. After ammonium is taken up by the cell or produced from $NO_3$ reduction, there are two possible pathways by which ammonium can be assimilated into amino acids.

Distribution of ammonia-N in the Mandovi estuary indicate that the concentration is high in the middle reaches of the estuary compared to the marine and freshwater ends. Large quantity of organic nitrogen as suspended sediments through river runoff is brought into the estuarine region which gets deposited in the middle reaches of the estuary. This organic nitrogen undergoes transformations (ammonification and nitrification) and the ammonia thus regenerated can accumulate in the porewater, diffuse out of the sediments into the overlying water column or be adsorbed onto the sediments. This ammonium can alter the concentrations at the overlying water to a considerable extent (Rosenfield 1979).

Relationship between chlorophyll *a* and $NH_3$-N at the Mandovi estuary was worked out (Fig. 5.61) and a non-linear relationship could be observed. Utilization of the regenerated ammonium may take place depending upon the phytoplankton activities. Probably the marine dominated area of the estuary is an active zone of phytoplankton production and utilization of the inorganic nitrogen compounds.

Zooplankton excretion has been recognised as a potentially important source of nitrogen for phytoplankton in coastal and oceanic waters. Most marine zooplankton are known to be primarily amonotelic (Corner and Newell 1967, Kremer 1977) excreting ammonia as a major end-product of amino acid and nucleic acid catabolism. Preference for excreted nitrogen (ammonium and urea) over other forms of nitrogen by phytoplankton has been reported (Carpenter et al 1972, McCarthy et al 1977). It has also been demonstrated that phytoplankton nitrogen uptake is tightly coupled with ammonium regeneration in aquatic systems (McCarthy and Goldman 1979). Harris (1965) first demonstrated that ammonia excretion by macrozooplankton accounted for more than 50 % of phytoplankton nitrogen demand in Long Island Sound. However, Vargo (1979) and Smith (1978) reported that macrozooplankton excretion contributed only 4 to 6 % of phytoplankton nitrogen demand in Narragansett Bay and in the New Port River estuary respectively.

Johannes (1965) suggested that Ammonia excretion as the dominant mechanisms of ammonification in surface waters and reviewed the previous work indicating that net zooplankton release amounts of dissolved nitrogen and phosphorus equal to their total body content of these nutrients. A second mechanism for ammonification is direct autolysis after cell death, which may account for 30 to 50 % of the nutrients released from plant and animal materials.

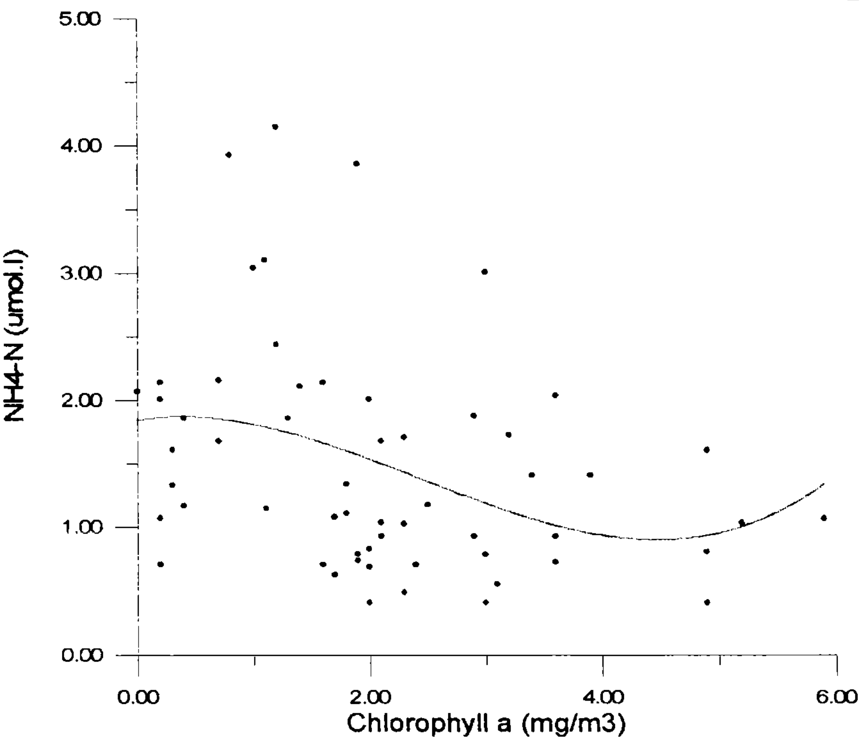


Fig. 5.61 Relationship between NH4-N and Chlorophyll a (Polynomial fit)

In the sediment environment there are continuous transformations of nitrogen operating at various rates, but some of the processes only operate under specific conditions. Ammonification can proceed aerobically and anaerobically over a wide pH and temperature range. However, nitrification can only be carried out by two groups of obligate aerobes, *Nitrosomonas* and *Nitrobacter* which are sensitive to pH and have an absolute requirement of oxygen.

Denitrification is accomplished by a limited number of bacteria, since nitrate replaces molecular oxygen and it occurs in an anoxic environment. The dissolved oxygen concentration in the waters of the estuary did not fall below 3 $ml.l^{-1}$ except at one occasion at the coastal station during post-monsoon (2.04 $ml.l^{-1}$). Therefore, in the present case due to high oxygen concentration chances of this process in the study area is ruled out.

The overall transformation of nitrogen in the present environment can thus be described as follows: ammonium the first product of the microbial decomposition of freshly deposited organic matter can be nitrified or immobilised by microbial processes or can migrate into the overlying waters or be fixed by the sediment clay minerals.

Relationships between chlorophyll *a* and $NO_3$-N and Total inorganic-N showed almost similar trends as that of $NH_3$-N. Chlorophyll *a* and $NO_3$-N plots shown in Fig 5.62 explains that the relationship was inverse and at higher concentrations of chlorophyll *a* almost all the $NO_3$-N present in the water column was used up. It is generally assumed that in marine environment $NO_3$ is the major constituent for plant growth. (Strickland 1965, Riley and Chester 1971). If the plankton contain sufficient amounts of $NO_3$, they can reproduce without diminishing the $NO_3$ concentrations in the environment to any appreciable extent. (Eppley et al 1977). From the $NO_3$-chlorophyll relationship it could be inferred that in the estuary where Chl a concentrations are fairly low, $NO_3^- - N$ was found in excess of the demand and at the region where Chl *a* is high $NO_3^- - N$ showed deficit.

Nixon (1981) has pointed out that high N concentration in combination with a characteristic salinity stratification pattern that restricts the phytoplankton to a shallow surface layer where more light is available can promote rapid growth rate and high Chl *a* values. The particulate nutrients which have reached the transition zone of the estuary during the high flow events should be available for cycling from the bottom sediments later in the year and could provide nutrients to sustain the phytoplankton biomass.

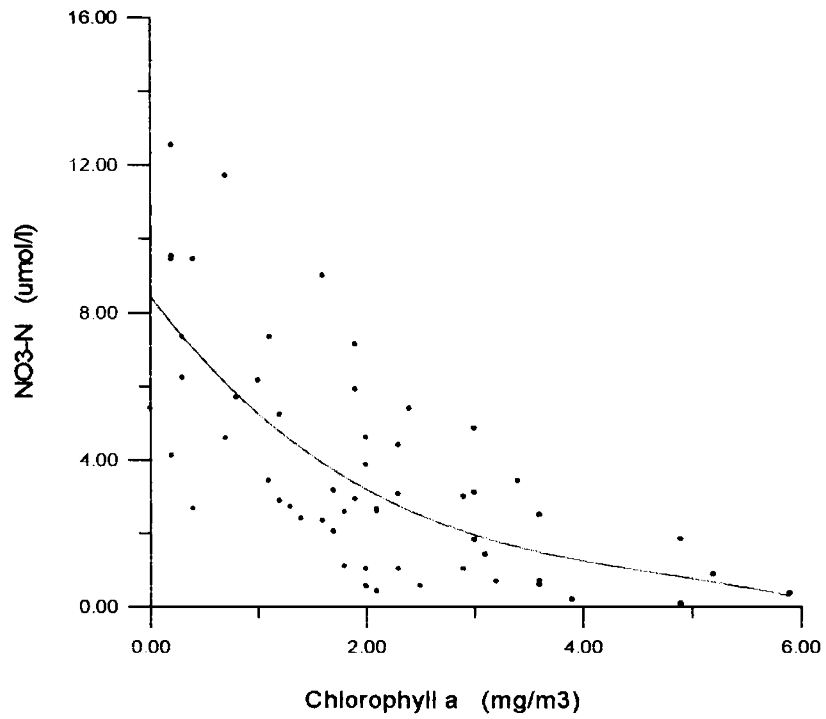


Fig. 5.62 Relationship between NO3-N and Chlorophyll a (Polynomial fit)

The stoichiometry of net benthic nutrient regeneration differs from that of pelagic regeneration, however, and simple Redfield (1934) type models probably cannot be applied. The amount of fixed inorganic N returned to the water across the sediment water interface appear to be a major factor in determining the nitrogen dynamics in this estuarine region. Combined nitrogen input from benthic regeneration, advective exchanges with adjacent water systems and riverine and ground water inputs do not appear to be sufficient enough to meet the phytoplankton demand. This could further be confirmed from the low N:P ratio obtained in the estuarine region.

$NO_3^- - N$ and carbon production relations have been worked out and the statistical plots are given in Fig. 5.63. A negative correlation with r = 0.72 could be obtained with a slope Y = -4.587 * X + 48.5693. Though, Chl a and inorganic nitrogen compounds relationships were separately worked out (Fig. 5.64) to understand the nutritional preferences of these

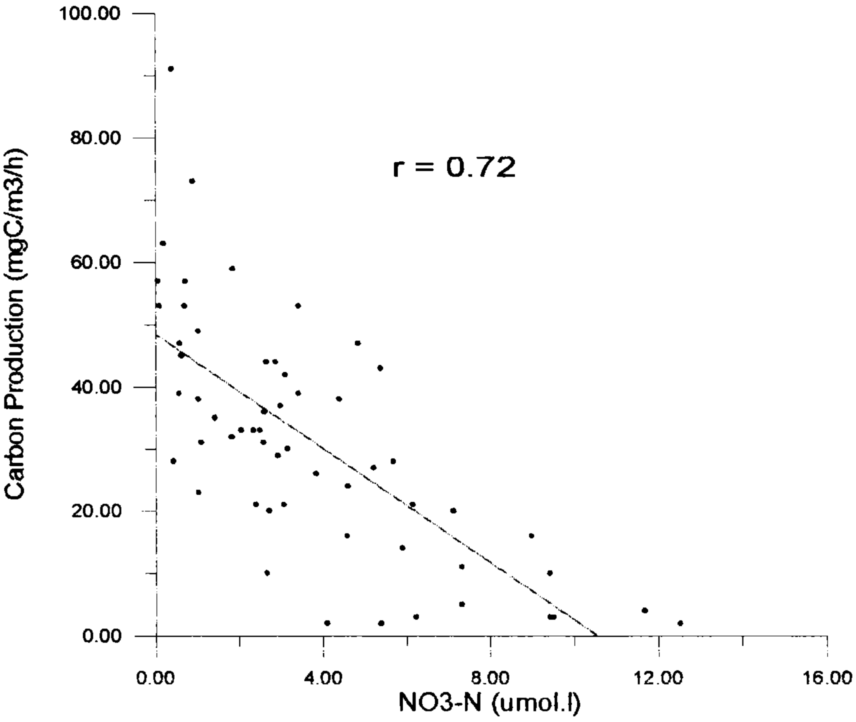


Fig. 5.63. Relationship between Carbon production and NO3-N

compounds in Mandovi estuary. Linear relationship between carbon production and total inorganic nitrogen compounds has also been attempted to generalise the nitrogen uptake processes in the estuary. Fig. 5.65. shows an inverse relationship between total inorganic -N and carbon production in Mandovi estuary with a correlation coefficient r = 0.74 and a slope of Y = -5.966 * X + 36.4454. $NO_2^-$ -N concentrations did not show a reasonable correlation with productivity and Chl *a* in the estuarine region.

The phytoplankton and nutrient data were treated with linear regression techniques to gain a better perspective on relationship by Meyers et al (1981). Linear correlation coefficients were determined between phytoplaknkton productivity and soluble nutrient concentrations. Phytoplankton productivity was more strongly correlated with soluble reactive phosphate concentrations (r = +0.73) than with either total dissolved inorganic nitrogen concentrations (r = +0.44) or with the

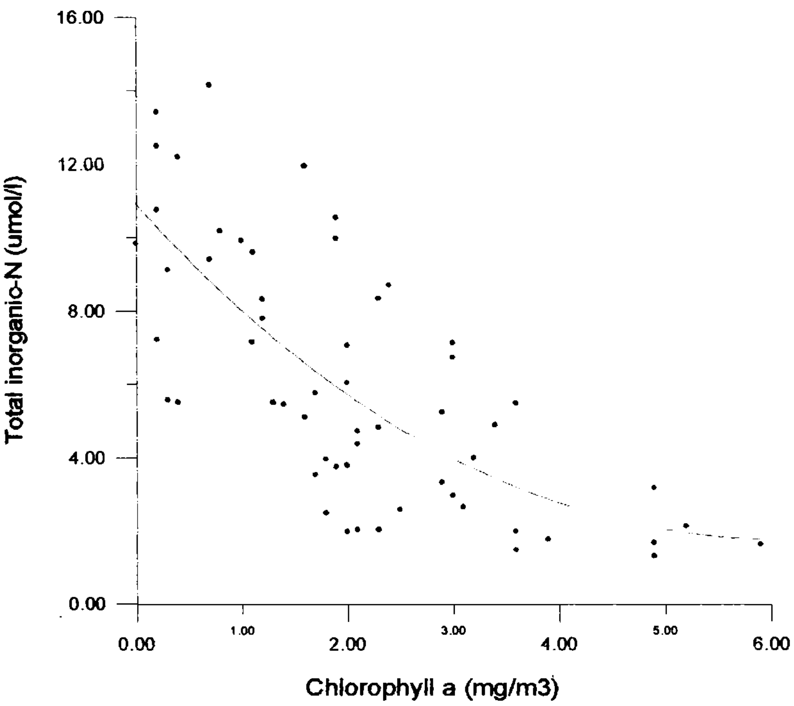


Fig. 5.64. Relationship between Total inorganic-N and Chlorophyll a (Polynomial fit)

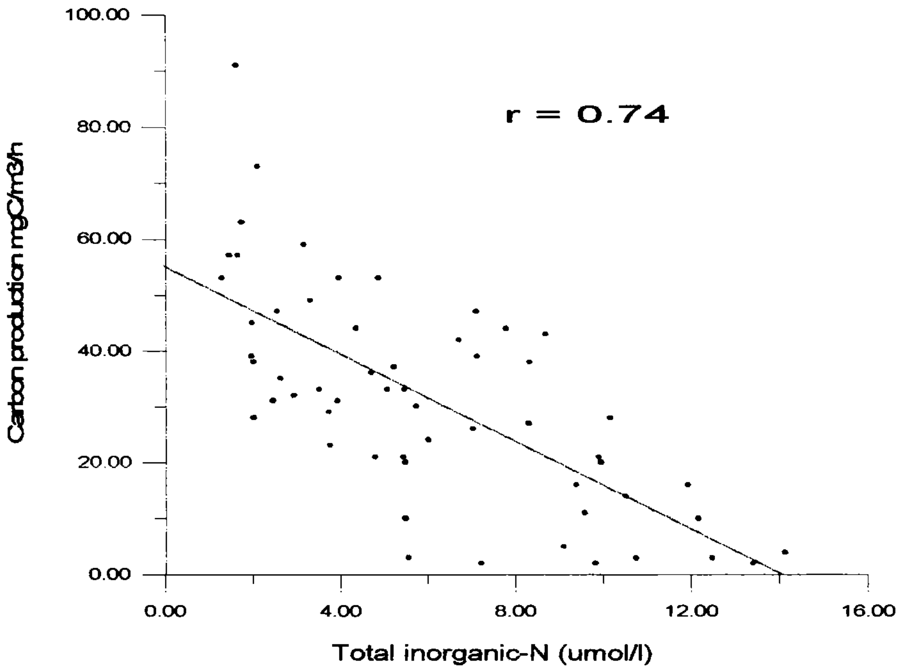


Fig. 5.65. Relationship between Carbon production and Total inorganic-N

individual nitrogen forms, soluble nitrite (r = +0.41) soluble nitrate (r = +0.23) or soluble ammonium (r = +0.31). This suggests that soluble reactive phosphate concentration was more important than the concentration of dissolved inorganic nitrogen forms in explaining phytoplankton productivity in the estuaries of the north eastern Gulf of Mexico.

The above studies indicate that estuaries are characterised by complex gradients of salinity, tidal action, sediment accumulation and nutrient fluxes. These factors are not constant, but shift in both short term and long term cycles. Furthermore, they are subject to major and often unpredictable variations in response to river flow as well as wind pattern. Thus, each portion of the estuary is subject to environmental variability in response to external perturbations. Against the background of a variable and heterogeneous physical environment, biological systems develop toward local biological equilibrium communities and some of the biological solutions are successful. As there are biological force working toward stability and equilibrium, there are also biological forces creating local instability.

Biological stability and constancy of nutrient flux are casually related however, the exact nature of the target equilibrium and the degree to which it is achieved reflect species availability and interaction, stability of the physical environment, and constancy of the nutrient supply. Ecosystem health is that state in which the components and processes remain well within specified limits of system integrity selected to assure that there is no diminution in the capacity of the system to render its basic services to society throughout the indefinite future.

# Resume

The thesis presents "Some Aspects on the Interrelationships between nutrients and plankton in the Estuarine and Nearshore Regions of Goa" based upon a comprehensive seasonal study carried out over one year in the Mandovi estuary (Goa) including its freshwater and nearshore regions.

The First Chapter "Introduction" gives an overview of the estuarine conditions, a review of the literature on the Indian estuaries and the work plan.

Description of the study area, -the Mandovi estuary - its geographic setting, general characteristics such as flow pattern, river discharge etc. are dealt with in detail in the Second Chapter.

Methodology followed for the determination of various biological and chemical parameters and the sampling techniques are described in the next Chapter. This include the analytical methodologies followed for the determination of various phosphorus and nitrogen compounds in the waters and sediments, the estimation of chlorophyll and carbon production and the enumeration of phytoplankton.

Seasonal variability of different environmental features in the Mandovi estuary and the nearshore regions are discussed in the Fourth Chapter. For this purpose the study area has been divided into three regions viz. seawater (marine) dominated area (MDA), Estuarine area (EA) and freshwater dominated areas (FDA).

Geomorphologically Mandovi estuary has been identified as 'drowned river valley' estuary and classified as a tide dominated 'coastal plain estuary'.

The monsoon brings about changes from typically marine to typically brackish-water conditions. This is followed by a reduction in the freshwater discharge during the post-monsoon period and the restoration of stable marine conditions in the pre-monsoon months.

The estuary remain vertically homogeneous for about 8 months and gets moderately stratified for about 3 to 4 months in a year.

There is a strong longitudinal variation in salinity in almost all the depths from mouth to the upstream. During the monsoon months, due to large influx of freshwater, a compensatory salt-water flow occurs below the freshwater in the form of a salt wedge.

No definite relationships between salinity and dissolved oxygen could be observed and the oxygen profiles indicated localised regions of oxygen saturation seaward of the estuary mouth. Part of the oxygen was consumed due to the industrial and domestic effluents released into the estuary and the rest to respiration of coastal phytoplankton following transport into an inimical lower salinity regime.

Short term variability in pH relative to salinity could be observed in the estuary. The rate of increase of pH with increasing salinity decreased progressively from 1 to 10 PSU. (Practical Salinity Unit) At salinities higher than 10 PSU, pH changes relative to salinity were less pronounced, although relatively sharp increase in pH occasionally occurred in the more saline ranges (25-35 PSU). Minor inflections in the pH profiles were invariably found either to covary with minor salinity perturbations in accordance with the general pH - salinity characteristics of the water.

Suspended sediment load was comparatively high in the estuary mainly due to strong tidal currents which cause disturbances of the loose bottom sediments and the mud flats. The theoretical best fit obtained by linear regression analysis showed that the suspended sediment load increased with freshwater content. The role of suspended sediment in regulating the nutrient concentrations in the estuary has been discussed in detail.

The turbidity variations in the estuary followed the pattern of distribution of suspended particulate material load. A moderately good correlation between salinity and turbidity could be observed.

In the Fifth Chapter evaluation of the distribution of various nitrogen and phosphorus compounds in the water and sediment environments have been discussed in detail. The third compartment - the phytoplankton - its distribution, species composition and carbon assimilation rates have also been studied to assess the interrelationships between plankton and nutrients in the estuarine and nearshore environments.

Mandovi estuary receives considerable nutrient inputs from terrigenous and oceanic sources and within the estuary proximate sources of nutrients such as regeneration from bottom sediments and oxidation of organic matter within the water column have been considered significant.

Estimations of the various nitrogen compounds in the estuarine system was carried out for understanding the variation with respect to season and location of the estuary. For this purpose the nitrogen compounds determined were $NH_4^+$-N , $NO_2^-$-N , $NO_3^-$-N and total N. From these total org. N and total inorganic N were computed.

Seasonwise variation of concentration of $NH_4^+$ -N showed that during pre-monsoon it was low between 0.43 and 1.73 µmol.l$^{-1}$, during monsoon it varied between 1.04 and 2.76 and during post-monsoon season the concentration was comparatively high (~3.93 µmol.l$^{-1}$).

$NO_2$ and $NO_3^-$ -N concentrations also showed seasonal variations. $NO_2^-$ -N data indicated that it was closely related to the biogeochemical processes taking place in the estuaries. Indications of intense ammonification and nitrification processes in the estuary could be ascertained from the data.

$NO_3$ showed a negative relationship with salinity in the estuary indicating the source at the freshwater-end.

The estuary in general showed fairly high concentration of $NO_3^-$ -N indicating the intensity of various N- transformations taking place in the environment. Similar to $NO_3$, total inorganic nitrogen also showed seasonal and depthwise variations with surface water showing less concentrations compared to bottom.

Total nitrogen concentration varied between 2.87 and 23.53 µmol.l$^{-1}$ and did not show a definite pattern, although it exhibited a relationship with freshwater inflow. Considerable amount of nitrogen is brought into the estuary during the river runoff and atmospheric precipitation.

Hypothetical behaviour of nitrogen and phosphorus in the estuarine environment was deduced from the property-property relationships. Through salinity dilution plots 'net gain' of 13 and 42 % of $NO_3$ for monsoon and post monsoon seasons respectively and a net loss of 21 % during pre-monsoon season could be estimated.

$NH_4^+ - N$ concentrations in the estuary did not show any linearity with salinity. Salinity $NH_4^+ - N$ plots showed that the concentration of ammonia was the highest in the salinity range between zero and 15 PSU. This probably means that $NH_4^+ - N$ production takes place in this region possibly through the breakdown of the nitrogenous organic material brought into the estuary from landward sources.

$NO_2^- - N$ - salinity scatter plots revealed that $NO_2^- - N$ distribution was uniform throughout the estuary irrespective of the freshwater source. Being an intermediate product $NO_2^- - N$ undergo is rapid transformation within the water column besides being assimilated by the phytoplankton.

Percentage of $NO_3^- - N$ dominated during the monsoon period reaching as high as 81.2 % of the total inorganic N and during this period the estuary experienced a low rate of biological assimilation due to high turbidity and varying salinity conditions.

Ammonia nitrogen showed considerably low percentage during monsoon and maintained an increasing trend during post-monsoon due to the breakdown of organic-N. As this process continued throughout the post-monsoon period, transformations of the released $NH_4^- - N$ took place during pre-monsoon which either got oxidized to the stable product $NO_3^- - N$ or partially used up by the phytoplankton.

Seasonal variation of phosphorus compounds indicates that though considerable inputs of phosphorus during river runoff takes place at the freshwater end of the estuary besides lateral entries through anthropogenic inputs, the concentration of $PO_4^{3-} P$ and other fractions within the estuary did not exhibit wide fluctuations.

Total phosphorus concentrations showed two maxima, a less pronounced one during pre-monsoon and a more pronounced one during monsoon. Concentration of inorganic N fraction dominated during the monsoon while organic-N fraction dominated during pre-monsoon sample.

Phosphate- salinity relationships to evaluate the behaviour of phosphorus during estuarine mixing was worked out and the scatter showing total-N and total-P indicated a positive correlation between the two parameters.

It is estimated that during pre-monsoon a net loss of 23 % of phosphates and during other seasons a net gain of 18 % (monsoon) and 53 % (post-monsoon) took place in the estuarine region.

It was observed that the distribution of phosphorus and nitrogen compounds in the water column in the estuary were not homogeneous. The dissolved phosphates tend to reach uniform concentrations but this tendency is counteracted by other compounds, either organic or inorganic.

In order to study the association of inorganic P in estuarine sediments an evaluation of the forms of sediment inorganic phosphorus through selective removal of certain forms of elements have been carried out. Although organic form of phosphorus are not themselves directly available for phytoplankton nutrition they do form the main source of available phosphorus.

Available phosphorus determined by chemical extraction procedure included all forms of phosphorus but predominantly associated with iron, aluminium and calcium. Estimations of the saloid bound-P, $NH_4F$-P, NaOH-P, CDB-P, $H_2SO_4$-P and Res-P were carried out to study their seasonal variations in sediments. The ability of sediments to sorb inorganic P at different pH has been worked out.

Aluminium-P fraction, though considerably low as compared to Iron and CDB-P form showed more or less a distribution pattern with increasing values towards the upper reaches of the estuary and the calcium bound P showed a reversing trend.

The largest pool of nitrogen in the estuarine environment can be the organic nitrogen brought into the estuary by river runoff. The process of ammonium adsorption relative to its production by organic matter decomposition has been evaluated by determining the relationships between the dissolved $NH_4^+$-N in porewater and the $NH_4^+$-N adsorbed on the sediments.

The relationships between exchangeable and dissolved ammonium in the estuarine sediments indicate that they are linearly correlated with $r = 0.96$. similarly the relationships worked out by linear regression method between dissolved ammonium and non-exchangeable ammonium (fixed) exhibited a positive correlation ($r = 0.93$) suggests that an equilibrium exists between these nitrogen compounds in the estuarine sediments.

Variations of concentrations of chlorophyll *a* with respect to seasons showed that both surface and column chlorophyll *a* were low (0.2-1.9 mg/m$^3$) during monsoon throughout the estuary. A recovery could be noticed during post-monsoon (1.1 - 3.6 mg/m$^3$) and during pre-monsoon the estuary exhibited the highest concentration (1.8-5.8 mg/m$^3$).

It was noticed that chlorophyll *a* values in the estuary generally follow changing environmental conditions in the estuaries. Though, during monsoon the supply of inorganic nutrients into the estuary was maximum the Chl *a* concentrations remained considerably low. During the rest of the periods nutrient concentrations and Chl *a* showed significant correlations.

Phytoplankton population also exhibited seasonal variations. The cell concentrations at the surface fluctuated from 12.2 x $10^3$ / l (July) to 1203 x $10^3$/l (May) in the estuarine region. It showed a bimodal peak in Mandovi showing a prominent peak during May and an occasional peak in October.

Post-monsoon period was very conducive for maximum proliferation of both diatoms and dinoflagellates and during this season blooms of *Nitzschia closterium* also occurred near the mouth and coastal regions.

The species diversity indices of phytoplankton showed variations from 0.49 to 4.2 and the values declined during bloom periods.

Primary productivity values indicated that the carbon assimilation was higher in the estuarine area compared to the marine dominated area. Surface primary production at the MDA varied between 4.0 (July) and 63 mgC/$m^3$/h (May). Estuarine area exhibited slightly higher production and it was between 2.0 (June) and 91 mgC/$m^3$/h (May).

Distribution of various phytoplankton species show that the population was considerably high in the nearshore regions compared to the estuarine areas.

It is established that the "ratio of changes of the nutrients in water is equivalent to the ratio of their concentrations in phytoplankton" (Redfield et al, 1963).

In order to understand the relationships between the observed concentrations of various nutrient fractions and the phytoplankton (as Chl *a*), their absolute concentrations in the water column have been correlated. Both linear regression as well as polynomial equations have been employed for obtaining the best fit.

A linear positive relation between Chl *a* and primary productivity could be obtained for Mandovi estuary with a correlation coefficient r = 0.90 and for column Chl *a* and column productivity r = 0.83 was obtained.

Salinity - chlorophyll *a* relation indicated that it was linear and positive with r = 0.79. However, polynominal equation when applied, the relationship showed more or less linear upto salinity 10 PSU and above that it was parabolic.

Salinity - suspended solid relation with polynomial equation showed that in the estuary 3 distinct zones - upper estuary with high concentration, a transition zone with rapidly decreasing concentration and area of slightly high concentration diminishing seaward. The suspended load was correlated with the particle-bound phosphorus equilibrations in the estuary.

Phosphate-chlorophyll *a* relationships showed that it was inversely correlated with r = - 0.76 and a non-linear best fit was found for these two components.

Relationships between Chl *a* and $NH_4^+$-N showed a non-linear relationship. Chl *a* and $NO_3$ and Chl *a* and total-N relationships also showed inverse relationships $NO_3^-$-N and Carbon production relationships have been worked out and a negative correlation with r = 0.72 could be obtained with a slope $Y = -4.587 * X + 48.5693$. Chlorophyll *a* and total inorganic N compounds also showed a linear inverse relationship.

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