PUBLISHED PAPERS
Estuarine Response of Fluoride - Investigations in Azhikode Estuary

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Concentrations of fluoride in Azhikode estuarine region were measured as a function of chlorinity during the different seasons. The type of behaviour indicated that fluoride was regulated by sea water incursion alone. Fluoride behaved conservatively during the postmonsoon season. However, during the premonsoon season 25% removal of fluoride was observed due to estuarine mixing. The possible mechanisms for the removal are explained.

INTRODUCTION
Fluoride has long been considered as an acute pollutant to natural environment because of its detrimental effects upon marine biota even by concentrations as low as 1.5 mg/L. The optimum level of fluoride in the drinking water for the prevention of tooth decay is 1 mg/L while fluoride concentrations in excess of 4 mg/L can cause molten stained teeth and fluorosis (De Souza, 1988). Though extensive work has been done on the behaviour of fluoride during estuarine mixing (Sankaranarayanan et al. 1986; De Souza, 1988) no such information on the behaviour of fluoride is available in Azhikode estuary. The present investigation was undertaken to understand the distribution of this element in Azhikode estuary during different seasons, and to find an explanation for any anomaly that may exist. Azhikode estuary is formed by the major arm of the Periyar river opening out at the Azhikode barmouth (Figure 1). The annual input of fresh water in this estuary is about 2.7 x 10^9 m^3/year, of which 60% is contributed by Periyar river and the rest by Chalakudy river (Pylee, 1990).

MATERIAL AND METHOD
Two stations one at Azhikode (barmouth) and the other at Kottapuram at a distance of about 6 km upstream from the river mouth were selected for sampling. Water samples at 2 hourly intervals were collected from the surface, mid-depth and near bottom of the water column during October '93 and May '94 (postmonsoon and premonsoon, respectively) for a complete tidal cycle. Sampling was also done from a station at the fresh water region where there is no sea water effect. Surface samples were collected using a clean bucket and the subsurface and the bottom samples using Niskin samplers. All samples were filtered using Whatman GF/C filter paper. The salinity was measured with an electrodeless induction type salinometer (DIGI-AUTO, model 3G, Tsurumic Seiki, Japan). The fluoride was estimated by the alizarine-complexone method of Greenhalgh and Riley (1961).

RESULT AND DISCUSSION
The highest chlorinity was observed during the premonsoon observations with a maximum of 19.37 x 10^{-3} at both stations. However, the influence of the high saline water mass was restricted to 2 hr coinciding with the high tide at Kottapuram, whereas this water mass persisted for 6 hr at Azhikode barmouth. During this period, the chlorinity values at Azhikode varied between 13.12 and 19.37 and at Kottapuram it varied from 8.42 to 19.37 x 10^{-3}. The surface to bottom chlorinity gradient was minimum during this period showing vertical homogeneity of the water column. The tidal variations of fluoride at both the stations followed the same pattern of distribution as that of chlorinity. This type of distribution indicates that fluoride is...
Fluoride levels at Azhikode bar mouth increased gradually with tide from 0.82 at low tide to a concentration in the range of 1.2 to 1.31 mg/L. At Kottapuram, the changes were found to be more pronounced with a rise in fluoride level from 0.42 to 1.31 mg/L.

During October, the influx of fresh water was at its maximum and the incursion of sea water into the estuary was restricted. This is reflected in the fluoride and chlorinity distributions. The chlorinity values varied markedly from 3.5 to 18 x 10^{-3} at Azhikode and 1.1 to 16.8 x 10^{-3} at Kottapuram. The fluoride concentrations ranged from 0.20 to 1.22 mg/L at Azhikode and 0.08 to 1.20 mg/L at Kottapuram. At both the stations, fluoride content observed was less than that observed in May. In both seasons, the average fluoride concentrations in river water was found to be in the range 0.035 to 0.15 mg/L.

Fluoride - chlorinity relationship
Plots of chemical constituents versus chlorinity or salinity have been used to demonstrate removal, addition or conservation of a given constituent within an estuary (Liss, 1976). Figure 2 are plots of fluoride against chlorinity for both the stations during October and May, respectively. The regression analysis shows a highly significant positive correlation (r = 0.98, r = 0.97) in both the observations. The F - Cl% relationship for Azhikode and Kottapuram during October was linear given by:

\[ F = 0.066 \text{ Cl} \% + 0.068, \quad r = 0.98 \]

It was observed that fluoride behaves conservatively during the month of October when there is fresh water influx. This linear relationship shows that its concentration is governed by physical processes of mixing and tidal variations and is not affected by any other geochemical factor. But during premonsoon season (May), a significant deviation was observed from theoretical dilution line (TDL drawn by joining the concentration of fluoride at zero chlorinity with that in coastal sea water) between chlorinity 2 - 14 x 10^{-3} indicating removal. The extent of removal of fluoride has been calculated to be 25% (-8) which is comparable to the earlier reports (25 - 28%) from Mandovi and Zuari estuaries (De Souza and Sen Gupta, 1988) and Baltic Sea (17 - 30%) and other rivers flowing into it (Kullenberg and Sen Gupta, 1973). Figure 2 shows that deviation from the TDL is experienced below chlorinity 13 x 10^{-3}. The removal may be attributed to some geochemical mechanism which predominates in this chlorinity range during premonsoon season. The studies on sediment dynamics in Azhikode estuary have shown that during premonsoon season, there was formation of a turbidity maximum at a distance 6 - 9 km upstream from bar mouth (Revichandran, 1993). The character
Figure 3. Variation of fluoride chlorinity ratio with chlorinity in the Azhikode estuary

the suspended sediment distribution strongly suggests that there existed a third source of material in mixing in the estuary and this source is sediments which are resuspended within the turbidity maximum.

In an estuary, ionic strength of dissolved material and surface charges on particulate material rapidly changes in turbulent mixing zones. Such conditions accelerate reaction between dissolved species and suspended particles (Liss, 1976). Thus fluoride may be absorbed on to the particles in suspension, the first step in the removal process. Similar observations of geochemical removal of fluoride have been reported earlier (Carpenter, 1969; Kullenberg, 1973; De Souza and Sen Gupta, 1988). Table 1 presents the range and mean concentrations of fluoride and F/Cl ratio in different chlorinity ranges (Figure 3). These values are in close agreement with reported values of fluoride to chlorinity ratio for ocean water (Riley, 1965; Brewer et al., 1970; De Souza and Sen Gupta, 1988).

REFERENCE


Non-conservative Controls on Distribution of Dissolved Silicate in Cochin Backwaters

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Abstract
Cochin backwater system was studied with regard to dissolved silicate (DSi) to understand its seasonal distribution and behaviour during estuarine mixing. Silicate had a linear relationship with salinity during the high river discharge period. During premonsoon period, a sharp decrease of silicate with distance in the middle regions between salinity range of 4 to 22 $10^{-3}$ in the estuary was observed. River discharge was found to modulate both estuarine residence time and the DSi supply. The substantial removal of DSi (approximately 50 %) during premonsoon was attributed to enhanced biological utilization, caused by the development of null zones in the middle areas of the estuary.

Introduction
Distribution of dissolved silica (DSi) in estuaries differs from other major micronutrients, since the main DSi source is river discharge coupled with an insignificant contribution from cycling by dissolution of siliceous diatoms (Patterson et al., 975; Anderson, 1986). Silica utilization is normally by hytoplankton in synthetic processes and by inorganic removal to suspended matter (Liss and Spencer, 1970). Although a few published informations are available on the distribution of silicate in this area (Sankaranarayanan and Qasim, 1969; Sankaranarayanan, Joseph, Jayalakshmi and Balachandran, 984; Sankaranarayanan, Varma, Balachandran, Pylee and Joseph, 1986) and other estuaries of India (Borole, Jishnaswamy and Somayajulu, 1977; Sarin, 1985; Burton, Liss et Venugopalan, 1970b) an exhaustive study on the silicate behaviour during the estuarine mixing is lacking. An attempt has been made here to study the behaviour of DSi in this marine system during different seasons of the year.

Materials and Methods
Water chemistry observations were made within 48 hrs as many as 20 stations in the mid-channel of the estuary between river mouth and the freshwater boundaries of northern Periyar and southern Muvattupuzha rivers during the flood tide. Monthly hydrographic studies were made for two years from 1989 to May 1991. Water samples collected from surface 10.5m and 0.5m above the bottom were filtered through Whatmann filter paper no.1. Salinity was estimated using a direct laboratory model salinometer (Tsurumi Seiki Model 6 DIGI AUTO, accuracy 0.01 x 10^{-3}). Silicate was measured by silicomolybdate method as given in Grasshoff et al. (accuracy + 4µg at/l).

Results and Discussion
Temporal and spatial variations
In order to understand the temporal and spatial variations in DSi, the study period is divided into 3 seasons viz., premonsoon (February - May), SW monsoon (June - September) and postmonsoon (October - January). The salinity intrusion in the northern and southern limbs of the estuary responds closely to the variations in river discharge. The intrusion of salt water into the estuary was deep, the distance being 25 km in Muvattupuzha and 21 km in Periyar from the barmouth (1989-90). For monsoon months the saline intrusion is limited to 10 km. During the premonsoon, the estuary becomes dominated by neritic waters leading to vertical homogeneity. During monsoon season, the entire estuarine water is flushed out and replaced by freshwater. There is a short fall in river discharge between September and October when again the northeast monsoon brings in moderate precipitation from late October to January resulting in considerable river discharge, though much less than that in the SW monsoon period. During this period, the estuary behaves as partially mixed one until December. The extent of saline intrusion was more in the southern part as compared to the northern part throughout the year. This is probably due to a higher river discharge through river Periyar compared to Muvattupuzha. Levels of silicate in the present study varied from 4.43 to 139.4 µg at/l at the surface and 6.14 to 133.4 µg at/l at the bottom. In Muvattupuzha, the average silicate concentration varied between 4.03 and 138.15 µg at/l, while in Periyar it ranged between 5.20 to 140.1 g at/l. Monsoon and postmonsoon peaks in silicate content for both rivers indicated that the silicate source to this estuary is by river run off, which is in clear agreement with earlier works (Sankaranarayanan and Qasim, 1969; Sai Sastry, 1990; Gouda and Panigraphy, 1992).

Plots of chemical constituents vs. salinity have been used to demonstrate uptake, addition or conservation of a given constituent within an estuary (Liss, 1976). These concepts were extended by Patterson, Conomos et al., 1975). DSi - salinity relations of the Cochin backwaters during monsoon, postmonsoon and premonsoon seasons are given in Figs.1 a,b.
and c respectively. For this the individual values were averaged out for each season and plotted. The DSI-salinity (S) relationship during monsoon 1989 and 90 is linear given (Fig.1a) by

$$DSI = 119.16 - 2.98 S$$

Correlation coefficient $r = -0.97$ and

$$DSI = 109.81 - 2.65 S$$

linear relation between DSI and salinity is also observed during postmonsoon season

$$DSI = 110.33 - 2.91 S$$ $r = -0.98$ and

$$DSI = 107.51 - 2.76 S$$ $r = 0.98$

for 1989 and 1990 respectively (Fig.1b). It is thus clear that dissolved silicate bears a linear relationship with salinity during monsoon and postmonsoon seasons. A linear distribution of this kind indicates that mixing rates between river and seawater dominate over non-conservative processes (Patterson et al., 1975). During premonsoon season, however, the DSI-Salinity relationship is not linear (Fig.1c), but forms a curvilinear shape. The relation is best explained by the exponential equations,

$$DSI = 95.32 \cdot e^{-0.05 S}$$ and $$DSI = 99.82 \cdot e^{-0.06 S}$$

The fractional loss of DSI within an estuary (G) influencing the loss of DSI from this estuary are the development of watermass with high residence time during premonsoon which favours enhanced primary productivity. The peculiar topography of this estuary with the two perennial rivers entering the estuary from opposite directions, a system of canals connecting the two and the seaward opening at right angle to their direction of flow makes the hydrodynamics of estuarine circulation complex. As the river discharge decreases, the estuary is gradually dominated by tidal influence which forces the neritic water into the upper reaches of the estuary, against a weak river discharge. In such conditions, there develops a non-tidal mean flow representing a body of water column with a high residence time compared to other seasons, called “null zone” (Patterson et al., 1975). The sections adjacent to this zone (both upstream and downstream) will be having a residual flow towards the zone, thus enriching the zone with nutrients. Flushing time of the estuary in general increases resulting in a net accumulation of any material discharged into the estuary towards the null zone. Available information also supports the view that primary productivity in this estuary remain high during premonsoon season and with occasional bloom of phytoplankton during the rest of the period (Joy, Balakrishnan and Joseph, 1990; Nair et al., 1975; Qasim, 1979; Gopinathan, 1984; Nair et al., 1988; Joseph and Pillai, 1975). The standing stock of Chlorophyll ‘a’ pigments (54.5 mg m$^{-3}$) and biomass recorded are highest during this season (Joy et al., 1990) and are mainly constituted by diatoms and dinoflagellates (Joseph and Pillai, 1975), which are the main consumers of silicic in the water.

Fig 1. Dissolved Silicate - Salinity relationship during different seasons for two years in the Cochin backwater system as a whole. (a) DSI vs. S% during monsoon 1989 and 1990, (b) DSI vs. S% during postmonsoon 89 and 90, (c) DSI vs. S% during premonsoon 1990 and 91.

In the light of above conditions, we can explain the salient features pointed out earlier. During monsoon and postmonsoon seasons, moderately high rate of supply of DSI through river discharge compensates the removal, if any, from the estuary explaining the near-linear relationship between DSI and salinity (Fig.1a and 1b). During premonsoon period, the river discharge becomes low, decreasing the rate of supply of DSI. The productivity can be increased due to enrichment of N and P fractions into the null zone. But the primary nutrients necessary for primary productivity are N, P and Si, of which the last is not in surplus. This leads to utilization of DSI from the river input, at a greater rate than its addition through river discharge. The net result is, an observed removal of DSI from the estuary between salinity range 4 - 22 x 10$^{-3}$ marked by the zone ‘B’ in Fig. 1c. Within the limitations of our field surveys carried out, we find that this 25 km stretch of Cochin backwaters with salinity range of 4 to 22 x 10$^{-3}$ behaves as a biologically active zone, during the premonsoon period of 1990. Another noticeable feature is that the null zone was found to extend more towards the southern side than towards the north. This can be explained by difference in the river discharge through these two rivers. The southern portion of the estuary is also characterised by seaward increase of cross channel area.

The fractional loss of DSI within an estuary (G)
proximated by the method of Hydes a and Liss (1977) and tended by Officer (1979) for this estuary is given as \( G = \frac{C_o - C_o^*}{C_o} \), where \( C_o^* \) is the extrapolated silicate value corresponding to zero salinity of the linear lower estuary silicate distribution and \( C_o \) as the freshwater end point DSi concentration. This fractional loss for the Cochin backwaters = 45.4% and 53.1% during premonsoon seasons of 1990 and 91 respectively (Fig.2) are comparable with with the values reported by Callaway and Specht, 1982, but high compared to values reported by Liss (1976).

Acknowledgements

We are thankful to Dr. E. Desa, Director, N.I.O, Goa for keen interest. Technical assistance rendered by Miss. Sammu Sebastian is gratefully acknowledged.

References

Lower reaches of river Periyar were studied to assess longitudinal extent of salt water intrusion into the system during different seasons and also its effect on the flushing of pollutants introduced by the industries. During SW monsoon season due to the influx of a large volume of fresh water longitudinal salinity gradient could be noticed only up to a few stations upwards from the barmouth. During postmonsoon season the estuary behaved like a partially mixed estuary with the saline intrusion extending further upstream up to 17 km. In the premonsoon season the intrusion length extended further upstream beyond 21 km. A steady downstream dilution of any pollutant introduced could be expected during these seasons. Fluoride concentration showed high values (>1.5 mg l^{-1}) during Nov. to May and minimum from July to Sept. The high values observed may be due to the effect of pollutants containing fluoride discharged into the river.

The Cochin backwater estuarine system is a part of the lower reaches of the river Periyar, which is one of the largest perennial rivers of this region. The hydrographic studies so far made are on physical and biological aspects and mainly centred around the Cochin harbour. However there is no attempt to evaluate the extent and nature of the salt water intrusion into the estuarine region and its variation from season to season with respect to varying tidal prisms at the Cochin harbour inlet and fresh water influx into the estuarine system. The present study pertains to intrusion of salt water into the estuarine region, assessment of its longitudinal extent in different seasons, and its effects on the flushing of pollutants introduced into the system from the industrial belt. As very little information is available on the distribution of fluoride in Indian waters, in this study the fluoride concentration is estimated in the Cochin backwater system and the river Periyar.

Materials and Methods

Monthly surveys (1982-83) were conducted from the Cochin harbour mouth towards upstream, a distance of about 21 km (Fig. 1), during the spring tide. From each of the 13 stations water samples were collected at the peak of high tide for the estimation of salinity, inorganic phosphate, fluorides and dissolved reactive silicate. The direction and speed of the currents were measured at 1 m interval from surface to 1/2 m above bottom after anchoring the boat at all the stations. Also current measurements were made from sts 9 and 13 at hourly interval during the spring tide for 1 complete tidal cycle.

This estuarine system is largely influenced by the influx of fresh water, which, in turn, is controlled by the rainy season facilitating the division of the observation period into 3 distinct periods, viz. premonsoon (Feb.-May), monsoon (June-Oct.) and postmonsoon (Nov.-Jan.).

Results

Distribution of saline water entering into this region is depicted in Fig. 2. Major incursion of saline water occurs from Jan. to May when the salinity is \(>30 \times 10^{-3}\). Even at a distance of about 18 km from the...
barmouth and beyond this high saline water can be traced to a distance of > 25 km from the barmouth. At st 1 salinity value remains high (> 25 x 10^{-3}) just after the monsoon. However at st 13 the salinity value shows only a gradual increase from 0 to > 20 x 10^{-3} from Dec. to May. The vertical salinity gradient is very small (< 3 x 10^{-3}) during this season.

With the onset of the monsoon fresh water or very low saline water of < 1 x 10^{-3} salinity is traceable even to a distance of 5 km from the barmouth. While the salinity at st 1 varies from 19 to 3 x 10^{-3}, the salinity at st 13 is 0 most of the period except in early June. During this period actually a fresh water regime would be established towards the head of the estuary after 5 km from barmouth (Fig. 3B). The vertical salinity gradient at stations near the barmouth is > 10 x 10^{-3} showing saline incursion through the bottom during high tide.

During the postmonsoon period a gradual increase in salinity could be noticed at all stations as the season progresses. While at st 1 salinity value increased to nearly 30 x 10^{-3}, at st 13 it increased from 0 to 2 x 10^{-3}. Similar gradual increase of salinity took place at all the intermediate stations (Fig. 3C). The salt water intrusion was restricted to a distance of about 19 km during this season.

The flow pattern studied, at the peak of the high tide, shows that the direction of current is towards the estuary at all the stations during the 3 seasons. However the current observations taken at st 9 and 13 for a complete tidal cycle showed the complete reversal of the tidal current according to the tide. The speed of the current varied from 10 to 42 cm. sec^{-1} at different regions of the estuary during the 3 seasons. Maximum speed was recorded near the narrow regions of the estuary especially at st 7, 8 and 13. Generally the speed increased from surface to 1-2 m depth layers and then reduced to the bottom. The water in the estuary remains partially mixed when the river water runoff was small and moderate. At high fresh water influx stratification is pronounced at st 1 to 5.

**Dilution and flushing**—The amount of fresh water at any given location in the estuary in terms of salinity (S) at the same location is given by:

\[
\frac{S_o - S}{S_o} = \frac{S - S_n}{S_o}
\]

where \(S_o\) is salinity of the coastal seawater, \(S\) salinity at any location inside the estuary, the fresh water fraction at different stations along the estuar
was calculated for different seasons (Fig. 4). The fresh water fraction was very large during the monsoon at almost all stations except at 1 and 2 where it was 0.69 and 0.89. During the postmonsoon season the fresh water fraction increased from 0.17 at st 1 to 0.86 at st 10 in a gradual way and is maximum there after. In the premonsoon season there was a gradual increase from 0.04 at st 1 to 0.63 at st 13 and was very low as compared to other seasons.

The dilution factor, inverse of the fresh water fraction, showed during premonsoon conditions a gradual decrease from 14.28 at st 4 to 1.58 at st 13. During monsoon period this factor was 1.47 at st 1 and 0 at st 13. During postmonsoon period it was 5.88 at st 1 and gradually decreased to 1.02 at st 11 and 0 at st 13.

Distribution of inorganic phosphate—During premonsoon high concentration of inorganic phosphate (Fig. 5) was seen at sts 13 (81 μmol.l⁻¹) and 12 (63 μmol.l⁻¹) and from st 12 down the estuary there was reduction in the concentration and reached a value of 3 μmol.l⁻¹ at st 1. During monsoon the distribution was irregular. While very low values below 10 μmol.l⁻¹ could be observed at sts 10 and 13, between st 9 and 3 values above 17 μmol.l⁻¹ reaching a value of approximately 50 μmol.l⁻¹ at st 8 could be noticed, and after that at stations near to barmouth the concentration was below 10 μmol.l⁻¹. In the postmonsoon months, a picture almost similar to that of premonsoon could be noticed with a difference that the maximum value (88 μmol.l⁻¹) was at st 11 instead of st 13. The phosphate level showed a gradual decrease from st 11 to st 1.

Silicate—Average silicate concentration varied from 0.37 to 5.96, 0.21 to 4.73 and 0.03 to 2.66 mg.l⁻¹ effectively in monsoon, postmonsoon and premonsoon seasons from barmouth to upstream (Fig. 6). There was a general decrease in the silicate content in Oct. to May. In the upper reaches of the river the salinity influence is less the silicate levels are relatively uniform throughout the year. The changes in the silicate content of estuarine waters are due to the difference in dilution and the net concentration is observed during the SW monsoon season when the fresh water discharge is minimum. During premonsoon season when the river discharge is minimum the longitudinal variation in the silicate content was minimum (0.03-2.66 mg.l⁻¹). Ranarayanan et al.⁹ observed atypical behaviour of dissolved silicate in this region. They also reported substantial removal of silicate by precipitation at different salinity ranges as compared to other areas.

Fluoride—There is a general increase in the fluoride concentration from upstream to barmouth.
Fluoride concentration (0.5 to >1.5 mg.l⁻¹) from Oct. to April. Maximum concentration is observed during Dec. to April. From May the values begin to decrease and minimum concentrations (<0.5 mg.l⁻¹) are observed at all stations except at st 1 during July to Sept. At st 1 fluoride content is high (>0.5 mg.l⁻¹) at the bottom. During this season the fresh water influx through the river is maximum. The extent of seawater incursion into the estuarine system during different months of the year considering the index of seawater penetration as 1 x 10⁻³ is shown in Fig. 3. Fluoride values at sts 8 to 13 are markedly high (>1.5 mg.l⁻¹) during Dec. to April (Fig. 7) and there is a general decrease in the concentration towards the river mouth. High concentration of fluoride observed is due to the effect of pollutants discharged from the fertilizer factory situated upstream near to st 13. It is also believed that the Aluminium Factory, which is also in the vicinity of the fertilizer factory, uses cryolite as one of the raw materials and this may be contributing fluoride substantially to the environment. The effect is conspicuous during the time of the year when the fresh water discharge through the river is minimum. Station near to the river mouth also shows higher levels than the usual sea water concentration except during March, but the values are less than the values observed at stations upstream. This indicates clearly the contribution from the river and afterwards dilution by the time the effluent mixed water reaches the river mouth.

Fluoride content of the river water at zero chlorinity collected from the upstream of the industrial belt showed a concentration from 0.18 to 0.24 mg.l⁻¹. This value is slightly higher than what has been reported for the river water from other regions. As already discussed there is a higher concentration of fluoride at station downstream of the industrial belt during Dec. to April. Absence of higher values at these stations during May to Oct. is due to the greater dilution of fresh water flow.

Fluoride data from the estuary and the river plotted against chlorinity showed no definite relationship. A linear relationship between fluoride and chlorinity was reported from the estuary when fresh water containing no fluoride mixes with seawater. Water samples of lower chlorinity showed a marked variation showing a higher fluoride-chlorinity ratio than chlorinities above 15 x 10⁻³ indicating contributions from the river.

The secondary maximum observed at chlorinity between 10 and 14 x 10⁻³ is also believed to be due to the effect of fluoride containing pollutant at upstream stations during Dec. to April, when chlorinity values increased from 0 to >10 x 10⁻³ to the decrease in the fresh water flow.

Discussion

Changes in the characteristics of this estuarine system reveal its dependence on the monsoonal cycle of this region. SW monsoon season accompanied by large volume of fresh water influx into the estuarine system creates stratification at the mouth of the estuary during the flood tide. At stations nearer to the barmouth the direction of flow was controlled by nature of the tide. Seawater dominated up to 2 km from there onwards fresh water dominated. Qaisar, Sen Gupta observed a salt wedge extending up to a distance of 10 km in Mandovi and 12 km in Zuari rivers during monsoon which is totally absent in this system during this period. The horizontal salinity gradient could be noticed only up to a few stations upwards from barmouth. Eventhough the inorgan...
Phosphate concentration was generally low compared to the other seasons, there was an accumulation between sts 3 and 9. This also depicted in the fresh water fraction which does not show much variation between these stations. This showed that even though the pollutant introduced near st 11 gets diluted, the flushing was less during the season, because seawater dilution factor was very negligible beyond st 3 towards the head of the estuary reaching zero value. Therefore any pollutant introduced into the estuary from factories located near sts 11 and 12 would only get diluted by the fresh water influx and would be cradled back and forth according to the tidal current up to st 3 near to barmouth, where it would get progressively mixed with seawater and get diluted further and flushed out of the estuarine system. High concentration of phosphate and fluoride observed between the sts 4 and 9 may be due to the effect of cradling of river water mixed with the effluent discharge in between tidal regimes.

During the postmonsoon period, the salinity gradient along the longitudinal axis of the estuary increases (fresh water fraction curve in Fig. 4). This showed that with the reduction in the river discharge intrusion of saline water was taking place more interior into the estuary (up to 17 km from barmouth). The slight vertical gradient of salinity with an upstream current from surface to bottom showed that the estuary behaved as a partially mixed estuary during the season. The fresh water fraction curve and the phosphate distribution also showed that there was partial mixing of river water and seawater. From the steep gradient of phosphate curve after st 11 up to st 4, it was evident that there was a progressive dilution downstream after the discharge point.

Comparatively high horizontal gradient of salinity from the barmouth to st 13 and beyond and less vertical gradient, with the flow pattern showing a steady upstream current from top to bottom at all the stations, showed that the estuary during the postmonsoon condition is a mixed estuary. This is also quite evident from the distribution of phosphate and fresh water fraction from st 13 downstream. A steady dilution of any pollutant introduced at sts 11 and 12 could be expected downstream up to barmouth.

As the estuary is a tide dominated one it is responding to the vagaries of the monsoon in a great way. The deepening of the harbour entrance channel has increased the tidal prism resulting in greater incursion of seawater into the estuary during the flood tide. Indiscriminate reclamation of the estuarine water area near the harbour entrance for various activities of the harbour has also helped in the horizontal extension of seawater into the river Periyar thereby increasing the salinity of the system considerably.

Acknowledgement
The authors express their gratitude to Dr H N Siddiquie, Director for his interest and to Dr M. Krishnan Kutty for all help.

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Atypical Behaviour of Dissolved Silicate in the Cochin Backwater & Periyar River

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Received 10 October 1983; revised received 7 March 1984

Dissolved silicate was determined for 1 yr (1982-83) covering a wide range of salinity from the estuarine mouth to the fresh water region. Silicate concentration ranged between 0.03 and 4.75 mg L⁻¹. Silicate - salinity relationship was linear and inverse in the salinity ranges 0-5 × 10⁻³ and 5-35 × 10⁻³. Since variability in the distribution of silicate explained by the significant linear regression model was small in the subranges of salinity 5-20 and 20-30 × 10⁻³, a curvilinear regression model was fitted and it gave a good fit at 5% level (P > 0.05). The expected removal of silicate at salinity range 0-5 and 5-35 × 10⁻³ given by linear relationship was 28.8 and 51.1 %, respectively. In 5-20 and 20-30 × 10⁻³ at 5 and 20 × 10⁻³ salinity the expected removal as given by curvilinear relationship was 31.94 and 6.068 %, respectively.

Distribution of dissolved silicate in the sea has been studied extensively. Several workers have studied the behaviour of silicate during the estuarine mixing. Very little information is available on the silicate distribution in the Indian estuaries, though it is of interest to note its behaviour during the estuarine mixing processes.

This paper presents the behaviour of silicate in relation to salinity in the Cochin backwater and in Periyar river.

Materials and Methods

Water samples were collected from Cochin backwater and Periyar River at monthly intervals during 1982-83 from marine zone to fresh water region covering a wide range of salinity (Fig. 1). The station depths varied between 2 and 7 m. Samples were collected from the surface and bottom and stored in polyethylene bottles and analysed immediately. Dissolved silicate by spectrophotometric method and salinity by titration method were estimated. A linear regression model was fitted and its significance tested using ANOVA technique, based on the significance of near correlation.

Salinity ranges in 0-35 × 10⁻³ were combined and grouped into 2 as 5-20 × 10⁻³ and 20-35 × 10⁻³. For each 2 groups separately and for the whole the same linear regression model was fitted and its significance tested as above. Since linear relationship was not significant for the subranges a curvilinear model was fitted for 2 groups. The fitted equation was

$$Y_i = \frac{X^2}{a_0 + a_1 X + a_2 X^2}$$

where $Y_i =$ silicate concentration at the $i$th salinity; $X =$ salinity; $a_0, a_1, a_2$ are curvilinear regression coefficients. This model was fitted for the average of silicate and salinity concentration in each interval of 5 units in each range. The fitted model was found to be good fit using $X^2$ statistic at 5% level. For linear and curvilinear relationships, the expected removal of silicate at 0 salinity in different ranges was computed.

Results and Discussion

There is a vast change in the salinity conditions at all stations except at the estuarine mouth where the salinity changes are less during the year (Table 1).
There is a general increase in the silicate concentration from the mouth of the estuary to upstream (Table 2). Average silicate concentration (mg $1^{-1}$) varies from 0.37 to 5.96, 0.21 to 4.73 and 0.03 to 2.66 respectively in monsoon, postmonsoon and premonsoon seasons from the barmouth to upstream. Highest silicate concentration is observed at the surface. There is a general decrease in the silicate content from Oct. to May. In the upper reaches of Periyar where the salinity influence is less, the concentration is comparatively uniform throughout the year. All samples have been collected at a similar stage of tidal cycle. Nevertheless the major changes in the silicate concentration observed are due to differences in dilution and the concentration is maximum when the fresh water flow is maximum. The silicate distribution appears to be largely governed by the river water discharge. Maximum concentration of silicate (1.7 to 6.7 mg $1^{-1}$) occurs during SW monsoon when the river water discharge is maximum. But during the premonsoon season when the river discharge is minimum the variation and the concentration of silicate are minimum (0.03-2.66 mg l $^{-1}$).

Variation in the concentration of salinity decreases steadily from 195 to 3‰. Whereas in silicate, it reaches to a maximum of 443‰ in the salinity range $10^{-3}$ and falls to a minimum of 47‰ in the lower range $10^{-2}$ and higher $30-35 	imes 10^{-3}$ ranges. Correlation coefficient is negative in all cases except in the salinity range $10-15 	imes 10^{-3}$ and it is significant only in $5-10 	imes 10^{-3}$. It is further suggested that dilution has significant inverse effect at $5\%$ level only in the salinity range $0.5 	imes 10^{-3}$.

The fitted linear regression equation for different salinity ranges ($\times 10^{-3}$) are:

$$Y = -0.4445X + 3.3808 \text{ for } 0-5$$
$$Y = -0.2566X + 4.0221 \text{ for } 5-10$$
$$Y = -0.1222X - 0.0049 \text{ for } 10-15$$
$$Y = -0.2099X + 5.1256 \text{ for } 15-20$$
$$Y = -0.0136X + 0.8482 \text{ for } 20-25$$
$$Y = -0.0055X + 1.0587 \text{ for } 25-30$$
$$Y = -0.1029X + 4.0212 \text{ for } 30-35$$

where $Y$ is silicate and $X$ is salinity.

The fitted linear regression model was significant only in salinity range $0.5 \times 10^{-3}$ (F ratio 30.25; < 0.05) and variability explained was only 7.82%. Since linear regression model was not significant for the remaining ranges, they were all combined in the analysis.
redistributed into 2 ranges 5-20 $\times 10^{-3}$ and 20-35 $\times 10^{-3}$. The correlation coefficient was calculated and the same model was again fitted for the 2 separately and together.

The fitted equations for the 2 salinity ($\times 10^{-3}$) ranges and the combined one are:

$$ Y = -0.0508 X + 2.3203 \text{ for 5-20} $$
$$ Y = 0.0147 X + 0.3594 \text{ for 20-35} $$
$$ Y = -0.0556 X + 2.3234 \text{ for 5-35} $$

Since linear model was significant only for the salinity range 5-35 $\times 10^{-3}$ (F ratio = 59.1776; P < 0.05), the fitted linear equation in this range was extended to salinity 0 and the expected removal was estimated as 51.1%. The variability explained was only 19.57% (Table 3). Therefore the unexplained variability may be due to different types of relationships between silicate and salinity; in the salinity sub-ranges 5-20 $\times 10^{-3}$ and 20-35 $\times 10^{-3}$. Since linear relationship did not hold good for these 2 ranges, a curvilinear model was fitted and it was:

for sal. 5-20 $\times 10^{-3}$

$$ Y = 1.047 + \frac{X^2}{-211.4349 + 13.8129 X + 2.7041 X^2} $$

for sal. 20-35 $\times 10^{-3}$

$$ Y = 0.6163 + \frac{X^2}{-46048.107 + 1748.5109 X + 0.9746 X^2} $$

The model was fitted using the average values of silicate and salinity in each interval of 5 units in each range. The fitted model gave a good fit for both ranges

### Table 2 — Silicate (mg.l$^{-1}$) Distribution at Different Stations

<table>
<thead>
<tr>
<th></th>
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<td>3.59</td>
<td>4.33</td>
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<td>1.81</td>
<td>0.54</td>
<td>0.11</td>
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<td>1.30</td>
<td>2.23</td>
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<td>0.38</td>
<td>0.72</td>
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<td>4.45</td>
<td>3.94</td>
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<td>0.12</td>
<td>0.31</td>
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<tr>
<td>B 2.62</td>
<td>2.47</td>
<td>2.84</td>
<td>4.05</td>
<td>4.10</td>
<td>3.42</td>
<td>3.75</td>
<td>0.50</td>
<td>0.28</td>
<td>1.20</td>
<td>1.28</td>
<td>1.34</td>
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<tr>
<td>1 S</td>
<td>3.00</td>
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<td>3.95</td>
<td>3.96</td>
<td>1.55</td>
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<td>0.48</td>
<td>0.10</td>
<td>0.33</td>
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<td>6.80</td>
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<td>3.51</td>
<td>4.22</td>
<td>0.41</td>
<td>0.54</td>
<td>0.64</td>
<td>0.76</td>
<td>2.22</td>
<td></td>
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</tbody>
</table>

* B = surface, B = bottom

### Table 3 — Removal of Silicate for All Salinity Ranges and Variability Explained by Linear Regression Model

<table>
<thead>
<tr>
<th>Sal. range ($\times 10^{-3}$)</th>
<th>0-5</th>
<th>5-20</th>
<th>20-35</th>
<th>5-35</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent silicate removed at</td>
<td>28.83 at (0)</td>
<td>31.94 at (5)</td>
<td>6.068 at (20)</td>
<td>51.09 at (0)</td>
</tr>
<tr>
<td>$\times 10^{-3}$</td>
<td>$\times 10^{-3}$</td>
<td>$\times 10^{-3}$</td>
<td>$\times 10^{-3}$</td>
<td>$\times 10^{-3}$</td>
</tr>
<tr>
<td>Explained variability (%)</td>
<td>7.36</td>
<td>—</td>
<td>—</td>
<td>19.57</td>
</tr>
</tbody>
</table>
by $\chi^2$ test at 5% level ($P > 0.05$). Therefore the reduction in the variability explained by the linear regression model in the salinity range $5-35 \times 10^{-3}$ can be attributed to different types of curvilinear relationships existing between silicate and salinity in the salinity ranges $5-20 \times 10^{-3}$ and $20-35 \times 10^{-3}$. Using these 2 equations the expected removal of silicate at 5 and $20 \times 10^{-3}$ salinity is 31.94% and 6.068% respectively (Table 3). Burton et al. observed only values 2% less than the measured concentration for the test estuary and thereby ruling out the possibility of any silicate removal by precipitation when the freshwater mixes with seawater. Substantial removal of dissolved silicate from river water entering the Mississippi Delta has been suggested by Bien et al. Burton has reported 10% removal of dissolved silicon in the upper estuary of the Vellar river. The variation in the concentration observed over the year in the estuarine mouth have been associated with the biological factors such as high phytoplankton production occurring in these waters. In other regions of the estuary the biological effect on the distribution of silicate seems to be minimal.

Eventhough linear model was found to be significant in $0.5 \times 10^{-3}$ salinity the explained variability is very low. This may be due to precipitation. Similarly, in the salinity range $5-35 \times 10^{-3}$ the explained variability is little more, but much less than 50%. Since curvilinear relationship gave a good fit in the subsalinity ranges $5-20 \times 10^{-3}$ and $20-35 \times 10^{-3}$, a part of the unexplained variability may be due to removal but at a lower rate.

Acknowledgement
The authors express their gratitude to Dr V V R Varadachari, Director, for his interest, to late C V G Reddy for going through the paper and to Dr M Krishnan Kutty, Scientist-in-Charge, RC of NIO for the help.

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3 Meed H & Takesue K, Rec Oceanogr Wks Japan, 6 (1960) 112.
Hydrochemical Characteristics of Chaliyar River Estuary

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National Institute of Oceanography, Regional Centre, Cochin - 682 018

Hydrochemistry of Chaliyar river estuary was studied for a period of one year taking tidal observations across 4 sections along 15 km distance. The important factors affecting the general hydrography were rainfall, freshwater inflow and seawater intrusion. Nitrate - N source was found to be due to land drainage and the source of inorganic phosphate as seawater. An inverse relationship was observed between inorganic and organic nitrogen fractions.

INTRODUCTION

Estuarine ecological environments are complex and highly variable compared to other marine environments. In an estuary, mixing occurs between natural waters of very different chemical composition and physico-chemical properties. Differences in the nature of the fresh and saline mixing components produce gradients and transitions of various parameters within this region. Estuaries receive highest inputs of nutrients through land drainage and industrial pollution. What happens to this large quantity of nutrients that enter the estuary is not only of ecological interest, but also relevant to water quality management. The Chaliyar river is one of the major west flowing rivers of the Kerala State. It originates from the Western Ghats and joins the Arabian Sea at Bevpore, near Kozhikode in the south west coast of India. Earlier, a few studies have been conducted in this estuary on salinity intrusion (James and Sreedharan, 1983) and general hydrography (Premchand et al., 1987). In the present work the distribution and seasonal variation of different hydrochemical parameters, such as pH, salinity, dissolved oxygen and nutrients in the estuary are discussed. The studies was mainly directed at identifying the sources and sinks of nutrients and defining the important geochemical and biochemical pathways of these nutrients in the estuary.

MATERIAL AND METHOD

Study area

Intensive sampling and analyses were made at 4 sections in Chaliyar river estuary. The study area with the 4 observation sections, namely S1, S2, S3, and S4 are shown in figure 1. S1 is near to the river mouth and the upstream sections are at 5, 10 and 15 km distances from S1. Two stations were selected along each section across the river which are almost equidistant from the shore, one on the northern side and the other on the southern side. Depths along these sections varied with tide and season, so that mean values and exceptions are stated below. The physical dimensions of the sections are:

<table>
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<tr>
<th>Section</th>
<th>Width, m</th>
<th>Mean depth, m</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.45 to 2.95</td>
</tr>
<tr>
<td>S2</td>
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<td>2.99 to 3.50</td>
</tr>
<tr>
<td>S3</td>
<td>200</td>
<td>4.00 to 4.54</td>
</tr>
<tr>
<td>S4</td>
<td>243</td>
<td>2.52 to 3.06</td>
</tr>
</tbody>
</table>

( The northern side is deeper with depth approx. 7.00 m )

Sampling and analysis

*Present address: St. Thomas College, Department of Chemistry, Pala, Arunapuram - 686 574
Monthly surveys were conducted in the estuary for a period of one year. 13 hr tidal observations were made simultaneously at 2 sections on consecutive days. Water samples were collected at 2 - hourly intervals from the surface, mid - depth and bottom of the water column. Hydrochemical parameters determined for each station included pH, salinity, dissolved oxygen, nitrite - N, Ammonia - N, nitrate - N, phosphate - P, total - N and total - P. Organic - N and organic - P are obtained by subtracting the inorganic fractions from corresponding total fractions. The pH measurements were conducted insitu using a portable pH meter (Philips model PP 9046) and salinity was measured using an electrodeless induction type salinometer (Digi - Auto model 3G, Tsurumi Seiki, Japan) after proper calibration. DO was determined using Winkler's method as described in Grasshoff (1983). NH₄ - N was measured using the indophenol blue method, NO₂⁻ - N by sulphanilamide diamin method, NO₃⁻ - N determined after reduction to nitrite and phosphate using the molybdenum blue method (Grasshoff, 1983). Total N and P were determined by simultaneous oxidation procedure using alkaline persulphate described in Grasshoff (1983).

RESULT AND DISCUSSION

Results of the present study on the hydrochemical characteristics of the estuary are summarised below. Based on rainfall, the period of study was divided into 3 seasons, namely Oct - Jan as post monsoon, Feb - May as pre monsoon and June - Sept as monsoon season.

General hydrography

The hydrogen ion concentration (pH) is an important indicator of the chemical conditions of the estuarine waters. Spatial variations in pH during each month of observation is shown in figure 2. The pH values were found decreasing from the marine towards the riverine end of the estuary. Tidal averages varied between 8.2 and 6.9 during post monsoon, 8.4 and 7.3 during pre monsoon and 7.8 and 6.7 during monsoon. The low pH values observed during the monsoon months are clearly due to the heavy fresh water inflow into the estuary. The increased pH values during pre monsoon and post monsoon seasons and the gradual increase in pH towards the marine end of the estuary are due to greater sea water intrusion. Spatial distribution of salinity during each month of observation is shown in figure 3. Salinity was mainly controlled by freshwater discharge through the river. During the monsoon months (June - July), when the rainfall and river discharge were maximum, saline intrusion was felt up to a distance of about 5 km from the river mouth. Sea water intrusion increased during post monsoon and the estuary was found to be marine dominated during premonsoon. These observations on salinity distribution lead to the classification of the estuary to be salt - wedge type during monsoon, a partially mixed type during post monsoon and a well mixed type during pre monsoon season.

Spatial variations in dissolved oxygen during each month of observation is shown in figure 4. Generally, dissolved oxygen concentration was higher during monsoon and comparatively low during the pre monsoon months. The variations in dissolved oxygen may be attributed to the variations in fresh water inflow, tidal ingress and water temperature. Although vertical differences in oxygen values were not conspicuous due to the shallow nature of the estuary, surface values were slightly higher than the bottom values. This may be due to the oxidation of organic matter at sub - surface levels. Thus the important factors effecting the general hydrography of Chaliyar river estuary were rainfall, freshwater inflow and seawater intrusion through the river mouth.

Distribution of nitrogen fractions

Ammonia - N: Seasonal variations in the integrated mean values of ammonia concentration in the 4 sections of the estuary are shown in figure 5. Ammonia concentration varied from non - detectable amounts during the monsoon months at certain sections to a gradual build up during the monsoon months and high concentrations (> 5.0 µg at/L) during the post monsoon season. Isolated high concentrations (> 15.0 µg at/L) were noticed in the month of January in the 2 upstream sections. Otherwise the ammonia concentration decreased gradually to lower values in the months of February to May.

Nitrite - N: Seasonal changes in the integrated mean values of nitrite concentration are shown in figure 6. Nitrite distribution did not followed a clear definite pattern. Very low concentrations (1 µg at/L) were observed throughout the estuary during the period of study with a few exceptions. The maximum value observed (1.9 µg at/L) was at the
Figure 2. Spatial variations in pH during each month of observation.

var mouth during June. A second maximum was observed during October at section 2.

Itrate - N: Seasonal changes in the integrated mean concentration of nitrate at 4 sections in the estuary are shown in figure 7. The annual cycle showed minimum nitrate concentrations at all sections during the premonsoon followed by high concen-

IDIAN J. ENVIRONMENTAL PROTECTION, VOL. 19, NO. 5, MAY 1999
ntrations during the monsoon and a decrease in levels during the post monsoon.

Organic-N: Seasonal variation in the Integrated mean values of organic nitrogen in the estuarine waters (Figure 8) showed an inverse trend with that of nitrate-N.
A discussion of the seasonal variation in the distribution of various nitrogen fractions in the estuary will help in understanding the nutrient chemistry of the estuary. The degree to which phytoplankton nitrogen uptake processes affect estuarine nitrogen concentration varies between different estuarine systems (McCarthy, 1981). Several factors including external environmental conditions, such as temperature, light, nutrient concentration and physiological state of the phytoplankton ultimately regulate the rate of nitrogen uptake in the estuary. The effect of these uptake processes on ambient nitrogen...
Table 1. Percentage of various nitrogen fractions

<table>
<thead>
<tr>
<th>Season</th>
<th>NO$_3^-$-N</th>
<th>NH$_4^+$-N</th>
<th>Org-N</th>
</tr>
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<tr>
<td>Premonsoon</td>
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<tr>
<td>S-1</td>
<td>13.80</td>
<td>4.80</td>
<td>81.40</td>
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<td>10.60</td>
<td>7.60</td>
<td>81.80</td>
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<td>S-4</td>
<td>10.00</td>
<td>1.50</td>
<td>88.50</td>
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<td>10.00</td>
<td>24.10</td>
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<td>72.30</td>
<td>8.20</td>
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<td>7.60</td>
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<td>85.70</td>
<td>6.10</td>
<td>8.20</td>
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<td>Postmonsoon</td>
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<tr>
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<td>48.80</td>
<td>26.60</td>
<td>24.60</td>
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Table 2. Interstitial nutrients of sediments at various sections in Chaliyar river estuary, in µg at/L

<table>
<thead>
<tr>
<th>Sections</th>
<th>NO$_3^-$-N</th>
<th>NO$_2^-$-N</th>
<th>NH$_4^+$-N</th>
<th>PO$_4^-$-P</th>
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<td>1.70</td>
<td>13.09</td>
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<td>14.44</td>
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<td>12.35</td>
<td>681.70</td>
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<td>3.59</td>
<td>73.90</td>
<td>106.20</td>
<td>2.46</td>
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<td>1.93</td>
<td>17.35</td>
<td>69.30</td>
<td>8.20</td>
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<td>16.41</td>
<td>770.00</td>
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<td>36.85</td>
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<td>1.64</td>
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<td>Postmonsoon</td>
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<td>2.37</td>
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<td>13.16</td>
<td>226.60</td>
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<td>S-3</td>
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<td>61.62</td>
<td>61.52</td>
<td>3.25</td>
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<td>S-4</td>
<td>1.88</td>
<td>24.92</td>
<td>27.80</td>
<td>4.92</td>
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The distribution of various nitrogen fractions in the estuary was affected by physical, chemical and biological processes. The contribution of various nitrogen fractions to the total nitrogen pool of the estuarine waters was found to vary spatially and temporally. The major source of inorganic nitrogen was through river discharge which was indicated by their maximum concentration during monsoon. During the premonsoon months when the riverine contribution was very little, percentage of inorganic nitrogen in the estuarine waters was found to be the minimum and the major form of nitrogen was organic. During postmonsoon season, the contribution of both these components were almost equal in the estuarine waters even though there existed a predominance in the inorganic form. Generally, dissolved nitrogen compounds are present throughout the estuary during all seasons of the year in one form or other and so nitrogen was not a limiting nutrient in the estuary.
Percentage of different nitrogen fractions at various sections in the estuary is given in Table 1. Contribution of ammonia to the total nitrogen pool of the estuary was < 10% during the monsoon and pre-monsoon periods. Maximum accumulation of ammonia (> 25% of total N) occurred during the postmonsoon period when the opposing forces, namely river runoff and tidal incursion were moderate. Ammonia-N did not constitute a major component in the river water; therefore its concentration is subjected to little influence by river discharge. Ammonia distribution in the water column clearly indicated the process of ammonification in the estuarine and riverine part, which is the ultimate step in the autoepuration of organic matter. Added to this also the transfer of ammonia from the interstitial water in the bottom sediments which was rich in ammonia (Table 2). An examination of ammonia data in the interstitial water at various sections during different seasons (Table 2) indicated that it is minimum during the post monsoon season and the values are lowest at sections 3 and 4. But the ammonia concentrations are uniformly high in the water column with maximum values at the upstream sections. The transfer of ammonia to the overlying water can only be minimal at sections 3 and 4 where the interstitial water values are low. Therefore, it strengthens the argument that the high amount of ammonia encountered can only be due to ammonification in the water column.

Nitrite concentration was found to be significantly high only during the postmonsoon season. A close look at the tidal variations during this period showed the sequence of a peak concentration of ammonium followed by an increase in nitrite at all sections (Jose K. Xavier, 1993). This was indicative of nitrification in the water column as reported by several workers, like Ward and Twilley (1986) and Fan and Jin (1989). Here nitrifying bacteria can play an important role because they are able to...
oxidise ammonium to nitrate with nitrite as an intermediate. Nitrite may also be formed in the reduction of nitrate and denitrification. Heavy rainfall and consequent land drainage was observed to be the main source of nitrate in the estuary. High nitrate concentration in the run-off waters can be related to the large amount of nitrogenous fertilizers used in agriculture. Nitrates are not well retained by the soil and if not utilised quickly are leached away along with land drainage. Since nitrates are highly water-soluble, most of it may be leached away during the initial runoff period and this could be the reason for the decrease in nitrate concentration during July and August even though the river discharge was high. A second nitrate peak observed during November is due to the influence of river runoff during the north-east monsoon. A gradual decrease in concentration was observed downstream and the fluctuations observed at the barmouth section was according to the phase of tide. Much of the nitrate was washed out of the estuary during the period of high runoff without being assimilated, due to short residence time and slow uptake rate of nitrate by phytoplankton.

Nitrate concentration decreased during December and January due to the decrease in contribution from the land source and increased uptake by primary producers. During the premonsoon months from February to May, the entire estuary was marine dominated and the contribution of nitrate from fresh water was practically absent. This together with the high biological activity brought nitrate concentration to a minimum. But during this period, there was an increase in organic-N concentration. The reduction in the inorganic nitrogen accompanied by a substantial increase in the percentage of organic-N indicated that the major source of organic-N in this system is not the river runoff. Organic-N was positively correlated with salinity during monsoon and post monsoon (r = 0.40 to 0.61). This indicated that the source of this nutrient during this period was from the sea. Dissolved organic compounds in the sea water come from the decay of organic matter produced in the body of water itself, from the excreted waste products of living organisms or by diffusion from the bodies of certain phytoplankton (Rao and Rao, 1974).

During the monsoon period, when land drainage and river discharge were maximum, 80 - 90 % of the total nitrogen pool in the estuary was contributed by nitrate alone. On the other hand during the premonsoon period, when the estuary was marine dominated, 75 - 85 % of the total nitrogen pool was organic-N. Generally an inverse relationship was observed between inorganic and organic forms of nitrogen in the estuary. Such an inverse relationship has been reported in the waters of western English Channel (Butler et al., 1979). A sharp rise in organic-N accompanied by a depletion of inorganic nitrogen during pre and post monsoon seasons is indicative of phytoplankton productivity and nutrient enrichment due to favourable physicochemical conditions.

Distribution of phosphorus in the estuary

Dissolved inorganic phosphate: Seasonal variation in the integrated mean concentration of phosphate is shown in figure 9. The seasonal trends observed in the phosphate distribution were less marked compared to the nitrate distribution. Phosphate concentrations were relatively low (< 1.0 μg/L) throughout the estuary with a few exceptions. The peak values observed were at the upstream sections during Dec - Jan. The peak value noticed at the river mouth was during July.

Organic phosphorus: Seasonal variation in the integrated mean concentration of organic phosphorus in the water column at different sections of the estuary are shown in figure 10. The temporal and spatial variation of inorganic phosphate differed from that of nitrogen fractions. The concentration that was generally low during the pre monsoon period picked up with the advent of monsoon and recorded the highest mean concentration during the post monsoon at all sections in the estuary. Except during December, January and June, higher concentrations of inorganic phosphate was found at the river mouth section. Organic phosphorus was higher at the river mouth except during November.

Therefore the source of inorganic phosphate as well as organic-P was mainly from the sea. Regeneration from sediments was found to be a major source and increased uptake by primary producers. During the premonsoon months from February to May, the entire estuary was marine dominated and the contribution of nitrate from fresh water was practically absent. This together with the high biological activity brought nitrate concentration to a minimum. But during this period, there was an increase in organic-N concentration. The reduction in the inorganic nitrogen accompanied by a substantial increase in the percentage of organic-N indicated that the major source of organic-N in this system is not the river runoff. Organic-N was positively correlated with salinity during monsoon and post monsoon (r = 0.40 to 0.61). This indicated that the source of this nutrient during this period was from the sea. Dissolved organic compounds in the sea water come from the decay of organic matter produced in the body of water itself, from the excreted waste products of living organisms or by diffusion from the bodies of certain phytoplankton (Rao and Rao, 1974).

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process is more under conditions of high terrestrial runoff. Higher interstitial phosphate concentrations at sections 1 and 2 during monsoon (Table 2) reveal this. High values of inorganic phosphate observed at the rivermouth during July and August could be due to the intrusion of upwelled water. The high concentrations observed during December and January can be accounted as due to local regeneration under favourable physical - chemical conditions. Pomeroy et al. (1965) pointed out that the exchange of phosphate consisted of a 2 step ion exchange process between clay minerals and water, plus an exchange between terrestrial micro - organisms and water. Further he suggested that the exchange rate and capacity of the sediments were ecologically important factors in maintaining the phosphate concentration at an optimum level favourable for plankton production.

It has been found that total productivity in aquatic biological communities is directly limited by the concentration of available phosphorus and that several geochemical processes are involved in regulating the availability of phosphorus in the nutrient cycle. One of these important processes in the aquatic environment is the incorporation of phosphorus into the sedimental phase, either by sorption mechanisms or by the formation of insoluble inorganic phosphate minerals (Storm and Biggs, 1982). The biological removal of phosphate in estuaries include uptake by both phytoplankton and bacteria (Lebo, 1990). The 'buffering' of phosphate concentrations in estuaries has been described as an equilibrium process where phosphorus is adsorbed or released from particles to maintain a constant concentration.

CONCLUSION

The important factors affecting the general hydrography of Chaliyar river estuary were rainfall, freshwater inflow and intrusion of sea water through the river mouth. Observations on salinity distribution lead to the classification of the estuary to be a salt-wedge type during monsoon, a partially - mixed type during postmonsoon and a well - mixed type during premonsoon.

The distribution of various nitrogen fractions in the estuary was found to vary spatially and temporally. Concentration of inorganic nitrogen compounds were high only during periods of heavy freshwater runoff. Nitrate - N was the predominant form among inorganic species and it showed a negative correlation with salinity. High nitrate concentration in the runoff waters can be related to the large amount of nitrogenous fertilizers used in agriculture. Nitrates are not well retained by the soil and are leached away along with land drainage. Organic nitrogen showed from the sea.

The distribution and seasonal variation of phosphorus in the estuary differed from that of nitrogen fractions. The source of phosphorus in the estuary was found to be mainly from the sea. Contribution from land drainage was very small and a significant contribution during postmonsoon was observed to be regeneration from the bottom sediment.

REFERENCE


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Changes in water quality at Cochin harbour dredging site, south west coast of India

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Received 2 December 1996; revised 26 December 1997

The water quality in the vicinity of the dredging did not show any appreciable change. All dissolved nutrients recorded sharp changes in the water column. After 20 minutes and 2 hours, the conditions at the dredging were much different from the pre-dredging site. As the surge in the nutrients was confined only to the end stage of the dredging, the possibility of any extensive water quality deterioration at the site or in its vicinity was remote.

The proposal to deepen the navigational channel of Cochin to 12.2 - 12.8 m draft level would increase the annual extent of dredging to $10 \times 10^6$ m$^3$ from the present level of $6 \times 10^6$ m$^3$. Deepening of the channel might lead to a greater incursion of salt water and silt into the harbour region and that may affect the benthic community. The release of the detritus and silt and their re-deposition over biota may even cause mass mortality. As part of a detailed study to establish prevailing conditions of the water body, with an aim to provide a scientific basis for future integrated management of the harbour area, a field experiment was devised to monitor the effect of extreme perturbation caused by dredging.

The dredging operations for deepening the channel for super tanker entry started in Ernakulam channel (Fig. 1) during October 1992. A field study was conducted on 15th December, 1992 in the Ernakulam Channel while dredging was operational. Observations were made just before the dredging, immediately after the dredging operations, after 20 minutes and 2 hours dredging respectively. From the vicinity of the dredging site, sea water samples were taken for the analysis of dissolved nutrients and other chemical parameters with a clean plastic bucket and the surface samples by a 1.71 Niskin water sampler. The ammonial nitrogen was analysed by Indophenol blue method and the nitrate, nitrite phosphate were done as in Grasshoff et al. In situ turbidity measurements were made with an OSK Model FN5 Turbidity meter and the light penetration in the water column by a sechi disk. The salinity is measured by an Inductive Salinometer. Water samples from three levels (surface, mid-depth and bottom) for salinity, dissolved oxygen and nutrient analyses and water samples from every 1m levels for sediment load were collected from the site. The transparency,
turbidity of the water column were measured. A small neutrally buoyant float was put into the sediment cloud formed at the dredging site with the hauling up of dredger and the movement of the patch and float was followed at a distance making least disturbances to the sediment patch immediately after dredging.

During the dredging operations (tidal ranges were between 1 and 1.3 m), and the water in the vicinity of the dredging had a sechi disk reading of 50 cm, turbidity of 10-15 ppm in the surface layer, 15-25 ppm at mid depth and 48.55 ppm just above the bottom. The suspended load in the surface water layer was 10-20 mg. l\(^{-1}\), 15-30 mg. l\(^{-1}\) in the mid layer and 35-50 mg. l\(^{-1}\) in the bottom layer during the dredging. As soon as the column of suspended sediment was introduced into the navigational channel along with dredger head lifting, it started to move away from the site by the average large scale tidal current, while at the same undergoing mixing by small scale turbulent eddies. On lifting up of dredger head, the sechi disc reading dropped to 5 cm, the turbidity reached 150 ppm at the surface, 900 ppm at the mid-depth and 1300 ppm in the bottom layer. The suspended load in the surface water reached to 120 mg. l\(^{-1}\) and the bottom water recorded 1150 mg. l\(^{-1}\) of sediment load. The sediment cloud formed during the lifting of dredging gear was extended to the bottom. The mixing process causes the initial sediment column to grow with time, thereby reducing the concentration within the sediment cloud.

The chemical features of the water column during the operation period were quite close to the average values of the parameters recorded for the month of October. A strong density stratification and a two layer structure of the water column was evident from the salinity and silicate distribution (Table 1). Phosphate profiles had a small vertical gradient within the range (0.50-0.71 \(\mu M\)). Nitrate recorded a decrease from the surface to the bottom within the range 0.2-0.54 \(\mu M\). Ammonia was generally absent except at the surface where its concentration was 0.41 \(\mu M\). Silicate varied inversely with salinity and decreased from 55.70 \(\mu M\) at the surface to 14.39 \(\mu M\) at the bottom.

Immediately 1 minute after the hauling of the dredging head, the sediment cloud patch was uniformly spread over the water column. All the nutrients in the water increased substantially. Phosphate levels increased four times, nitrite levels had doubled and ammonia levels underwent a five

<table>
<thead>
<tr>
<th>Depth</th>
<th>Salinity</th>
<th>Phosphate-P</th>
<th>Nitrite-N</th>
<th>Ammonia-N</th>
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<td>0.58</td>
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<td>S</td>
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<td>11.24</td>
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<tr>
<td>S</td>
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S=surface, M=mild layer, b=bottom
fold jump. Within 20 minutes after dredging, the water column regained its vertical density stratification. The phosphate and nitrite levels had returned to the pre-dredging ambient levels. But the ammonia and phosphate in the bottom layer still remained high. Normal suspended load values were attained within 30-45 minutes.

After 2 hours of dredging, the sediment plume completely mixed with the surrounding waters. Nitrite and phosphate had reverted to their pre-dredging levels. It could be seen that the disturbance due to the dredging was confined to a short span and to a limited area and was unlikely to cause any intense environmental damages to the entire system. The environment may be considerably affected increase of frequent lifting of dredging gear and total collapse/ failure of the system of dredging or accidental release of dredged material in the channel on its route in the designated dumping site.

This study forms a part of EIA study prior to deepening of the navigational channel, sponsored by Cochin Port Trust.

References
Heavy metals in fishes from coastal waters of Cochin, southwest coast of India

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Received 9 October 1995, revised 10 October 1996

The concentration levels of copper, zinc, manganese and iron have been determined in marine fishes from Cochin area which is one of the major fishing zones along the west coast of India. The concentration of heavy metals varied from species to species. Copper, Zn, Fe and Mn showed increased levels in the gills and alimentary canal compared to the muscle. Difference in heavy metal concentration in various species studied is attributed to the varying feeding habits. The observed levels were below the toxic limit.

Accumulation of certain toxic metals in different organs of marine organisms and their subsequent transfer to man through the food chain is of great concern. Fish musculature is a major path through which heavy metals can enter the human body and therefore, it has been investigated more than other organs. The present study was confined to the assessment of the level of some heavy metals in the muscle, liver, alimentary canal and gills of fishes collected from the inshore waters of Cochin in the south west coast of India.

Fish samples for analysis were collected from the Chinese dipnets deployed off Cochin during the summer 1992. Most of these fishes were confined in their distribution to shallow waters which subsist on phytoplankton and zooplankton strained from the surrounding waters by the well developed and feathery gills. The fish samples of same size were weighed individually and dissected to remove the various tissues which were washed in double distilled water. The alimentary canal was first removed carefully to avoid any contamination. The samples were dried to constant weight at 40 - 50°C, powdered and stored. The composite samples were digested in aquaregia using teflon bombs. Parallel replicate measurements were made on all the samples and the mean value has been tabulated. This method was calibrated by analysing one BCSS-1 standard reference material supplied by the National Research Council, Canada. The standard deviation found for each metal are Cd (±7%), Cu (±5%), Zn (±11%), Fe (±19%) and Mn (±15%) respectively. Determination of heavy metals were performed with a flame atomic absorption spectrophotometer (Perkin-Elmer 2380).

The details of the concentration of various metals in fourteen different species fishes are given in Table 1. Though the concentrations of metals in different tissues of fishes varied widely, the musculature which forms the edible part showed much lower concentration than other tissues. The concentration of Cu in the muscle tissue of Sphyrna zygaena was 1.54 µg.g⁻¹, while in the case of liver it was 35.49 µg.g⁻¹. This corresponds to an average enrichment ratio of about 1:23 in respect of liver as compared to the musculature. Similarly, the enrichment ratio for Zn and Mn in the same species were 1:26 and 1:3 respectively.

In the case of Chirocentrus dorab the liver to muscle ratio for Cu, Zn, and Fe were 11:1, 38:1 and 2:1 respectively. The enrichment ratio for each element between the pair of organs for different species of fishes varied considerably. The absolute increase of heavy metals in muscle tissue of contaminated fish is often much lower than in other organs and as mentioned earlier, it becomes enriched by metals only when the contamination is extremely high.

The estimated concentrations of Cu, Zn and Mn in the muscle tissue compared well with those of reported values in fishes from different parts of the western Indian Ocean. Elevated levels of Zn were observed in the alimentary canal and gills of Stolephorus devisi, Chirocentrus dorab, Sardinella longiceps, Rastrelliger kanagurta, Mini maculata and Mugil cephalus. It is generally believed that fish activity regulates Zn concentration in their muscle tissue and as a result do not reflect changes in
Table 1—Heavy metal concentration in different tissues of fish from coastal waters of Cochin (µg. g⁻¹ dry weight).

<table>
<thead>
<tr>
<th>Species</th>
<th>Common name</th>
<th>Tissue</th>
<th>Cu (SD)</th>
<th>Zn (SD)</th>
<th>Fe (SD)</th>
<th>Mn (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Sardinella longiceps (14)</td>
<td>Indian oil Sardine</td>
<td>M</td>
<td>1.54 (±0.09)</td>
<td>20.52 (± 1.80)</td>
<td>148.50 (± 32.0)</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AC</td>
<td>6.94 (±0.41)</td>
<td>63.42 (±11.10)</td>
<td>2255.40 (±609.0)</td>
<td>6.14 (±1.10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>G</td>
<td>2.72 (±0.11)</td>
<td>110.83 (±12.02)</td>
<td>428.39 (±68.0)</td>
<td>16.39 (±2.40)</td>
</tr>
<tr>
<td>2 Dassumieria auta (8) Rainbow sardine</td>
<td>M</td>
<td>1.59 (±0.06)</td>
<td>24.63 (± 1.66)</td>
<td>57.97 (± 9.5)</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AC</td>
<td>9.92 (±0.65)</td>
<td>64.45 (±9.20)</td>
<td>376.81 (±80.1)</td>
<td>8.19 (±1.10)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>ND</td>
<td>58.25 (±6.67)</td>
<td>224.63 (±40.4)</td>
<td>2.73 (±0.60)</td>
<td></td>
</tr>
<tr>
<td>3 Stolephorus devii (18) Anhovy</td>
<td>M</td>
<td>2.20 (±0.15)</td>
<td>29.90 (± 3.20)</td>
<td>119.04(± 18.0)</td>
<td>NO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AC</td>
<td>27.00 (±0.56)</td>
<td>123.15 (±16.09)</td>
<td>443.84(±96.0)</td>
<td>6.14 (±1.10)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>ND</td>
<td>172.41 (±15.50)</td>
<td>1009.32(±122.0)</td>
<td>64.40 (±8.20)</td>
<td></td>
</tr>
<tr>
<td>4 Rastrelliger kanagurta (4) Mackerel</td>
<td>M</td>
<td>2.01 (±0.12)</td>
<td>14.99 (± 1.60)</td>
<td>127.59(± 21.0)</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AC</td>
<td>9.28 (±0.32)</td>
<td>71.25(±6.50)</td>
<td>3773.30(±540.0)</td>
<td>14.68 (±2.10)</td>
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<tr>
<td></td>
<td>G</td>
<td>ND</td>
<td>117.87(±12.00)</td>
<td>419.25(±85.4)</td>
<td>11.70 (±1.20)</td>
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<tr>
<td>5 Chirocentrus dorab (3) Wolf herring</td>
<td>M</td>
<td>1.52 (±0.08)</td>
<td>6.56(± 0.42)</td>
<td>33.77(± 6.6)</td>
<td>NO</td>
<td></td>
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<tr>
<td></td>
<td>L</td>
<td>16.53 (±0.74)</td>
<td>247.62(±31.00)</td>
<td>72.46(± 14.5)</td>
<td>4.39 (±0.62)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AC</td>
<td>4.63 (±0.21)</td>
<td>462.64(±64.00)</td>
<td>318.84(±72.0)</td>
<td>62.84 (±11.00)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>6.17 (±0.35)</td>
<td>396.96(±55.00)</td>
<td>64.40 (±8.20)</td>
<td>ND</td>
<td></td>
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<tr>
<td>6 Mini maulata (6) Torpedo</td>
<td>M</td>
<td>4.63 (±0.21)</td>
<td>38.58(± 2.90)</td>
<td>250.00(± 51.0)</td>
<td>6.83 (±1.02)</td>
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<tr>
<td></td>
<td>AC</td>
<td>15.43 (±0.69)</td>
<td>159.68(±18.00)</td>
<td>536.25(±98.0)</td>
<td>6.98 (±1.50)</td>
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<tr>
<td></td>
<td>G</td>
<td>4.92 (±0.32)</td>
<td>137.52(±16.00)</td>
<td>692.03(±125.0)</td>
<td>2.73 (±0.50)</td>
<td></td>
</tr>
<tr>
<td>7 Megalaspis cordyla- (9) Trevally</td>
<td>M</td>
<td>1.43 (±0.07)</td>
<td>19.29(± 2.10)</td>
<td>362.32(± 70.0)</td>
<td>1.36 (±0.22)</td>
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</tr>
<tr>
<td></td>
<td>AC</td>
<td>7.71 (±0.46)</td>
<td>90.72(±8.70)</td>
<td>833.33(±178.0)</td>
<td>2.73 (±0.50)</td>
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</tr>
<tr>
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<td>G</td>
<td>4.60 (±0.25)</td>
<td>83.74(±9.20)</td>
<td>347.82(±68.4)</td>
<td>17.75 (±2.11)</td>
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</tr>
<tr>
<td>8 Psuedoscaena diacoants (11) Sciaenids</td>
<td>M</td>
<td>1.55 (±0.06)</td>
<td>19.07(± 2.50)</td>
<td>79.71(± 11.2)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>AC</td>
<td>6.17 (±0.29)</td>
<td>68.14(±9.50)</td>
<td>333.33(±178.0)</td>
<td>ND</td>
<td></td>
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<tr>
<td></td>
<td>G</td>
<td>ND</td>
<td>82.58(±8.70)</td>
<td>306.90(±55.0)</td>
<td>ND</td>
<td></td>
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<tr>
<td>9 Johnilies sp. (4) Jew fish</td>
<td>M</td>
<td>1.50 (±0.04)</td>
<td>18.06(± 1.80)</td>
<td>112.31 (± 20.0)</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AC</td>
<td>9.25 (±0.46)</td>
<td>67.73(±8.00)</td>
<td>239.13(±49.5)</td>
<td>ND</td>
<td></td>
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<tr>
<td></td>
<td>G</td>
<td>ND</td>
<td>66.05(±7.00)</td>
<td>306.32(±61.5)</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td>10 Sphyrna zygaena (2) Shark</td>
<td>M</td>
<td>1.54 (±0.08)</td>
<td>13.13(±0.90)</td>
<td>90.58(± 16.2)</td>
<td>1.26 (±0.19)</td>
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<tr>
<td></td>
<td>AC</td>
<td>15.43 (±0.84)</td>
<td>58.55(±5.20)</td>
<td>173.91 (±35.0)</td>
<td>4.29 (±0.73)</td>
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</tr>
<tr>
<td></td>
<td>G</td>
<td>3.70 (±0.14)</td>
<td>54.67(±2.50)</td>
<td>49.13 (±2.1)</td>
<td>3.27 (±0.33)</td>
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<td>L</td>
<td>35.49 (±2.01)</td>
<td>341.97(±49.00)</td>
<td>94.20 (±11.5)</td>
<td>4.09 (±0.80)</td>
<td></td>
</tr>
<tr>
<td>11 Mugil cephalus (4) Grey mullet</td>
<td>M</td>
<td>1.51 (±0.04)</td>
<td>26.68(±1.20)</td>
<td>72.46(± 17.9)</td>
<td>ND</td>
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<tr>
<td></td>
<td>AC</td>
<td>24.69 (±1.89)</td>
<td>137.93(±18.60)</td>
<td>167.00 (±26.4)</td>
<td>17.75 (±3.20)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>2.72 (±0.15)</td>
<td>140.53(±11.00)</td>
<td>479.54(±86.0)</td>
<td>26.51 (±4.00)</td>
<td></td>
</tr>
<tr>
<td>12 Petrica filamentosa (3) Silver bellies</td>
<td>M</td>
<td>ND</td>
<td>33.66 (± 4.40)</td>
<td>144.92 (±22.5)</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AC</td>
<td>40.12 (±3.11)</td>
<td>110.01(±20.10)</td>
<td>166.30(±40.4)</td>
<td>30.05 (±4.40)</td>
<td></td>
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<tr>
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<td>G</td>
<td>1.54 (±0.08)</td>
<td>84.03(±7.20)</td>
<td>262.14(±45.6)</td>
<td>2.41 (±0.50)</td>
<td></td>
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<tr>
<td>13 Gobius plassa (5) Goboid</td>
<td>M</td>
<td>ND</td>
<td>18.06 (± 2.10)</td>
<td>101.44(± 17.0)</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AC</td>
<td>12.34 (±0.78)</td>
<td>100.16(±13.00)</td>
<td>264.49(±42.3)</td>
<td>4.09 (±0.60)</td>
<td></td>
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<tr>
<td></td>
<td>G</td>
<td>2.72 (±0.15)</td>
<td>138.36(±14.00)</td>
<td>1419.44(±320.0)</td>
<td>24.10 (±3.19)</td>
<td></td>
</tr>
<tr>
<td>14 Parastracmeus niger (3) Black pomfret</td>
<td>M</td>
<td>3.08 (±0.16)</td>
<td>15.18(± 0.60)</td>
<td>45.29 (± 5.5)</td>
<td>9.56 (±1.50)</td>
<td></td>
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<tr>
<td></td>
<td>AC</td>
<td>7.71 (±0.48)</td>
<td>12.15(±0.90)</td>
<td>91.66 (±14.0)</td>
<td>20.49 (±4.90)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>9.25 (±0.44)</td>
<td>91.54(±11.00)</td>
<td>398.55(±70.4)</td>
<td>24.59 (±3.20)</td>
<td></td>
</tr>
</tbody>
</table>

M - muscle, AC - alimentary canal, G - gill, L - liver (SD) - standard deviation for triplicate analysis
(Values in parentheses give the no. of samples analysed)
ambient available levels of this element in the environment. Therefore, the high levels of Zn concentration reported here infers that the regulation of this element may not be complete. In all the species, Fe was found to be the most abundant of the metals analysed. Acceptable limits for other elements for human consumptions are: Zn (150ppm), Cu (10ppm) and Pb (1.5ppm) wet weight, respectively. No maxima is specified for Mn.

Dussumiera acuta, Chirocentros dorab, Mini maculata and Megalaspis cordyla contained trace metal levels in the order of alimentary canal > gill > musculature, while in the others the order was gill > alimentary canal > musculature. The possible explanation for the latter trend is that the principal mode of uptake of metal is through the gills. As the gills are constantly exposed, the mucus exposed to seawater acts as a surface adsorption sheet for either selective or general accumulation of metals.

The variation in concentration of metals in different tissues may be attributed to the feeding habits. In detrital feeders like Mugil cephalus which feed by grazing on submerged materials and plant surfaces or by sucking the surface layer of the mud, ingestion of sediment which could be enriched with heavy metals as a result of contamination, would probably lead to the ingestion of greater quantities of heavy metals by the fishes.

From the data it is clear that the concentration of all the metals analysed were within the prescribed limits for human consumption.

Authors thank Dr (Mrs). V. Santhakumari and Sri. P. Venugopal for identifying the species.

References
CHLOROPHYLL ‘a’ AND PARTICULATE ORGANIC CARBON IN RELATION TO SOME PHYSICO-CHEMICAL PARAMETERS ALONG SOUTHWEST COAST OF INDIA

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National Institute of Oceanography, Regional Centre, P.B. No. 1913, Cochin-18.

ABSTRACT

Chlorophyll ‘a’, Particulate Organic Carbon and other environmental parameters were studied along Kerala coast during October 1987 and 1988. High chlorophyll ‘a’ content at surface water and decreasing trend towards offshore was observed. Spatial gradient in the Chl ‘a’ and POC distribution exhibited appreciable difference in the inshore and offshore region. Gaylor and Hopper conditions tested to apply Satterthwaites approximation for unequal sets of sample observations showed that chlorophyll ‘a’ and environmental parameters except NO3-N varied spatially, while POC and NO3-N diurnally. For total and 60 µm size fractioned chlorophyll ‘a’ a negative relation of high gradient with salinity while, for 20 µm size fraction a positive relation of low gradient was observed. Inverse relation was observed between size fractioned chlorophyll ‘a’ and other parameters.

INTRODUCTION

BIOMASS of phytoplankton in the seas in terms of chlorophyll ‘a’ concentration is one of the most widely accepted methods in the study of primary production. Chlorophyll ‘a’ indicates total plant material available in the water at primary stages of food chain. An assessment of particulate organic carbon provides a more meaningful estimation of the available energy to the next trophic level where herbivore grazing is proposed to control phytoplankton within the limits set by nutrient concentration. The control of phytoplankton production by nutrient availability in the euphotic zone is the basis of any geochemical model calculation of bioreactive element cycling, particularly in the coastal and estuarine systems dominated by detrital material. Further, it is increasingly recognised that the physico-chemical characteristics prevailing in the water column play an important role in selecting the size structure of the phytoplankton community (Malone, 1980; Platt, et. al., 1983; Charez, 1989; Legendre and Le-Ferre, 1989). The spatial and temporal gradients in environmental parameters offered by the inshore/offshore waters make this ecosystem suitable for examining the relationship between physico-chemical parameters and phytoplankton pigment (size fraction) which forms the main objective of the present study.
Lot of information is available regarding the productivity and related parameters from the southwest coast of India. But all these are confined to a particular region or season, but the present work concentrates on the entire southwest coast of India.

Authors wish to thank the Director, National Institute of Oceanography, Dona Paula, Goa for the encouragement and help.

MATERIAL AND METHODS

This study is based on the samples collected along the southwest coast of India extending from Kasargod to Cape Comorin during the 187th and 204th cruises of RV Gaveshani during October, 1987 and 1988 respectively. The stations along the continental shelf (< 200 m depth) were taken as near shore and those on the continental slope (> 200 m depth) were classified as offshore stations. During October 1987, 12 nearshore stations, including 6 anchor stations were occupied covering 43 day and 26 night observations and also 6 offshore stations were occupied covering 43 day and 26 night observations. Collection during October 1988 included 18 nearshore stations, with 6 anchor stations covering 44 day and 21 night collections and 9 offshore stations covering 4 day and 5 night observations. Each anchor station was sampled 3 hourly intervals. Surface water was analysed for hydrographic parameters like temperature, salinity, DO and nutrients such as phosphate, nitrite, nitrate and silicate. Chlorophyll 'a' and Particulate Organic Carbon were determined by standard methods (Strickland and Parsons, 1968). For numerical interpretations the data of the two cruises were pooled and 7 anchor stations viz; Kasaragod, Cannanore, Calicut, Cochin, Quilon, Vizhinjam and Cape Comorin, 6 nearshore non-anchor stations and 6 offshore stations were considered. The numerical analysis include intraparameter association, box model for Chlorophyll 'a' distribution over the parameters POC, temperature, salinity, DO, PO4-P, NO2-N, NO3-N and SiO4-Si (Snedecor and Cochran 1967, Fisher and Yates 1963), critical ratio test and student's t test for single sample and student's two sample test for comparison of independent samples (Federer, 1967), two way nested analysis for testing significance of difference between offshore, nearshore and anchor stations and difference between day and night with respect to the concentration of parameters stated earlier using Gaylor and Hopper conditions for Satterthwaites approximation, Kruskal-walls non parametric test for comparing day and night collections of offshore, nearshore and anchor stations (Sokal and Rholf, 1981). Based on these results day and night collections were combined together or not according as the difference was not significant or otherwise, for further analysis. Duncan's multiple range test was applied to determine the highly different shore types and significant differences are presented in the form of a Trellis diagram for each parameter (Sanders, 1973). For size fractioned Chl 'a' studies, total water sample, 60 µm, and 20 µm size filters were used (Arantza Iriarte, 1993).

RESULTS AND DISCUSSIONS

Environmental features: A slight increase in temperature was observed towards offshore during both years showing an upward gradient from nearshore to offshore. Salinity and dissolved oxygen did not show much variations. Well oxygenated conditions prevailed throughout the study period. Of the four micronutrients only phosphate showed a wide range (0-2µg atom/l) in the near shore regions during October 1987 and most of the values were less than 1 µg at/l. Nitrate was found in trace level in most of the collections. Nitrate showed considerable increase during October 1987 compared to 1988. Moderate values for silicate content was noticed during both cruises. The values ranged between 1.01 and 26.21 µg at/l and mostly the values were between 5 to 10 µg at/l irrespective of space and time.

Distribution of chlorophyll 'a' and Particulate Organic Carbon: In October 1987, Chl 'a' during day ranged between 0.007 to 3.32 mg/m³, lowest being near Cochin and...
TABLE 1. Mean, Standard Deviation (SD) & Coefficient of variation (C. V. %) of the parameters

<table>
<thead>
<tr>
<th>OFFSHORE :</th>
<th>DAY</th>
<th>NIGHT</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Chl 'a'</td>
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<tr>
<td></td>
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<tr>
<td></td>
<td>SD</td>
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<tr>
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<td></td>
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<td>NIGHT</td>
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<td>NIGHT</td>
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<tr>
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<td>POC</td>
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<td>4.426</td>
</tr>
<tr>
<td></td>
<td>CV</td>
<td>147.73</td>
</tr>
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</tr>
<tr>
<td></td>
<td>X</td>
<td>22.490</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>22.01</td>
</tr>
<tr>
<td></td>
<td>CV</td>
<td>97.86</td>
</tr>
<tr>
<td></td>
<td>DAY</td>
<td>NIGHT</td>
</tr>
<tr>
<td>-------</td>
<td>--------------</td>
<td>---------------</td>
</tr>
<tr>
<td></td>
<td>(\bar{x})</td>
<td>SD</td>
</tr>
<tr>
<td></td>
<td>(\bar{x})</td>
<td>SD</td>
</tr>
<tr>
<td></td>
<td>(\bar{x})</td>
<td>SD</td>
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<td>(\bar{x})</td>
<td>SD</td>
</tr>
<tr>
<td></td>
<td>(\bar{x})</td>
<td>SD</td>
</tr>
<tr>
<td></td>
<td>(\bar{x})</td>
<td>SD</td>
</tr>
</tbody>
</table>

Table 1. Contd.
The values during night were low ranging between 0.02 and 1.99 mg/m³, minimum being near Cape Comorin and maximum near Quilon. The day and night Chl 'a' concentration of the offshore region varied from 0.27 to 2.01 mg/m³ and 0.05 to 6.5 mg/m³ respectively. The particulate organic carbon of the nearshore region ranged between 0 and 6.60 mg/m³ and 0.22 and 4.14 mg/m³ during day and night respectively. High POC values were recorded near Cochin, Quilon and Vizhinjam and low values at Kasaragod and Calicut. In the offshore region, the values ranged from 0.11 to 6.6 mg/l during day and 0.22 to 4.15 mg/l during night. The mean Chl 'a' values for the 9 observations of the anchor stations ranged between 0.3 and 1.76 mg/m³ during day and 0.21 to 1.48 mg/m³ during night. From Kasaragod to Quilon Chl 'a' content was almost the same except a high value at Quilon (3.32 mg/m³) and from Vizhinjam to Cape Comorin low chl 'a' <1 mg/m³ was noticed. POC was low at Kasaragod and Calicut and high at Cochin.

During October 1988, chl 'a' of the nearshore region ranged between 0.17 and 66.65 mg/m³ during day and 0.88 to 10.99 mg/m³ during night, both at Calicut. In the offshore region the values ranged between 0.21 and 3.51 mg/m³ during day and between 0.32 and 2.18 mg/m³ during night. POC in the nearshore ranged between 0.12 and 1.81 mg/l during day and between 0.24 and 1.89 mg/l during night and in the offshore it ranged between 0.22 and 1.64 mg/l during day and 0.28 to 3.84 mg/l during night. The average chl 'a' value for the anchor stations ranged between 1.33 and 36.44 mg/m³ during day and 0.95 and 22.26 mg/m³ during night. The peak value of both were observed at Calicut and lowest value at Quilon. Comparatively high values were noticed at Kasaragod, Cochin and Vizhinjam irrespective of time. Cannanore and Quilon showed low levels of pigment concentration. Mean POC values were almost low at all anchor stations, the peak value 2.77 mg/l being at Vizhinjam (Table 1). Based on the combined data, it was observed that mean chl 'a' ranged between
Higher variations for all parameters were observed for night collections taken from offshore and nearshore stations whereas for the day collections taken from anchor stations. \( \text{NO}_2^{-}-\text{N} \) is the parameter with the maximum variations (Table 1). Also in the offshore region, the set of parameters, (temperature, silicate, \( \text{(} .763\text{)} \), \( \text{(NO}_2^{-}-\text{N}, \text{NO}_3^{-}-\text{N}, \text{.999)} \) were highly associated during day and (salinity, silicate, \( \text{(} -.803\text{)} \) and (chl 'a', POC, \( \text{(} .904\text{)} \) were significantly correlated during night. In the nearshore region, during day, (POC, Chl 'a', \( \text{(} -.528\text{)} \), (salinity, POC, \( \text{(} -.594\text{)} \), (POC, PO4, \( \text{(} .580\text{)} \) and (POC, Temp, \( \text{(} -.596\text{)} \) which are highly correlated while \( r \) of (Chl 'a', temp., \( \text{(} -.967\text{)} \), (DO, \( \text{NO}_2^{-}-\text{N}, \text{NO}_3^{-}-\text{N}, \text{(} .974\text{)} \) during night were also high. In the nearshore anchor stations, intraparameter relationships were all highly significant except at Calicut and Vizhinjam during day and at Cape Comorin during night (Table 5).

The box model fitted to the normalised data of chl 'a' and other parameters showed that silicate was the relatively most important factor (being the factor with the highest value or the next highest value for partial regression coefficient), in controlling the total chl 'a' concentration, the primary production at anchor stations Quilon, Calicut and Cape Comorin and at other non anchor nearshore stations during night.

Nutrients were also found to be contributing substantially in controlling the distribution of chl 'a' in the offshore, nearshore and at the anchor stations viz. Calicut, Cape Comorin and Cannanore during day. Similarly nutrients play a prominent role in limiting chl 'a' distribution in the nearshore stations and anchor stations, namely Kasaragod, Calicut, Cape Comorin and Cannanore during night. This implies that availability of several elements particularly nutrients, control phytoplankton production at different oceanic locations whereas nonavailability generally limited primary production at different oceanic locations.

### Table 2: Relative importance of parameters in the box model

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Offshore</th>
<th>Nearshore</th>
<th>Kasaragod</th>
<th>Cannanore</th>
<th>Quilon</th>
<th>Cochin</th>
<th>Calicut</th>
<th>Cape Comorin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Day</td>
<td>Night</td>
<td>Day</td>
<td>Night</td>
<td>Day</td>
<td>Night</td>
<td>Day</td>
<td>Night</td>
</tr>
<tr>
<td>Salinity</td>
<td>0.47</td>
<td>0.18</td>
<td>0.10</td>
<td>0.06</td>
<td>0.36</td>
<td>0.04</td>
<td>4.35</td>
<td>0.17</td>
</tr>
<tr>
<td>D.O.</td>
<td>1.07</td>
<td>3.08</td>
<td>2.29</td>
<td>2.29</td>
<td>3.30</td>
<td>2.02</td>
<td>3.92</td>
<td>0.90</td>
</tr>
<tr>
<td>PO4-P</td>
<td>2.80</td>
<td>0.22</td>
<td>3.89</td>
<td>0.28</td>
<td>4.31</td>
<td>0.23</td>
<td>4.15</td>
<td>0.65</td>
</tr>
<tr>
<td>NO2-N</td>
<td>3.15</td>
<td>3.80</td>
<td>1.34</td>
<td>1.00</td>
<td>1.99</td>
<td>0.36</td>
<td>0.51</td>
<td>0.63</td>
</tr>
<tr>
<td>NO3-N</td>
<td>0.80</td>
<td>0.76</td>
<td>2.90</td>
<td>0.38</td>
<td>0.18</td>
<td>0.28</td>
<td>4.15</td>
<td>0.23</td>
</tr>
<tr>
<td>POC</td>
<td>0.63</td>
<td>0.36</td>
<td>0.15</td>
<td>0.14</td>
<td>0.14</td>
<td>0.28</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>
| 0.23 (Vizhinjam, day) to 22.490 (Cannanore, day) with c.v.\% ranging between 7.74 (Cape Comorin, night) to 147.73 (Kasaragod, night).
production in coastal environments. The prominence of NO$_3$N in Chl $'a'$ distribution implies that it is used in the formation of phytoplankton biomass on a global ocean basis. It has been observed that the physical process that control NO$_3$N supply to the euphotic zone also controls the magnitude of primary production. The functional relation between phytoplankton and NO$_3$N is however the result of the processes that occur to the food chain after NO$_3$N has been introduced into the euphotic zone and it is evident at all trophic levels of the marine ecosystems. The high negative correlation between chl $'a'$ and DO during day at Cochin indicates high respiratory demands for oxygen by the biota (Yakobi, et al., 1993) (Table 2).

Gaylor and Hepper conditions were tested to apply Satterthwaite's approximation when the sample sizes are unequal. It showed that chl $'a'$ distribution is significantly different between offshore, nearshore and anchor stations with more or less same form of distribution during day and night. But in the case of POC, day and night difference was high irrespective of the region. Temperature, salinity, DO P0$_4$-P, NO$_3$-N and silicate distribution varied between regions irrespective of the time of collection whereas NO$_3$-N concentration was almost same at all regions, being more during day than night (Table 6).

The non-parametric Kruskall-wallis test showed that chl $'a'$, salinity, POC, temperature, DO and silicate distribution are more or less in the same pattern throughout the investigation whereas the nutrients differed between day and night, irrespective of the shore type (Table 3).

The disparity in the distribution pattern obtained by parametric and non-parametric analysis reveals that the assumption of normal distribution and additivity property for treatment effect is satisfied only for the parameters temperature, chl $'a'$, salinity (except nearshore), DO and silicate while for nutrients such as PO$_4$-P and NO$_3$-N and for POC, the observed data is to be subjected to Tukeys test of additivity to satisfy the additivity property by suitable transformations for treatment effects in nested two way ANOVA.
Based on the informations gathered from Kruskal-Wallis test, day and night data were combined for temperature, chl ‘a’, salinity, DO and silicate to test the difference between the regions using the same test and for the rest of the parameters day and night data were treated separately. The test showed that in the case of POC and silicate, difference between the regions was within the significance limit (Table 4). The result based on non-parametric test is to be considered because, it is better to use the distribution-free test when transformation is required.

**Fig. 1.** Trellis diagram showing the similarity between offshore, nearshore and anchor stations with respect to (a) chl ‘a’ (b) POC, (c) temperature, (d) salinity, (e) dissolved oxygen, (f) PO4-P (g) NO2-N, (h) NO3-N and (i) SiO4-Si. O-‘t’ Not significant, ⊗ ‘t’ significant at 5% level, ⊠ ‘t’ significant at 1% level.

Multiple range test was applied based on the results of the nested two way ANOVA and similarity index in terms of student’s range statistic, ‘t’ is presented in the form of a Trellis diagram. High similarity was observed at all
regions except Trivandrum for NO$_2$-N, Cape Comorin and Cannanore for NO$_3$-N and Calicut for POC with respect to their concentrations (Fig. 1).

### Table 4. Kruskal-Wallis test statistic (H*) for significance of the difference between the shore types

<table>
<thead>
<tr>
<th>Parameters</th>
<th>H*</th>
<th>N</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorophyll 'a'</td>
<td>44.914</td>
<td>9</td>
<td>*</td>
</tr>
<tr>
<td>POC</td>
<td>13.422</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>28.569</td>
<td>9</td>
<td>*</td>
</tr>
<tr>
<td>Salinity</td>
<td>61.078</td>
<td>10</td>
<td>*</td>
</tr>
<tr>
<td>D.O.</td>
<td>80.917</td>
<td>9</td>
<td>*</td>
</tr>
<tr>
<td>PO$_4$-P</td>
<td>17.904</td>
<td>9</td>
<td>*</td>
</tr>
<tr>
<td>NO$_2$-N</td>
<td>19.106</td>
<td>11</td>
<td>*</td>
</tr>
<tr>
<td>NO$_3$-N</td>
<td>22.776</td>
<td>12</td>
<td>*</td>
</tr>
<tr>
<td>SiO$_4$-Si</td>
<td>148.37</td>
<td>9</td>
<td></td>
</tr>
</tbody>
</table>

* — Calculated H* is significant at 5% level, P < 0.05

From the relation between chl 'a' and salinity at different size fractions and total, it was observed that total chl 'a' ranged between 0 and 10 mg/m$^3$, lowest values were recorded at salinities ranging between 34 and 35 ppt, nearly 18.54% of the samples, mostly that collected from Cannanore and Calicut fall in the lowest range of chl 'a' ($< 1$ mg/m$^3$) and salinity the range 29 to 33.9 ppt. In the 60 $\mu$m size fraction, chl 'a' ranged between 0 and 3.5 mg/m$^3$ and salinity ranged from 31.6 to 35.5 ppt. Most of the values were between 34 and 35.6 ppt of salinity. In the size fraction 20 $\mu$m, chl 'a' ranged between 0 to 3 mg/m$^3$ and salinity between 34.4 to 35.6 ppt. For total and 60 $\mu$m, a negative relationship of high gradient with salinity while for the 20 $\mu$m size fraction, a positive relation of low gradient with salinity was observed.

The size fraction of chl 'a' when plotted with respect to DO, observed ranges for chl 'a' were 0-5, 0-2.5, 0-3 mg/m$^3$ which vary with DO in the ranges 3.75 to 6, 4.1 to 6 and 4.1 to 5 ml/l with inverse relation but prominent only in the lowest size fraction. Silicate-chl 'a' relation showed 3 narrowing ranges viz; 0 to 5, 0 to 2 and 0 to 1 mg/m$^3$ for chl 'a' and 0 to 15, 0 to 6 and 0 to 8 for silicate concentration for total, 60 $\mu$m and 20 $\mu$m size fractions respectively. However the relationship between the two, in the lowest range of silicate (0 to 1), was not significant and it constituted about 22% of the samples. Only in the range of 1 to 10 $\mu$g/at/l for silicate, inverse relation was observed. Inverse relation was also observed between chl 'a' and nitrite + nitrate, and chl 'a' and phosphate with high values of chl 'a' falling in the lower range 0-2 of NO$_2$ + NO$_3$ and in 0 to 0.5 of phosphate. The ranges for chl 'a' were 0 to 5, 0 to 3.5 and 0 to 3 in the case in NO$_2$ + NO$_3$ relation and 0 to 8, 0 to 3.3 and 0 to 3 in the case of phosphate for total, 60 $\mu$m and 20 $\mu$m size fractions respectively.

The positive relationship of chl 'a' with salinity observed in 20 $\mu$m size fraction is likely to reflect the obligate regress for high amounts of ions (Waturburry et al. 1986). Phyco erythrin containing Synechococcus spp. in agreement with this observation. But the negative relationship of chl 'a' with salinity observed for total water sample and 60 $\mu$m size fraction as against the positive relation in 20 $\mu$m size fraction suggests that these discrepancies could be a reflection of strain specific variation in salinity tolerance. It was also observed that small size phytoplankton rarely attain concentration of bloom level ($> 10$ mg chl 'a' /m$^3$); ie; concentration is more tightly controlled and less frequently subjected to larger variations and it can be suggested that it is mainly the variations in the abundance of the larger phytoplankton that determine the size structure of phytoplankton communities.

The major changes in chl 'a' content are associated with varying nutrient levels in the euphotic zone and appears to be necessary adaptation to provide these slowly growing population at low nutrient concentration. High chlorophyll 'a' content at surface water and a
significant correlation between parameters

**Table 5. Significant correlation between parameters**

<table>
<thead>
<tr>
<th>Anchor Station 1 (Kasaragod)</th>
<th>Anchor Station 2 (Cannanore)</th>
<th>Anchor Station 3 (Calicut)</th>
<th>Anchor Station 4 (Cochin)</th>
<th>Anchor Station 5 (Quilon)</th>
<th>Anchor Station 6 (Vishinjam)</th>
<th>Anchor Station 7 (Cape Comorin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C, DO) = .616 (T, Si) = .724</td>
<td>(C, Si) = .743 (S, Si) = .930</td>
<td>(C, Si) = -.707 (T, DO) = .701</td>
<td>(S, DO) = -.620 (SNO3) = -.819</td>
<td>(S, DO) = .632 (NO2, NO3) = .727</td>
<td>(POC, Si) = .842 (DO, S) = .940</td>
<td>(S, DO) = -.842 (SNO2) = -.935</td>
</tr>
<tr>
<td>(S, P) = .651 (S, Si) = .559</td>
<td></td>
<td>(SNO3) = -.684 (P, NO3) = .905</td>
<td>(S, DO) = -.700 (S, P) = -.735</td>
<td>(S, DO) = .632 (NO2 S) = -.617</td>
<td>(S, S) = -.838 (T, NO3) = -.879</td>
<td>(S, P) = -.935 (S, Si) = -.935</td>
</tr>
<tr>
<td>(T, P) = -.639 (S, DO) = .580</td>
<td></td>
<td>(C, DO) = -.651</td>
<td>(S, NO2) = -.632 (NO3 S) = -.617</td>
<td>(S, NO2) = .632 (NO2, NO3) = .727</td>
<td>(S, S) = -.863 (T, NO3) = -.914</td>
<td>(NO2, NO3) = .951</td>
</tr>
<tr>
<td>(SNO2) = -.617 (P, Si) = .693</td>
<td></td>
<td></td>
<td>(P, NO3) = .738 (S, P) = -.954</td>
<td>(P, NO3) = .738 (S, P) = -.954</td>
<td>(P, NO3) = .738 (S, P) = -.954</td>
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</tr>
</tbody>
</table>

**DAY**

<table>
<thead>
<tr>
<th>NIGHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C, T) = -.943 (C, P) = .980</td>
</tr>
<tr>
<td>(C, Si) = -.947 (P, NO3) = .967</td>
</tr>
<tr>
<td>(S, Si) = -.976 (P, Si) = -.969</td>
</tr>
<tr>
<td>(C, Si) = .929 (P, Si) = .863</td>
</tr>
<tr>
<td>(C, S) = .717 (C, NO2) = -.770</td>
</tr>
<tr>
<td>(P, NO2) = .737 (S, NO2) = .953</td>
</tr>
<tr>
<td>(P, NO2) = .750 (C, P) = -.771</td>
</tr>
<tr>
<td>(P, POC) = .738 (S, P) = -.954</td>
</tr>
<tr>
<td>(S, NO3) = -.874 (POC, S) = -.773</td>
</tr>
<tr>
<td>(C, PO) = -.868 (POC, DO) = -.866</td>
</tr>
<tr>
<td>(T, P) = -.735 (T, Si) = -.821</td>
</tr>
<tr>
<td>(P, NO2) = .894 (NO2, NO3) = .876</td>
</tr>
<tr>
<td>(S, NO2) = -.772 (T, DO) = .841</td>
</tr>
<tr>
<td>(T, NO2) = -.755 (S, DO) = .894</td>
</tr>
<tr>
<td>(Si, P) = .876 (S, NO2) = .876</td>
</tr>
<tr>
<td>(T, NO3) = -.766 (S, DO) = .680</td>
</tr>
<tr>
<td>(DO, NO2) = -.946 (S, NO3) = .876</td>
</tr>
<tr>
<td>(POC, Si) = -.998 (P, NO2) = .999</td>
</tr>
<tr>
<td>(DO, P) = -.946 (Si, NO3) = .876</td>
</tr>
<tr>
<td>(T, NO2) = -.946 (S, NO3) = .876</td>
</tr>
<tr>
<td>(DO, P) = -.946 (Si, NO3) = .876</td>
</tr>
<tr>
<td>(POC, Si) = -.998 (P, NO2) = .999</td>
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<tr>
<td>(DO, P) = -.946 (Si, NO3) = .876</td>
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<tr>
<td>(POC, Si) = -.998 (P, NO2) = .999</td>
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<tr>
<td>(DO, P) = -.946 (Si, NO3) = .876</td>
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<tr>
<td>(POC, Si) = -.998 (P, NO2) = .999</td>
</tr>
<tr>
<td>(DO, P) = -.946 (Si, NO3) = .876</td>
</tr>
</tbody>
</table>

Decreasing tendency towards offshore as noticed in the present study was also reported by Radhakrishna et al. (1977). They also could not observe any relation between POC and chl 'a'. The coastal and nearshore waters of west coast of India are enriched by heavy rainfall and land runoff from June to September every year (Bhargava et al. 1978). Devassy (1983) noticed high concentration of chl 'a' (10.2 mg/m³) at the surface during October and November in the southwest coast of India. Bhargava et al. (1978) reported an average chl 'a' value of 6.44 mg/m³ and 10.6 mg/m³ during October and December respectively, when the concentration of nutrients were also high along this coast. Balachandran et al. (1989) reported high values (8 mg/m³) during October 1987 and 1988 in the inshore waters of Cochin. They stated that the variation in the observed values during 1987 and 1988 can be attributed...
to the intensity of freshwater discharge. The spatial gradients in the chl 'a' and POC exhibited such as convergence and divergence as stated by earlier workers (Bhattathiri and Devassy

Table 6. Showing the significance of the difference between shore type and between day and night using 2 way ANOVA for unequal number of samples.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Shore type</th>
<th></th>
<th>Day and night</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>F. value     d.f.</td>
<td>F. value</td>
<td>d.f.</td>
</tr>
<tr>
<td>Chlorophyll 'a'</td>
<td>(a)</td>
<td>8.0388*       (8,132)</td>
<td>1.1326</td>
<td>(9,132)</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>7.8068*       (14,6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>POC</td>
<td>(a)</td>
<td>3.8746*       (8,132)</td>
<td>3.0756*</td>
<td>(9,132)</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>3.3056        (14,7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>(a)</td>
<td>2.3893*       (8,132)</td>
<td>1.7589</td>
<td>(9,132)</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>2.1533        (14,7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salinity</td>
<td>(a)</td>
<td>10.1250*      (8,132)</td>
<td>0.6424</td>
<td>(9,132)</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>11.7008*      (8,4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D.O.</td>
<td>(a)</td>
<td>23.4512*      (8,132)</td>
<td>0.7771</td>
<td>(9,132)</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>25.2920*      (8,5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P04-P</td>
<td>(a)</td>
<td>3.0731*       (8,132)</td>
<td>0.4968</td>
<td>(9,132)</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>4.1368        (8,3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO2-N</td>
<td>(a)</td>
<td>1.4395        (8,132)</td>
<td>2.5176</td>
<td>(9,132)</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>1.2485        (8,7)</td>
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<td></td>
</tr>
<tr>
<td>NO3-N</td>
<td>(a)</td>
<td>2.4246*       (8,132)</td>
<td>0.7416</td>
<td>(9,132)</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>2.6591        (8,5)</td>
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<tr>
<td>SiO4-Si</td>
<td>(a)</td>
<td>4.5855*       (8,132)</td>
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<td></td>
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<tr>
<td></td>
<td>(b)</td>
<td>6.5916        (8,3)</td>
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</tbody>
</table>

(a) — Actual F ratio for groups considered under shore type.
(b) — F ratio on applying Satterthwaite's approximation.

appreciable difference in the nearshore and offshore region. This difference in the distribution can be taken as due to the variations in depth, currents prevailing in the area, sinking of water masses and other oceanic phenomena (1977). Krey (1976) opined that variability in temporal distribution and heterogeneity in spatial distribution which are naturally inherent in oceanic biological parameters make comparison of data rather troublesome.

References


Hydrochemical Studies Along the Coastal Waters off Mangalore

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Cochin - 682 018

ABSTRACT

Environmental parameters such as temperature, salinity, dissolved oxygen, BOD, pH, nutrients, suspended load and chlorophyll 'a' were estimated in the coastal waters of Mangalore. Four transects, each consisting of four stations extending from old Mangalore port to Surathkal were monitored bi-monthly and different parameters were compared seasonwise. Inorganic phosphate values registered high values at all the transects during September, with a maximum of 2.24 umol/l. Nitrite was found to be absent except during January. Low bottom values of dissolved oxygen with corresponding high inorganic phosphate were indicative of monsoonal upwelling along the Mangalore coast during September. This period was characterised by a drop in pH values, though not very significant. Low BOD values encountered indicated the absence of any organic pollution in the area.

Key words: Coastal waters, Nutrients.

Introduction

The nutrients determine the potential fertility of the water masses and therefore, it is important to understand their distribution and behaviour in different geographical locations and seasons. Some information on the spatial and seasonal distribution of nutrients is available in different estuarine and coastal environments of India. The earlier reports on the physico-chemical characteristics of the coastal waters of Mangalore are that of (Suresh et al., 1978 and Rivonkar et al., 1990). It is considered worthwhile to study the changes in the environmental parameters in the coastal waters of Mangalore, especially as the coastal belt is getting industrialised and this region supports a good fishery both pelagic and demersal. In the present investigation, spatial and temporal variations of different environmental parameters in the region between old Mangalore port and Suratkal are reported.

Materials and Methods

The study area covering coastal stretch of about 20 km is shown in Fig. 1. Four transects were selected between old Mangalore Port and Suratkal at equidistant points. With four stations at 5, 10, 15 and 20 meters depth. Surface, mid and near bottom water samples were collected from 16 stations for a year during rough monsoon months. Surface samples were collected using a clean plastic bucket and subsurface samples using Niskin water sampler. Bucket thermometer and reversing thermometers were used to measure the surface and subsurface temperatures respectively. In suit pH determinations done with a portable digital pH meter (Philips 9046). The nitrite, nitrate, phosphate and silicate were done as of (Grasshoff 1983) and dissolved oxygen, BOD, and Chlorophyll 'a' were estimated as in (Strickland and Parsons 1972). Known volume of samples for Chlorophyll 'a' were filtered through a GF/C filter paper at the shore laboratory and the filter papers were kept in the deep freezer until analysis.

Results and Discussion

The monthly means of the chemical parameters for each transect are shown in figures 2 and 3. Water temperatures were high during March.
Surface temperatures ranged from 29.0°C to 31.2°C during this period and those at the bottom from 28.8 to 30.6°C. Relatively cooler conditions prevailed during the remaining period at all the transects. Lower temperatures were recorded during September (26 to 27°C for surface samples and 26.0 to 28.4°C for bottom samples).

Salinity values were found to vary in a narrow range at all the transects, surface values ranged from 27.02 × 10⁻³ (September, off old Mangalore port) to 34.8 × 10⁻³ (May, off Surathkal). The values at the bottom varied between 32.94 × 10⁻³ (September, off Surathkal) and 36.32 × 10⁻³ (October, off old Mangalore Port). Vertical gradient was either absent or small at all the transects which could be largely the result of strong turbulence favoured by the near shore geometry.

Maximum values of dissolved oxygen (DO) were recorded during premonsoon months (months) (4.79-5.12 ml/l) along all the transects. Generally surface waters were found to be well oxygenated. Very low levels of DO (0.31 to 1.00 ml/l) were recorded for bottom waters during the months of May and September. More pronounced reduction in DO content was noticed during September at transects 3 and 4.

pH values for the surface and bottom waters remained more or less same along all the transects. Comparatively low values of pH (7.9-8.27) observed
during September may perhaps be due to the dilution of the waters by the monsoonal discharge.

High values of phosphate (1.73-2.95 μmol/l at transects 4) were noticed during September at all stations. Minimum values (0.23-0.59 μmol/l) were observed during post monsoon months (October, December and January). Higher concentrations were found to be associated with bottom waters at all transects. This may be due to the lesser uptake of this nutrient. The high values of inorganic phosphate at all the four transects were conspicuous during September. The oxygen depleted water column with high nutrient content is indicative of the occurrence of upwelled waters along the coast during this period. Seasonal changes in hydrographic parameters due to upwelling were prevalent in this region from May to September. Sastri and D' Souza (1972) observed that cyclonic circulations prevailed in this region during this period which can induce coastal upwelling. They concluded that from June to September this region is subjected to direct wind mixing and indirect effect of wind induced circulation, which probably brings the cold subsurface waters to the surface.

Nitrate-N showed the fluctuation between surface and bottom waters. Nitrate remained low, but for a few exceptions. Nitrites were found to be practically nil at all the transects except during January, which could be treated as an exception. Seasonal changes in nitrate concentrations suggest that the availability of this nutrient is adequate to meet the required demand for primary production.

An inverse relation of silicate for surface waters with salinity during September was observed. Generally, during this period, silicate levels in surface water increased (5-254 μmol/l). The erosion of loose solid strata from the catchment areas may be bringing in high silicate to the water column. A vertical gradient could be noticed only in September. Similar observations have been reported in this area by Rivonker et al. (1990). Bottom waters during that time originated from deeper layers and permeated the area.

The BOD₅ values were below 3 mg/l along all the transects during most of the observation which indicated the absence of organic pollution in this area of study. High values noticed in September could be attributed to the extraneous input from land runoff (Table 1).

Monthly pattern of Chlorophyll 'a' distribution was found to be more or less the opposite of those of nitrate and phosphate suggesting that the seasonal reduction of these inorganic nutrients could be due to assimilation by phytoplankton.

The suspended solids ranged from 8 to 255 mg/l at
the surface and from 8 to 290 mg/l at the bottom (Table 1). The higher suspended load was associated with the bottom water. The prevailing physical climate seems to control the quantum of suspended sediment by activating resuspension and settling cycles in time.

The various environmental parameters along the four transects between old Mangalore port and Suratkal encountered very little variations between each transects except along transect 4 during September, which could be the result of the fresh water discharge through the two rivers. During this period, comparatively higher values of phosphate, nitrate and silicate were encountered along transect 4 which could be due to the influence of the river Nethravati which opens to the sea closer to transect 4. The water remained well mixed due to turbulent mixing in this shallow coastal zone and thus the stability of the water column is maintained. The assessment of the impact of release of waste water on the marine environment becomes easier and reliable if baseline water quality is known against which the existing conditions can be compared.

Acknowledgement

Authors thank Dr. E. Desa, Director, NIO, Goa for the encouragement and support.

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Knowledge of the fluxes of suspended sediment, salt and water are important to understand the dynamics of the estuarine system. In the present study, an attempt has been made to estimate and compare various dispersion mechanisms such as residual fluxes of water, Stokes drift and vertical shear in the tidal and residual current at 4 stations in the lower reaches of the Muvattupuzha river, under varying dilution intensities. Emphasis has been given to study intra-tidal variation of suspended sediment concentration with concurrent salinity and current observation.

The study area (Fig. 1) is characterised by the presence of the two large basins of the Periyar and Muvattupuzha rivers. The Muvattupuzha river empties into the Cochin backwaters, which is subjected to the tidal effects through the Cochin barmouth. Average depth of the study area is 5.5 m. Width of the cross section—1 is 633 m and that of section-II is 1012 m. Tides in the region of study being—semidiurnal, synoptic field measurements for 13 h were made at 4 stations during May and August 1990, which respectively represent the low and high fresh water discharge period (data from Central Water Commission, Cochin). Measurement include vertical profiles of current speed, direction, salinity and suspended sediment concentration. Vertical profiles of current speed and direction were made using indigenous rotor current meter (accuracy for velocity ± 2 cm.s\(^{-1}\) and direction ± 2.68°, designed at NIO, Goa, India). Vertical profiles of salinity is accomplished by Beckman salinometer (accuracy 0.01 \(\times 10^{-3}\)). Water level at the observation site was recorded using a graduated tide pole, suspended sediment concentration at surface, mid depth and bottom were determined by vacuum filtration of water samples through pre-weighed 0.45 \(\mu\)m millipore filter paper. Cubic splines were used to interpolate data at fixed fraction of the non-dimensional depth (\(\eta = 0\) at the surface and \(\eta = 1\) at bottom).

Basic properties of the stations are given in Table 1. Tide averaged depth was higher during August 1990 at all stations by an amount < 50 cm. Appreciable salinity gradient of < \(3 \times 10^{-3}\) was observed in the upstream direction. Vertical salinity gradient of 5 to \(8 \times 10^{-3}\) was observed during May at all stations.

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**Fig. 1—Study area with location of stations**
Longitudinal salinity gradient did not exhibit seasonal fluctuation as it depends both on the tide and the river discharge. Higher vertical salinity gradient at section-I could be attributed to the influx of Chitrapuzha river which joins the system 1 km upstream of this section. Tide-depth average suspended sediment (Table 1) concentration did not vary much between May and August.

**Residual flux of water**—A summary of the observed residual fluxes of water is given in Table 2. Negative sign shows that transport is directed upstream and positive sign indicates the downstream transport. Eulerian residual flow ($u_E$, Table 2) was upstream at all stations during May and changes its direction towards downstream in August. Direction of the Stokes drift ($u_s$, Table 2) was upstream irrespective of the season. Stokes drift arises because of the partially progressive nature of the tide, resulting from the frictional dissipation of tidal energy in the estuary. Langrangian residual flow which is the sum of residual current and stokes drift follows the direction of the residual flow as the magnitude of Stokes drift was very low.

**Residual fluxes of salt**—Values of the observed fluxes of salt computed are given in Table 2. Residual transport salt due to residual discharge of water ($F_d$) was upstream during May and downstream during August. Generally the salt transport due to tidal pumping ($F_{TP}$) was directed upstream. Magnitude of Stokes drift was higher at section-I due to the strong tidal influence available there, since its close proximity to the barmouth. Large transverse variation in $F_{TP}$ was observed in section-I. This indicates the predominant flood channel in the eastern flank of the estuary. Residual transport of salt due to vertical shear was directed upstream irrespective of the season. Net salt transport was upstream during May and August though the magnitude was less in August. Fischer accredited this net upstream transport even during high freshets to the transverse shear.

### Table 1—Basic properties of stations

<table>
<thead>
<tr>
<th>St No.</th>
<th>H (m)</th>
<th>S ($\times 10^{-3}$)</th>
<th>T (°C)</th>
<th>F (mg l$^{-1}$) ($\times 10^{-3}$)</th>
<th>$S_b$</th>
<th>$S_s$</th>
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<tbody>
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<td></td>
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H: Tide averaged depth
T: Tide-depth averaged temperature
F: Tide-depth averaged suspended sediment concentration
$S_b$, $S_s$: Tide averaged salinity at bottom and surface respectively

### Table 2—Axial component of residual fluxes

<table>
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<tr>
<th>St No.</th>
<th>$u_E$</th>
<th>$u_s$</th>
<th>$u_E$</th>
<th>$F_L$</th>
<th>$F_{TP}$</th>
<th>$F_V$</th>
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Units: $* = \text{cm sec}^{-1}$, $S = 10^{-3}$ cm sec$^{-1}$, $+ \text{mg l}^{-1}$ cm sec$^{-1}$

$u_E$: Depth averaged Eulerian residual current
$u_s$: Stokes drift
$F_L$: $G^*$: Net transport of salt (suspended sediment)
Residual transport of suspended sediment—Residual transport of suspended sediment due to the residual discharge of water was directed upstream during May and August (Table 2). Tidal pumping of suspended sediment was directed upstream during May, probably due to resuspension of bed sediment and associated upstream transport, whereas in August tidal pumping of suspended sediment was irregular both in magnitude and direction. Suspended sediment transport by the tidal pumping was in general high at section-I, particularly at st.1. This was possibly due to the easily erodible bed material at st.1 and the presence of flood channel described earlier in the salt transport mechanism. Suspended sediment transport associated with vertical shear was downstream at section-I during May and August. At section-II, direction of the vertical shear transport was not consistent.

Authors thank Dr. B.N. Desai, Director and Dr. V.N. Sankaranarayanan, for their keen interest and encouragement.

References