

## **BEHAVIOUR OF ALUMINIUM, SILICON AND IRON IN TAPI ESTUARY**

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Behaviour of dissolved Al, Si and Fe in high energy and well-mixed Tapi estuary was studied under varied tidal cycles. The observed trend of variation in concentration of dissolved Al has been explained in terms of release from suspended particulate materials (SPM) dispersed by strong tidal currents to low dissolved Si containing coastal water and its subsequent removal in the estuary, enriching the estuarine SPM. This view was supported by markedly high Al content of estuarine SPM as compared to that associated with the end members. Higher percentage of removal during spring tides as compared to neaps was attributed to large scale disturbance of bed sediment by high energy spring tides. An inverse relationship between dissolved Al and dissolved Si supported the mechanism of removal of dissolved Al through formation of authigenic clays. Behaviour of dissolved Si has been explained keeping in view the occurrence of substantial biogenic removal in the river water as supported by the profiles of pH, dissolved oxygen,  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N which were also suggestive of some biogenic removal of dissolved Fe. In the estuary however, dissolved Fe was randomly distributed and poorly correlated with chlorinity as well as pH.

### **INTRODUCTION**

The concentration of dissolved Al in fresh water is highly variable ranging from 2 to 3500  $\mu\text{g l}^{-1}$  (Bowen, 1979) unlike in marine water where its concentration is generally low (2  $\mu\text{g l}^{-1}$ ). The short oceanic residence time of around 100 years (Brewer, 1979) reflects the inherent instability

of dissolved Al and relative ease of its removal from solution through inorganic precipitation processes (Moore, 1981; Moore and Millward, 1984) and biological uptake (Stoffyn and Mackenzie, 1982). Varying degrees of removal of dissolved Al from solution within estuarine low salinity regions have been reported (Hosokawa *et al.*, 1970; Hydes and Liss, 1977; Crerar *et al.*, 1981; Mackin and Aller, 1984a,b,c; Morris *et al.*, 1986). In contrast an input at low salinities with a maximum at  $5 \times 10^{-3}$  has been observed in the Zaire River plume (Van Bennekom and Jager, 1978). Flocculation during mixing of river and sea water (Eckert and Sholkovitz, 1976; Sholkovitz, 1976, 1978) and authigenic alumino-silicate formation (Mackin and Aller, 1984a,b,c) have been considered as principle removal mechanisms.

Estuarine behaviour of Si is fairly well studied. No significant removal has been observed in some estuaries and when removal occurred its magnitude was less than 30%, (Aston, 1978). The mechanism of silicon removal from solution in estuaries however, is not clearly understood and Liss (1976) has summarised the reasons for observed discrepancies.

Due to its relative high concentration in river water of lower pH than in sea water, dissolved Fe is often removed in estuarine mixing zones (Liss, 1976; Aston, 1978; Paulson *et al.*, 1984; Windom *et al.*, 1988; Byrd *et al.*, 1990) though conservative behaviour has also been reported (Paulson *et al.*, 1989).

## STUDY SITE

Though Tapi River is a major and important river opening in the Arabian Sea, very little information is available on the hydrography and the general circulation. Hence, a brief description of tides, currents and sea water incursion is worthwhile for better understanding of the processes occurring within the estuary.

The 720 km long Tapi River commanding a catchment area of  $6.5 \times 10^4$  km<sup>2</sup> initially flows through the basaltic terrains of the Deccan traps and then through the alluvial deposits, before emptying into the Arabian Sea at the mouth of the Gulf of Cambay. The alluvial deposits are mainly of unconsolidated fine sand, silt and clay mainly transported and deposited by Tapi River.

The average rainfall of 1200 mm a year in the coastal plains largely occurs during south-west monsoon (June to September) with highest precipitation during July, resulting in high river discharge of  $8000 \text{ m}^3 \text{ s}^{-1}$ . The fresh water flow to the estuary during dry weather is controlled by the Ukai and Kakrapar dams at 116 km and 87 km respectively upstream of Surat City. The average fresh water discharge in the estuary decrease considerably after September and is  $10 \text{ m}^3 \text{ s}^{-1}$  during November–December and  $45 \text{ m}^3 \text{ s}^{-1}$  during January–May (periods of present study). Although numerous tributaries join the river in upper reaches, a few inlets in the lower 70 km stretch are rain-fed and do not bring any fresh water to the estuary after the withdrawal of monsoons, thus eliminating the interpretative problems due to additional sources of freshwater.

Due to its proximity to the Gulf of Cambay, the mouth estuarine region of Tapi experiences significantly high semidiurnal tides with spring rise of 5.5 m at the mouth decreasing to 4.5 m at station 4 (Fig. 1) and further down to 2.3 m at station 6, 25 km from the mouth. This decrease during neap is from 2.3 m at the mouth to 1.7 m at station 4 and to 0.4 m at station 6. Although the durations of flood and ebb are roughly similar of 6 h in the off shore, the flood period decreases with increase in the ebb period in the estuary and is variable between 2 to 3 h at station 6.

The salinity incursion within the estuary which generally varies between 25 to 30 km is governed by the tidal phase and the fresh water flow during the dry season while during monsoon salinity incursion upstream of 10 km is unusual. The strong currents often exceeding  $1 \text{ m s}^{-1}$  sweeping the shallow estuary renders it vertically well-mixed except around the period of tidal slacks.

## SAMPLING AND METHODS

Water samples over complete tidal cycles were collected hourly during November–December 1983 and April–May 1984 in acid rinsed polyethylene bottles of the bow of a wooden power boat at 7 locations within the estuary and at one location (station 0) near the coast. River water was sampled at stations 8 and 9 which were beyond the range of tidal influence. The surface samples were collected using a polyethylene bucket while Niskin sampler mounted on a nylon rope was used to obtain sub-surface samples.

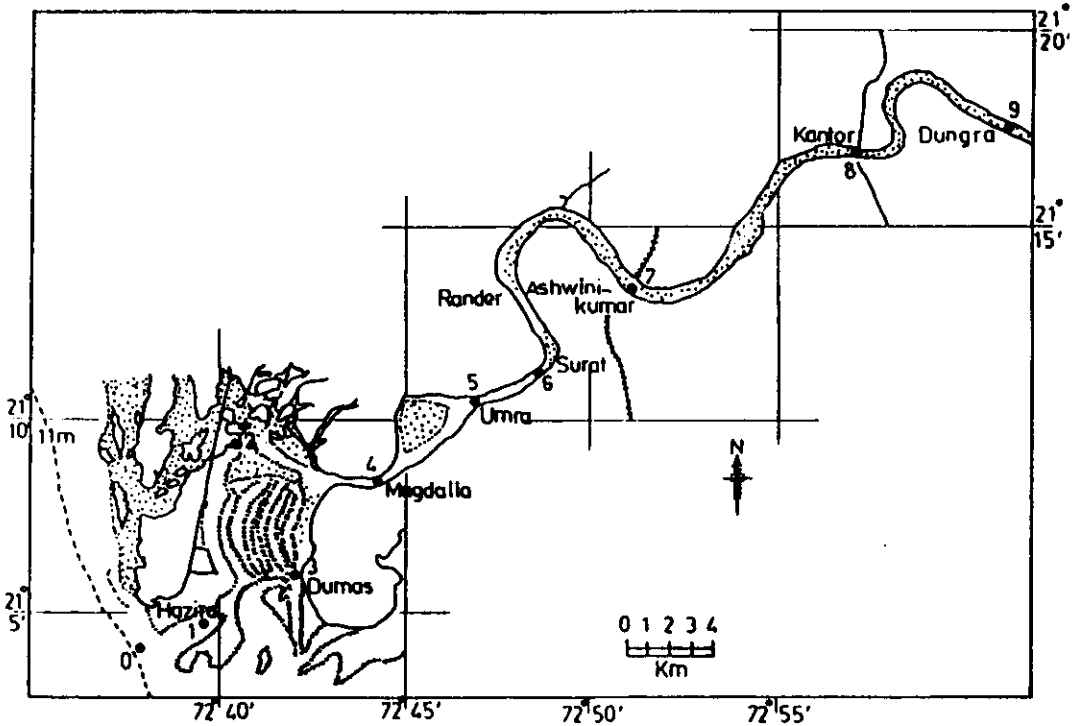


Fig. 1. Location of Tapi River showing positions of sampling stations.

The samples were immediately filtered in a random order through 0.45  $\mu\text{m}$  pore-size Millipore (R) membrane filters mounted in Millipore glass holders.

### Analytical methods

Dissolved Al concentrations were determined with a precision of <5% by pyrocatechol violet method of Wilson and Dougan reported elsewhere (FAO, 1975). Dissolved Fe was estimated colorimetrically using 2,4,6-tripyridyl-S-triazine (FAO, 1975) with a precision of <5%. Filtered samples for Fe analyses were stored acidified (pH 2) prior to analysis. Dissolved Si was determined with a precision of <2% using the silicomolybdate method (Strickland and Parsons, 1972; Fanning and Pilon, 1973). Chloride was determined by argentometric titration with  $\text{AgNO}_3$  (Grasshoff, 1976) with a precision of <1%.  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N,  $\text{PO}_4^{3-}$ -P and dissolved oxygen (DO)

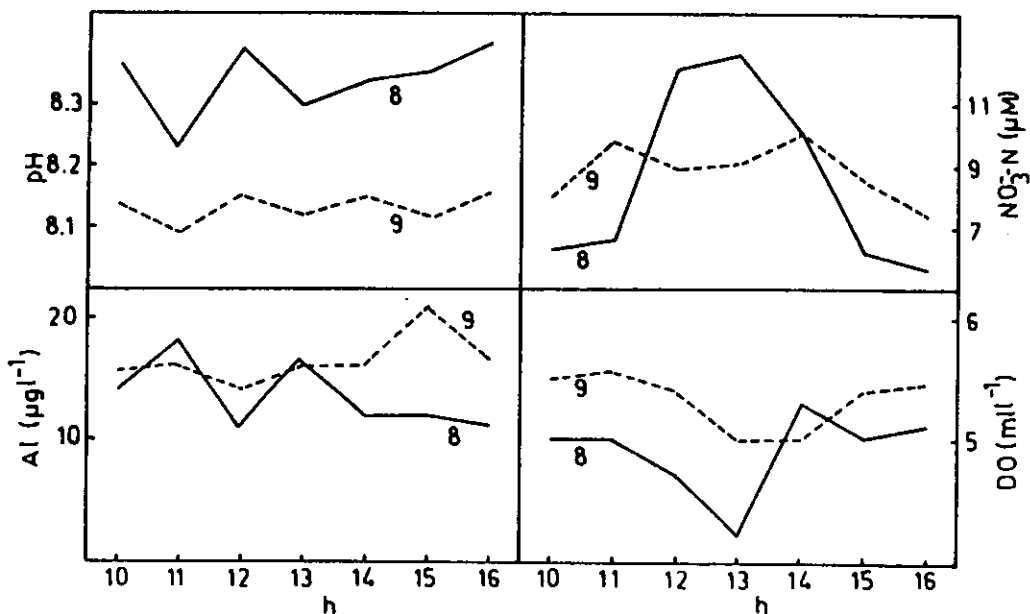


Fig. 2 Dissolved Al, pH, DO and  $\text{NO}_3^-$ -N as a function of time at station 8 on 19 May 1984 and station 9 on 20 May 1984.

TABLE I: Addition or removal (%) of dissolved Al at some stations.

Station	Spring tide		Neap tide*	
	Addition	Removal	Addition	Removal
2	0 -30	0 -23	Nil	32 -54
3	0 -23	0 -31	Nil	32 -47
4	0 -20	0 -38	Nil	43 -94
5	Nil	20 -73	-	-
6	0 -14	0 -47	-	-
	Nil	33 -88	-	-

\*There was no incursion of chlorinity at stations 5 and 6 during neap tide.

were determined by standard procedures (Grasshoff, 1976; Koroleff, 1976). The pH was measured on unfiltered samples with a microcombination electrode with a precision of  $\pm 0.02$  pH units on a Philips portable pH meter. All analysis were completed within 12 h from the collection of the last sample.

Dissolved Al was determined in April–May samples, dissolved Fe in November–December samples and dissolved Si and other constituents in all the samples.

The suspended particulate materials (SPM) recovered as described above from sets of samples collected during January–February 1985 was analysed for Al after complete digestion (Buckley and Cranston, 1971) by flame AAS (Varian Spectra-30) with nitrous oxide–acetylene flame. The precision of measurements of <3% was estimated by replicate analyses of W-2 and BIR-1 standard rocks.

## RESULTS AND DISCUSSION

The behaviour of dissolved Al, Si and Fe in lower 60 km of Tapi River was studied diuranally at 9 locations. Stations 8 and 9 were in the riverine zone unaffected by the tides while weak tidal influence was observed at station 7 during certain spring tides coinciding with low riverine flows.

### River water

The data from stations 8 and 9 were used to fix riverine end members of the theoretical dilution lines (TDLs) which was an important consideration in studying the behaviour of elements in estuaries as improper selection could lead to doubtful interpretations (Liss, 1976; Aston, 1978). The dissolved Al concentration varied in 11 to 21  $\mu\text{g l}^{-1}$  range (Fig. 2) with a mean of 16  $\mu\text{g l}^{-1}$  which was considered as a representative of fresh water tie end of the TDL. The observed variations were not due to analytical uncertainties since replicate analyses of a sample with a mean concentration of Al of 14  $\mu\text{g l}^{-1}$  gave values of  $14 \pm 2 \mu\text{g l}^{-1}$ . The changes due to biological uptake as in the case of Si (See discussion below) was less likely in May as the profiles of pH, nutrients and DO did not support this view. The pH is considered to be an important factor controlling the levels of dissolved Al in water (Aston, 1978). The difference in pH by about 0.2 units did not influence the concentration of dissolved Al at the two stations though small local variations in pH at station 9 were closely followed by the changes in concentration of dissolved Al. The low levels of dissolved Al in Tapi River was perhaps due to high pH of river water ascribed to the patches of lime

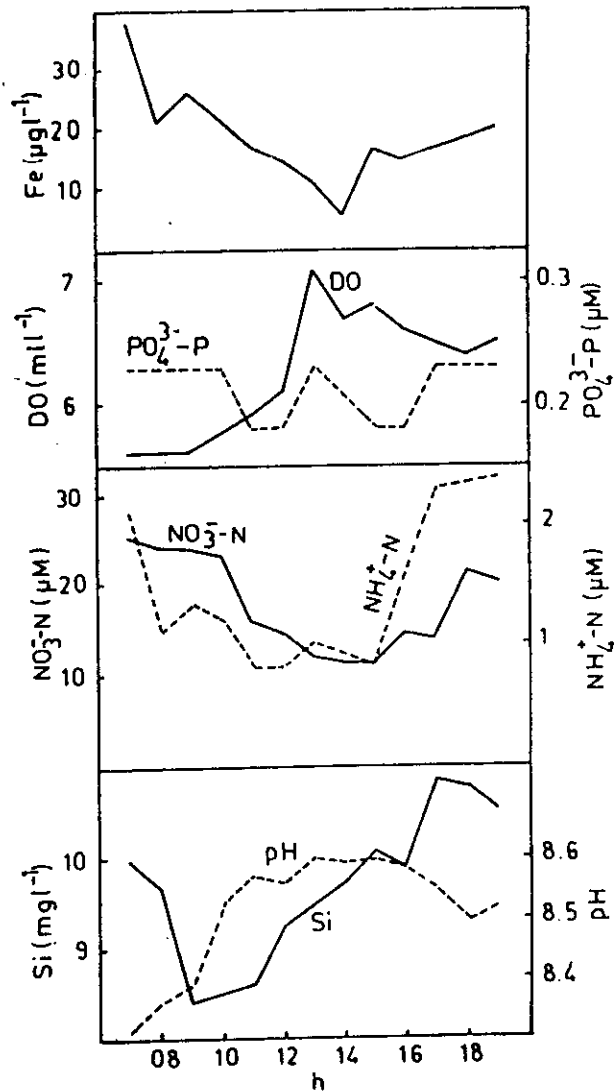


Fig. 3 Dissolved Si, Fe, pH, DO,  $\text{NO}_3^- \text{-N}$ ,  $\text{NH}_4^+ \text{-N}$  and  $\text{PO}_4^{3-} \text{-P}$  as a function of time at station 8 on 20 Nov 1983.

stone and sand stone strata through which many of the rivers of this region flow (Zingde *et al.*, 1981).

The profile of dissolved Si in fresh water however revealed (Fig.

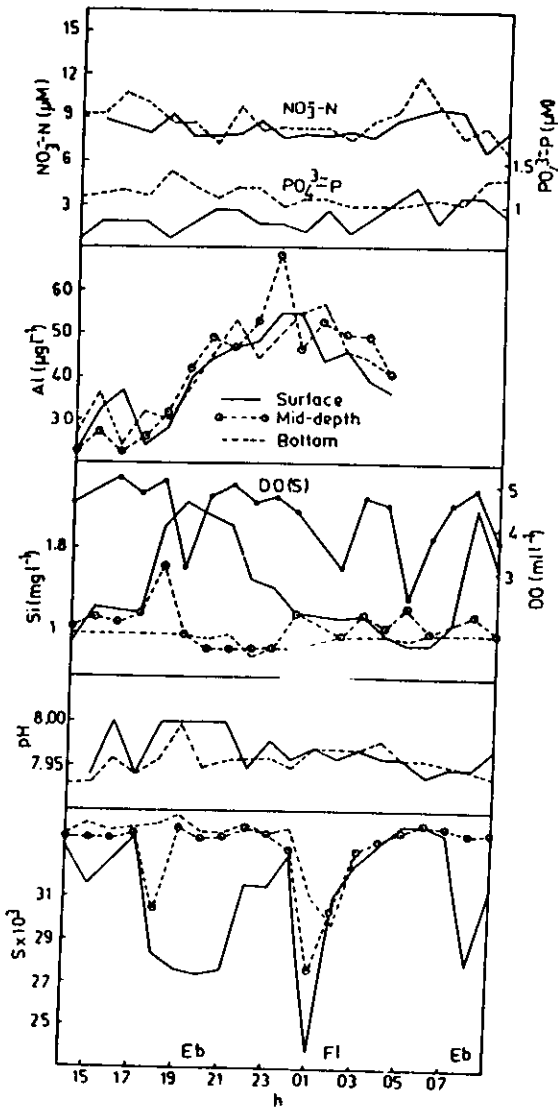


Fig. 4 Dissolved Al, Si, pH, DO, NO<sub>3</sub><sup>-</sup>-N, PO<sub>4</sub><sup>3-</sup>-P and salinity as a function of time at station 0 on 11-12 April 1984.

3) a sharp decrease from 10.00 mg l<sup>-1</sup> at 0700 h to 8.49 mg l<sup>-1</sup> at 0900 h followed by a steady increase to attain a peak value of 10.92 mg l<sup>-1</sup> around 1700 h. In view of the presence of high concentrations of chlorophyll



a with dominating populations of diatoms during November–December at this location (NIO, 1985), the observed trend was suggestive of biological uptake. The profiles of pH, DO,  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N also supported high rate of photosynthesis in the marine stretch. The initial high uptake of Si,  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N was perhaps due to rapid rise in the rate of photosynthesis on exposure to sunlight after a period of darkness as reported by Yentsch and Reichert (1963). Surprisingly the  $\text{PO}_4^{3-}$  remained more or less constant around  $0.2 \mu\text{M}$  with minor perturbations. To support high primary productivity, the supply of  $\text{PO}_4^{3-}$ -P should be ensured in Tapi River. The release of  $\text{PO}_4^{3-}$ -P from SPM or sediment in certain circumstances when the water concentrations become low, so that the  $\text{PO}_4^{3-}$ -P is replenished for meeting the requirements of phytoplankton growth has been reported (Aston, 1978). Such a mechanism could be operative in Tapi River and was supported by higher  $\text{PO}_4^{3-}$ -P concentration in the bottom water as compared to the surface (NIO, 1985). If we assumed N:P ratio of 16 as commonly observed for phytoplankton, than for the uptake of N of  $12.5 \mu\text{M}$  (Fig. 3) the requirement of P would be  $0.8 \mu\text{M}$  that would be released from the SPM or sediment.

We have used low ( $8.49 \text{ mg l}^{-1}$ ), high ( $10.92 \text{ mg l}^{-1}$ ) as well as mean ( $9.69 \text{ mg l}^{-1}$ ) values of dissolved Si to represent the riverine end member for estimating the behaviour of dissolved Si in Tapi estuary.

The dissolved Fe also decreased systematically from  $38 \mu\text{g l}^{-1}$  at 0700 h to a low of  $5 \mu\text{g l}^{-1}$  around 1300 h followed by an increase to  $20 \mu\text{g l}^{-1}$  at 1900 h. The observed profile (Fig. 3) was supportive of biological uptake of Fe. Iron in trace quantities is essential for the growth of phytoplankton (Aston, 1978) and can even become a limiting factor for primary production. The increase of pH by about 0.4 unit as a result of photosynthesis would also favour inorganic removal as the chemistry of inorganic Fe in aqueous solutions is highly pH dependent (Liss, 1976). The profile in Fig. 3 could be the result of both these factors.

### Sea water

The results of diurnal sampling at the offshore station (station 0) were used to fix the seaward end member. Unlike in the fresh water, the concentration of dissolved Al ranged between 22 and  $68 \mu\text{g l}^{-1}$  without

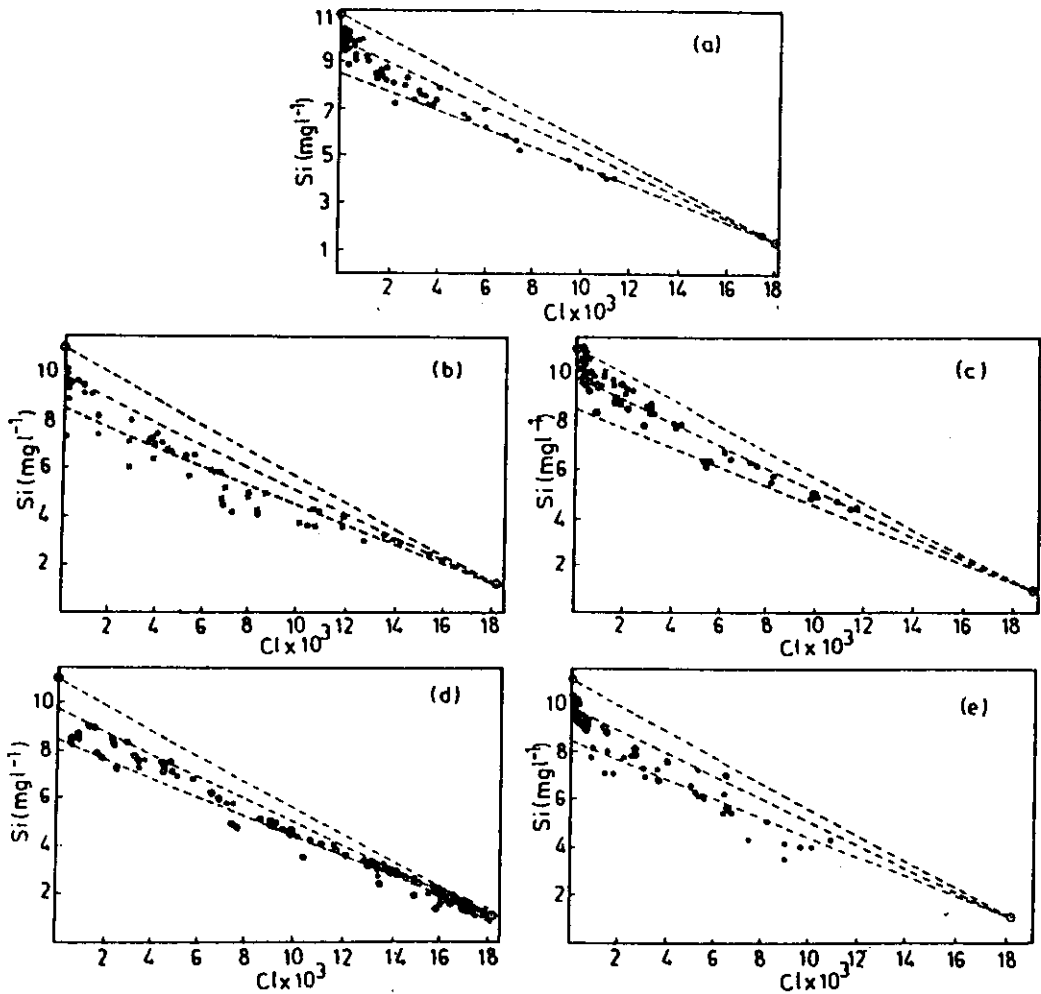


Fig. 5 Dissolved Si as a function of chlorinity at (a) station 4 on 22–23 Nov. 1983, (b) station 3 on 8 Nov 1983 (.) and 1–2 Dec 1983 (x), (c) station 4 on 6–7 April 1984, (d) station 0 on 28–29 Nov 1983 [x] and station 1 on 25–26 Nov 1983 [.] and (e) station 2 on 4–5 Dec 1983. Broken lines indicate TDLs drawn with riverine Si concentrations of 10.92, 9.69 and 8.49 mg l<sup>-1</sup> respectively.

any significant correlation with salinity (Fig. 4). The pH was relatively constant and could not be an important factor for the observed diurnal changes. The higher concentrations in the sea water as compared to the river water

was suggestive of the release of Al from SPM and/or the bottom sediment. It has been shown (Mackin and Aller, 1984c) that the estuarine sediment is very reactive towards dissolved Al due to rapid adsorption, dissolution and precipitation reactions. In addition the geochemistry of dissolved Al is complicated by a number of other reactions such as complexation by organic matter, adsorption to Fe-oxyhydroxides and reaction with dissolved Si. In settled sediment dissolved Al is rapidly consumed at the sediment water interface and is subsequently released upon reduction of Fe-oxyhydroxides (Mackin and Aller, 1984c). Such a mechanism is unlikely at station 0 because the sediment off Tapi mouth is silty with low organic carbon content (NIO, 1985). Moreover, the surficial sediment is constantly under agitation in this high energy tidal regime. Also with the subsurface currents often exceeding  $1 \text{ m s}^{-1}$ , the water body was well-stirred and dissolved oxygen was high in the water overlying the sediment, preventing anoxic conditions at the water sediment interface.

Although SPM was not estimated in the present study, investigations undertaken during January–February 1985 revealed that the SPM content in the offshore varied widely between 300 and 2600  $\text{mg l}^{-1}$  in the bottom layer (1 m above the bed sediment) due to the dispersion of the silt by strong tidal currents (NIO, 1985). We expect that the precipitation reaction of dissolved Al with dissolved Si proposed by Mackin (1986) should be reversible when the sediment is resuspended into relatively Si-depleted waters resulting in release of Al to the water. Evidence that Al is released to solution upon dissolution of detrital clays is provided through clay and sediment resuspension experiments (Hydes, 1977; Mackin and Aller, 1984b; Mackin, 1986). The Al released to the solution would be complexed with the dissolved organic matter as uncomplexed Al is rapidly removed from solution (Willey, 1975). The dissolved organic matter is expected to be high in the Gulf of Cambay receiving discharges from several rivers draining forest and agricultural areas. Thus for instance in Yangtze River plume depleted in organic matter and with low biological productivity, dissolved Al concentrations could be described by an apparent equilibrium with respect to authigenic aluminosilicate (Mackin and Aller, 1984a). The lower pH of water (7.7–8.0) at station 0 as compared to that of the inner estuary (8.0–8.6) would also favour complexation of dissolved Al (Kerndorff and Schnitzer, 1980). Although complexation weakens with increasing pH due to the

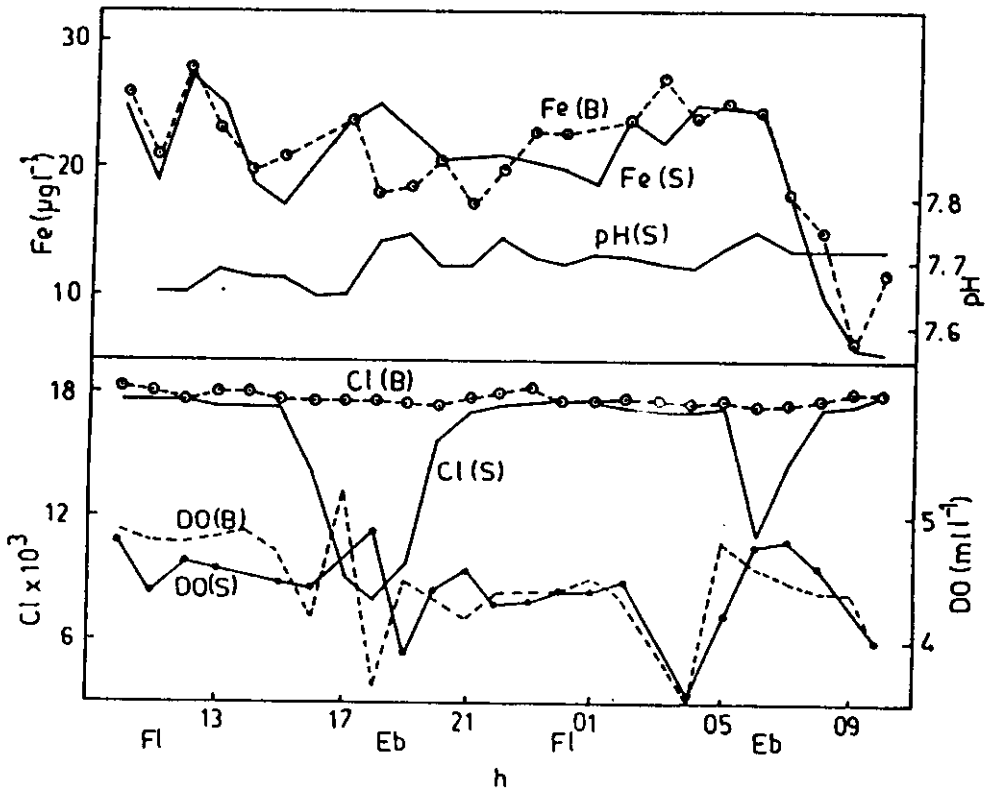


Fig. 6 Dissolved Fe, pH, DO and chlorinity as a function of time at station 0 on 28–29 Nov 1983.

displacement of Al from organic complexes owing to change from positively to negatively charged species, the effect should be significant at pH upto 8.0 (Mackin and Aller, 1984b). We have used the average concentration of dissolved Al of  $50 \mu\text{g l}^{-1}$  to define the seaward end member.

As evident from Fig. 4, the influence of riverine discharge was seen at station 0 particularly at the surface. To fix the seaward end member the concentrations of dissolved Si at chlorinities lower than  $17.8 \times 10^{-3}$  were not considered. The variation of dissolved Si concentration in the chlorinity range of  $17.8 \times 10^{-3}$  to  $18.3 \times 10^{-3}$  was from  $1.10$  to  $1.42 \text{ mg l}^{-1}$  (41 values) with a mean of  $1.23 \text{ mg l}^{-1}$  at a mean chlorinity of  $18.24 \times 10^{-3}$  during November–December. The concentration in the chlorinity range from

$18.7 \times 10^{-3}$  to  $19.1 \times 10^{-3}$  varied from  $0.81$  to  $1.16 \text{ mg l}^{-1}$  (37 values) with a mean of  $1.00 \text{ mg l}^{-1}$  at a mean chlorinity of  $18.9 \times 10^{-3}$  during April–May. These mean values of  $1.23$  and  $1.00 \text{ mg l}^{-1}$  were used as seaward end members for the construction of TDLs. As evident from Fig. 5 the relative position of these seaward end members did not substantially alter the slope of the TDLs. Unlike in the fresh water, the diurnal profiles (Fig. 4) of pH, DO,  $\text{NO}_3^-$ -N and  $\text{PO}_4^{3-}$ -P did not indicate (Fig. 4) substantial biological uptake and hence biogenic removal of dissolved Si was not dominant. Reduction in chlorophyll *a* concentration by at least five times in the lower estuary as compared to its levels at stations 8 and 9 (NIO, 1985) also supported this view. The low primary productivity of the lower estuary has been attributed to multifold increase in SPM due to the dispersion of the bed sediment in the water column by strong tidal currents sweeping the estuary (NIO, 1985).

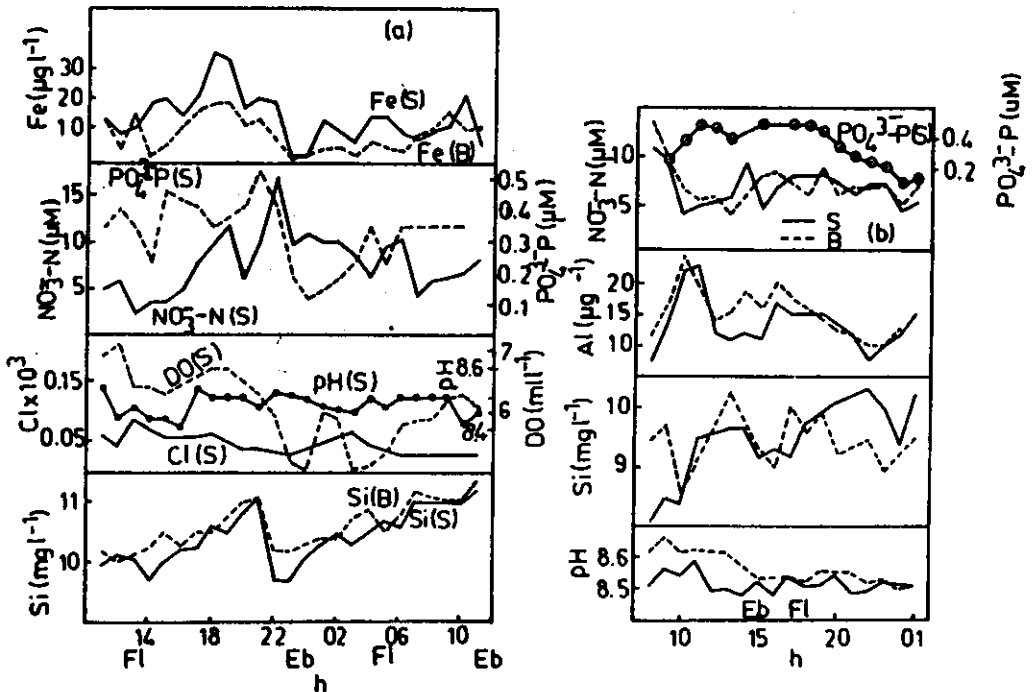


Fig. 7 Dissolved Al, Si, Fe, pH, DO,  $\text{NO}_3^-$ -N,  $\text{PO}_4^{3-}$ -P and chlorinity as a function of time at station 6 on (a) 16–17 Nov 1983 and (b) 2–3 April, 1984.

TABLE II: Al content (%) of SPM in Tapi estuary\*

Station	Chlorinity ( $\times 10^{-3}$ ) Range	SPM ( $\text{mg l}^{-1}$ ) Range	Al in SPM Range	Al in SPM Mean	No. of estima- tions
0	18.64 - 19.26	488 - 632	6.01 - 7.00	6.36	3
1	0.28 - 14.71	130 - 2223	7.31 - 7.53	7.44	6
2	0.19 - 2.17	48 - 1887	7.80 - 8.61	8.26	6
3	0.64 - 12.64	160 - 2076	9.32 - 19.19	12.66	5
4	1.10 - 4.68	94 - 1366	7.83 - 8.36	8.09	5
5	0.03 - 0.23	136 - 1162	7.38 - 7.62	7.46	3
6	0.02 - 0.14	131 - 1675	7.70 - 8.14	7.93	6
9	0.02	3 - 12	5.89 - 6.74	6.06	4

\*For January-February 1985

The concentration of dissolved Fe at station 0 (Fig. 6) varied randomly in the range 3 to 17  $\mu\text{g l}^{-1}$  with a mean of 22  $\mu\text{g l}^{-1}$  which was considered as the seaward end member.

### Zone of weak sea water influence

Although spring tidal range of 2.3 m was observed in the inner estuary (station 6) the incursion of sea water as indicated by increase in chlorinity occurred only during high spring tides and the water rise was mainly due to the piling of fresh water due to the advancing tidal front in the lower estuary. This zone of weak sea water incursion stretched down upto station 4 around neap tides particularly during April-May when average riverine discharge was 45  $\text{m}^3 \text{s}^{-1}$ . In this stretch of the estuary of low or weak sea water incursion (chlorinity below  $0.5 \times 10^{-3}$ ) the diurnal variations in concentrations of dissolved Al, Si and Fe were irregular (Fig. 7) with a general tendency to decrease around the ebb tide. Unlike in the fresh water zone, pH, DO,  $\text{NO}_3^-$ -N and  $\text{PO}_4^{3-}$ -P also varied randomly. We feel that the random variations of dissolved Al, Si and Fe were perhaps due to high and widely variable SPM in this section of the estuary as evident from the diurnal SPM range of 150-3300  $\text{mg l}^{-1}$  measured at stations 5 and 6 (NIO 1985). The importance of sediment disturbance due to variable tidal energy inputs in depletion at very low salinity and augmentation of dissolved Al at intermediate salinities has been reported in Tamar estuary (Morris *et al.*, 1986).

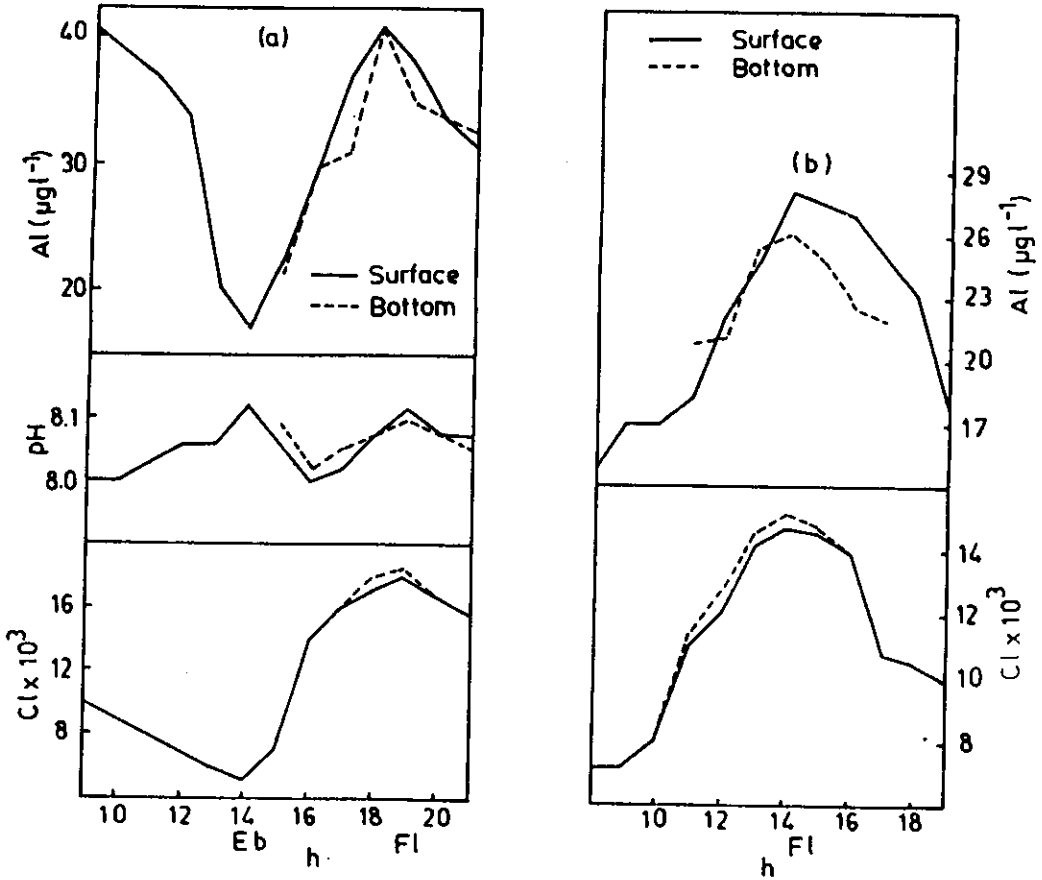


Fig. 8 Dissolved Al, pH and chlorinity as a function of time at station 8 on (a) 18 May 1984 – Sp and (b) 26 May 1984 – Np.

### ZONE OF SUBSTANTIAL SEAWATER INFLUENCE

The tidal incursion of sea water with higher concentration of dissolved Al dominated its concentration in the estuary as evident from Figs. 8 and 9. Similar profiles were obtained at all the stations when there was intrusion of chlorinity. The measurements undertaken 1 or 2 days around spring or neap tide are termed as spring or neap. The surface values are represented by (S) and bottom values by (B) in some Figures. The position of points of concentration of dissolved Al with respect to TDL (Fig. 10) was indicative of considerable removal in the estuary with distinct dependence on the tidal

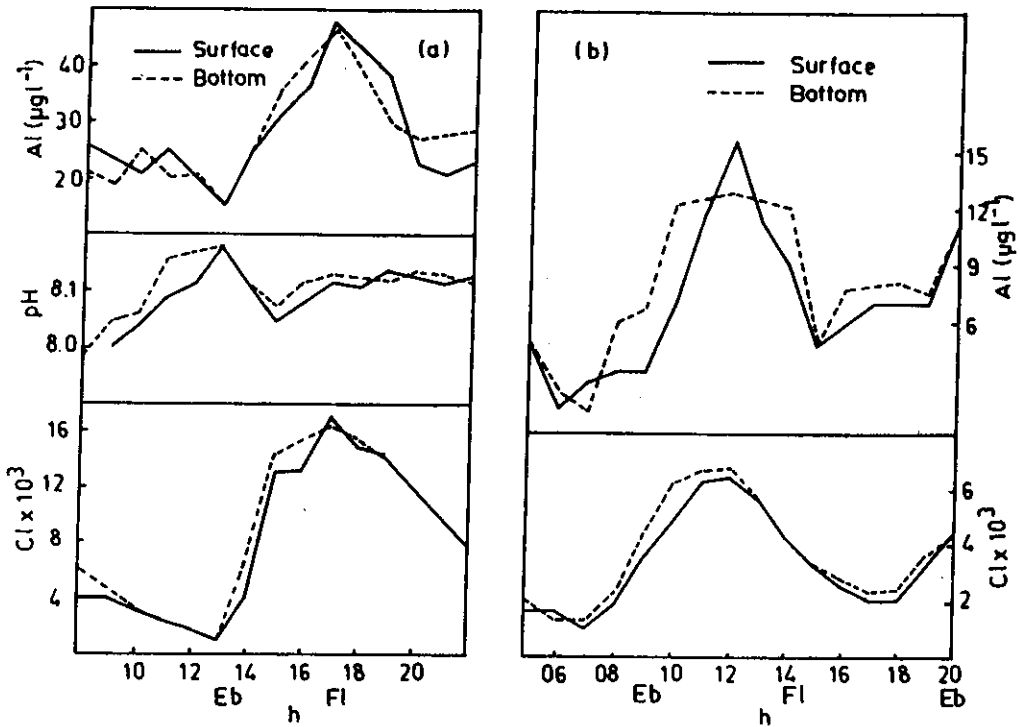


Fig. 9 Dissolved Al, pH and chlorinity as a function of time at station 4 on (a) 16 May 1984 - Sp and (b) 24 May 1984 - Np.

phase. Lower percentage of removal with instances of addition occurred during springs upto station 4 (Table I) (Lower estuary) while removal of 32–94% was evident during neaps. The lower percentage of removal during spring as compared to neap tide can be explained on the basis of release of Al through large scale resuspension of bed sediment facilitating partial augmentation of dissolved Al removed by the settling sediment through the type of mechanism suggested by Mackin and Aller (1984c). In actual situations both these processes would be occurring simultaneously in the estuary with the predominance of removal barring instances of addition during springs. Except in one case at station 6 removal was predominant at stations 5 and 6. Removal to the extent of 0–47% with addition of 0–14% was possibly influenced by large diurnal changes in pH as reflected in Fig. 10(c) by association of higher concentration of dissolved Al with lower pH favouring



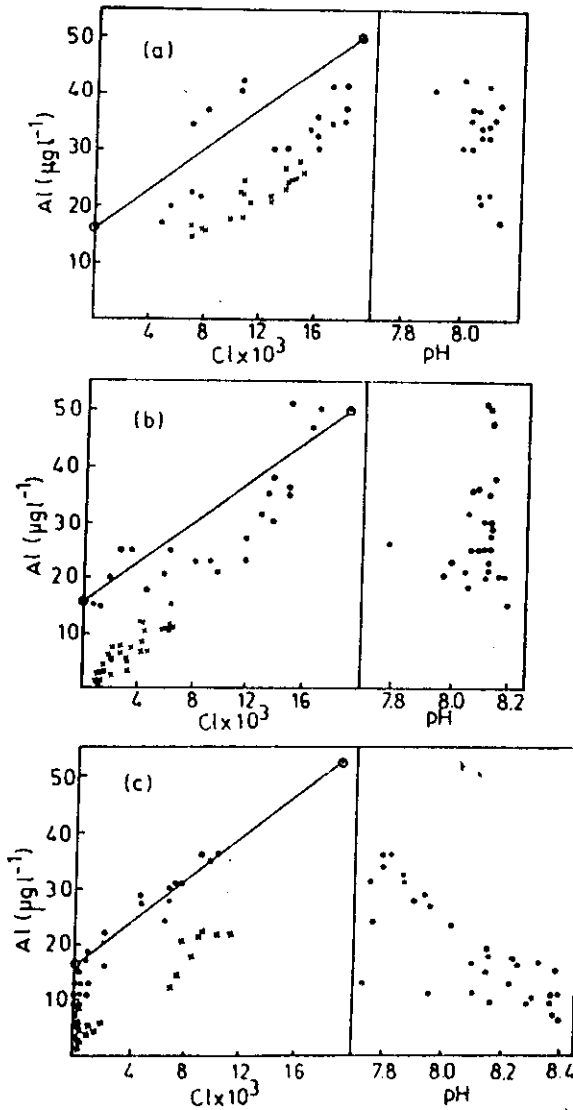


Fig. 10 Dissolved Al as a function of chlorinity and pH at (a) station 3 on 18 May 1984 – Sp [.] and 26 May 1984 – Np [x], (b) station 4 on 16 May 1984 – Sp [.] and 24 May 1984 – Np [x], and (c) station 6 on 15 May 1984 – Sp [.] and 31 May 1984 – Sp [x].

release of Al from SPM. The pH which varied in narrow ranges (Fig. 10) at other stations, did not seem to influence the concentration of dissolved Al, as expected. The mechanism of removal of dissolved Al in estuaries

is not clearly understood and has been attributed to flocculation of riverine micro-colloids (Sholkovitz, 1976, 78; Eckert and Sholkovitz, 1976), authigenic aluminosilicate formation (Mackin and Aller, 1984a,b; Mackin, 1986) and sorption onto suspended sediment particles (Morris *et al.*, 1986). The flocculation of riverborne micro-colloids, established by an increase in ionic strength was not a dominating factor in Tapi estuary since it failed to explain observed higher concentrations of dissolved Al in the estuary as compared to levels in fresh water. Removal through non-specific sorptive uptake onto SPM in line that occurred in Tamar estuary (Morris *et al.*, 1986) was not supported by the diurnal changes in SPM in the Tapi estuary which were not significantly correlated with chlorinity (NIO, 1985) unlike dissolved Al, and were largely controlled by the variation in tidal energy. Hence, it is possible that authigenic clays may be forming by dissolution - precipitation mechanism whereby relatively siliceous detrital clays are converted into more aluminous products causing net release of Si to the solution supported by quantitative treatments of the inverse relationships between dissolved Al and dissolved Si after long equilibration times in resuspension experiments (Mackin and Aller, 1984a; Mackin, 1986). In support of occurrence of such mechanism in Tapi estuary, an inverse relationship between dissolved Al and dissolved Si was observed (Fig. 11). As the concentrations of the dissolved Si in Tapi estuary are generally much greater than the concentrations of dissolved Al, this mechanism though an important factor in controlling the levels of dissolved Al, it should not be a controlling factor for dissolved Si.

From the above discussion it appears that the resuspension of nearshore sediments (station 0) due to strong tidal currents resulted in release of Al to low Si containing water column while in the estuary the dissolved Al was removed from solution perhaps through the formation of authigenic clays. Such a mechanism would lead to the enrichment of estuarine SPM and depletion in the nearshore SPM with Al, over a period of time.

Since, the SPM in the estuary and the coastal waters was mainly associated with the bed materials, the estuarine sediment should be enriched in Al as compared to the nearshore coastal sediment. The bed material in Tapi estuary however, is highly patchy varying from sandy to sandy silt with localised areas of clayey silt. Hence, the elemental composition of the bed sediments varied considerably with location in the estuary (Sharma,

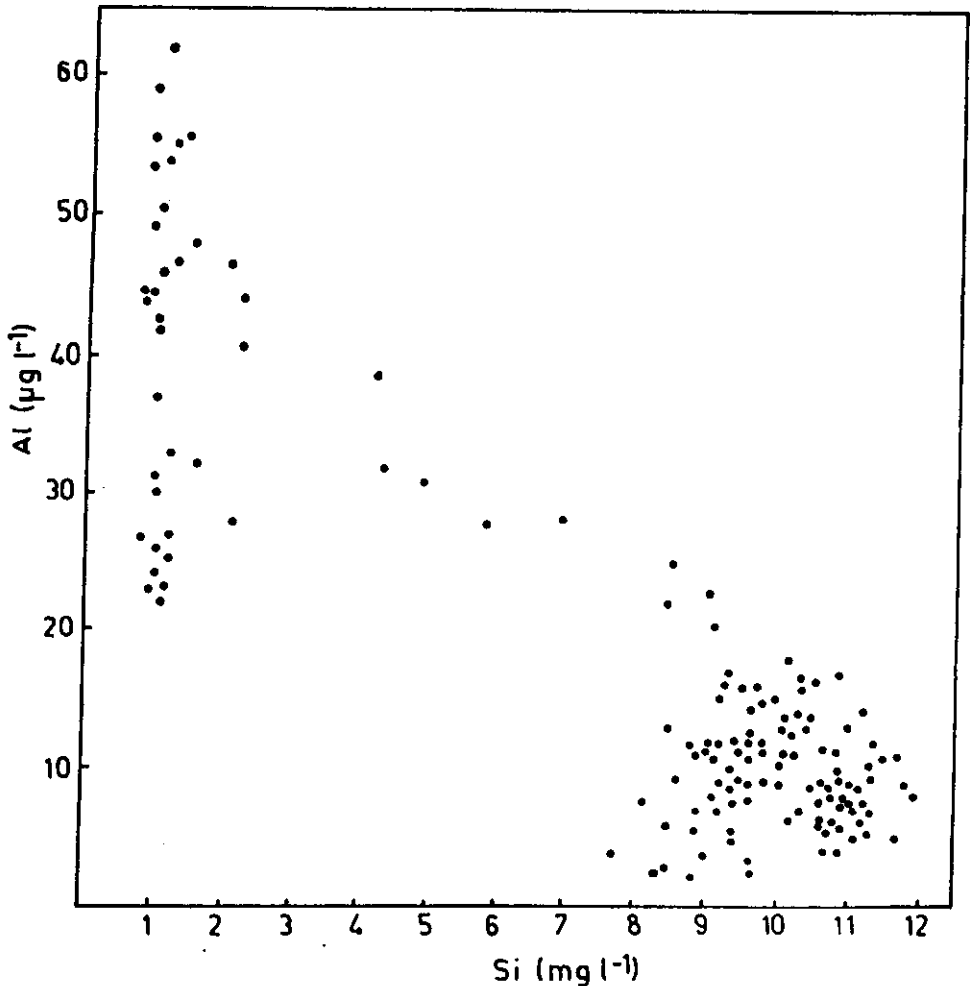


Fig. 11 Dissolved Al as a function of dissolved Al.

1985). However, it was clayey silt or silty clay which was preferentially dispersed in the water column along with the clay by the tidal energy, particularly in the surface water. Evidently, the elemental composition of SPM would be a better indicator of Al enrichment and/or depletion. Hence, the concentration of Al in SPM was determined in the subsequent study undertaken during January–February 1985 and the results shown in Table II supported the above view with estuarine SPM (stations 1 to 6) exhibiting

markedly higher levels of Al as compared to its concentration in SPM associated with the end members (Stations 9 and 0). The swift currents in the estuary induced long and variable tidal excursion of 5 to 15 km (NIO, 1985) because of which the mixing of SPM from different estuarine sections was expected resulting in marked variation in Al concentration at the same location though the trend was maintained. The SPM of the mid-estuarine region (Stations 2 to 4) – particularly at station 3, had higher concentration of Al. From Fig 1, it was evident that the station 3 was in the southern channel of the estuary. It has been shown that the major water exchange with the sea was through the northern branch (station 2). Hence, the currents were relatively weak in the southern channel favouring preferential deposition of SPM and hence higher removal of dissolved Al. Elemental composition of SPM of Tapi River reported by Borole *et al.*, (1982) was also supportive of higher Al content of estuarine SPM as compared to that associated with the fresh water and SPM associated with water of chlorosity 17 to 19 g l<sup>-1</sup> had lower levels of SPM. However, the locations of sampling have not been specified and it was not clear whether high chlorosity samples were obtained from the coastal water or from the lower estuary.

Interpretation regarding the behaviour of dissolved Si in Tapi estuary becomes ambiguous because of significant variation in its concentration in fresh water and resulting uncertainties in fixing the riverine end member. The TDLs drawn with 8.49 mg l<sup>-1</sup> (Lower value), 10.92 mg l<sup>-1</sup> (Highest value) and 9.69 mg l<sup>-1</sup> (Mean value) drawn in Fig. 5 indicated addition as well as removal depending on the choice of the tie end. However, it was apparent from Fig. 3 that dissolved Si was depleted to low levels only over a shorter duration of about 3 h. Moreover, during April when the primary productivity was relatively low the dissolved Si concentration varied in a narrow range of 9.51 and 9.94 mg l<sup>-1</sup> with a mean of 9.69 mg l<sup>-1</sup>. Hence, we feel that the mean value of 9.69 mg l<sup>-1</sup> is the appropriate choice to explain the behaviour of dissolved Si. Phytoplankton productivity estimated on the basis of chlorophyll *a* content (NIO, 1985) decreased by half upto station 5, by one third between stations 4 and 3 and by one fifth in the lower estuary. The profile of dissolved Si at station 9 (Fig. 3) indicated removal of around 23% due to biological uptake during November–December. If we assumed that this uptake was roughly proportional to the primary productivity than the biogenic removal of dissolved Si would decrease from

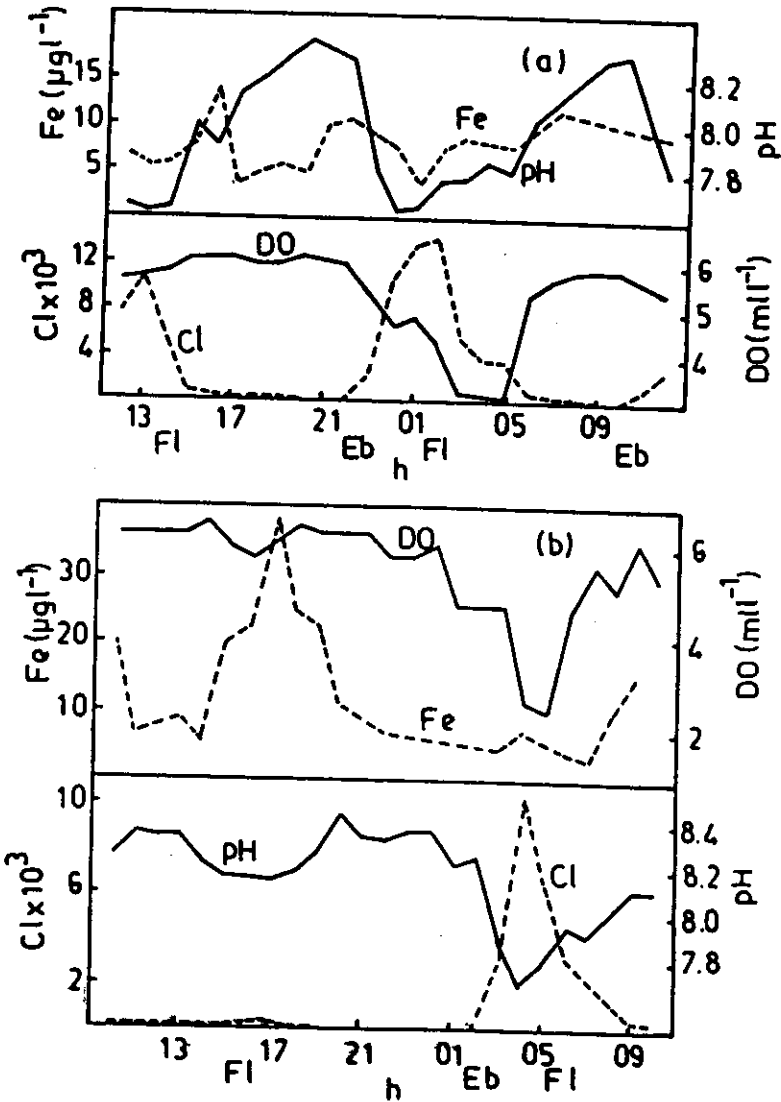


Fig. 12 Dissolved Fe, pH, DO and chlorinity as a function of time at (a) station 2 on 4-5 Dec 1983 and (b) station 3 on 1-2 Dec 1983.

11% in the inner estuary to 5% in the outer estuary. With the mean value (9.69  $\text{mg l}^{-1}$ ) for the fresh water tie end for TDL, the average removal varied between 10 and 15% in the chlorinity range of  $2 \times 10^{-3}$  to  $10 \times 10^{-3}$ . It therefore, appears that the inorganic removal if at all, would be

small in Tapi estuary. Comparison of November–December results with those of April–May in Fig. 5 indicated markedly lower percentage of removal during April (Av. 4–8% which could be due to decrease in primary productivity during this period. Addition observed below chlorinity of  $2 \times 10^{-3}$  on some occasions was due to the influence of river water containing variable concentration of dissolved Si.

The variation in concentration of dissolved Fe in Tapi estuary was neither correlated with chlorinity nor pH and in this respect differed from removal (Liss, 1976; Aston, 1978; Paulson *et al.*, 1984; Windom *et al.*, 1988; Byrd *et al.*, 1990) as well as conservative behaviour (Paulson *et al.*, 1989) reported in some estuaries. Unlike in the instances of removal due to decrease in solubility of Fe as the acidic river water mixed with the estuary water of higher pH, the high pH of Tapi River water (Fig. 3) favoured lower levels of dissolved Fe that entered the estuary. Although, the pH of the estuary was generally lower and varied diurnally (Fig. 12), the concentrations of dissolved Fe did not seem to be controlled by pH changes. Even in the offshore where the pH was low (Fig. 6) the dissolved Fe concentrations were comparable to the levels in the estuary and the random variations made the assessment difficult. However, the average concentrations of the dissolved Fe in the fresh water, estuary and the coastal water appeared to be of the similar order. The random variations could be due to the adsorption–desorption mechanism under highly varying load of SPM.

## CONCLUSIONS

Study of the behaviour of dissolved Al, Si and Fe in Tapi estuary led to the following conclusions :

- (a) Al was released to low dissolved Si containing coastal water and was subsequently removed to a varying degree in the estuary, enriching the estuarine SPM.
- (b) The inorganic removal of dissolved Si in the estuary was small though reliable estimate was hindered by biological uptake of Si.
- (c) Dissolved Fe varied randomly in the estuary.

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