

SEAWATER INTRUSION AND BEHAVIOUR OF DISSOLVED BORON, FLUORIDE, CALCIUM, MAGNESIUM AND NUTRIENTS IN VASHISTI ESTUARY

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Behaviour of dissolved B, F, Ca, Mg and nutrients in partially stratified estuary of Vashisti River has been studied under stable conditions of riverine flow. The dominance of Mg over Ca concentration in river water resulted in unusually low Ca/Mg molar ratio of 0.32 while the levels of B and F compared well with the composition of average global river water. F, Ca and Mg, were conservative at chlorinities above 4×10^{-3} while variable addition was evident in case of B, Ca and Mg at low chlorinities. Upto 25% removal of B also occurred in the intermediate chlorinity range. Mineralization of organic matter in the mid-estuarine region supplemented the nutrient budget of the estuary along with that associated with the tidal influx of sea water. However, low and variable N/P ratio was suggestive of other source of P in addition to mineralization.

INTRODUCTION

The behaviour of several elements which is conservative in seawater often differs in estuaries due to widely changing physico-chemical environment through mixing of natural waters of very different chemical composition. Boron was conservative in Chikugogawa (Hosokawa *et al.*, 1970), Beaulieu (Liss and Pointon, 1973), Zaire (Fanning and Maynard, 1978), Magdalena (Fanning and Maynard 1978) and Tamar (Liddicoat and Whitfield (1983) estuaries while varying degrees of removal have been reported for Alde (Liss and Pointon 1973), Mindola (Narvekar *et al.*, 1981) Zuari (Rajagopal

et al., 1981) and Ambika (Narvekar *et al.*, 1983) estuaries. Estuarine behaviour of F is mostly conservative (Liss 1976) though at least two instances of deviation have been reported. Kullenberg and Sen Gupta (1973) concluded that 17% of the F entering into the Gulf of Bothnia was removed at chlorinities below 4×10^{-3} . Addition of upto 30% of F observed in Mindola estuary (Zingde and Mandalia 1988) was attributed to the anthropogenic inputs to the mid-estuarine stretch. Similarly although Ca and Mg behaved conservatively in several estuaries (Liss 1976) exceptions have been reported in Ambika (Narvekar *et al.*, 1983). Purna (Narvekar and Zingde 1987). Mandovi and Zuari (Se Gupta and Naik 1981) estuaries.

We report the behaviour of dissolved B, F, Ca and Mg in Vashishti estuary in which significant deviations were observed in certain cases, particularly at low chlorinities.

Study area

Till date there is no published information regarding Vashishti River. Hence, a brief description of the study area is given below.

The 55 km long Vashishti River rises in the Sahyadrian scarp of Western Ghats and drains to the Arabian Sea through a region that is rugged, hilly and largely bare. In its mountainous course, it takes a narrow and steep profile, while on reaching the plain tract, it develops into a meandering course through low mud banks and rich mangroves with promontories on either side. The Jagbudi River, the principal tributary of the Vashishti also rises in the Sahyadrian scarp and drains a similar terrain. Geologically, the river bed and the adjoining regions are part of the Deccan trap consisting of hard and undulating laterite and basalt formations with scattered laterite and alluvial soil cover of varying thickness.

The catchment area is under profound monsoonal influence with an average yearly rainfall of 3500 mm at Chiplun (Fig. 1) 90% of which occurs during June-September transforming the river into rushing torrents of water. Following the withdrawal of monsoon the stable flow conditions are attained after October. The riverine flow is then regulated by the tailrace water from the hydal power station at Popheli and varies between 32 and 108 $\text{m}^3 \text{S}^{-1}$ with an average of 80 $\text{m}^3 \text{s}^{-1}$.

TABLE 1: Relative standard deviations (n = 15) of some analytical methods.

Element	Mean conc.	RSD
B (mg Kg ⁻¹)	4.12	±0.05
	0.045	±0.0013
F (mg Kg ⁻¹)	1.028	±0.005
	0.515	±0.005
	0.056	±0.004
Ca (g Kg ⁻¹)	0.369	±0.0006
	0.062	±0.0008
Mg (g Kg ⁻¹)	1.193	±0.0040
	0.004	±0.0001

Though detailed tidal data is lacking, short-term water level measurements indicated that the spring tidal range of 3.1 m at the estuary mouth marginally increases to 3.3 m at station 6, 35 km inland, and then falls to about 2 m at station 7 (45 km inland). The neap tidal influence was weak with tidal ranges of 0.7 m at the mouth and 0.9 m at station 6 with negligible water rise at station 7. The increase in range with distance in the estuary upto the station 6 indicate piling-up of freshwater as the tidal front advanced through the estuary.

METHODS

FIELD SAMPLING

Hourly sampling over tidal cycles was undertaken at 7 stations shown in Fig. 1 using a mechanised wooden trawler during February-March 1983. The riverine freshwater was sampled at station 8. A clean polyethylene bucket was used for sampling at the surface while Niskin sampler mounted on a nylon rope was used to sample at 1 m above the bed and at mid-depth. The samples were filtered through 0.45 µ Millipore membrane filter papers prior to analysis.

ANALYTICAL METHODOLOGY

The procedure developed by Hulthe *et al.* (1970) modified and applied

manually as described by Narvekar (1979) was used for the determination of boron. Propionic anhydride, oxalyl chloride and acetone were replaced by acetic anhydride, hydrochloric acid and methyl isobutyl ketone respectively. Boron in low chlorinity samples was determined as follows; a sample volume of 40 ml was pipetted into a polyethylene beaker and 0.2 ml of 0.0185 M solution of mannitol was added. The solution was carefully evaporated to dryness under infrared light, and then 2 ml of freshly prepared and boron-free deionised water was added to dissolve the precipitated salts. Boron was determined as above. Samples concentrated by this procedure did not show any loss of B due to evaporation.

F in water was estimated using the alizarine complexone procedure of Greenhalgh and Riley (1961). Correction was made for interference due to Mg.

Titrimetric procedure of Culkin and Cox (1966) was employed for the determinations of Ca and Mg. Ca in the sample was titrated to photometric end point (475 nm) with standard EGTA (0.005 M) using Zincon+Zn EGTA indicator. A sum of Ca+Mg+Sr concentrations was obtained after titrating the sample (635 nm) with EDTA (0.024 M) using eriochrome black T indicator. Mg concentration was obtained by difference which was further corrected for Sr and 1% overestimate in the titration (Sen Gupta *et al.* 1978). Suitably diluted EGTA and EDTA solutions were used for low chlorinity samples. All titrations were performed using precision burette (Metrohm Herisau, E 415) and spekol colorimeter. The precision of determinations of B, F, Ca and Mg was confirmed by analysing standard seawater.

$\text{PO}_4^{3-}\text{-P}$, $\text{NO}_3^- \text{-N}$, $\text{NO}_2^- \text{-N}$, $\text{NO}_4^+ \text{-N}$ and chlorinity were determined as described elsewhere (Grasshoff, 1976; Koroleff, 1976). All samples were analysed for B, F, Ca, Mg and chlorinity while samples collected over tidal cycles at stations 2, 4 and 6 and high tide and low tide from other stations were analysed for nutrients.

The relative standard deviations of some analyses are given in Table 1.

TABLE 2: Average composition of Vashishti River and coastal waters.

Parameter	No. of analysis	Range	Mean	Ratio ^a with (Clx10 ⁻³)
Vashishti River (Station 8)				
B (mg Kg ⁻¹)	12	0.009 - 0.018	0.012	9.23x10 ⁻⁴
F (mg Kg ⁻¹)	23	0.06 - 0.117	0.093	7.15x10 ⁻³
Ca (mg kg ⁻¹)	23	9.75 - 13.16	11.30	0.869
Mg (mg Kg ⁻¹)	23	19.93 - 23.60	21.59	1.660
Cl x 10 ⁻³	37	0.010 - 0.018	0.013	
PO ₄ ³⁻ -P (µM)	15	0.15 - 0.36	0.24	
NO ₃ ⁺ -N (µM)	15	0.14 - 0.52	0.21	
NO ₂ ⁻ -N (µM)	15	0.14 - 0.21	0.16	
NH ₄ ⁺ -N (µM)	15	0.92 - 2.86	2.74	
Coastal water (Station 1)				
B (mg Kg ⁻¹)	30	4.47 - 4.88	4.85	2.33x10 ⁻⁴
F (mg Kg ⁻¹)	30	1.29 - 1.45	1.41	6.77x10 ⁻⁵
Ca (g Kg ⁻¹)	25	0.39 - 0.47	0.44	0.0211
Mg (g Kg ⁻¹)	25	1.26 - 1.42	1.39	0.0668
Cl x 10 ⁻³	30	19.26 - 21.21	20.81	
PO ₃ ³⁻ -P (µM)	30	1.52 - 2.73	2.28	
NO ₃ ⁻ -N (µM)	28	1.78 - 3.12	2.52	
NO ₂ ⁻ -N (µM)	30	0.53 - 1.31	0.85	
NH ₄ ⁺ -N (µM)	27	0.85 - 2.34	1.82	

^aCalculated using concentrations of B, F, Ca and Mg in g kg⁻¹.

RESULTS AND DISCUSSION

RIVERINE ZONE

River water was sampled thrice during the study period at station 8 away from the influence of any seawater incursion. The Jagbudi River which brought some freshwater into Vashishti was also sampled. The concentrations of all the constituents studied were closely comparable in the two rivers as expected since they drained similar terrains. The mean values given in Table 2 were used to fix the riverine end members of the theoretical dilution lines (TDLs). This is an important consideration while studying the

behaviour of elements in estuaries as improper selection can lead to doubtful interpretations (Liss 1976). While the concentrations of B and F (Table 2) were comparable to the average global river water (Holland 1978), marked deviation was observed in case of Ca and Mg. The relative concentration of Mg was higher by about two times than that of Ca in Vashishti River resulting in low Ca to Mg molar ratio of 0.32 as against more than 1.5 for majority of river waters (Holland 1978). Two explanations are plausible for the observed low ratio. The rain-fed Vashishti River drains a basin which is highly leached due to the tropical environment and torrential rainfall, as evident from the low concentrations of dissolved salts in river water (Table 2). In such a situation the river may be receiving major part of the dissolved salts through the precipitation over the drainage area.

The strong south-west monsoon winds blowing on the coast during May-September can transport marine aerosols influencing the composition of river water. The molar ratio of 0.198 of Ca to Mg in seawater is closer to the ratio (0.32) of these constituents in the river water. However, even if we assumed that all the Cl in Vashishti River was derived from the atmospheric transport, it could account for only about 3% of the concentrations of dissolved Ca and Mg. Moreover, the rain water analysis of samples regularly collected from 1974 to 1989 from Bombay (Fig. 1), a coastal location about 150 Km to the north-west and also strongly influenced by south-west monsoons, have shown that Cl, Ca and Mg levels were low and varied in narrow ranges of 3.10-7.95, 1.30-3.40 and 0.28-0.58 mg l⁻¹, respectively (Meenakshy *et al.*, 1992). Hence the major proportion of these elements would be derived from the laterite and basalt formations in the drainage area.

The Poladpur and Ambevali basalts of the Western Ghats where the river rises contain 9.5 to 11.1% CaO and 4.6 to 6.5% MgO (Mitchell and Cox 1988). From the composition of several samples reported by these workers Ca to Mg molar ratio was calculated to be 1.2 to 1.5. Considering that the relative mobility of Ca and Mg in water from basaltic terrain is similar (Holland 1978) we expect much higher Ca to Mg molar ratio if the basalt was the major source of these elements in Vashishti River water since preferential leaching of Mg with respect to Ca, to account for observed low ratio (0.32) is less likely. The drainage basins of Vashishti and Jagbudi Rivers have extensive spread of laterite formations and the riverine course is partly through these laterites. The laterites are highly leached rocks rich

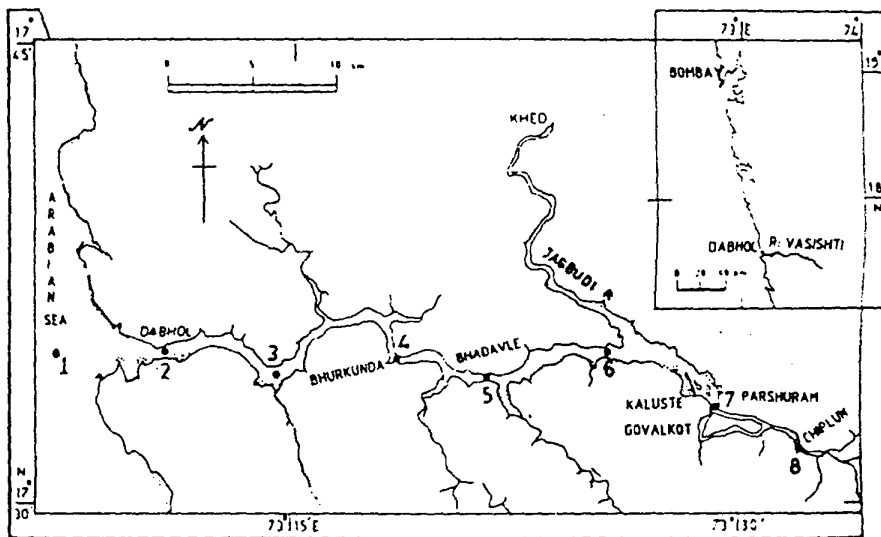


Fig. 1: Locations of sampling stations in Vashishti estuary.

in sesquioxides but poor in Ca and Mg. The Ca to Mg molar ratio calculated from the available literature reports for the region (Thomas 1979; Chandrasekharam and Ushakumari 1987) gave values in 0.2 to 0.6 range and hence markedly lower than the ratio for basalt. This ratio for laterite is comparable to that observed for water of Vashishti River (0.32). Hence, we believe that the Ca and Mg in these river systems are largely derived from the laterite.

ESTUARINE ZONE :

The intrusion of seawater as a salt wedge within the estuary was upto 35 km inland (Fig. 2) during spring as well as neap tides, and the flood tide rise upstream of this point was largely due to the piling-up of freshwater by the advancing tidal front in the lower estuary. Although numerous small streams and Jagbudi River joined the estuary, their influence on the chlorinity distribution was not evident as during dry season (except for Jagbudi River) they were mainly tide-fed and did not bring freshwater to alter the chlorinity regime of the estuary.

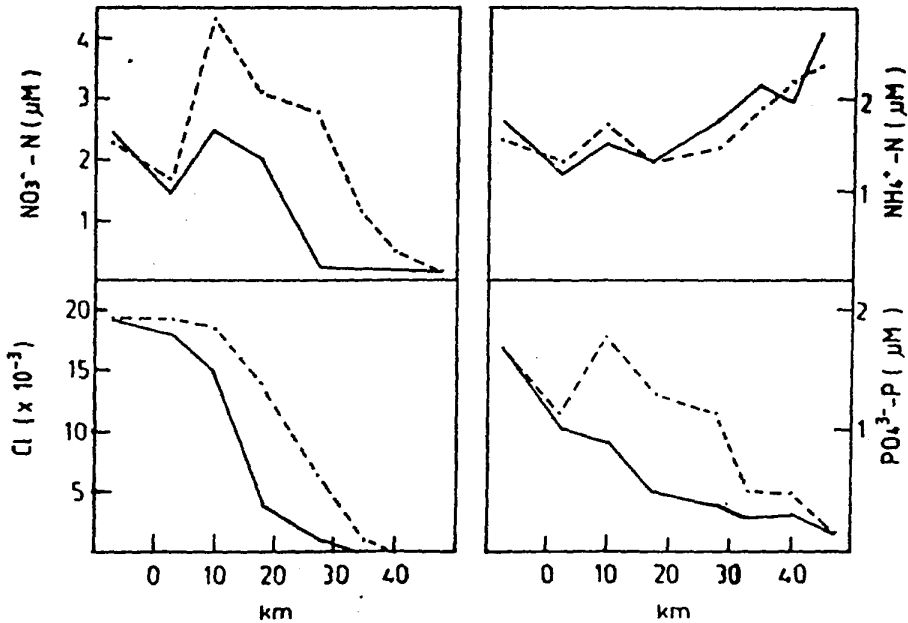


Fig. 2 Mean concentrations of chlorinity, NO_3^- -N, NH_4^+ -N and PO_4^{3-} -P in Vashishti estuary in surface (—) and bottom (---) waters

The temporal chlorinity profiles within the estuary varied in a relatively smooth manner (Fig. 3) with minor perturbations inherent to a dynamic estuarine system. The vertical chlorinity stratification persisted throughout the tide cycle attaining maximum around the high tide and decreasing considerably as the low tide approached rendering the estuary stratified to a varying degree. At station 6, it was near freshwater most of the time at the surface though chlorinities of 4×10^{-3} to 8×10^{-3} were recorded at the bottom during flood (Fig. 3). The turbulence generated owing to major topographic irregularities at the estuary mouth due to the presence of sand bars rendered the water column fairly well-mixed in the mouth region while increase in depth on the landward side of station 3 attaining maximum around station 4 coincided with the high vertical chlorinity gradient which decreased in the shallow inner estuary.

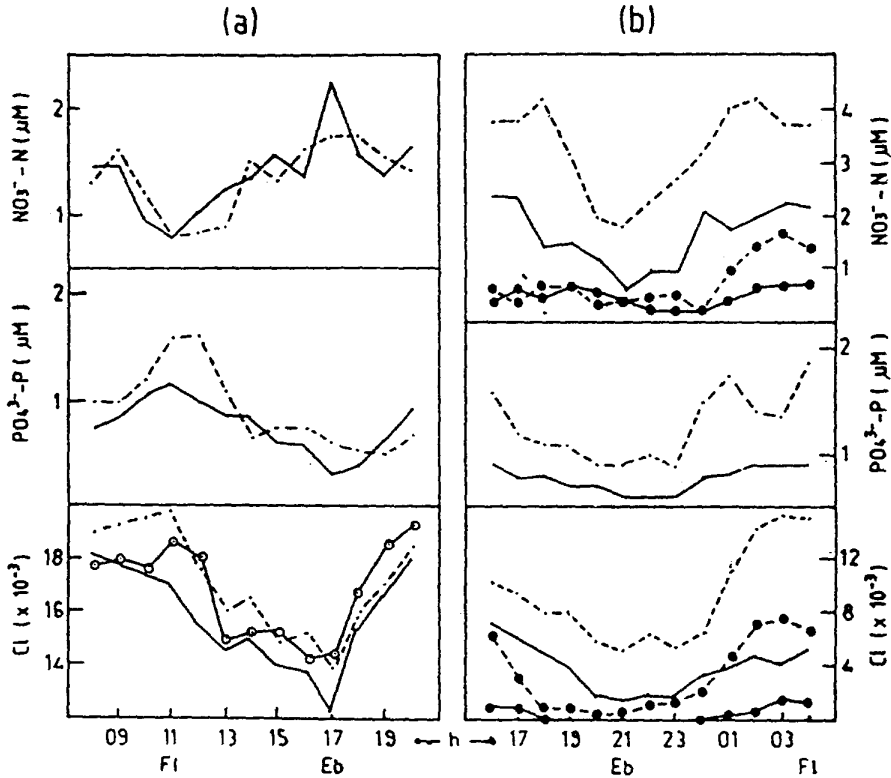


Fig. 3 Temporal changes in chlorinity, $\text{PO}_4^{3-} - \text{P}$ and $\text{NO}_3^- - \text{N}$ in surface (—), mid-depth (o—o) and bottom (—) water at (a) station 2 on 12.2.83 and (b) station 4 on 18-19.2.83: stations 6 profiles are shown as (●—●) for the surface and as (●—●) for the bottom water. $\text{PO}_4^{3-} - \text{P}$ values at station 6 were low and hence not shown in the figure to maintain clarity.

The results of diurnal sampling at the coastal location (station 1) were used to fix the seaward end members (Table 2) of the TDLs. Here the chlorinity varied in a narrow range of 19.26×10^{-3} to 21.21×10^{-3} with small and variable vertical chlorinity gradient unlike in the estuary where considerable gradient occurred.

The equation of the TDLs illustrated in Fig. 4 was derived in the form.

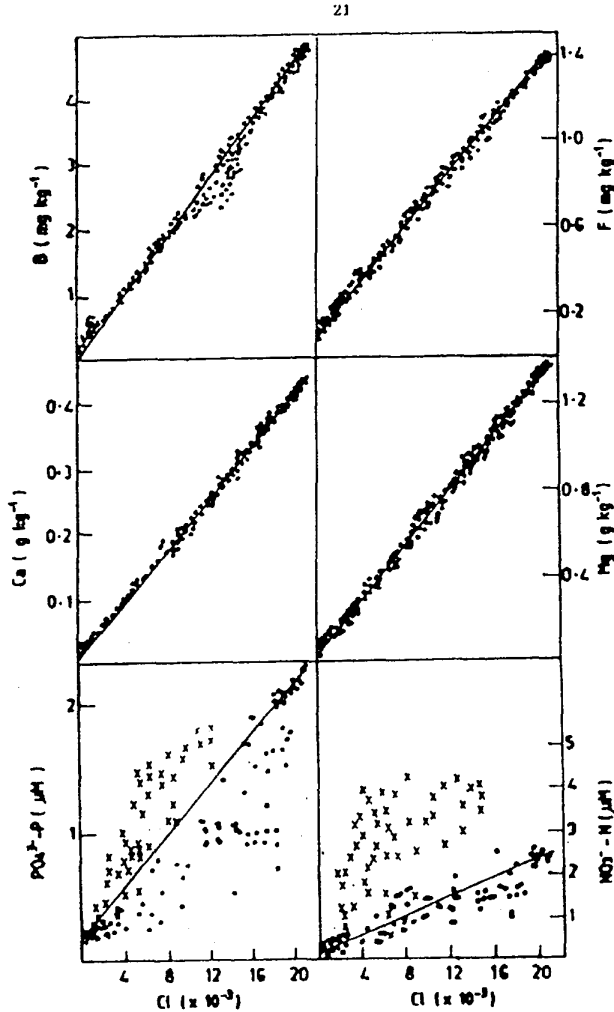


Fig. 4 Variations of B, F, Ca, Mg, $\text{PO}_4^{3-}\text{-P}$ and $\text{NO}_3^- \text{-N}$ with chlorinity in Vashishti estuary.

$$Pt = \frac{[(Ps - Pr) Ct + (PrCs - PsCr)]}{(Cs - Cr)}$$

Where Pt is the theoretical concentration of the element
 Ps is the mean concentration of the element in seawater endmember
 Pr is the mean concentration of the element in riverwater endmember

Cs is the mean chlorinity of seawater endmember
Cr is the mean chlorinity of riverwater endmember
Ct is the chlorinity of the sample

The percentage addition or removal (PAR) of the elements was computed from the relation

$$\text{PAR} = \pm 100 (\text{Pm}/\text{Pt}-1)$$

Where Pm is the measured concentration of the element. This equation is assigned negative sign to PAR in the event of removal ($\text{Pm} < \text{Pt}$) and positive sign for addition ($\text{Pm} > \text{Pt}$).

Dissolved F, Ca and Mg behaved conservatively at chlorinities above 4×10^{-3} with their respective ratios with chlorinities close to the seawater values (Table 2). Definite deviations however occurred at low chlorinities (Fig. 4) with addition of B (upto 200%), Ca (upto 20%) and Mg (upto 50%). Although considerable scatter in percent addition or removal was perhaps associated with uncertainties in analytical determinations at low concentrations of the elements as illustrated in Fig. 5 in which per cent addition or removal was shown at chlorinities below 6×10^{-3} , the trends were quite evident. F was conservative throughout the chlorinity range though small changes could not be ascertained due to the scatter, and there was no evidence for removal of the type reported in the Gulf of Bothnia (Kullenberg and Sen Gupta 1973). The addition of Ca and Mg which was significant between chlorinities 1.5×10^{-3} and 3×10^{-3} indicated that these additions were perhaps related to $\text{Na}^+ - \text{Ca}^{2+}$ and $\text{Na}^+ - \text{Mg}^{2+}$ type base exchange reactions occurring when the riverine clays were reacted with seawater (Sayles and Mangelsdorf Jr. 1977; Nadler *et al.*, 1980). It is possible that the clays in Vashishti River have predominantly Mg occupying majority of ion-exchange sites unlike in other rivers, because of the dominance of Mg in river water, which on entering the saline zone is exchanged by Na^+ and K^+ thus accounting for high percentage of release of Mg as compared to Ca.

The studies also suggested removal of B upto 25% at chlorinities between 12×10^{-3} and 116×10^{-3} . Removal of B has been reported for

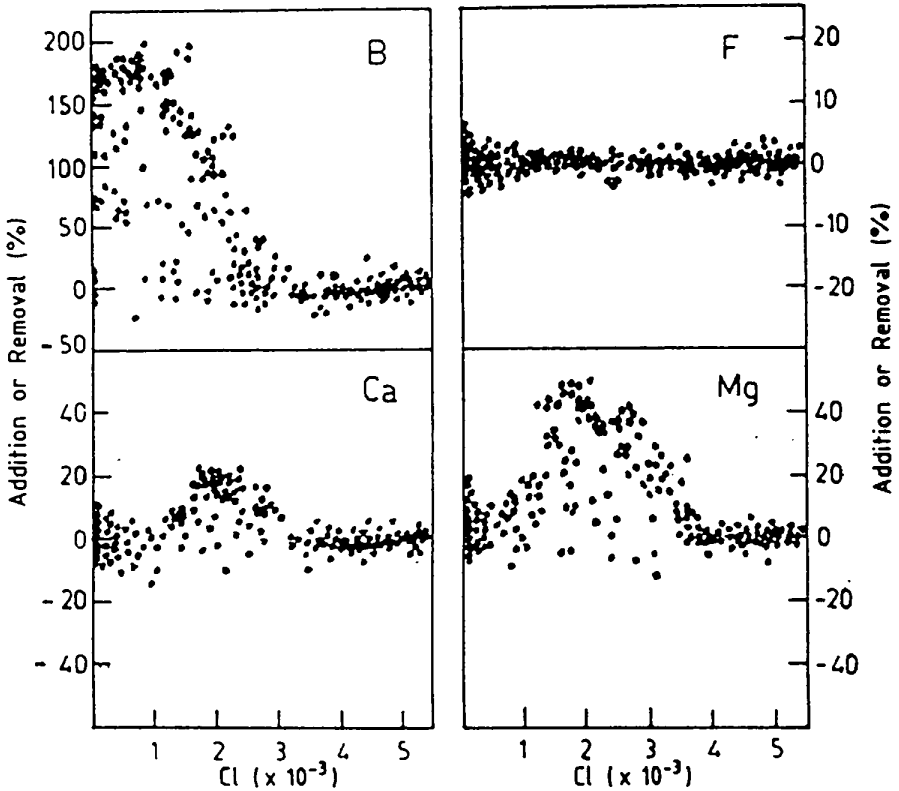


Fig. 5 Percent addition or removal of B, F, Ca and Mg at low chlorinities in Vashishti estuary.

Alde (Liss and Pointon 1973), Mindola (Narvekar *et al.*, 1981), Zuari (Rajagopal *et al.*, 1981), Ambika (Narvekar *et al.*, 1983) and Purna and Auranga (Narvekar and Zingde 1987) estuaries. Such removal can occur by adsorption onto clays, through a conversion from trigonally to tetrahedrally coordinated boron species at the clay surface (Palmer *et al.*, 1987). However, with the available data we are unable to explain the addition of B at low chlorinities and its subsequent removal at higher chlorinities.

Concentrations of soluble nutrients and their temporal variations in

Vashishti estuary are illustrated in Figs 2 and 3. The river water draining highly leached non-agricultural, rugged terrain contained low levels of nutrients and its contribution to the nutrient budget of the estuary was significantly low. The concentrations of NO_2^- -N were generally low (0.11-0.8 μM) within the estuary except at stations 3 and 4 where occasionally levels of 0.9 to 1.2 μM were encountered particularly in the bottom layer. The concentrations of NH_4^+ -N also varied in a narrow range (Fig. 2). In the absence of substantial nutrient fluxes through freshwater, the relatively high levels in the estuary particularly in the bottom layer, could result either from the ingress of seawater and its slow mixing dictated by the vertical stratification or from the additional supply within the mid-estuarine zone. Any anthropogenic influence to alter the nutrient budget was considered unlikely as the estuary had scarce human settlements in the vicinity and lacked industrial establishments. The profiles in Figs 2 and 3 supported benthic regeneration of nitrate and phosphate in the mid-estuary resulting in enhanced levels in the bottom water. Topographically the estuary with shallow mouth and shallow inland regions (upstream of station 5) forms a relatively deeper basin between stations 2 and 5 which traps the particulate suspended matter. Thus the bed sediment at stations 1 and 2 is sandy, but in the mid-estuarine zone it is composed of silty sand with silt-clay content of 40 to 50% (Govindan, 1989). However, N/P ratios, calculated combining measured dissolved forms of nitrogen, in the coastal water (1.5 - 2.7) as well as the estuary (1.0-8.5) were much lower than Redfield value with markedly higher ratios in the mid-estuary (4.2 - 8.5). Hence, although remineralisation was probably a source of soluble nutrients within the estuary, the low N/P ratios indicated another source of P which was not associated with nitrogen, i.e. not from mineralization. It was possible that the bottom sediment suspended by the tidal movements released significant quantities of adsorbed inorganic phosphate to the estuary water decreasing the N/P ratio. Such a release at a rate of approximately 0.2 $\mu\text{M day}^{-1}$ when sediment was suspended in mixtures of seawater and deionised water shown to occur in Amazon estuary (Fox *et al.*, 1986). The concentrations of PO_4^{3-} -P and NO_3^- -N are plotted as a function of chlorinity in Fig 4. The values observed at stations 4 and 5 are represented by crosses in this figure. Except for these values which indicated considerable addition, the concentration of NO_3^- -N decreased almost linearly, with chlorinity while PO_4^{3-} -P was removed in the outer and inner estuary.

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