

## Behaviour of Boron, Calcium & Magnesium in Purna and Auranga Estuaries (Gujarat), West Coast of India

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Ratios of B:Cl, Ca:Cl, and Mg:Cl were generally within limit of river water at one end and seawater at the other. Percentage addition or removal (PA & PR) of B, Ca and Mg was calculated using the concept of the theoretical dilution line. High percentage of removal of B at low chlorinities indicated its rapid removal in the initial encounter of river water with seawater. On the contrary, Ca was preferentially added at low chlorinities. Addition decreased as the chlorinity increased and removal was observed near-to seawater chlorinity. Mg was more conservative when compared to B and Ca.

Behaviour of many elements in estuarine mixing zones often differs considerably from their well known conservative nature in seawater due to interactions between solid solution components, adsorption, ion-exchange and variation in ionic strength<sup>1-3</sup>. Factors controlling the behaviour of an element in the mixing zone of one estuary may differ from those of another and could result in its differential behaviour in different estuaries. Removal of B is not significant in Chikugogawa<sup>4</sup> and Beaulieu<sup>3</sup> estuaries while the same is considerable for Alde<sup>3</sup> and Mindola<sup>5</sup> estuaries. Release of wastes containing B in the grossly polluted Ambika estuary<sup>6</sup> has resulted in its addition to the extent of 263% at the ebb tide in the inner estuary and in a mixed behaviour of removal as well as addition in the mouth region. Likewise, Ca and Mg are conservative in Chikugogawa<sup>4</sup> and Ambika estuaries<sup>6</sup> whereas only calcium is conservative in Potomac estuary<sup>7</sup>. Therefore it is of interest to investigate the behaviour of B, Ca and Mg in Purna estuary which is located in between Ambika and Mindola estuaries. The behaviour of B in the adjacent Auranga estuary is also studied.

### Materials and Methods

Sampling over complete tidal cycles during Oct.-Nov. 1978 was undertaken at 4 stations (Fig. 1) in Purna and Auranga estuaries. Freshwater was sampled further upstream at a point where there was no tidal influence. The surface samples were collected using a polythene bucket while Niskin sampler was used to obtain bottom samples 1 m above the sediment level. Samples were filled in prerinsed polyethylene bottles with leak-proof stoppers and preserved in a refrigera-

tor till analyses, which was completed within a month from the date of collection. Samples preserved in refrigerator gave unaltered results even after 1 month of storage.

The procedure developed by Hulthe *et al.*<sup>8</sup> was modified and applied for the determination of boron. Propionic anhydride and oxalyl chloride available locally gave erroneous results. Hence, these were replaced by acetic anhydride and hydrochloric acid respectively. Acetone was also replaced by methyl isobutyl ketone to avoid uncertainties due to evaporation of acetone. The procedure used was as follows: Seawater sample (0.10 ml) was pipetted in a B-free reaction tube dried in oven just before use. Reagent A (glacial acetic acid-90 ml + conc. sulphuric acid-10 ml), 1 ml;

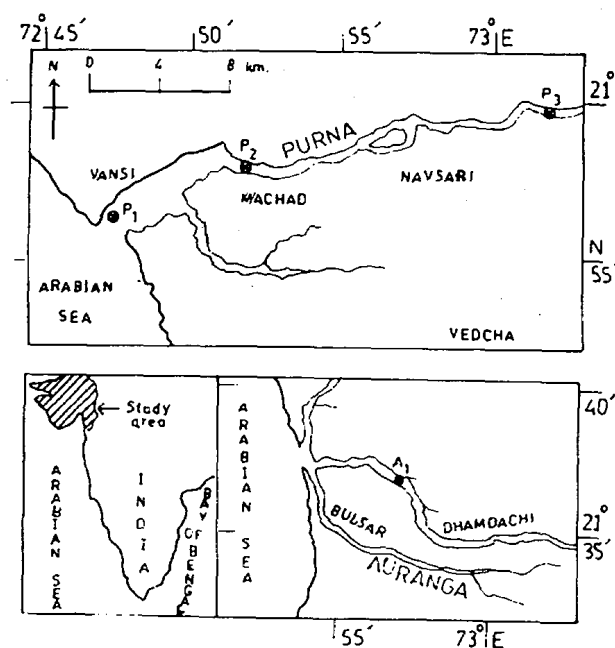


Fig. 1 — Sampling locations in Purna and Auranga estuaries

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acetic anhydride, 1 ml; and conc. hydrochloric acid, 0.1 ml were added successively. Reagent B (glacial acetic acid + conc. sulphuric acid-equal volumes), 0.7 ml and curcumin reagent, 0.4 ml were added after 15 min and the tube was immersed in a water bath maintained at  $40^{\circ} \pm 1^{\circ}\text{C}$ . Buffer (ammonium acetate-100 g + isopropyl alcohol-90 ml + glacial acetic acid-135 ml-made up to 1 l) 5 ml, was added and the absorbance measured at 540 nm on Spekol (Carl Zeiss, Germany) after cooling the tube to room temperature. Beer's law was obeyed up to a B concentration of  $5 \text{ mg.l}^{-1}$ . Relative standard deviation (RSD) for B in the range  $2.40\text{-}4.56 \text{ mg.l}^{-1}$  was  $\pm 1.2\%$ .

B in river water was determined after concentrating the sample at least 10 times by evaporation as follows: a sample (20 ml) was taken in a polyethylene beaker and 0.1 ml of a  $0.0185 \text{ M}$  solution of mannitol was added. The sample was carefully evaporated to dryness under infrared light. Then 2 ml of freshly obtained and B-free deionized water was added to dissolve the precipitated salts. B was then determined as above. Concentration by this procedure did not show any loss of B. This was evident from the evaporation of seawater containing  $4.56 \text{ mg.l}^{-1}$  B which gave unaltered results after dilution to its original volume. Duplicate analyses of a river-water sample gave B values of  $0.0698$  and  $0.0682 \text{ mg.l}^{-1}$  with a mean of  $0.069 \text{ mg.l}^{-1}$ .

Ca and Mg were analysed following the procedure of Culkin and Cox<sup>9</sup>. Photometric titration with EGTA and Zincon Zn-EGTA indicator yielded the concentration of Ca while complexometric titration with EDTA and Eriochrome Black T indicator gave combined concentrations of Ca, Mg and Sr. Appropriate correction<sup>9</sup> for Sr (calculated using relation,  $\text{Sr mg.kg}^{-1} = 0.42 \times \text{chlorinity}$ ) and for a systematic overestimate of about 1% in the titration end point<sup>10</sup> were applied. For Ca at  $0.4540 \text{ g.kg}^{-1}$  and Mg at  $1.3353 \text{ g.kg}^{-1}$  conc, RSD was  $\pm 0.13$  and  $\pm 0.15\%$  respectively.

Chlorinity was determined by argentometric titration procedure<sup>11</sup>, with RSD of  $\pm 0.1\%$ .

### Results and Discussion

The narrow and shallow Purna and Auranga rivers broaden into wide estuaries barely navigable during low tides. The regions around the mouth are largely marshy and sparsely populated with little commercial activity. The estuaries<sup>12,13</sup> are well mixed with excellent flushing characteristics due to high seawater influx and strong tidal currents; the flushing time being  $< 5$  tide cycles. The spring tidal height of 4.5 m in the mouth region of Purna estuary (Table 1) decreases to 1.5 m at 30 km upstream. This decrease is sharp in

Auranga estuary with tidal height of 1.1 m only at 10 km inland. The estuaries are freshwater dominated during July-October while seawater influence is predominant during May-June when riverine flow is weak. Although both the estuaries receive<sup>12,13</sup> pollutants from domestic and industrial sectors, the water-quality has not deteriorated appreciably<sup>12,13</sup> except in the immediate vicinity of the wastewater release locations.

Analyses of wastewaters reaching these estuaries indicated that they did not make any significant contribution of B, Ca and Mg to the receiving water.

The observed concentrations of B, Ca and Mg in water were plotted against chlorinity (Fig. 2) and the theoretical dilution lines (TDL) joining the seawater and river water end members (Table 2) drawn to evaluate their behaviour in the estuarine mixing zones<sup>1</sup>.

The mean element value for samples having chlorinity  $< 0.07 \times 10^{-3}$  was considered as the low chlorinity end member and the upper chlorinity end member was obtained by analysing the samples collected outside the mouth of the estuary. Mean ratios of B, Ca and Mg to chlorinity for the coastal water were  $0.24 \pm 0.0009$ ,  $0.0225 \pm 0.0006$  and  $0.0660$  respectively. These are slightly different from the normal

Table 1 — Comparison of Purna and Auranga Estuaries

	Purna	Auranga
State of mixing	Well mixed	Well mixed
Spring tide (mouth) (m)	4.6	4.5
Neap tide (mouth) (m)	3.1	3.3
Range of		
Cl ( $\times 10^{-3}$ ) <sup>*</sup>	1.2-17.9	1.1-16.4
B ( $\text{mg.kg}^{-1}$ )	0.3-4.2	0.2-4.0
Ca ( $\text{g.kg}^{-1}$ )	0.08-0.41	—
Mg ( $\text{g.kg}^{-1}$ )	0.09-1.17	—
Range of		
B:Cl	0.187-0.281	0.112-0.283
Ca:Cl	0.0213-0.0668	—
Mg:Cl	0.0598-0.0798	—
Range of addition (%)		
B	0-17	0-9
Ca	0-33	—
Mg	0-8	—
Range of removal (%)		
B	0-27	0-60
Ca	0-7	—
Mg	0-10	—
Equation for TDL		
B ( $\text{mg.kg}^{-1}$ )	$0.2376 \text{ Cl} + 0.0457$	$0.2366 \text{ Cl} + 0.0557$
Ca ( $\text{g.kg}^{-1}$ )	$0.0205 \text{ Cl} + 0.0387$	—
Mg ( $\text{g.kg}^{-1}$ )	$0.0651 \text{ Cl} + 0.0172$	—
Correlation coefficient		
PA & PR (B) & Cl	0.53	0.54
PA & PR (Ca) & Cl	-0.81	—
PA & PR (Mg) & Cl	0.00	—

\*Values below  $0.5 \times 10^{-3}$  not included

seawater ratios of 0.232, 0.02127 and 0.0666 respectively. The differences however are very small.

In the case of simple mixing of sea and river waters and in the absence of any loss due to biological or abiological removal, all the points in Fig. 2 would lie on TDL. When a chemical constituent is removed from or added to the water, the points would lie either below or above the TDL depending on removal or addition of the constituent under study. Theoretical con-

centrations (Pth) were directly obtained from the equations derived for TDL (Table 1) and the percentage addition (PA) or removal (PR) was obtained from the knowledge of the measured concentration of dissolved property (Pm) by using the relation

$$PA \& PB = 100 \left( \frac{P_m}{P_{th}} - 1 \right)$$

The positive sign for the result would indicate addition and negative sign would indicate removal. Correlation coefficient between PA & PR of element and chlorinity was calculated after converting all negative PR values to positive by raising all values (PA & PR) through certain positive number.

**Boron** — Wide changes in chlorinity resulted not only in change in B concentrations (Figs 3-5) but also in considerable variations in the B:Cl ratio in Purna (Figs 6 and 7) as well as in Auranga (Fig. 5) estuaries. The removal of B was more at low chlorinities and it decreased at high chlorinities and some addition was also observed in Auranga estuary (Fig. 5). Removal was observed in all samples at st P<sub>2</sub> (Fig. 7) and the extent of removal was greater as compared to st P<sub>1</sub> (Fig. 8). It appeared that the B entering the estuary through river water was rapidly removed during its encounter with the salinity gradient. It is suggested<sup>14,15</sup> that the removal of boron is through uptake by clays in two steps, viz. adsorption of B, perhaps on Mg(OH)<sub>2</sub> and other hydrous metal oxide phases, followed by more permanent incorporation into the tetrahedral sites of mica structure. The chlorinity and PA & PR of B gave positive correlation coefficients of 0.53 and 0.54 for Purna and Auranga estuaries respectively (Table 1). A negative correlation coefficient of -0.82 between chlorinity and PA & PR of B observed for the nearby Ambika estuary<sup>6</sup> was considered to be due to the release of B containing wastewater in the upper reaches of the estuary.

Ten samples collected at st P<sub>1</sub> were also analysed for suspended load by filtration through Millipore membrane filter paper. The high suspended load which varied from 90 to 389 mg.l<sup>-1</sup> was typical of the estuaries of south Gujarat and was due to the strong tidal currents dispersing the bottom sediments into the overlying water column<sup>13</sup>. A fairly good correlation coefficient of -0.73 observed between the suspended solids and PA & PR in the mouth region of Purna estuary tends to suggest the importance of suspended load in controlling the levels of dissolved B. However, it must be emphasised that only a limited number of analysis for suspended solids were available. Also such a relation was not very significant in Ambika estuary<sup>6</sup> although an inverse relationship between PA & PR of B and suspended solids was ob-

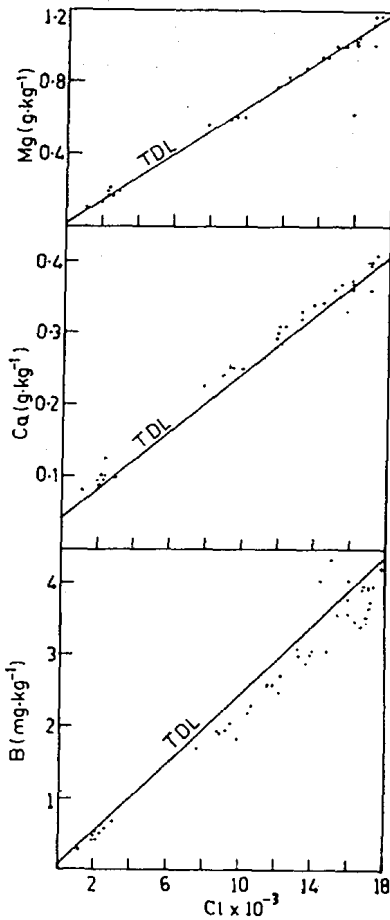


Fig. 2 — Variation of B, Ca and Mg with Cl and their theoretical dilution line (TDL) in Purna estuary

Table 2 — Average Boron, Calcium and Magnesium in Freshwater and Seawater

	River water			Seawater	
	Purna	Auranga	World average	Gulf of Cambay	World average
Cl (%)	0.060	0.069	0.01	19.375	19.375
B (mg.kg <sup>-1</sup> )	0.060	0.072	0.013	4.65	4.50
Ca (g.kg <sup>-1</sup> )	0.0399	—	0.0150	0.4359	0.4282
Mg (g.kg <sup>-1</sup> )	0.0211	—	0.0041	1.2788	1.2923

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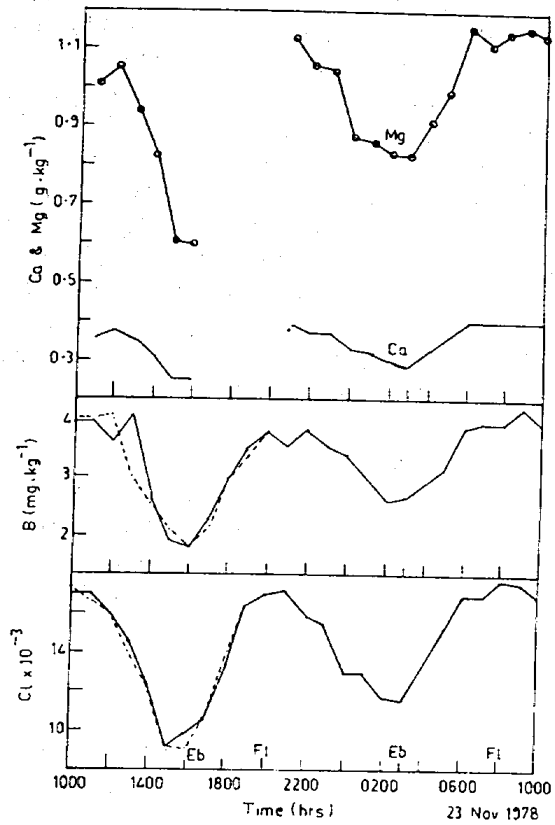


Fig. 3 — Temporal variation of Cl, B, Ca and Mg at P<sub>1</sub> on 22-23 Nov. 1978 (Dotted lines indicate bottom values. Discontinuity in lines is because few samples could not be analysed)

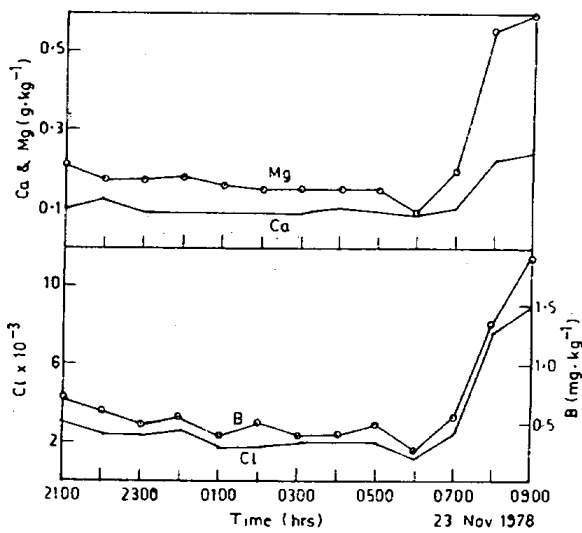


Fig. 4 — Temporal variation of Cl, B, Ca and Mg at st P<sub>2</sub> on 22-23 Nov. 1978

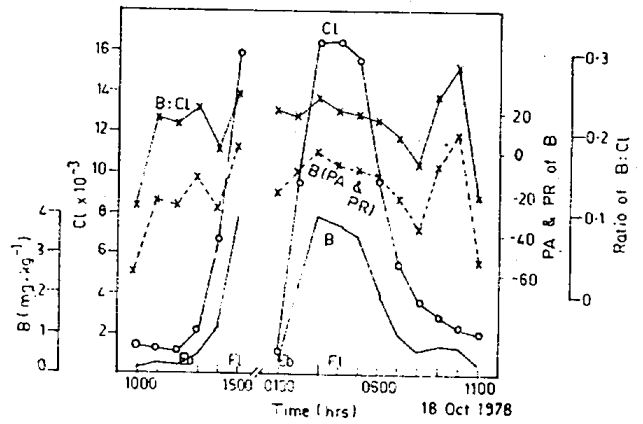


Fig. 5 — Temporal variation of B, Cl, B:Cl and B(PA & PR) at st A<sub>1</sub> on 17-18 Oct. 1978

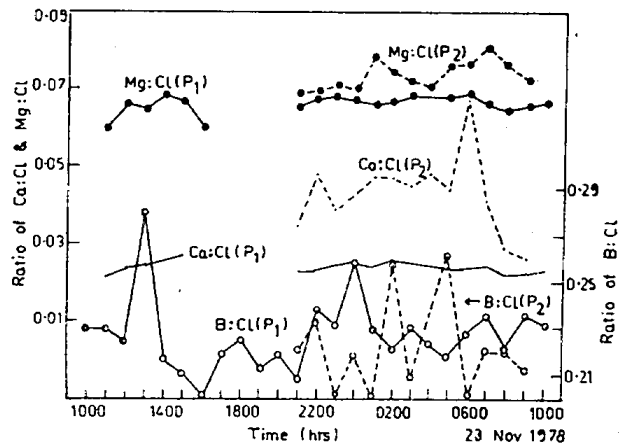


Fig. 6 — Temporal variation of B:Cl, Ca:Cl and Mg:Cl at sts P<sub>1</sub> and P<sub>2</sub> on 22-23 Nov. 1978

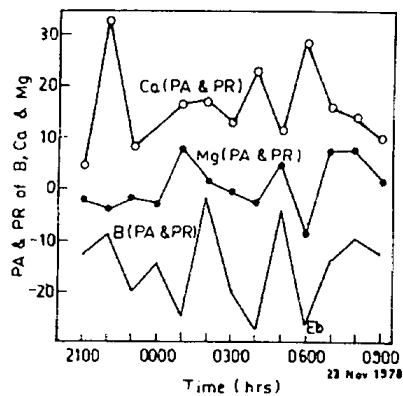


Fig. 7 — Temporal variation of PA & PR of B, Ca and Mg at st P<sub>2</sub> on 22-23 Nov. 1978

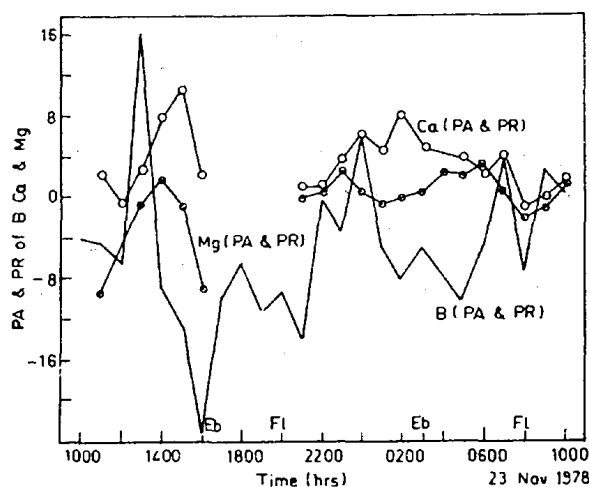


Fig. 8 — Temporal variation of PA & PR of B, Ca and Mg at st P<sub>1</sub> on 22-23 Nov. 1978

served. Fair to excellent correlations between PA & PR of B and chlorinity (Table 1) and similar pattern of B removal at low chlorinities in these estuaries strongly suggest that the ionic strength also plays an important role in the behaviour of B in the estuaries of south Gujarat.

**Calcium** — The levels of Ca varied with chlorinity and the plot for TDL revealed consistent, though small addition with only a few instances of removal (Fig. 2). Ca:Cl ratio varied considerably with high values during the ebb tide (Fig. 6). The excellent correlation between PA & PR of Ca and chlorinity obtained for Purna estuary is in concurrence with those of other estuaries<sup>5,6</sup> of the region. The addition of Ca which was more at low chlorinities was observed over the entire tidal cycle at st P<sub>2</sub> (Fig. 7) and over 90% of the time at st. P<sub>1</sub> (Fig. 8). A similar behaviour was observed for Ambika<sup>6</sup> and Mindola<sup>5</sup> estuaries though the magnitude of addition was small for the latter estuary. In the absence of external Ca inputs such as through wastewater, the addition of Ca appears to be due to the replacement of Ca<sup>2+</sup> ions which occupy the majority of ion-exchange sites in riverine clays, by Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> during their first encounter with seawater as observed for the clays of Rio Ameca, Mexico<sup>16</sup>. The observed inverse relation between PA & PR of Ca and chlorinity also supports this view.

The addition of Ca decreased at high chlorinities and removal was observed near seawater chlorinity. It was possible that the Ca added to the inner estuary at low chlorinities might be precipitating as the ionic strength increased down the estuary.

**Magnesium** — The behaviour of Mg was more conservative as compared to B and Ca with maximum removal of 8% and addition of 10%. Mg:Cl ratio was relatively high at st P<sub>2</sub> as compared to st. P<sub>1</sub> (Fig. 6) perhaps because of greater influence of freshwater at st P<sub>2</sub>. The correlation between PA & PR of Mg and chlorinity was not significant (Table 1) in line with the other estuaries<sup>5,6</sup> of the region.

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