

## Distribution of Dissolved Boron in the Waters of The Zuari Estuary (Goa)

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Dissolved boron varies from 0.02 to 5.42 mg/kg along the length of the estuary. The data suggest that a considerable portion of boron is removed from the waters by sedimentary uptake during monsoon and postmonsoon seasons. There is also a variation in the removal at different chlorinity values, maximum being between 11 and 17‰. Variations in B/Cl in different seasons in the estuary are also discussed.

Boron is an essential plant micronutrient and occurs in sea water to the extent of  $4.5 \text{ mg kg}^{-1}$  at salinity  $35\text{‰}$ <sup>1</sup>. According to Levinson and Ludwick<sup>2</sup>, boron is differentially adsorbed and deposited on suspended matter during estuarine mixing. Harriss<sup>3</sup> has attributed the removal of boron from waters to adsorption on detrital clays. Similar observations have been made by Liss and Pointon<sup>4</sup> in their studies in Alde estuary, England. There is no report on the behaviour of dissolved boron during estuarine mixing of sea and river waters in Indian estuaries. In the present study distribution and behaviour of boron during estuarine mixing are examined in order to identify any similarity or difference as compared to other estuaries in the intensity of the process.

### Materials and Methods

Regular monthly collections of water samples were carried out for 1 yr (Jan. 77 to Dec. 77) from the mouth of Zuari estuary to the upstream farther away at Saverdem (Fig. 1) so that a complete coverage of salinity range from zero to  $35\text{‰}$  could be obtained. The total stretch covered in the estuary was approximately 46 km from the mouth. Salinity (and chlorinity) were obtained using a Guildline Autosol model 8400 salinometer. After filtering the samples through  $0.45 \mu\text{m}$  Millipore filter, the dissolved boron was estimated spectrophotometrically as a complex with curcumin using the method of Uppstrom<sup>5</sup>. The coefficient of variation was 2.7%. The data collected were treated seasonwise, viz. premonsoon (February-May), monsoon (June-September) and postmonsoon (October-January), and to understand the general conditions the data were pooled. Measured concentrations of boron were plotted against a conservative index of mixing, such as chlorinity and a theoretical dilution line (TDL) was drawn by joining

the points corresponding to the fresh water and sea water boron concentrations and their respective chlorinities. If the boron during estuarine mixing processes behaves conservatively then all the points corresponding to different chlorinities should be on this line. The deviation above the line indicates addition and the points falling below the line show removal<sup>4</sup>. The amounts of suspended matter in the samples were determined (twice in a season) by filtering 1 litre aliquots of the sample through Millipore ( $0.45 \mu\text{m}$ ) filters which were dried at  $105^\circ\text{C}$  and weighed before and after the filtration.

### Results and Discussion

Variations in chlorinity during the period of study in different seasons in Zuari estuary are given in Fig. 2. There was only a narrow range of variation ( $18.27$  to  $20.15\text{‰}$ ) at the mouth during premonsoon and postmonsoon while during monsoon, it was between  $9.41$  and  $12.18\text{‰}$ . From the mouth of estuary to 10 km upstream the mean chlorinity was more or less the

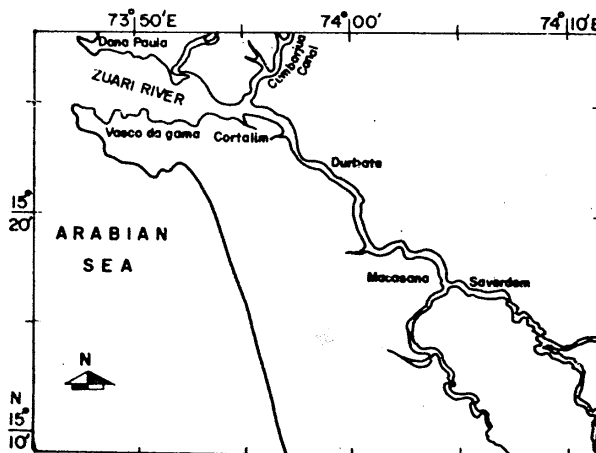


Fig. 1—Zuari estuary

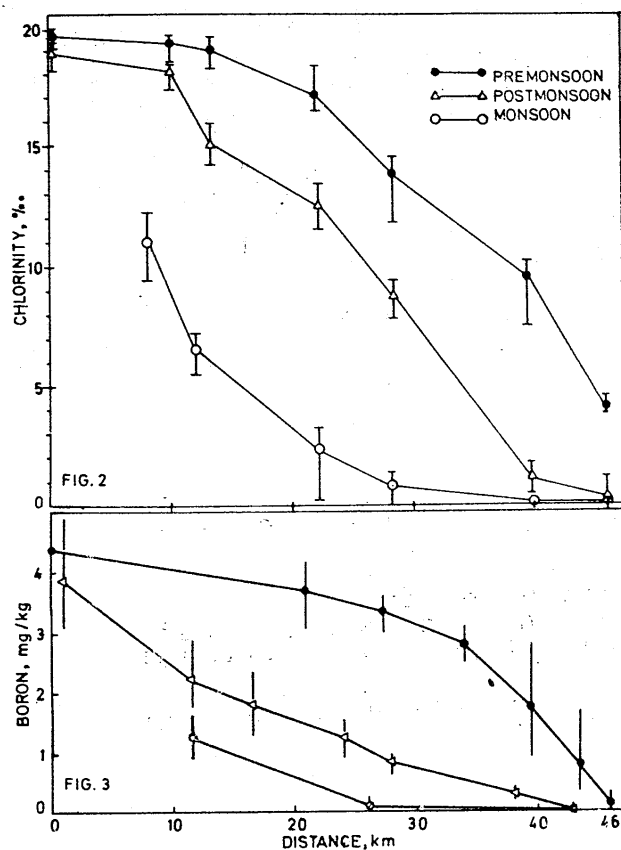


Fig. 2—Chlorinity variations in Zuari estuary in different seasons

Fig. 3—Variation in boron concentration in different seasons

same in all seasons and after 10 km, the chlorinity decreased steadily. During monsoon it dropped below  $1^{\circ}/_{\infty}$  at 27 km and was nearly fresh at and beyond 38 km. Near the head of the estuary at Macasana and Saverdem, the chlorinity varied between  $0.28^{\circ}/_{\infty}$  and  $1.66^{\circ}/_{\infty}$  during postmonsoon, but it never dropped below  $3.9^{\circ}/_{\infty}$  at Saverdem during premonsoon, mostly due to low river runoff and relatively higher evaporation. The quantity of freshwater discharging during premonsoon is negligible<sup>6</sup> ( $c. 0.03 \times 10^3 \text{m}^3/\text{yr}$ ). In the present study, chlorinity is taken as an index of estuarine mixing.

Boron varied widely between 0.03 and 5.42 mg/kg during premonsoon (Fig. 3). There was also a very wide variation between 2.98 and 4.87 mg/kg at the mouth of the estuary during postmonsoon. Beyond 25 km from the mouth in the upstream, the range of variation in boron was very low (0.02-1.4) during monsoon and postmonsoon, while during premonsoon the range was large (0.06-4.2) throughout the estuary. The mean concentration of boron varied from 3.88 to 0.02 mg/kg from mouth to the head of the estuary during postmonsoon and the same was observed between 1.54 and 0.02 mg/kg during monsoon.

Fig. 4 shows the relationship between boron and chlorinity during premonsoon, during which there was a steady marine condition prevailed at the mouth of the estuary, with an average chlorinity of  $19.76^{\circ}/_{\infty}$ . The concentration of boron also was high with a mean value of 4.59 mg/kg. Below the chlorinity  $8^{\circ}/_{\infty}$  there was a sudden drop in boron concentration, to 0.2 mg/kg. During this season, between the chlorinity value of 8 and  $20^{\circ}/_{\infty}$ , boron behaved, more or less conservatively (Fig. 4). Chlorinity and boron relationship was linear in this season with  $r=0.94$ . From the regression analysis, it was found that the expected boron concentration at  $19.37^{\circ}/_{\infty}$  chlorinity was 4.54 mg/kg and the measured values of boron varied between 4.09 and 4.8 mg/kg with a mean value of 4.6 mg/kg.

During monsoon, the estuary was flooded and almost throughout its course, it was predominant with freshwater. Simultaneously the concentration of boron was also considerably low and ranged from 0.02 to 1.54 mg/kg for a chlorinity range of 0 to  $3.13^{\circ}/_{\infty}$ . The regression analysis showed an expected boron concentration of 6.84 mg/kg at  $19^{\circ}/_{\infty}$  during this season, but due to flooding the chlorinity of this value never reached. Removal of boron during this season occurred above the chlorinity value of  $0.75^{\circ}/_{\infty}$  and it was  $11.23\%$  (Fig. 5).

Removal of boron was more in the postmonsoon than in other seasons and it was between 20 and  $45\%$  (Fig. 6). There was variation in the removal at different chlorinity values and the removal of boron was maximum between 11 and  $17^{\circ}/_{\infty}$  chlorinity values.

From the least square regression equation

$$\text{Boron} = -0.1579 + (0.1860) \text{chlorinity}$$

it was found that the expected boron concentration at  $19^{\circ}/_{\infty}$  chlorinity was 3.69 mg/kg and that the mean value of boron measured in these samples was 3.38 mg/kg. Variation in removal rate at various chlorinity values is given below:

| Cl <sup>o</sup> / <sub>∞</sub> | 0-5 | 5-10 | 10-15 | 15-20 |
|--------------------------------|-----|------|-------|-------|
| Av. removal rate (%)           | 20  | 35   | 45    | 29    |

To get a general idea of the distribution of boron in relation to chlorinity in the Zuari estuary, the values collected throughout the 12 month period were combined and processed separately (Fig. 7). The least square regression equation

$$\text{Boron} = 0.1743 + (0.2045) \text{chlorinity}$$

was obtained with  $r=0.93$ . The average annual removal rate of boron in Zuari estuary was 10-35%. Almost a similar magnitude of removal for boron (25-30%) was observed in the Alde estuary<sup>4</sup>.

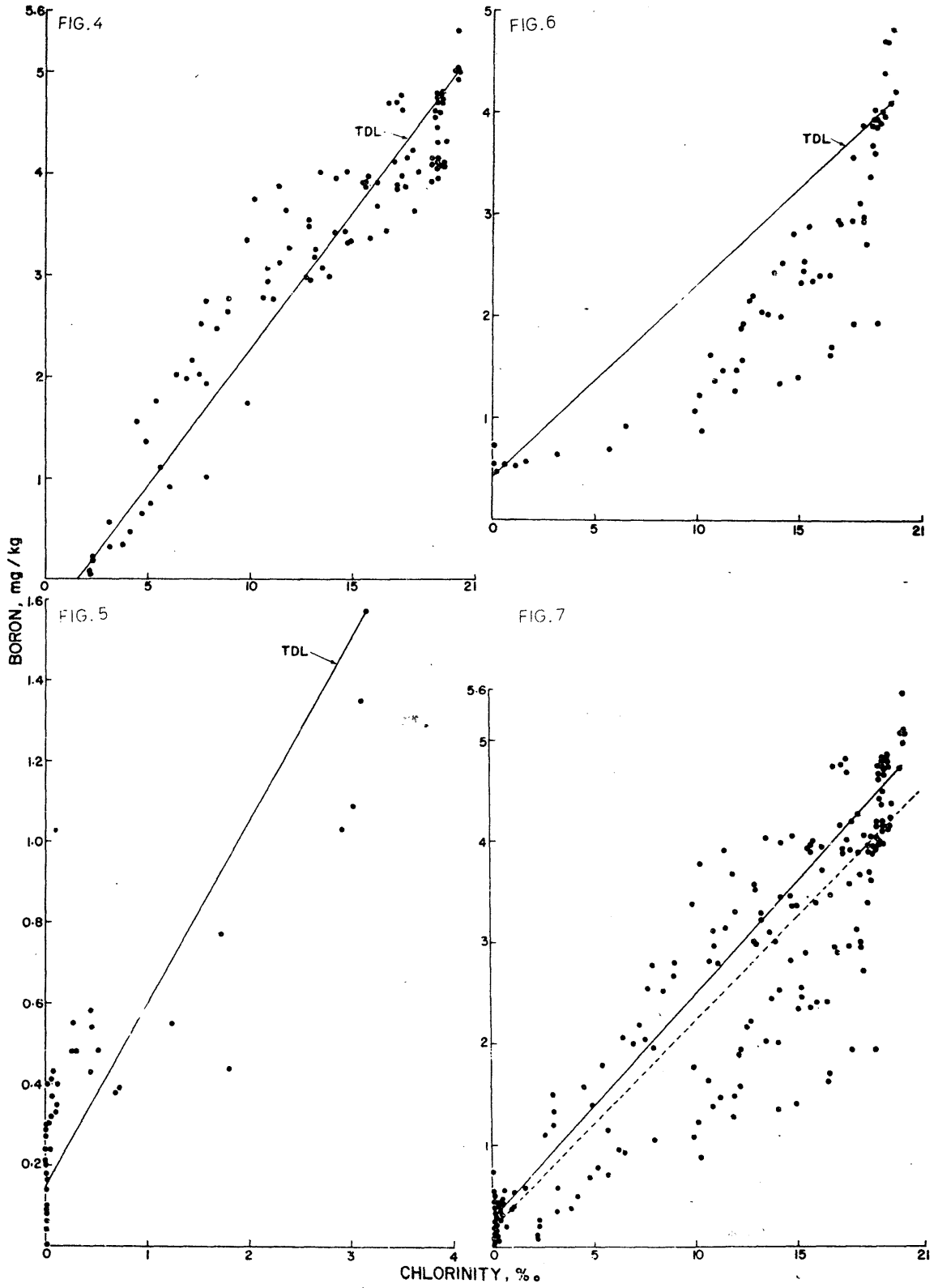


Fig. 4 to 7—Relationship between chlorinity and boron in the premonsoon (4), monsoon (5), postmonsoon (6), and for all seasons combined (7) [In Fig. 7: -----, regression line; —, TDL]

Boron/chlorinity ratio varied very widely in the estuarine environment. From the regression analysis, it was found that the B/Cl varied between 0.186 during postmonsoon and 0.351 during monsoon. B/Cl in the premonsoon with prevailing marine conditions, was 0.234. Narvekar *et al.*<sup>7</sup> found that significant scatter in B/Cl beyond the limit of the experimental error was 0.230-0.261 which indicated that the ratio was not truly constant, even in an oceanic region. Similarly, a wide range of variation was also found by Dyrssen and Uppstrom<sup>8</sup> in the Baltic waters (0.212 to 0.272). Culkin<sup>9</sup> gave an average B/Cl of 0.240 (range of 0.222 and 0.264). Very low value of B/Cl in postmonsoon (0.186) may be attributed to the high rate of removal of dissolved boron from the water and being fixed on the suspended particles. Eventhough chlorinity of the water dropped to zero during monsoon, B/Cl was very high (0.351) because the removal of boron was not to the extent as found in the postmonsoon. Annual mean value of B/Cl obtained from the regression analysis was only 0.205.

Though there was a high rate of removal of boron in postmonsoon, the quantum of the suspended load was comparatively low (17.4 mg/litre). The suspended matter was maximum during premonsoon (35.3 mg/litre), while in monsoon it was 26.7 mg/litre. This indicates that though the removal takes place due to adsorption on suspended particles, it is not controlled only on the quantity of the suspended load. The degree and nature of equilibrations of the solid phase with the water are probably more important than the total quantity of suspended material<sup>4</sup>.

Levinson and Ludwick<sup>2</sup> proposed that boron is adsorbed from solutions on to clay minerals. They further suggested that this process may lead to the non-conservative behaviour of boron during estuarine mixing. Natural clay minerals, especially illites, are the best adsorbents and remove boron from solution<sup>10</sup>. Along the west coast of India, the minerals that dominate in the sediments generally are in the order: montmorillonite, kaolinite and illite<sup>11</sup>. Perhaps the differences in the composition of the minerals in the suspended matter account for the observed variations of boron in place and time.

It is pertinent here to mention some of the mechanisms suggested for the incorporation of boron into marine sediments. Levinson and Ludwick<sup>2</sup> suggested the formation of a precipitate phase in which colloidal co-precipitation of boron with silica occurs on suspended solids in estuaries. Harder<sup>12</sup> showed through laboratory experiments that formation of new hydrous metal (M) oxide phases (M = Al, Fe, Mn, Mg, etc.) can remove dissolved boron from natural waters. Harriss<sup>6</sup> mentioned that riverborne input load of boron was removed by adsorption on detrital clays on

passing through the high ionic strength of sea water. Any of the mechanisms mentioned above may be operative in Zuari estuary.

The results presented in this paper show that dissolved boron is removed from the waters of the Zuari estuary during monsoon and postmonsoon. The enhanced process of inorganic removal in postmonsoon may be due to increased ionic strength or salinity, higher temperature, higher boron concentration in solution and longer exposure times<sup>13</sup>. Unlike silicon, boron enters the estuary from sea water which is rich in this element relative to most river waters. In river Zuari, an average annual freshwater runoff has been estimated<sup>6</sup> as 9 km<sup>3</sup>. At zero salinity, the average concentration of boron was 0.2 mg/kg and therefore, the river Zuari receives from the freshwater runoff a substantial amount (1800 metric tons) of boron every year.

It is still an unresolved problem as to why removal of dissolved boron should occur in some estuaries but not in others. Detailed studies on the types and composition of clay minerals present, degree of equilibrium established between the solid phase and the estuarine water and possible formation of new hydrous metal oxide phases during the estuarine mixing processes, etc. are to be carried out to establish the dominant mechanisms responsible for the removal of boron in estuarine environments.

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