BEHAVIOUR OF BORON IN MANDOVI ESTUARY (GOA)

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ABSTRACT

Boron in the waters of Mandovi estuary varied with tides and seasons with concentrations decreasing from mouth towards upstream. Higher concentrations of 0.51 — 5.83 mg kg$^{-1}$ and 0.03 — 4.42 mg kg$^{-1}$ respectively were observed during the pre and postmonsoon season as compared to relatively low levels in monsoon (0.01 — 2.70 mg kg$^{-1}$) due to increased suspended sediment loads and high dilution resulting from large quantities of freshwater influx. Addition of boron to the extent of 27.74% during the postmonsoon and removal upto 31.30% in the monsoon were observed. In the postmonsoon months, removal of boron to some extent was observed due to phytoplankton. The pH and dissolved oxygen showed a negative correlation with boron whereas chlorinity and alkalinity gave positive correlations with a linear variation. Though the overall behavioural pattern of boron indicated a non-conservative nature, it showed a quasi-conservative character during premonsoon and a non-conservative during rest of the seasons.

Key-words: Boron, Mandovi estuary, Goa coast.

INTRODUCTION

The mixing of riverine fresh water and the coastal/oceanic saline waters in the estuary imparts certain characteristics to the estuarine waters. River waters, though relatively less uniform in the composition of major constituents viz. boron, calcium, magnesium, compared to seawater, are important as principal suppliers of these constituents to the sea. This transport, however, depends largely on the geological nature of the drainage area. The levels of such major constituents generally do not exhibit appreciable changes in the oceanic and in coastal waters. They bear a relatively constant ratio with chlorinity.

The concept of constant ratio becomes a misnomer when one considers an estuarine environment. The rapid response of the estuarine environment to the time-dependent physico-chemical parameters such as land runoff, precipitation and evaporation due to changing seasons, brings about changes in the behaviour of most of the major elements of these waters. In addition, the highly productive features of the estuaries alter the level of some important bio-geo-chemical elements (Barnes & Green, 1970).
The present paper deals with the investigations on the behaviour of boron in the waters of Mandovi estuary, studied during the period June 1982 to May 1983.

MATERIALS AND METHODS

Water samples were collected from near-surface, mid-depth and near-bottom, every month by using Niskin samplers, from eight stations (M_2 to M_8) selected in the estuarine region along with two reference stations representing coastal (M_1) and freshwater (M_10) zones, (Fig. 1). These two reference stations are situated about 10 km apart on the two extremes of the estuary. The samples collected were well preserved in polyethylene bottles and kept under refrigeration till analyses. A systronic digital pH meter was used for measuring pH. Salinity, alkalinity, D.O. and suspended solids have been analysed following the normal and standard methods (Strickland and Parsons, 1972 and APHA 1976). Boron was analysed by the spectrophotometric method of Hulthe, Uppstrom and Ostling (1970) with standard deviation of ± 1.11% and standard error of 0.0021, while primary production was estimated following Vollenweider (1974).

RESULTS

The region under investigation was divided for convenience into coastal, estuarine and freshwater areas. The salient features on the distributions of boron and salinity are presented as follows:
Fig. 2 Horizontal profiles showing the distribution of boron in (a) surface (b) mid-depth and (c) bottom waters.
Fig. 3 Horizontal profiles showing the distribution of salinity in (a) surface (b) mid-depth (c) and bottom waters.
Boron — The concentrations of boron in the waters of the three areas; [Fig. 2(a, b & c)] varied widely (0.1 to 5.83 mg/kg) barring the freshwater stretch where the values were less than 0.1 mg/kg throughout the period of investigation. The coastal waters (M₁) with higher levels of concentration did not show appreciable variations. These varied between 3.03 to 4.49 mg/kg with a mean of 4.1 mg/kg. In addition, this station (M₁) did not show any conspicuous vertical gradient in B levels, though the water depth at this station was around 30 m. The stations in the estuarine stretch; 65 km during the premonsoon months (Qasim and Sen Gupta, 1981) however, exhibited a wide range in the magnitude of boron concentration. A gradual decrease in an upstream direction (M₂ to M₃), during any given month, was noticed though occasionally values as high as 5.83 mg/kg have been recorded (Fig. 2b. stn. M₃). With the progress of season, even the extreme stations M₈ and M₉ indicated values of considerable importance. Such rapid increase in the concentrations could not be seen in the lower reaches of the estuary.

Consequent to the onset of SW-monsoon and the associated rainfall, greater stretches of the estuarine region come under the influence of land drainage and river runoff. This results in a rapid fall in boron concentration. This situation continues till August. Subsequently, the concentration increased till October towards the upper reaches. As far as the vertical distribution is concerned, one fails to notice increase or a decrease of boron with depth. This reflects the inconsistent pattern of boron distribution (Fig. 2).

Salinity — The distribution of salinity (Fig. 3) at all the three depths exhibited similarity in its trend with, values varying from 0.04 to 36.67%. As expected, a linear decrease in the distribution of salinity from stns. M₁ to M₉ was observed. Salinity at stn. M₁₀ remained less than 0.04% all the time but its distribution within the estuarine areas, however, presented interesting patterns. By about May, highly saline waters could be seen with weak longitudinal gradients up to stn. M₇ beyond which these gradients become weak. From June, the salinity showed rapid decrease commencing from stn. M₄. By July, the full estuarine stretch (upstream of stn. M₃ and M₄) showed much lower salinity (Fig. 3). This situation prevailed for over a month. From the middle of August, the picture indicated above, reversed. Increase in salinity though less rapid initially, was observed till middle of September. The weaker longitudinal gradients from stns. M₇ to M₉ almost presented a mirror image of the conditions observed during the premonsoon months.

In the vertical distribution of salinity one can notice higher values even at stn. M₉ during the pre- and postmonsoon months with the values almost intermediate at mid-depth. During the SW-monsoon season the water column did not exhibit any interesting features in the vertical profile (Fig. 3). It is worth-
while to record a relatively lesser variation in salinity at the coastal station M.

High salinity during February, March and April probably indicates the effect of upwelling in addition to other physical processes.

**DISCUSSION**

Mandovi estuary is one of the duplex estuaries of Mandovi and Zuari situated geographically close to each other (Fig. 1). The observed distributions of salinity within the Mandovi estuary based on instantaneous samples collected in the present study could fairly be taken as a representative of the general long-term (monthly) trends. This also reflects the dependence of water properties on the seasons and the magnitude of concentrations. The results are in good agreement with the earlier published work carried out during the survey of Mandovi and Zuari river (NIO Technical Report, 02/79). Basically one can realize more or less well mixed conditions in dry seasons. Considering the weak or nearly less significant vertical gradients (Figs. 2 & 3), the progress of saline waters after the monsoon towards the upstream reaches and their recession during monsoon probably help in better understanding of the residential times (150-180 days). This gives a feeling that a given water mass moves up and down the estuary under the influence of the available tidal energies and undergoes gradual changes in characteristics through diffusion at both molecular and turbulent levels simultaneously.

Existence of the non-linear pattern of isohalines at the estuary entrance could be considered as the effects of the mixed semi-diurnal tide with the associated flows, generally directed in a N-NE direction during the flood phase and S-SW, in the ebb phase with slight asymmetry. This feature and the observed frontal movements (Stommel, 1953) up and down the longitudinal axis of the estuary could give rise to pockets of less saline water as seen in Fig. 3a, and high salinity as in Fig. 3b. Incidentally this frontal movement was believed to be one of the mechanisms associated with red tide phenomenon (Devassy, Bhattathiri and Qasim, 1978).

The behaviour of boron presented earlier resembles closely with that of salinity with minor variations. The coastal waters which are associated with relatively higher salinity but with lesser vertical variations, exhibited features similar to that of B content. This could be due to less solids in suspension and weak mixing caused by weak tidal flows, low wave energies and weak winds compared to the estuarine areas where the tidal currents give rise to maximum turbulence. The estuarine areas exhibited greater variations in B content primarily due to higher variability in suspended solids during the monsoon.

When the estuarine system is composed of freshwater the sediment loads in suspension have been found to vary from 2.6 to 18.4 mg l⁻¹ and are likely
to adsorb the dissolved boron as could be seen from their low values particularly at surface and mid-depths; Fig. 2 (a, b & c). The removal of dissolved boron by adsorption as proposed by Harder (1963), and Liss & Pointon (1973) has been observed in this season. The correlation of boron with suspended solids was found to be highly significant \( r = -0.63 \). During the pre- and post-monsoon months the B concentrations are contrastingly higher in magnitude with no vertical variations. This is due to the tidal input of B from coastal seawater as well as due to the settling of sediment in suspension through the processes of flocculation (Barness and Green 1970) commencing from Stn. \( M_2 \) and extending in an upstream direction with time. The slight vertical variations observed in B concentrations are the effect of settling particles adsorbing boron to various degree depending on the concentration of sediment load e.g. in the month of February, the high values of B observed at Stn. \( M_0 \) and during May at Stn. \( M_4 \) indicate insignificant concentrations of suspended solids. These locations are situated close to sizeable tidal marshes which are exposed during low tide and inundated during high tide. The strong horizontal tidal flow leads to greater turbulence and bring larger quantities of unconsolidated bottom sediments into suspension. This is evident from the relatively lower values of boron. In the extreme upper reaches of the estuary boron concentrations are not very insignificant and indicate larger sediments in suspension.

Giving due importance to the relation between boron and chlorinity, the scatter plots for the pre-, post and monsoon seasons together with their annual variation indicate a linear relationship (Fig. 4 a, b, c, & d). The correlation

![Fig. 4, Behaviour of Boron during (a) Pre-Monsoon (b) Monsoon (c) Post-Monsoon and (d) Annual.](image-url)
coefficient \( r \) shows variations from \(+0.89\) to \(+0.94\). During monsoon the scatter of points (boron concentrations) around the theoretical dilution line (TDL) is fairly large; (Fig. 4b). The plausible reasons for this observed feature is the removal of dissolved B by suspended solids, the dilution by land runoff and riverine freshwater discharge. Boron values when correlated with suspended solids gave a negative correlation \((r = -0.63)\) significant at 95% confidence limit indicating the removal of B. Its significant relationship with pH \((r = -0.32)\) and alkalinity \((r = +0.83)\) and no relationship with D.O. were also found in this season. The percentage addition and removal have been found to be 16.78 and 31.30 respectively. During the premonsoon season a balance for the addition and removals of B which are 8.56 and 7.61% respectively was noticed while these values were 27.84 and 10.71% respectively during the post-monsoon.

Little or insignificant addition of boron (0.95%) observed during pre-monsoon seems to be due to the decomposition of organic matter apart from the tidal input. This is evident from the significant correlation between B/Cl ratio and D. O. \((r = -0.73)\). Boron also showed significant correlation with alkalinity and insignificant with pH and suspended solids in this season. During

![Graph](image)

**Fig. 5. Variation in Boron and primary productivity in the (1) Coastal region (2) mouth region, and (3) Upstream Boron (-o-o-), pp (-x-x-).**
post-monsoon, its correlation with pH as well as with alkalinity were significant at 95% confidence limit ($r = -0.81$ and $0.84$ respectively).

From the above, it is noticed that during the post-monsoon months the percent addition and removals are significantly larger compared to pre-monsoon months. This anomaly is attributed to the primary production of these waters (Harris 1972; Subba Rao 1981 and Shiradkar, Singbal & Sen Gupta 1982) which exhibits peaks during February, July and October. This feature is more or less similar in the coastal areas while in the vicinity of the estuary entrance the pattern is slightly complex (Fig. 5) as a result of frontal movement and the sharp horizontal gradients in salinity particularly during pre-monsoon months.

A comparison of results with that of the adjoining river Zuari (Rajagopal, Rajendran and Reddy, 1981) indicates difference in many aspects. In Zuari, the biological removal of B predominates in monsoon and post-monsoon, whereas in Mandovi, it is only in the monsoon season. This indicates that the tidal currents in Zuari are strong and associated with high tidal energies that encounter turbulence and set the settled sediment in suspension, which in turn remove dissolved B by adsorption. Also, Zuari river is more saline up to a considerable distance along its length as compared to Mandovi and so, the alleviated flocculation of sediment particles reduce considerable B in the upstream; while in Mandovi, the freshwater content or rather the low chlorinity of the water in the upstream gives rise to low boron values. On the contrary, the highest boron content (5.83 mg kg$^{-1}$) as observed in this study agrees well with that of Zuari river (5.42 mg kg$^{-1}$).

Wide variations in B/Cl ratios observed during the three seasons indicate considerable addition as well as a significant decrease in B levels in partly independent ways (Dyrsen and Uppstrom, 1977). These variations were from 0.0 to 0.445 in monsoon; 0.197 to 0.310 in postmonsoon and 0.140 to 0.320 in premonsoon. Based on the concept of TDL the observed behaviour of B in these waters from all these areas (Fig. 4a, b & c) leads to non-conservative tendency in monsoon and post-monsoon with quasi-conservative nature during the premonsoon seasons.

Considering the whole data and linear relationship of B with chlorinity (correlation coefficient $r = +0.89$ significant at 95% confidence limit) it can be concluded that the physical and bio-chemical processes operating in these waters contribute to the observed departure of B concentrations from TDL (Fig. 4d) thereby indicating the non-conservative behaviour of this element in Mandovi estuary.

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REFERENCES


