

Boron chemistry in relation to its variations in eastern Arabian Sea

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Boron varied from 3.96 to 5.3 mg.kg⁻¹ in the coastal and from 3 to 4.74 mg.kg⁻¹ in the offshore waters. B/Cl showed a wide variation from 0.202 to 0.269 in the coastal region while significantly low ratios (< 0.2) to as high as 0.238 were observed in the offshore waters. Percent addition and removal of boron computed by taking into consideration the world average B/Cl of 0.232 indicated an addition up to 16% and removal up to 11.65% resulting in a net addition of boron to the coastal waters. At few stations boron was found to be released from the oxidation of organic matter while its removal was attributed to the net effects of suspended solids and the primary productivity. In the offshore waters, significant decrease of boron in the euphotic zone was mainly due to biological removal during high productivity.

Boron is an essential micronutrient for the growth of phytoplankton¹. However, the tolerance range between toxicity and deficiency of boron is narrow and due to this it can be a pollution hazard in the productive areas of the sea. An attempt has been made to study the chemistry of boron in the coastal waters of the eastern Arabian Sea in relation to its spatial variation and its inter-relationship with chlorinity, dissolved oxygen and primary productivity.

Materials and Methods

Following conventional methods, the water samples in eastern Arabian Sea (Fig. 1) were collected from coastal region during 15 June to 13 July 1987 at standard depths (0, 10, 30 and 50m) from selected stations on board *ORV Sagar Kanya* and from the offshore region from 17 March to 27 March 1981 on board *R.V. Gaveshani*. Boron (inorganic) was estimated by spectrophotometric method² with slight modification^{3,4}, replacing propionic anhydride and oxalyl chloride with acetic anhydride and the hydrochloric acid respectively. Methyl-isobutyl ketone was used in place of acetone. The standard deviation of the method was calculated to be $\pm 1.17\%$. Simultaneously, dissolved oxygen (DO) and salinity were estimated by the modified Winkler's method⁵ and by the Autosol salinometer respectively. The data on primary productivity however were taken from data bank.

Results and Discussion

Coastal waters—Boron concentrations in the

water column of 0 to 50 m depth vary from 3.96 to 5.3 mg.kg⁻¹ and gives an average value of 4.56 ± 0.05 mg.kg⁻¹ (Fig. 2). Salinity varies from 33.16 to 36.55 $\times 10^{-3}$ and indicates an apparent increase with depth. B/Cl ratio shows a wide spatial variation from 0.202 to 0.269 (Fig. 3). DO shows high concentrations mostly from > 4 to 5.93 cm³.dm⁻³ in the upper 10 m layer below which it decreases significantly with depth to as low as 0.45 cm³.dm⁻³. The relationship of boron with DO is inverse with correlation coefficients

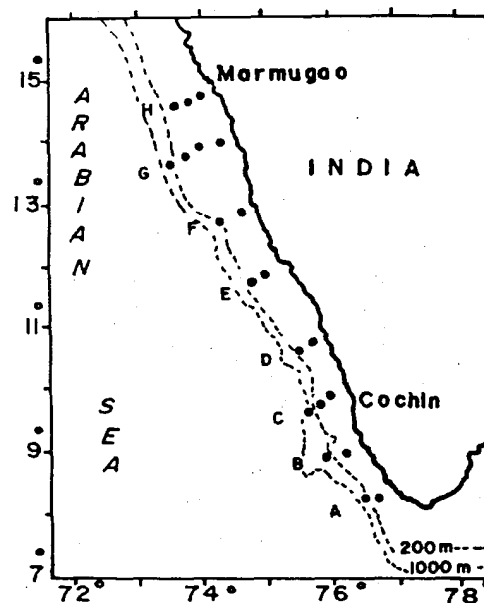


Fig. 1—Station locations

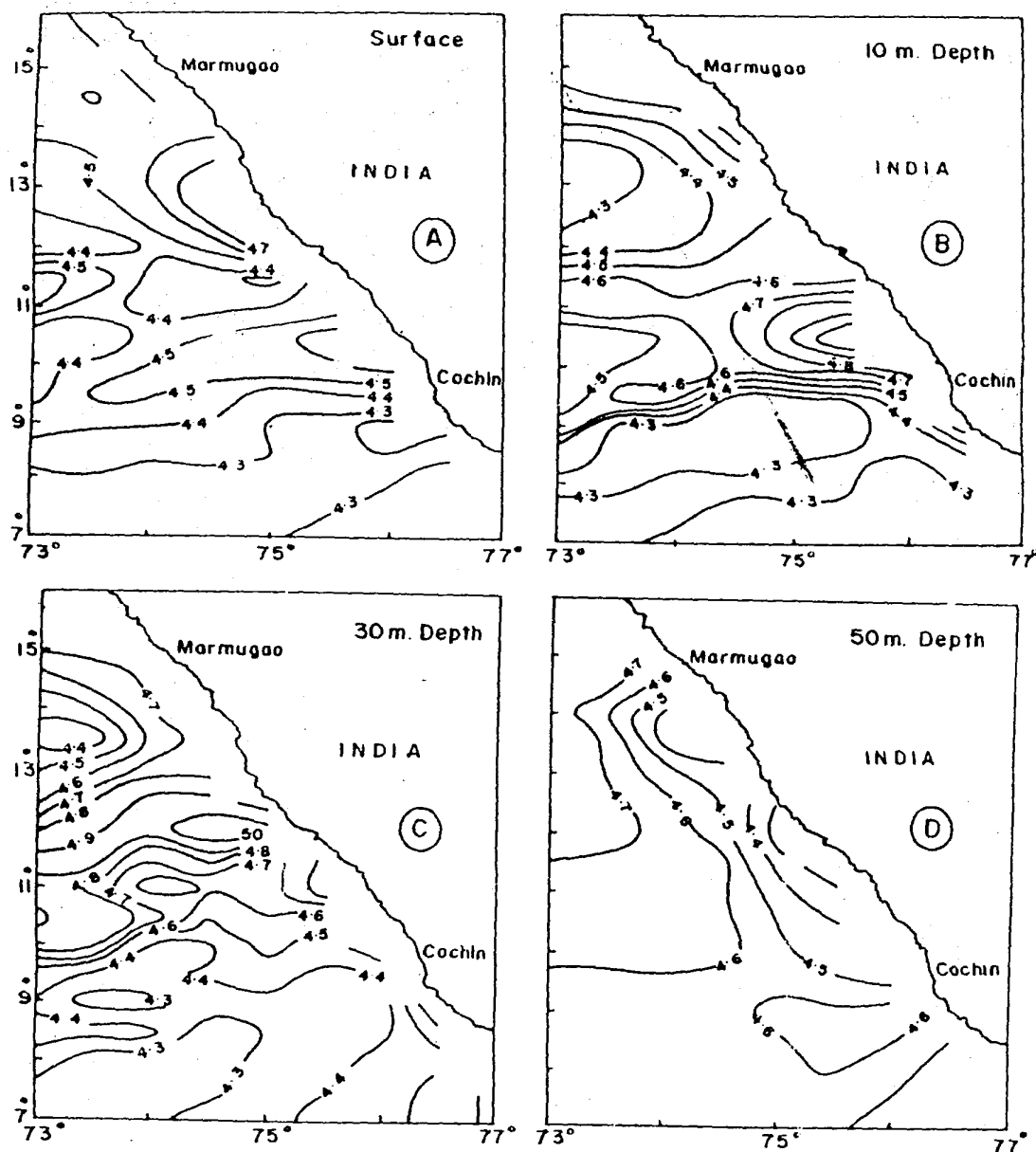


Fig. 2—Vertical profiles indicating the distribution of boron at 0,10,30 and 50 m in the coastal water

(r) varying from -0.22 to -0.4 along sections A,B,D,E and H in the coastal region (Fig. 1).

Offshore waters—In the upper 90 m layer boron showed variation from 2.89 to as high as 4.75 mg.kg^{-1} (av. $3.33 \pm 0.045 \text{ mg.kg}^{-1}$) while in deeper layer it was from 1.17 to 3.50 mg.kg^{-1} . B/Cl ratios varied from 0.171 to 0.238 in the upper layer and from 0.192 to 0.241 in the deeper layer. DO in the upper 90 m layer varied from 4.5 to $4.72 \text{ cm}^3. \text{dm}^{-3}$ while in the deeper

layer it showed a significant decrease ($0.5 \text{ cm}^3. \text{dm}^{-3}$). Primary productivity showed variation from $0.7 \text{ mg C.m}^{-3}.\text{day}^{-1}$ at 90 m depth to $54.9 \text{ mg C.m}^{-3}.\text{day}^{-1}$ at surface. The correlation of boron with DO and primary productivity indicated a depthwise inverse relation (Fig. 4).

Boron at surface (Fig. 2A) shows alternate low and high concentrations along the coast indicating a patchy distribution. The offshore region though

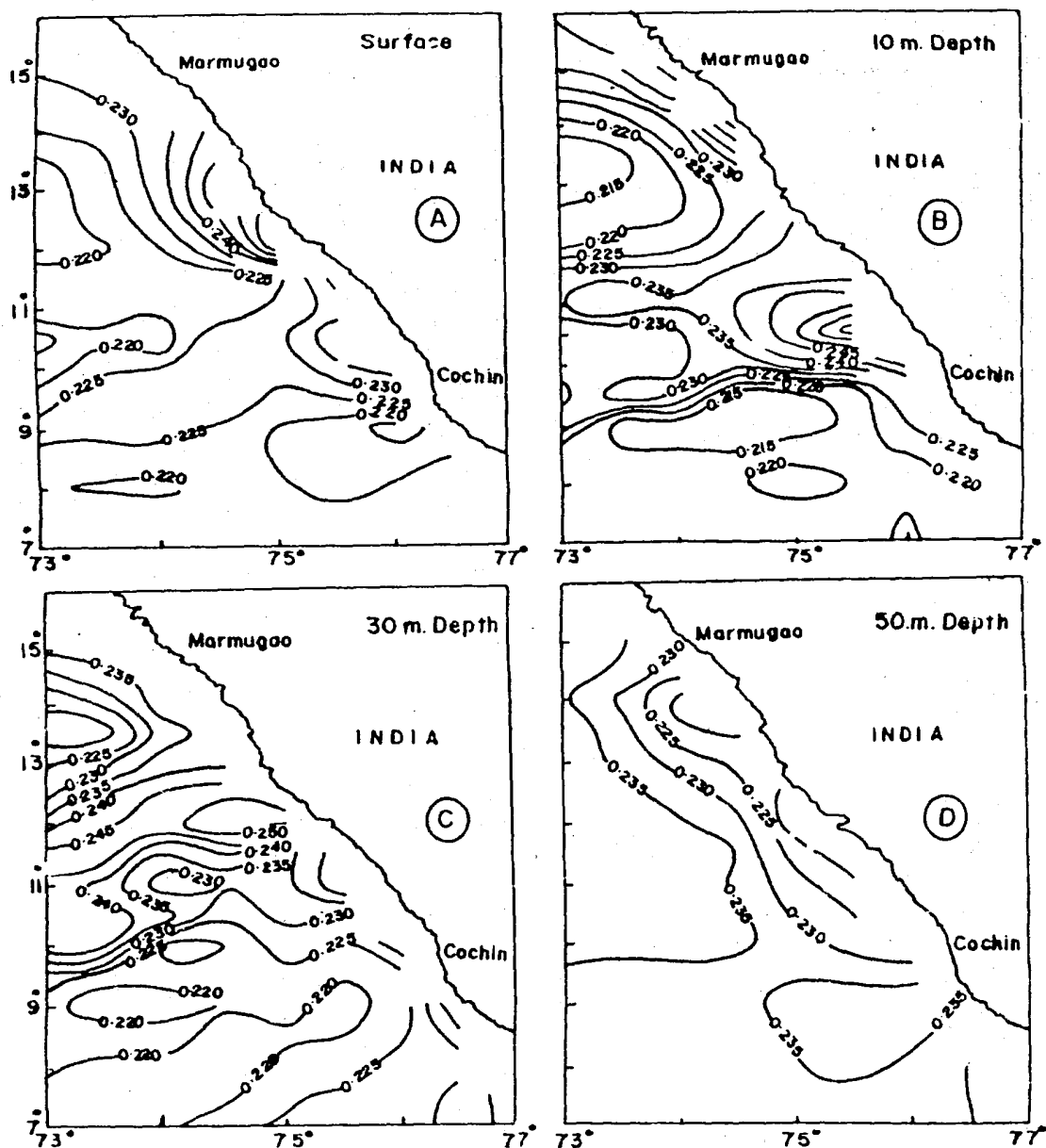


Fig. 3—Vertical profiles indicating the variation of B/Cl at 0,10,30 and 50 m in the coastal water

shows boron variation from 4.3 to 4.5 mg.kg^{-1} (close to normal) the B/Cl ratios from 0.22 to 0.225 indicate a significant decrease. This decrease is more prominent towards south along the coast. The distribution in general tends to be more zonal.

Similar features are also seen at 10m depth level with increased gradients. Figs 2A and 3A show a well developed intense frontal system prevailing around 9°N lat. in the coastal region off Cochin. This feature is in contrast to the similar feature seen in the north that encompasses a high and low cellular

distributions. The 30m depth layer in Fig. 2C shows identical features of boron as observed in the upper layer. However, at 50m depth the distribution of these parameters becomes more organized with alternate increase and a decrease all along the coast. The general pattern of distribution of boron in the coastal region also reflects the circulation of water indicating that along the coast the circulation is mostly cellular.

Alternate high and low concentrations of boron observed all along the coast are because of some of the

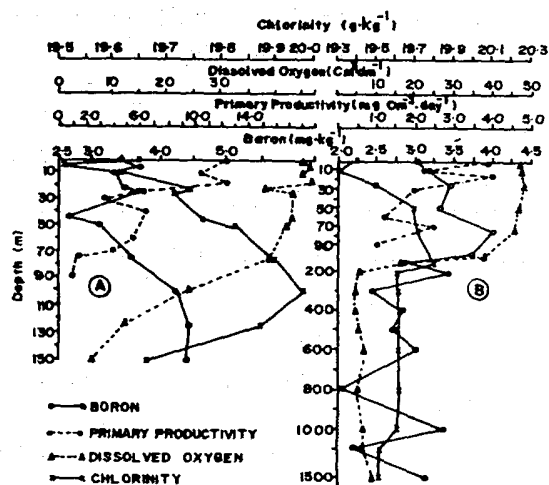


Fig. 4—Vertical profiles of the pooled values of salinity, DO, B and PP in the offshore water

sections such as A, B, D, E and H (Fig. 1) show an average high boron. They also show an inverse relation of boron with DO.

High and low B/Cl ratios with the highest ratio of 0.269 and the lowest of 0.202 observed in this study indicate addition as well as removal of boron along the coast. The percentage addition and removal of boron calculated by taking into consideration the world average B/Cl ratio for seawater⁶ (0.232), gave an addition from 0.43 to 16% and a removal from 0.43 to 11.6% in the coastal waters. This shows that boron is getting added to the coastal waters from some other sources. Addition of boron can be either due to the *in situ* production or due to addition from external sources or both. The former includes oxidation of organic matter, weathering of rocks and endothermal release of boron from sediments^{7,8}. The latter includes external sources such as industrial effluents and/or sewage discharges either drained directly or indirectly into the sea and the land drainage.

The first and foremost of these reasons, if considered, may contribute very significantly towards the addition of boron to the extent of 16%. The correlation coefficient (r) values between boron and DO though negative at most of the transects they are weak at some transects. Secondly, the river water⁹ contains on an average $13 \mu\text{g.l}^{-1}$ of boron so it need not necessarily contain high boron unless and until the river water flows over the bed rock containing boron and is therefore not a significant contributing factor. Except in very shallow and turbulent waters the boron released from sediments due to the endothermal reactions shows high values in bottom water. The alternate source, for boron could therefore be the

external one such as the industrial and/or the sewage discharges and the land drainage. As no investigations were made regarding the type of industries present and the effluent discharges along the west coast, the fact cannot be ascertained. However, the distribution profiles (Fig. 2) indicated increased concentrations of boron at 13°N off the coast of Mangalore. Similar increases were seen occurring at 9°N of the coast of Cochin.

Along the coast of Mangalore, Mangalore Chemicals and Fertilizers, Kudremukh Iron Ore Company Limited - the biggest iron ore producing plant - alkali manufacturing plant and other industries drain their effluents into the coastal water off Mangalore and the enhancement of boron levels resulting from such discharges cannot be ruled out. Shirodkar¹⁰, while working on the behaviour of boron in the Mandovi estuary found exceptionally high values in the upstream due to the drainage from mining wastes.

The reason for the removal of boron observed from 0.43 to 11.65% at some locations in the coastal region could be either due to the biogenic and/or the abiogenic processes. The biogenic processes include the uptake of boron by marine organisms. The area under investigation is a very productive and a dynamic region^{11,12} with primary productivity generally remaining high for most part of the year. The column productivity of the coastal waters off Goa studied by several workers varied from 0.15 to 270 $\text{mg Gm}^{-2}.\text{h}^{-1}$. Similarly, along the west coast of India, the primary productivity in the coastal waters was almost thrice the offshore values. The average column value reported^{13,14} for primary productivity was $474.56 \text{ mg Gm}^{-2}.\text{day}^{-1}$. Such high plankton production can greatly deplete boron levels in the sea. Subba Rao¹⁵ while studying the primary productivity of nanoplankton observed significant depletion of boron from seawater. This shows that the dissolved boron is being depleted by the plankton during their productivity.

The abiogenic processes include complexation of boron with some major elements like Na, Mg and Ca and with organic cis-diols; the adsorption of boron on to suspended sediment particles which removes boron from water and deposits it in the sediments and the evaporation of boric acid from seawater. In the coastal water, intense turbulence and the churning action caused by winds resuspend the settled sediment which has a great potential for boron removal by adsorption^{16,17}. Byrne and Kester¹⁸, indicated that 76% of the total inorganic boron occurs as undissociated boric acid and the rest as borate anion and of the total borate anion, 44% is

complexed with major elements. The result of all these processes is to decrease the boron content. It is for this reason in the coastal region, high and low values are observed. Thus in the euphotic zone boron is utilized by phytoplankton. In addition, the abiological processes remove dissolved boron from seawater. This abiogenic material along with the undigested organic matter settling from top finally reaches the sediment. This study when compared with the one in the offshore water gives a skeletal picture of boron cycle in seawater. The data in the offshore region show relatively low concentrations of boron from 2.89 to 4.75 mg.kg⁻¹. The highest values of B/Cl observed were from 0.241 for the deeper layer and 0.238 for the upper layer. However, the variation in B/Cl in the upper 90 m euphotic layer from as low as 0.171 to as high as 0.238 indicates the deviation towards negative side showing removal. The surface values of boron (3.26 ± 0.045 mg.kg⁻¹), primary productivity (8.161 mg C.m⁻³.day⁻¹) and DO (4.62 cm³.dm⁻³) show lower boron concentrations increasing slightly below and again decreasing further down up to 40m (Fig. 4). Boron starts increasing from 50 m onwards and this variation of boron shows an antipathetic relationship with primary productivity indicating removal of boron during high productivity. The increasing values of boron at depth show an inverse relation with DO indicating that the boron utilized during the productivity in the euphotic layer is released into the water at depth where the concentration of oxygen is low.

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