

INFLUENCE OF POLLUTION OF BORON CHLORINITY RATIO

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Presence of boron in domestic wastewater has resulted in high B/Cl ratio at some locations in the coastal water around Bombay. A widest range (0.215-0.281) of B/Cl was observed at a location with high influence of wastewater release. The mean B/Cl decreased at locations situated away from the polluting sources. In the histograms showing the frequency distribution of B/Cl the range in which most B/Cl values prevailed was same as that of unpolluted coastal water (0.224-0.230) whereas, at a location affected by severe sewage pollution the range of the most frequent B/Cl occurrence was higher (0.230-0.236). Nearly 45-71 per cent of B/Cl values at all stations were higher than the highest limit (0.230) for unpolluted coastal water, giving a graphic clue to B addition through external sources. Among the higher values, the frequency of occurrence decreased with the magnitude of B/Cl range, indicating a slow rate of removal of the externally added B.

A negative intercept on the B axis after the linear least square regression analysis of B and Cl data pairs revealed B loss at one location perhaps due to absorption by clay minerals. However, at other locations, the positive intercept on the B axis increased directly in line with the severity of pollution at those locations.

INTRODUCTION

Boron, considered as one of the major elements in seawater, is present at a concentration of 4.5 mg kg^{-1} at $35 \text{ (} \times 10^{-3} \text{)}$ salinity and bears a constant ratio of 0.232 with chlorinity (Cl) (Culkin, 1965). However, significant scatter in B/Cl observed at some coastal and oceanic regions has suggested that B may not be considered as a conservative element. The natural composition of seawater in the coastal zone may be subjected to changes arising from the runoff from agricultural lands or mining activities and discharge of sewage, and industrial wastes. Hence a widely varying B/Cl in the coastal water may be expected if the wastewaters transport significant quantities of B.

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The presence of B in domestic wastewater results from the use of borates and perborates in detergents and washing powders. B is shown to be present in free form in sewage and passes unchanged through biological treatment processes (Waggott, 1969; Mathews, 1974). The soluble nature of boric acid implies that high B/Cl may result in aquatic system affected by pollution unless all the added B is removed by physical or chemical processes. The fate of B added through the industrial wastewater was studied in Ambika River estuary (Narvekar and Zingde, 1983) where B/Cl gradually decreased in the seaward direction before the excess B was completely removed.

The domestic wastewater ($1.8 \times 10^6 \text{ m}^3 \text{ day}^{-1}$) generated in Bombay city was released untreated or partially treated to nearby creeks, bays or directly to the coastal water through point discharges. It has been estimated that around 450 t of BOD, 63 t of N, 11 t of P, 0.18 t Cu, 0.36 t of Zn and 0.09 t of Pb entered the marine waters every day through domestic wastewater alone (Zingde, *et al.*, 1979; Zingde, 1989). In addition the coastal waters also received industrial wastewater major fraction of which was released in Thana Creek and Ulhas River. Hence, the creeks and bays around Bombay have shown distinct deterioration of water quality. In this paper we have presented a one year data of B and Cl variation at four locations in the coastal water surrounding Bombay which are polluted to various extents.

The distribution of B has been used in identifying and tracing the water masses in the regions such as Tokyo Bay (Miyake and Sakurai, 1952) and Bay of Bengal (Narvekar *et al.*, 1980). This paper concentrates on the variable B/Cl ratio revealing its importance as an indicator of the spread of pollution in the coastal water around Bombay. The B/Cl ratio is expressed as B (mg kg^{-1})/Cl ($\times 10^{-3}$) throughout this article.

MATERIALS AND METHODS

Sampling : Surface and bottom water samples were collected from four stations (sts 1 to 4; Fig. 1) every month during high and low tides. Surface samples were collected using a clean polycyethylene bucket and a plastic Niskin sampler was employed to collect water from 1 m above the bottom sediments. Samples from surface and bottom were also collected from 37 stations (Fig. 1) during heavy downpour in August and September. Nine surface samples were collected from a known unpolluted region off Navapur (Latitude $19^\circ 48'N$; Longitude $77^\circ 39'E$), located 100 km north of Bombay, to serve as a reference for comparison. To measure the B levels in raw sewage, 26 samples were collected from seven sewage treatment plants situated in Bombay (Fig. 1).

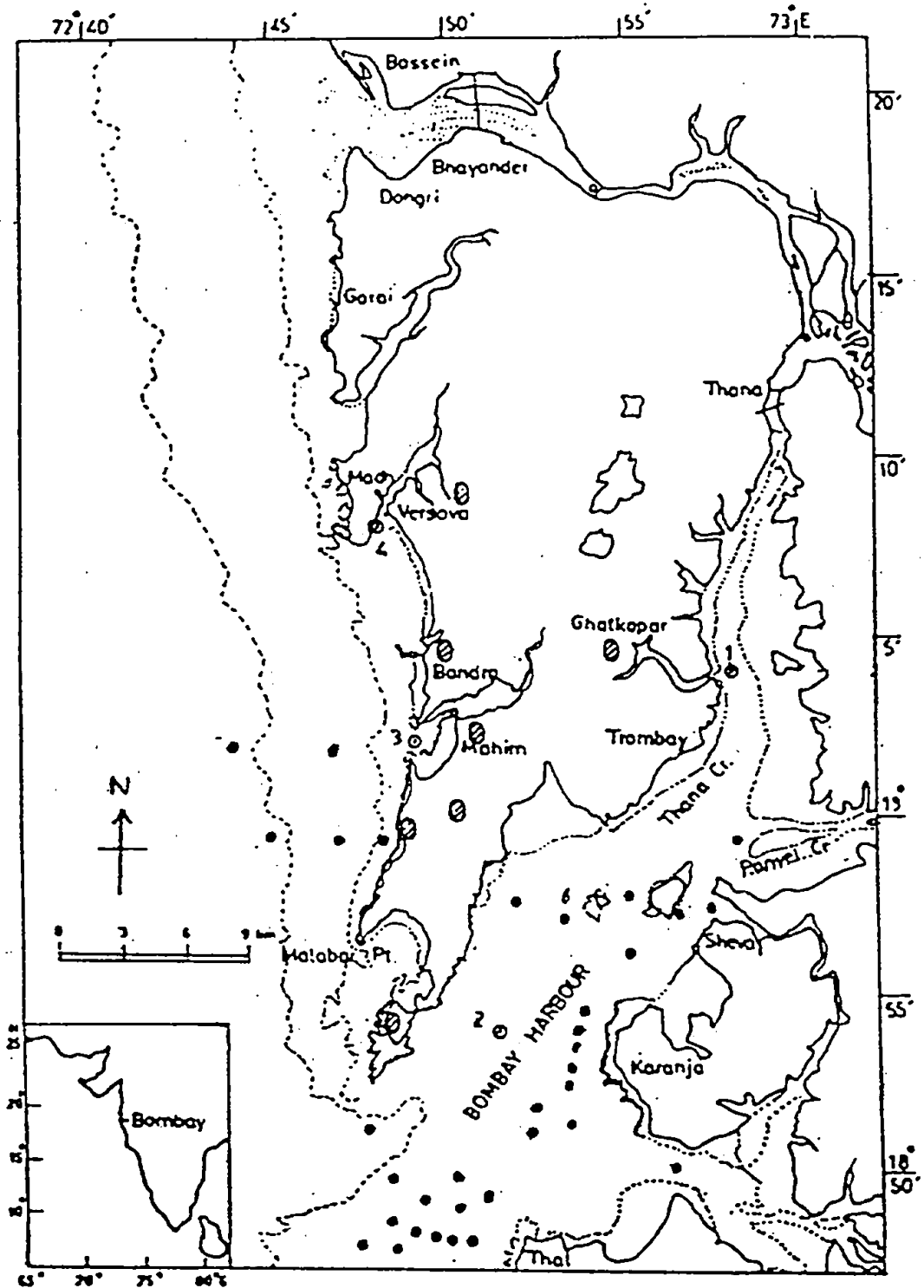


Fig. 1. Locations of sampling stations : (●) year round sampling; (○) monsoon sampling; (⊙) wastewater treatment plants.

Sample storage and analyses : Sample were collected in precleaned 100 ml capacity hard polyethylene bottles which were half filled and closed with

leak-proof stoppers. Samples were thereafter stored deep-frozen until the analyses which were completed within 30 days after collection.

The automated procedure of Hulthe *et al.* (1970) was modified and applied manually for the determination of B. Propionic anhydride, oxaly chloride and acetone were replaced by acetic anhydride, hydrochloric acid and methyl isobutyl ketone respectively. Vigorous reaction between water and acetic anhydride was controlled by taking 0.1 ml of sample. Replacement of acetone by methyl isobutyl ketone eliminated probable errors due to the evaporation of acetone. Beer's law was obeyed upto a B concentration of 5 mg l^{-1} and the standard deviation (SD) in the concentration range from 2.40 mg l^{-1} to 4.56 mg l^{-1} was ± 1.2 per cent (Narvekar, 1979). Chlorinity was determined by argentometric titration of samples (Grasshoff, 1976) with 0.15 M solution of silver nitrate using an automatic precision burette (Metrohm Herisau, E415, Switzerland). The SD in the chlorinity determinations above chlorinity 1 ($\times 10^{-3}$) was ± 0.05 per cent.

RESULTS AND DISCUSSION

Unpolluted coastal water:

Mean values of Cl, B and B/Cl and their variations in 9 samples from coastal waters of Navapur are shown in Table 1. Cl and B levels varied over a narrow range while B/Cl ranged within 0.224-0.230. The relative SDs of the methods of B and Cl determinations allowed a limit of ± 0.003 for the spread of B/Cl due to the experimental uncertainties. The B/Cl range in Navapur samples were covered by this limit and a mean B/Cl value in these samples (0.228) was considered as representative of the unpolluted coastal water.

Polluted coastal water around Bombay:

Station 1: Thana Creek where st 1 was located (Fig. 1) formed the upper reaches of the Bombay Harbour. The creek is open at its south-west approach to the Arabian Sea and connected at its northern extremity to the Ulhas River and Bassein Creek. The creek received industrial wastewater estimated at $1.5 \times 10^5 \text{ m}^3 \text{ day}^{-1}$ (MCGB, 1979). The major industries included fertilizer, petrochemicals, thermal power station, nuclear, pharmaceuticals and chemicals. The tidal effect is felt earlier in Thana Creek as a result of which water may flow from the former into the latter during high tide. Since water recedes earlier in the Thana Creek, the Ulhas River water carrying pollutants may also flow into the Thana Creek (Zingde, *et al.*, 1979).

To have an idea about the quantity of B introduced through domestic wastewater we analysed 26 samples of sewage collected from seven sewage treatment plants marked in Fig 1. Boron levels in these samples measured from 0.10 mg l⁻¹ to 0.85 mg l⁻¹ with a mean of 0.32 mg l⁻¹. With a flow of 5 x 10⁵ m³ day⁻¹ of domestic wastewater in Thana Creek the boron fluxes through this source alone would be 160 kg day⁻¹.

Strong influence of monsoonal freshwater flow was evident from the decline in Cl levels from July to August (Fig 2) which increased thereafter due to the reduction in freshwater flow. B levels in different months varied in line with the corresponding Cl values. The linear least square regression analysis of 39 B and Cl data pairs revealed the following relationship :

$$B \text{ (mg kg}^{-1}\text{)} = 0.231 \times Cl \text{ (} \times 10^{-3}\text{)} + 0.028 \text{ (} r = 0.99\text{)}$$

It should be noted at this point that the intercept should not be mistaken as B level at the point of its entry. The positive intercept on the B axis represented a net B addition in time and space that overbalanced any loss of B from the water in the immediate vicinity of the sampling location. B addition at st 1 was most likely through domestic and industrial wastewaters for the following reasons:

In the histogram (Fig. 3) showing the frequency of B/Cl occurrence, we have chosen a class interval of 0.006 which was equivalent to the spread of B/Cl due to the experimental uncertainties. It was noticed that the most frequently occurring values fell in the range represented by the unpolluted coastal water i.e. 0.224-0.230. Among all values, 64 per cent were beyond 0.230 indicating predominant B addition. Survey of literature showed no evidence of salinity-induced desorptive release of B from the suspended sediments which would give rise to high B/Cl. It was, therefore, possible that any contribution over and above the naturally occurring B levels must come from external sources.

Station 2: The Cl range at st 2 throughout the year was narrow (Fig. 2) and on the higher scale as compared to st 1 (Table 1) which was due to the proximity of st 2 to the open sea. B levels varied in line with Cl (Fig. 2) and yielded the following equation:

$$B \text{ (mg kg}^{-1}\text{)} = 0.236 \times Cl \text{ (} \times 10^{-3}\text{)} + 0.103 \text{ (} r = 0.99\text{)}$$

The negative intercept on the B axis implied the net B removal from the water in the vicinity of st 2. The harbour region also received sewage and industrial discharges and the B addition, therefore, could be possible directly as well as through the polluted creek water that influenced st 2 during ebb

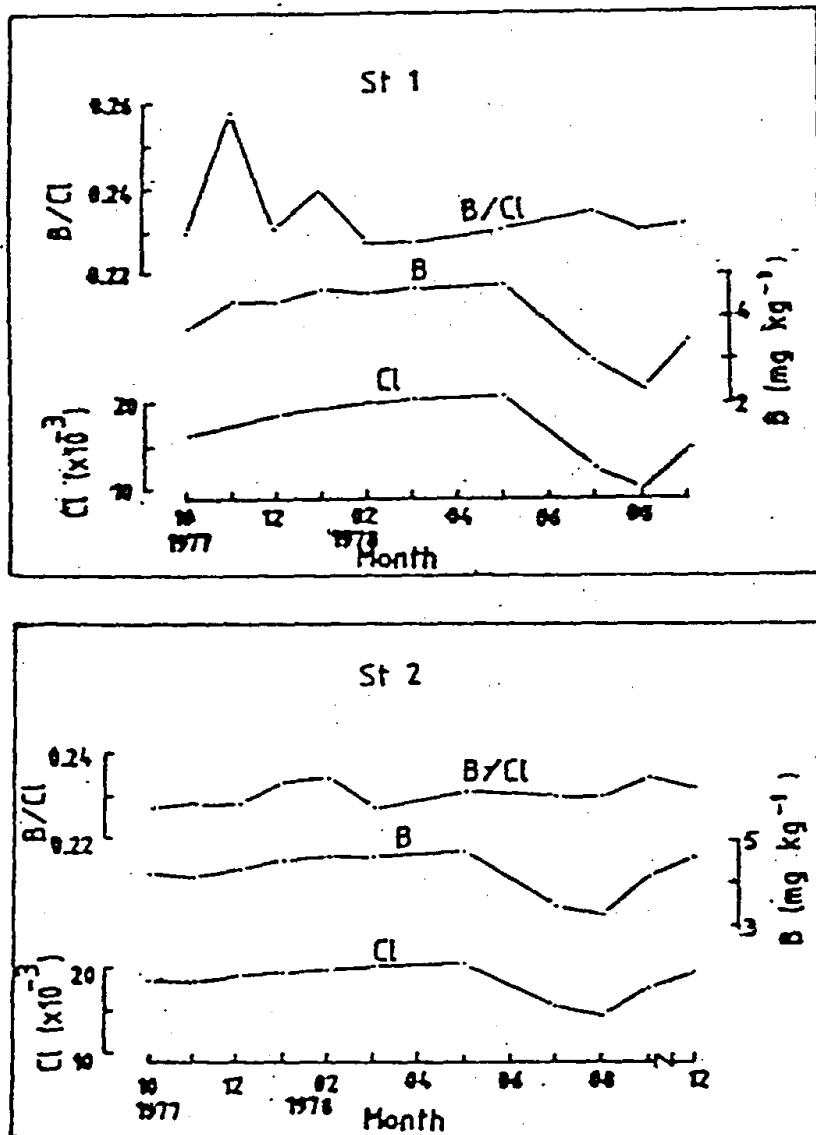


Fig. 2: Variation of B, Cl and B/Cl during different months at sts 1 and 2.

tide. The strong currents sweeping the bay dispersed fine grained and poorly sorted bottom sediment into the water column resulting in high and variable suspended matter in water. The load was generally below 100 mg l^{-1} during the dry season. The increased turbulence during monsoon and the high particulate matter associated with the runoff resulted in substantial increase in suspended matter and the values exceeding 200 mg l^{-1} were commonly observed. The suspended matter was largely inorganic in nature as evident from its low carbon content (<6 per cent) (Zingde, 1989). It was possible that B added was partially removed by suspended clay minerals similar to 25-30 per cent removal in Alde River estuary (Liss and Pointon, 1973) or removal upto 34, 27 and 25 per cent in Anbika, Purna and Mahi River estuaries

respectively (Narvekar, *et al.*, 1983; Narvekar and Zingde, 1987; Narvekar, 1986). It has been shown that natural clay minerals, especially illites are the best adsorbants for the element. Furthermore, the uptake of B by clays was suggested to occur in two steps; adsorption of B perhaps on the hydrous metal oxides, followed by more permanent incorporation in the tetrahedral sites of the mica structure of the clay minerals (Harder, 1970).

Table-1: Range of Cl, B and B/Cl at various locations.

Station	1	2	3	4	Monsoon	Navapur
No. of samples	39	36	38	45	80	9
Cl ($\times 10^{-3}$)	1.61 -21.00	13.02 -21.36	5.25 -20.32	13.12 -20.47	0.70 -18.57	19.67 -19.72
B (mg kg^{-1})	0.39 -4.90	2.99 -4.96	1.13 -4.79	2.99 -4.74	0.17 -4.30	4.50 -4.61
B/Cl	6.224 -0.262	0.223 0.244	0.215 -0.281	0.223 -0.249	0.207 -0.255	0.224 -0.230

From the histogram (Fig. 3) it was noticed that the most repeatedly occurring B/Cl values were in the range 0.224-0.230. About 50 per cent of the total values were on the higher side of this range despite the removal occurring at st 2. The high values in the histogram suggested that the continuous addition of B from external sources dominated the subsequent removal in the lower span of the bay. The high values beyond 0.230 therefore represented a transient stage towards the attainment of the equilibrium state of a nearly constant ratio observed in the open sea. The highest value of B/Cl at st 2 was less accentuated (Table 1) as compared to other stations, which was due to removal at st 2.

Station 3 : Mahim Bay where st 3 was located was fed by highly polluted Mahim River estuary. The strong tidal influence prevailing in Mahim Bay reduced considerably in the estuary due to an abrupt bed elevation and sudden narrowing of the channel cross-section. The release of $1.2 \times 10^5 \text{ m}^3 \text{ day}^{-1}$ of domestic wastewater in addition to industrial wastes through variety of sources, had resulted in abnormally high levels of $\text{PO}_4^{3-}\text{-P}$, $\text{NO}_3^{-}\text{-N}$, $\text{NH}_4\text{-N}$ and BOD in the bay with wide temporal variations. Dissolved oxygen (DO) was generally low and reduced close to zero particularly around low tide. The estuary on the contrary was totally devoid of DO with the presence of sulphide in the water

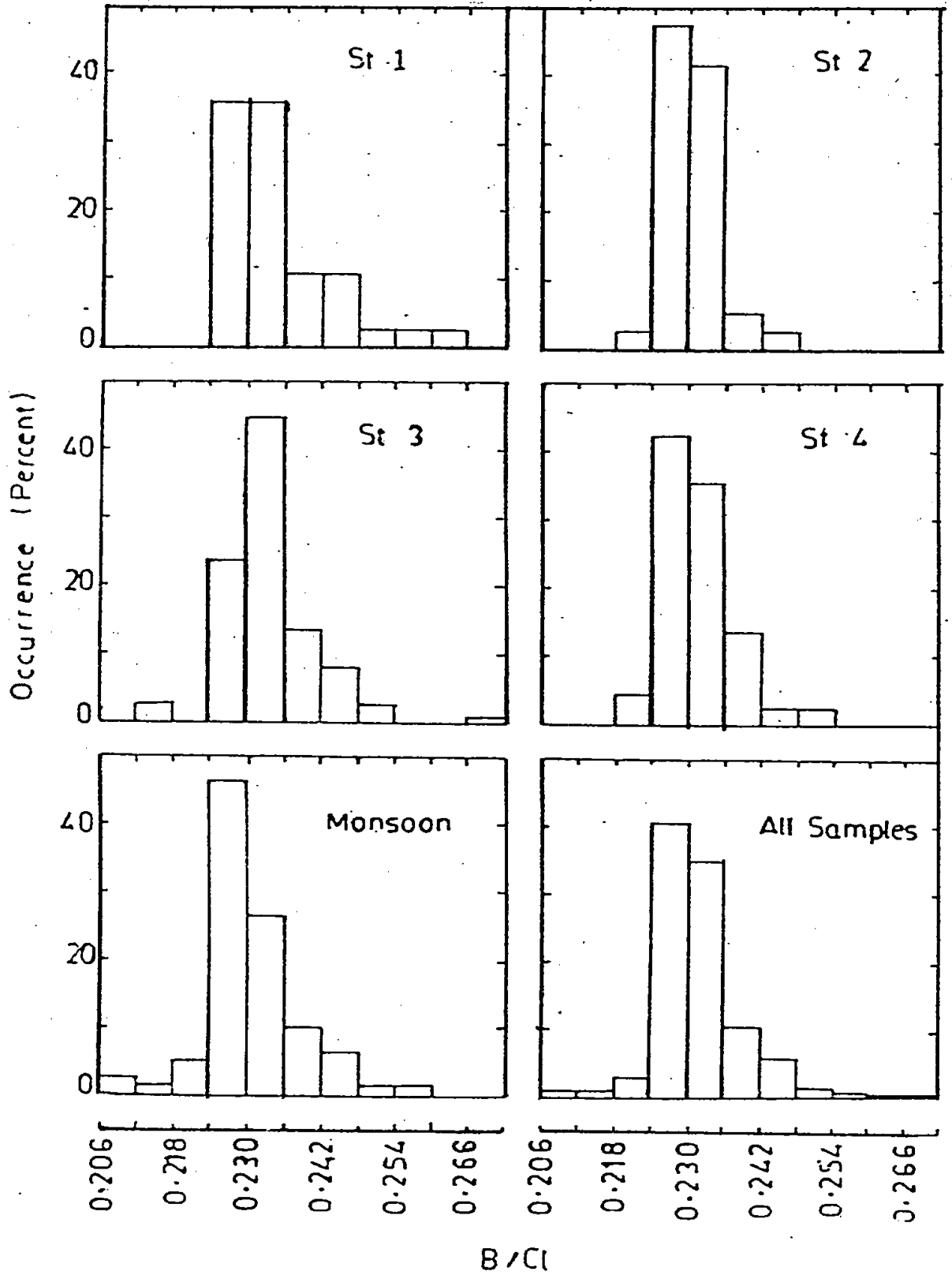


Fig. 3: Frequency of B/Cl occurrence at different locations.

column (Sabnis, 1984). Markedly low diversity of fish larvae and low mean biomass of zooplankton with the dominance of *Paracalanus*, *Oithona* and *Acartia* has been observed off Mahim (Gajbhiye *et al.*, 1982). The benthic fauna though abundant at the bay entrance, was either absent or sparse in the inner regions.

The domestic wastewater transported 58 kg day⁻¹ of B into Mahim Bay. Monthly variations in B, Cl and B/Cl are shown in Fig. 4. The regression analysis of B and Cl data in 38 samples resulted in the following relation:

$$B \text{ (mg kg}^{-1}\text{)} = 0.219 \times Cl \text{ (} \times 10^{-3}\text{)} + 0.258 \text{ (} r = 0.99\text{)}$$

The high intercept value of 0.258 which was close to the mean B level in the sewage (0.32 mg l⁻¹) suggested high addition of B through the combined wastewater discharge in which the sewage component was dominant. The similarity between the magnitude of intercept and the mean B level in sewage was obvious in the light of high influence of domestic wastewater at st 3.

Histogram (Fig. 3) showed that the range 0.230-0.236 encompassed the largest number (45 per cent) of B/Cl values as compared to other ranges. This was unlike the other stations where the encountered ranges of most frequent B/Cl occurrence were similar to the one represented by unpolluted coastal water i.e. 0.224-0.230. This was a single station where maximum number (71 per cent) of the total values were higher than 0.230. The entire range of B/Cl variation was also the widest among the ranges observed at other stations (Table 1). All these variations were the effects of the excessive external B addition augmented further by the proximity of st 3 to the discharge point.

Station 4: St 4 was located outside the mouth of the Versova Creek and indicated only marginal influence arising from 8.2 x 10⁴ m³ day⁻¹ of domestic wastewater released near the head of the creek (Fig. 1). The wastewater was considerably diluted by the time it reached st 4. This was evident from the narrow Cl range (Table 1) which was similar to that at st 2. Biochemical oxygen demand and levels of nutrients were also lower and comparable to the locations further away from the coast (Zingde *et al.*, 1979). The equation of the best fitting line after linear regression of 45 B and Cl data pairs was:

$$B \text{ (mg kg}^{-1}\text{)} = 0.226 \times Cl \text{ (} \times 10^{-3}\text{)} + 0.094 \text{ (} r = 0.98\text{)}$$

The higher intercept compared to st 1 was expected in light of the B addition through sewage discharge in the nearby Versova Creek. The histogram

(Fig. 3) exhibited the most frequently occurring B/Cl (42 per cent) falling within the range 0.224-0.230. About 53 per cent of values exceeded the upper limit of this range indicating remnant B addition after it's partial removal,

Monsoon : The monsoon collection included 65 samples from the east coast and 15 samples from the west coast of Bombay. The samples covering almost the entire Cl range [$0.70 (x 10^{-3}) - 18.57 (x 10^{-3})$] showed a wider B/Cl range (0.207-0.255) with a mean of 0.230 (Table 1). Following relationship was observed between B and Cl data pairs:

$$B \text{ (mg kg}^{-1}\text{)} = 0.229 \times Cl \text{ (} \times 10^{-3}\text{)} + 0.013 \text{ (} r = 1.00\text{)}$$

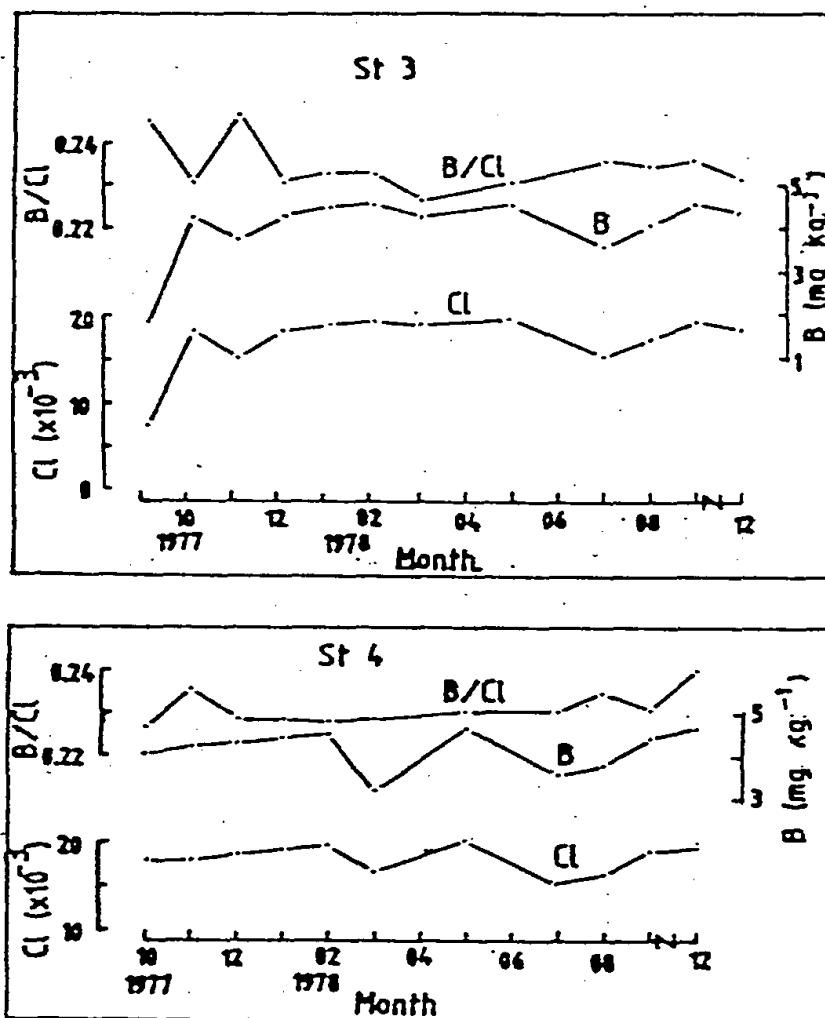


Fig. 4: Variation of B, Cl and B/Cl during different months at sts 3 and 4.

A small positive intercept and 45 per cent values exceeding 0.230 (Fig. 3) could be explained as a combined effect of pollution and higher B/Cl observed in the rainwater. Handa (1969) has reported B and Cl values in the samples of monsoon rains over Calcutta from which B/Cl was calculated. B/Cl in these samples was found to vary from 1.3 to 130. Similarly a mean B concentration in a rainwater sample collected from the coastal town of Daman (Latitude 20 5'N; Longitude 72° 52'E) was 0.04 mg l⁻¹. The associated Cl in this sample was <0.01 (x 10⁻³) giving a magnitude of >4 for the B/Cl ratio (Narvekar, 1979). A high B/Cl ratio (1.5) decreasing in the seaward direction was observed in Damanganga River during a period of rainwater floods. Also, very high addition of B (23-109 per cent) was encountered in Mahi River estuary during monsoon (Narvekar, 1986). These examples are compatible with the high B/Cl encountered in the rainwater and point to the rainwater as a possible source of B addition to water.

When all 238 samples collected from the coastal water around Bombay were taken together for the analysis, the mean B/Cl (0.232) was higher than the value for unpolluted coastal water (0.228). Also, the linear least square regression analysis of all B and Cl data pairs (Fig. 5) resulted in the following equation:

$$B \text{ (mg kg}^{-1}\text{)} = 0.230 \times Cl \text{ (x } 10^{-3}\text{)} + 0.023 \text{ (r} = 1.00\text{)}$$

The positive intercept gave an idea of average B addition to the coastal water around Bombay after accounting for the quantity removed through adsorption/removal by the suspended clays. An intercept of 0.054 reported for the Baltic seawater (Dyrssen and Uppstrom, 1972) was attributed to the contribution by rivers that brought freshwater to the Baltic Sea.

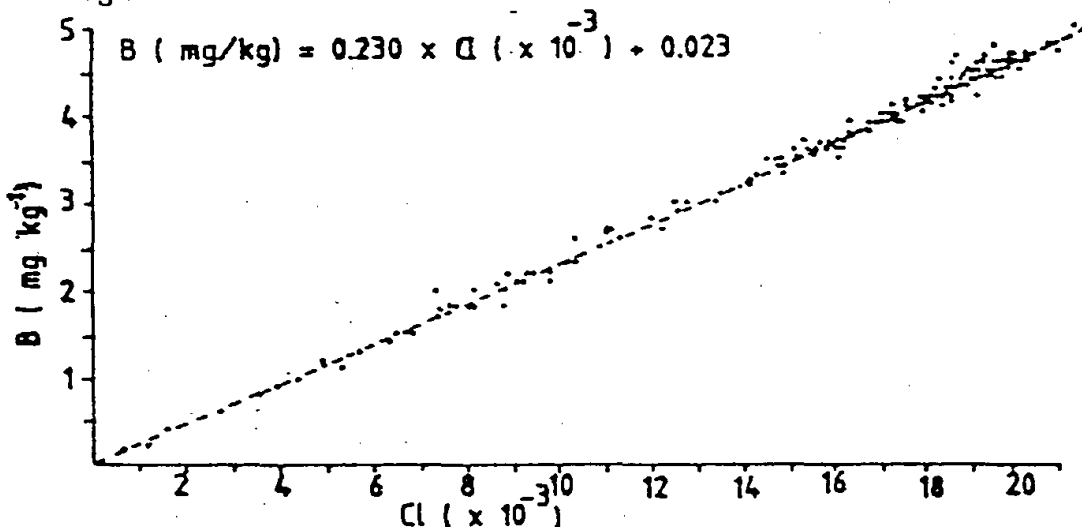


Fig. 5: Variation of B against Cl in the coastal waters of Bombay.

Histogram (Fig. 3) for 238 samples revealed 40 per cent of B/Cl values accumulated over the range of unpolluted coastal water i.e. 0.224-0.230, the observed 55 per cent values beyond 0.230 were due to excess B that remained in solution. The frequency of occurrence decreased with an increase in the magnitude of B/Cl range. This observation further supported the slow removal of externally added B from water. A gradual removal of B was also observed in Ambika and Mahi River estuaries (Narvekar *et al.*, 1983; Narvekar, 1986) where B was added through industrial effluents.

The range of mean B/Cl and intercept at four stations in the order st 2,4, 1 and 3 increased directly in line with the extent of influence by wastewater. Sts 2 and 4 which were located away from wastewater releases and less affected by pollution revealed decreased influence on B/Cl. It followed, therefore, that as the open sea conditions are approached, the externally added B would eventually be removed by the suspended clays.

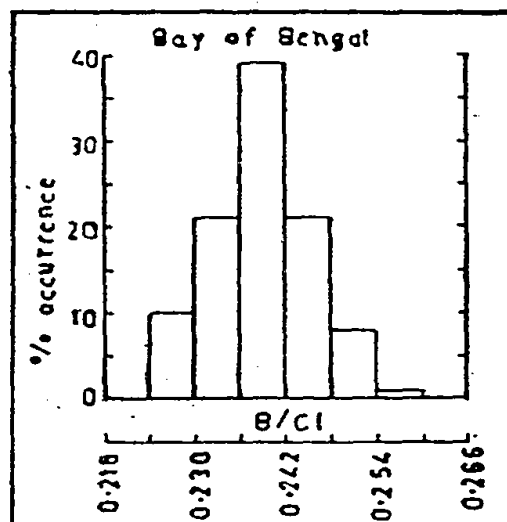


Fig. 6: Frequency of occurrence of B/Cl in Bay of Bengal.

Fluctuations in B/Cl in the absence of external addition have been observed in the depth profiles of deep oceans which are attributed to processes of introduction and elimination of B from seawater in partly independent ways (Dyrssen and Uppstrom, 1972). These fluctuations are due to the intrusion of water mass carrying a signature of its characteristic B/Cl ratio (Miyake and Sakurai, 1952) and/or the release of B due to oxidative breakdown of organic borate complexes in the oxygen minimum zone (Gast and Jhomson, 1958; Noakes and Hood, 1961). In the Bay of Bengal, a general trend of B and Cl variation at seven stations separated by a distance of 500 km was similar (Narvekar *et al.*, 1981) which suggested that the B loss by uptake in the surface layer was balanced by the release in the oxygen minimum zone. A histogram drawn for

100 samples of seven depth profiles in the Bay of Bengal, therefore, showed (Fig. 6) a nearly normal distribution of B/Cl ratio. On the other hand, 45-71 per cent values which were higher at four stations around Bombay (Fig. 3) suggested B addition through external sources and subsequent slow removal from water.

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