

Chemistry & Behaviour of B, Ca & Mg in Interstitial Waters of Sediments from the Coastal and Estuarine Regions of Mandovi River along the West Coast of India

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Interstitial waters of coastal and estuarine sediments show enrichment of B and Ca and a decrease in Mg. Increase in interstitial B in sediments is due to the downward diffusion from overlying water and release from solid phases by physico-chemical endogenous processes. Mg decrease is due to its uptake by clay minerals having a greater cation exchange capacity under reducing conditions. Ca^{2+} and Mg^{2+} released from carbonates at lower pH in sediments are governed by some physico-chemical processes. Salinity remains high in most of the sediments rich in clay and silt as compared to the sandy sediments, due to the semi-permeable character of clay and silt. Organic carbon in sediments (av. 1.6%) does not seem to indicate a definite relation with B but affects pH, indicating the releases of acidic compounds by the breakdown of organic matter.

Differences in behaviour exhibited by some of the major elements in an aquatic environment when they migrate from one aquatic phase to another are observed in one of the most critical boundaries of the aquatic system—the interstitial water. This pore water reflects the reactions of post depositional stages of the sediments which occur between the sediment components and the interstitial water and thus participate in the marine geochemical cycle in acting as a zone in migrating the soluble products and the reactants of diagenesis from sediments back to seawater and vice-versa.

Studies in the estuarine environment have indicated that the chemistry of pore water depends on the salinity of the overlying water¹. Some of the major elements like Ca, Mg^{2+} and B⁴ are enriched in pore water relative to overlying water.

Diagenesis controls the geochemistry of interstitial water and pronounced diagenetic effects are observed in sediments rich in clays, organic carbon, higher rate of deposition and greater continental influence⁵. Oxidation of organic matter leads to a loss of some major interstitial ions like Ca^{2+} , Mg^{2+} and K^+ etc. with concomitant increase of these ions in silicate and carbonate minerals. Oceanic sediments are characterised by a gain in Ca^{2+} for a mole by mole loss in Mg^{2+} .

While working on the interstitial waters of the sediment cores off the Gironde estuary, Ghobary⁶ has observed Ca^{2+} dissolution at the first 10 cm of the core and down below precipitation of Ca^{2+} as carbonate. The observed Mg^{2+} depletion is found to be due to Mg-silicate reaction.

In estuaries, the sediments are exposed to overlying water of varying salinities. The objectives of this

investigation is to understand the response of estuarine pore water chemistry to the changing physico-chemical factors and to study the behaviour and chemistry of interstitial B, Ca and Mg of sediments in coastal and estuarine regions of Mandovi river, west coast of India. An attempt has also been made to study the interrelationships between elements in pore water and in overlying water.

Materials and Methods

Sediments were collected during monsoon (Sept. 1982); post-monsoon (Dec. 1982 and Jan. 1983) and premonsoon (Feb. 1983) from different stations as shown in Fig. 1. The stations occupied were in the coastal (M_1 to M_2); estuarine (M_3 - M_6) and upstream (M_7 - M_9) regions of the estuary.

Water samples were also collected simultaneously at the same stations from surface, mid-depth (av. 3 m) and bottom levels (av. 6.5 m). Observed concentrations of different water properties in these samples were

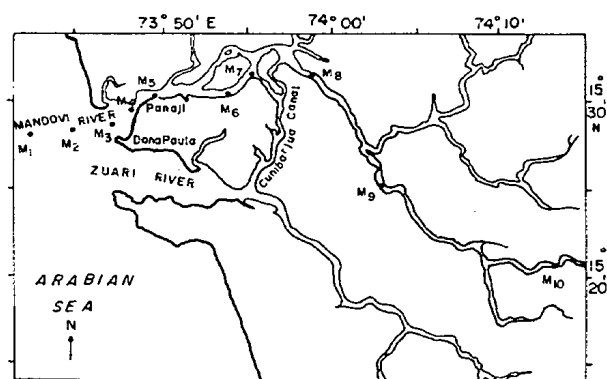


Fig. 1— Map showing the location of stations

integrated as this river remains well mixed from surface to bottom during the dry seasons, except during monsoon when stratification develops to some distance from its mouth. As no facility was available to find the *in situ* pH, the 'punch in' method was adopted for pH and Eh measurements⁷. The porefluid was extracted by vacuum filtering of the sediment (pressure 12 mm Hg) through 0.45 μ membrane filter paper. Mud squeezer was not used in order to avoid the anomalies that develop in some major interstitial cations during squeezing⁸. The interstitial water (3-5 ml) obtained from the sediment samples was divided into 2 parts. One part was acidified and used for the analyses of B, Ca and Mg whereas, the other non-acidified portion was used for the estimation of salinity. The samples were stored in deep freeze and were analysed within 2-3 days.

Salinity was determined by Knudsen's method⁹, B was analysed by curcumin method¹⁰ with appropriate dilution of the sample wherever necessary. Standard deviation for the method was $\pm 1.15\%$ and the standard error was 0.00206. Ca and Mg were analysed by atomic absorption spectrophotometer (Hilger and Watts, model H-1550). The coefficient of variation for Ca was $\pm 0.05\%$ and $\pm 0.03\%$ for Mg. Grain sizes were determined by sieving and pipette analyses¹¹ whereas the nomenclature based on sand-silt-clay ratio was found out as per the model given by Shepard¹². Glycolation method was used for mineral analyses¹³ and percentage of clay minerals was determined by the weighted peak area method¹⁴.

Results

Sediments in the coastal and estuarine regions had a reducing environment during post-monsoon and pre-monsoon seasons (Oct. - May), with Eh varying from -10 to -217 mv, whereas during monsoon season (June - Sept.) oxidising conditions prevailed with Eh ranging from +190 to +322 mv. In the coastal region, sediments were muddy being rich in silt and clay whereas upstream they were mostly sandy (Table 1).

The important clay minerals found were montmorillonite, illite, kaolinite and chlorite with montmorillonite being the most abundant in nearshore sediments (Table 2). Organic carbon varied from 0.07 to 2.9% (av. 1.6%).

pH—Interstitial waters had lower pH relative to the overlying water ranging from 6.7 to 7.44 and 7.03 to 7.39 in the estuarine and coastal regions respectively. The seasonal variations in interstitial pH followed the same trend as in the overlying water. In few cases, pH was close to the overlying water probably because tidal currents alternately resuspend the settled

Table 1—Texture and Grain Sizes of Sediments during Different Sampling Periods

St	Grain size (%)			Texture
	Sand	Silt	Clay	
	Premonsoon			
M ₁	1.67	60.2	38.15	A
M ₂	18.62	60.64	20.74	A
M ₃	82.95	13.61	3.44	B
M ₄	59.38	31.29	9.33	C
M ₅	22.14	23.33	54.33	D
M ₆	30.09	24.00	45.90	D
M ₇	80.46	5.01	14.53	B
M ₈	75.12	4.85	20.03	B
M ₉	69.09	3.17	27.47	E
	Monsoon			
M ₄	14.03	58.02	27.95	A
M ₅	62.19	26.13	11.68	C
M ₆	25.21	45.78	29.01	D
M ₇	88.98	7.34	3.68	B
M ₈	16.04	54.27	29.49	E
	Postmonsoon			
M ₁	24.71	50.81	24.48	D
M ₂	80.04	14.76	5.20	B
M ₃	16.35	55.65	28.32	A
M ₄	33.89	45.93	20.19	D
M ₅	31.74	54.47	13.79	F

A. clayey-silt; B. sand; C. silty sand; D. sand-silt-clay; E. clayey sand; and F. sandy-silt

Table 2—Clay Mineral Abundance in Nearshore Sediments

St.	Weighted peak area percentages			
	Montmorillonite	Kaolinite	Illite	Chlorite
M ₁	54-67 (av.60.8)	27-41 (av.34.35)	2-6 (av.4)	1
M ₂	57-66 (av.61.50)	32-38 (av.35)	2-5 (av.4.5)	1

sediment that retain large amounts of water and thereby lower the pH.

Salinity—Water salinity remained high in the coastal region than in the estuarine region with a decreasing trend upstream (Fig. 2). In the estuarine region, interstitial salinity remained higher than in the coastal during all the seasons.

Boron—Interstitial B remained high relative to the overlying water and ranged from 0.02 to 6.11 mg.kg⁻¹ (av. 3.46 mg.kg⁻¹). The concentration decreased from mouth towards upstream; with lowest values during monsoon (Fig. 3). Boron values when plotted against pore water chlorinity gave a linear relation ($r = +0.76$, significant at 95% confidence limit).

Calcium—Interstitial Ca appeared to be enriched

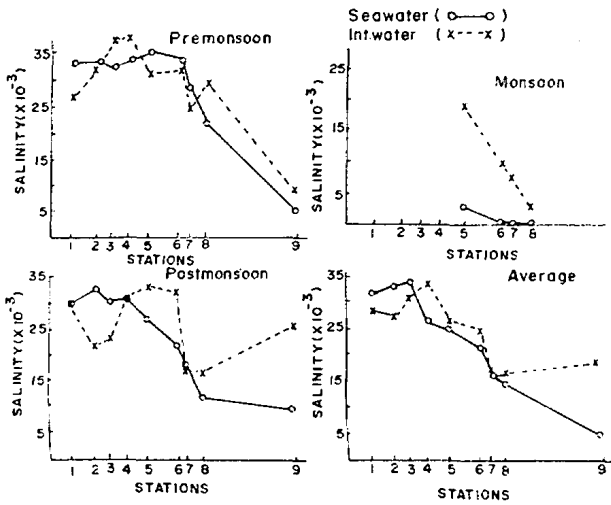


Fig. 2—Sptial variation in salinity of interstitial water and the seawater [In Figs 2-7 numbers 1,2,3 9 given under stations (X-axis) represent respectively sts M₁, M₂, M₃ M₉]

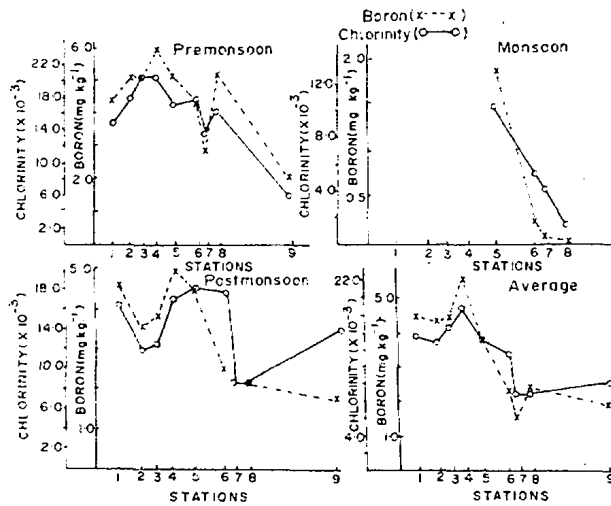


Fig. 3—Spatial variation in boron and chlorinity in interstitial water

(0.066 to 1.523 g.kg⁻¹) relative to overlying seawater. It did not indicate significant linear relationship with chlorinity. Both these factors indicate the non-conservative behaviour of pore water Ca. It generally decreased from mouth towards upstream with occasional higher concentrations in the upstream relative to the overlying water (Figs 4 and 5).

Magnesium—Variation of interstitial Mg was identical to that of the overlying water, Mg remaining higher than Ca. In contrast to Ca, interstitial Mg remained somewhat lower than seawater Mg except for 1 or 2 stations (Fig. 6). No good linear relationship existed between Mg and porewater chlorinity indicating its non-conservative behaviour. Low levels of Mg were observed at st M₆ in premonsoon and monsoon probably due to its involvement in the

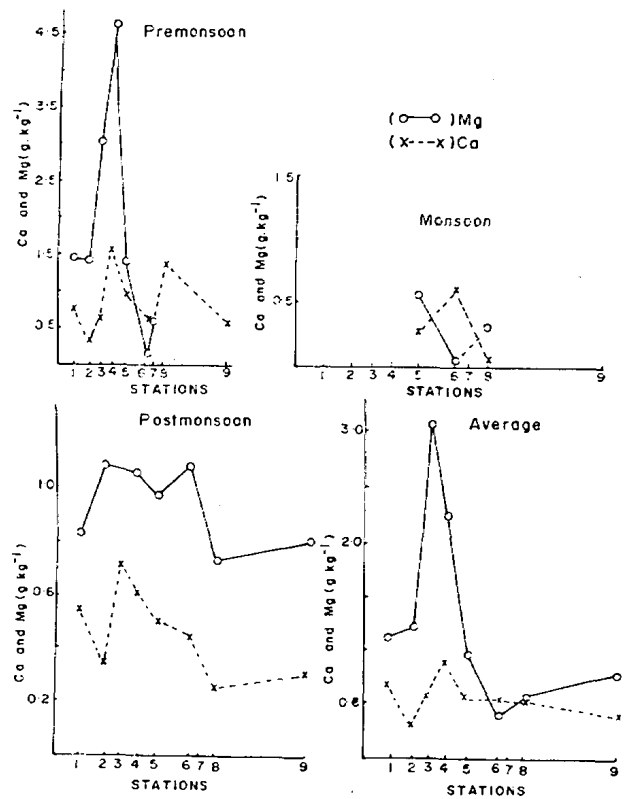


Fig. 4—Spatial variation in Ca and Mg in interstitial water

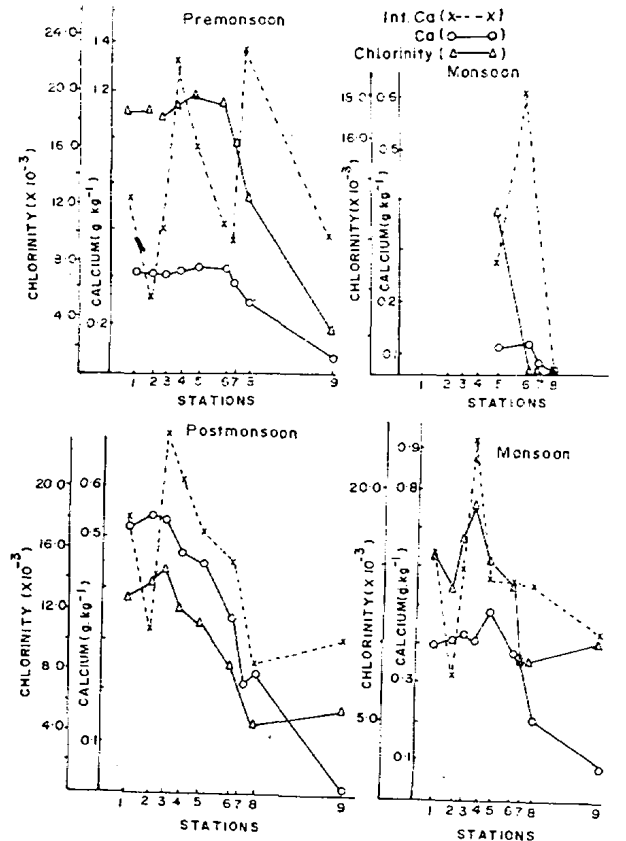


Fig. 5—Spatial variation in Ca in interstitial water and seawater with respect to overlying water chlorinity

precipitation or in other physico-chemical processes; whereas the higher concentrations were due to its greater mobilization in the pore fluids.

Discussion

Chemical characteristics of interstitial water from sts M_1 to M_9 throughout the period of investigation when compared with those of overlying seawater indicated an enrichment of B in both the reducing and the oxidising sediments. Observed positive gradients (Table 3) indicate the addition of major ions to interstitial water due either to diffusion or to release

from solid phases. Close to the river mouth (st M_4) the concentrations of B and Ca in the interstitial water remained elevated throughout the period of observation, whereas, Mg remained low compared to those in the overlying bottom water (Figs 3 and 4). At this station, the enrichment of B was calculated to be of a factor of 1.5 whereas at stations upstream the increase was by factors of 1.9 to 2. Along the estuarine transect the enrichment factor was on an average of 1.36. At the same station, the enrichment of Ca was by a factor of 3.6 (maximum) with an average of 1.8 along the transect. Higher B was thought to be due to the release from organic matter in the sediments by oxidation¹⁵. But, interstitial B and organic matter did not show significant correlation thereby indicating no clear picture of the source of B to be the organic matter, although the sediments were rich in organic matter. Horizontal profiles of B, pH and organic matter showed an inverse relation of B with pH whereas the organic matter followed the trend as B variation indicating organic matter to be a partial source of B. This is clearly seen at st M_1 and M_4 (Fig. 7).

B was more enriched in sediments of low

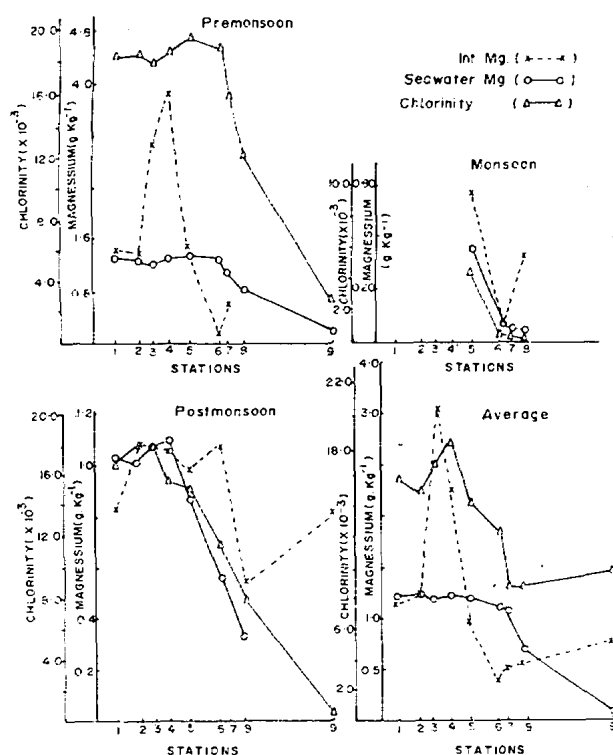


Fig. 6—Spatial variation in Mg in interstitial water and seawater with respect to overlying water chlorinity

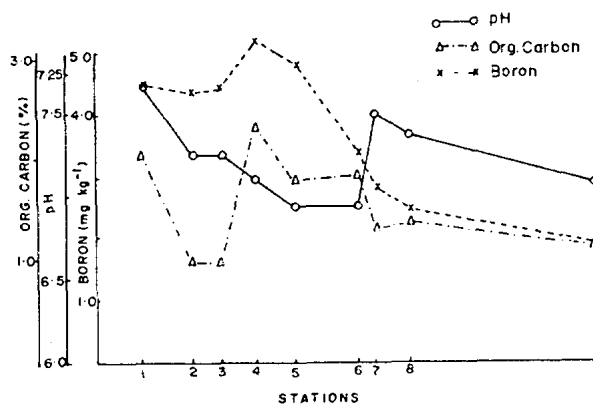


Fig. 7—Spatial variation in boron and pH in interstitial water (average)

Table 3—Changes in Concentration of Major Ions in Interstitial Water
[Values indicate enrichment (+) or decrease (–) relative to overlying water]

	Premonsoon			Monsoon			Postmonsoon		
	B	Ca	Mg	B	Ca	Mg	B	Ca	Mg
M_1	+0.49	+0.327	+0.202	—	—	—	+0.58	+0.127	–0.297
M_2	+0.85	–0.146	+0.044	—	—	—	–0.43	–0.092	–0.032
M_3	+1.12	+0.145	+1.713	—	—	—	–0.20	—	—
M_4	+2.07	+1.111	+3.365	—	—	—	+1.98	+0.391	–0.216
M_5	+1.12	+0.514	+0.032	–0.43	+0.149	+0.185	+0.56	+0.235	–0.011
M_6	–0.62	+0.196	–1.206	–0.06	+0.478	+0.036	—	—	—
M_7	–0.56	+0.165	–0.572	+0.018	—	—	—	—	+0.469
M_8	+2.54	+1.068	—	–0.034	+0.037	+0.132	—	—	—
M_9	+1.01	+0.497	—	—	—	—	—	—	—

depositional rates and the observed increases were calculated to be due to the dissolution of feldspar or illite^{16,17}. Present results indicated an increase of B by a factor of 1.5 relative to seawater at st. M₄ which is not due to the low depositional rate of suspended sediment but may probably be due to the transfer of sediments from the coastal region with tides. Turbulence is high at stations close to the river mouth and the sediments here are muddy with more clay and silt. This results in shifting of the sediments from coastal region into the estuary mouth.

Low values of B observed during monsoon seem to be due to the upward eddy diffusion¹⁸; which involves the physical stirring of the superficial sediments by tidal currents that exert a shear on the superficial sediments. This churning of the sediments by freshwater influx lowers the interstitial salt content and in the process, the sediments with more clay and silt release leachable B during transportation of sediments resulting in low concentrations during monsoon. It can thus be inferred that a change in the ratio of major ion to chlorinity in interstitial water is not necessarily due to the involvement of these ions in chemical reactions or migration. B/Cl ratio showed a range of 0.015 to 0.366, the lowest value appearing during the monsoon. The increases, in ratio may be due to the release of adsorbed B by mineral phases in the sediment or due to downward diffusion and advection from the overlying water.

In the upstream stations located in the mining area, B/Cl ratios remain higher than the average (0.22). This may be due to the effect of mine drainage containing some B. By molecular diffusion, this B enters the interstitial water in the sediments giving rise to higher values. The physico-chemical endogenous processes liberate B from sediments into the interstitial water¹⁹⁻²¹ which in turn is returned to the overlying water causing concentration gradients. It is found that B uptake by sediments is more at higher pH²² and vice-versa. The observed values of pH were lower, sometimes below neutral pH. This seems to be one of the important factors responsible for the increase of interstitial B in Mandovi estuary. The role of diffusion of ions and molecules in the geochemical processes of mass transport between the sediment and the overlying water depicts that the ionic interaction resulting from the requirements of electroneutrality may extensively modify the fluxes of diffusing ions and may also affect the relative distribution of both migrating and non-migrating ions.

Increase in interstitial Ca indicates its under-saturation with CaCO₃ at most of the stations and with partial saturation at few stations. At st. M₂, interstitial Ca is decreased (0.305 g.kg⁻¹) relative to seawater Ca (0.414 g.kg⁻¹) and this can be mostly due

to its precipitation as carbonate⁴. Interstitial water from the boarderland sediments showed greatest depletions in Ca in those sediments which has low phosphate content and high organic matter²³. Comparatively the sediment at st. M₂ was reduced ($Eh = -141$ mv) with high organic matter (2.45%) and this must have lowered the Ca content. Decrease in Ca was due to its precipitation as carbonate resulting from the metabolic activities of micro-organisms degrading organic matter²⁴. On the contrary, lower pH of interstitial water has dissolved the carbonate to increase the interstitial Ca.

Various factors seem to affect the decrease in Mg²⁺ content of pore water. One of such cases observed was in the reducing sediments from the open seas and oceans where low Ca²⁺ and Mg²⁺ and in oxidising sediments slightly higher K⁺ and low Mg²⁺ were observed²⁵. This was due to Mg²⁺ which was lost in exchange to montmorillonite with an increased cation exchange capacity (CEC) under reducing conditions^{26,27}. Secondly, under the reduced conditions, sulfide may react with Fe³⁺ in clays thereby, substituting the loss of Fe by Mg²⁺ and the formation of Mg-clays²⁸⁻³⁰.

In some cases, B increase was mirrored by Mg²⁺ depletion and it was due to the authigenic chlorite formation at the expense of illite - K - feldspar and also montmorillonite³¹. Also, in some of the reduced sediments, Mg²⁺ removed was due to the cation exchange³² and very recently such Mg²⁺ depletion was shown to be due to the Mg - silicate reaction⁶. Percentage of clay is higher at st. M₆ during monsoon and in premonsoon with highly reduced sediments rich in organic matter. One of the above mentioned factors seem to be responsible for indicating the observed low levels of Mg in Mandovi river sediments. On the other hand, the increase in Mg²⁺ seems to be due to the dissolution of carbonate under low pH.

Above observations show that B behaves semi-conservatively whereas Ca and Mg behave purely non-conservatively in the interstitial waters of the sediments of Mandovi river estuary.

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