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Short Communications

Behaviour of Boron, Calcium & Magnesium in Mindola River Estuary (Gujarat)

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The well mixed Mindola River estuary experiences considerable tidal influence with a tidal range of about 3.5 m in the mouth region which reduces to 0.9 m at a point 21 km upstream during neap tide. Boron is preferentially removed over the entire tidal cycle; the maximum removal being 9%. On the contrary calcium and magnesium are preferentially added over the same period though to a small extent. An inverse relationship between calcium and magnesium is probably indicative of ion-exchange reaction between calcium in clays of riverine origin and magnesium in water when the river water encounters sea water.

Exchange of solid solution components under varying chlorinity conditions in estuaries often result in non-conservative behaviour of several ions which normally bear a constant ratio with chlorinity in oceanic waters. The behaviour of silicon in estuarine mixing zones has been studied in some detail, while, boron, calcium and magnesium have been studied only in a few instances and further information on their behaviour is needed to establish definite trends[1]. Reported results for boron in estuaries differ considerably. Liss and Pointon[2] have found non-linear relationship between dissolved boron and salinity for the Alde River estuary and reported 25-30% removal of boron from solution. In contrast, no significant removal has been observed in Chikugogawa[3] and Beaulieu[2] River estuaries. Calcium and magnesium have been reported to be conservative in Chikugogawa River estuary[3], while, in Potomac River estuary[4] only calcium and not magnesium was conservative.

Studies on the estuarine behaviour of boron, calcium and magnesium in Mindola River estuary are reported in this paper.

Samples in estuarine region were collected at 1 hr intervals over complete tidal cycle at st 1 (Fig. 1) on 19.11.1978 and normally every 2 hr on 21.11.1978 at st 2. Samples in the coastal region up to a distance of 10 km from the mouth of the river were also collected thrice for analyses. Surface samples were obtained by a clean polyethylene bucket and Niskin sampler was used for subsurface collections. After collection, the samples were stored in clean, pre-rinsed polyethylene bottles with leak-proof stoppers and preserved in a refrigerator till the time of analysis. The analyses were completed within 30 days from the date of collection.

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The procedure[5] developed for autoanalyser was applied for manual analysis with a few modifications for the determination of boron. Propionic anhydride and oxalyl chloride were replaced with acetic anhydride and hydrochloric acid, respectively and acetone was replaced with methyl isobutyl ketone. Beer's law was observed to be obeyed up to a boron concentration of 5 mg/litre. Standard deviation for the concentration range 2.4-4.56 mg/litre was $\pm 1.2\%$ and is quite comparable to the value reported by Uppstrom[6] for the similar concentration range. Boron in fresh water was determined after concentrating the sample at least 10 times by evaporation under infrared light in presence of mannitol. Samples thus concentrated did not show any loss of boron due to evaporation[7]. Chlorinity was determined by the argentometric titration procedure[8]. Calcium was estimated by titrating the sample to the photometric end point with EGTA using Zincon Zn-EGTA indicator[9]. Calcium, magnesium and strontium were determined together by complexometric titration with EDTA using Eriochrome Black T as indicator. Values for calcium were subtracted to obtain magnesium concentrations. Corrections for strontium and for systematic over estimate of about 1% for the titration end-point were applied[10]. Replicate analyses of water samples gave standard deviation of $\pm 0.13\%$ for calcium and $\pm 0.15\%$ for magnesium.

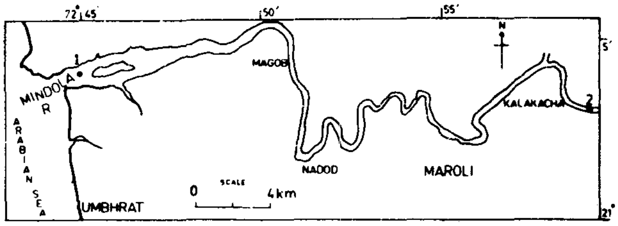

Fig. 1—Location of sampling stations in Mindola River

Mindola River estuary which opens into the Arabian Sea in the region south of Gulf of Cambay experiences substantial tidal influence. Water level measurements conducted at st 1 during sampling by installing graduated staff gauge indicated a tidal range of about 3.5 m during neap tide. The effect was considerably reduced at st 2 where the range was only 0.9 m. The estuary experienced pronounced cycle of fresh water flow during July-September due to monsoon which decreased considerably during the postmonsoon. Strong tidal currents[11] and shallowness of the basin rendered the estuary well mixed and the vertical chlorinity gradient was negligible throughout the tidal cycle. Suspended load exceeding 200 mg/litre was common in the mouth region due to dispersion of silt into the water body by strong currents.

The measured concentrations of boron, calcium and magnesium were plotted against chlorinity as the conservative index (Fig. 2). For straight forward mixing without any loss due to removal (biological or abiological) all points would be on the theoretical dilution line (TDL) joining the end members of the estuarine mixing series that is river water at one end and sea water at the other end. When a chemical constituent is removed from or added to the water, the points will lie below or above TDL indicating, respectively, removal or additon. The mean boron value for samples having chlorinity $<0.1°/_{oo}$ was considered as the low chlorinity end member. To obtain upper chlorinity end member, 6 samples were collected outside the mouth of the estuary and the mean values of boron, calcium and magnesium were 4.15 mg/kg, 0.3888 g/kg and 1.1419 g/kg, respectively. Mean B/Cl ratio of 0.24 was the same as that observed[7] for the coastal region of South Gujarat. The respective ratios for boron and calcium were 0.24 ± 0.0009 and 0.0225 ± 0.0006 respectively and were marginally higher than the normal sea water ratios of 0.232 and 0.02127 respectively[8]. Although the difference lies almost within the reproducibility of analytical methods, the contribution by fresh water through several perennial rivers with high element/Cl ratios cannot be ruled out. Mg/Cl of 0.0671 after an appropriate correction for strontium and end point error[10] reduced to 0.0660 which is little lower than the normal sea water value of 0.0666[8]. Mean concentrations of boron, calcium and magnesium in river water samples collected from st 2 were 0.09 mg/kg, 0.0389 g/kg and 0.0194 g/kg respectively with element/Cl ratios of 0.928, 0.4206 and 0.1937 respectively. Some of the rivers of Gujarat region have higher levels of calcium and magnesium[7] as compared to the world averages of 0.0150 and 0.0040 g/litre respectively[12].

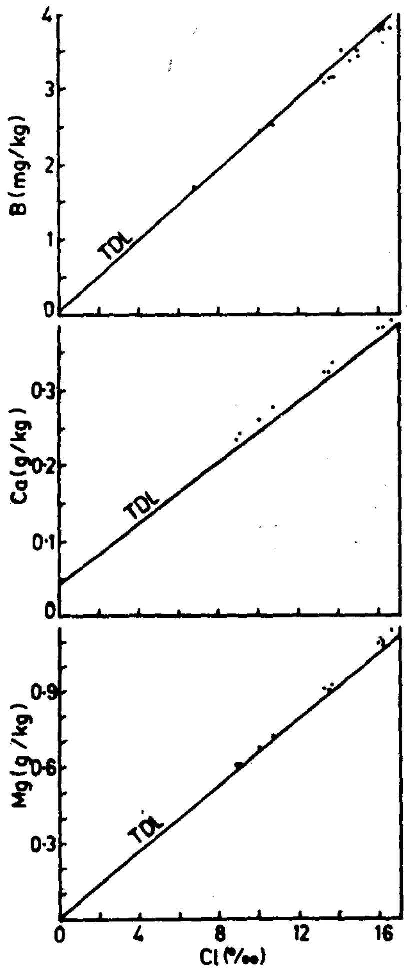

Fig. 2—Variation of boron, calcium and magnesium with chlorinity at st 1

For an ideal behaviour of physical mixing the following equations were derived for TDL (Fig. 2):

$$B\ (mg/kg) = 0.2364\ Cl°/_{oo} + 0.0697$$
$$Ca\ (g/kg) = 0.0201\ Cl°/_{oo} + 0.0453$$
$$Mg\ (g/kg) = 0.0656\ Cl°/_{oo} + 0.0065$$

These equations were used to calculate per cent addition/removal.

Boron was preferentially removed over the entire tidal cycle (Fig. 3) except at 3 instances. The addition though small, was observed at the ebb period. The maximum removal was only 9% as against 25-30% observed for Alde River estuary[2].

Calcium and magnesium were added over the entire period of observation; the maximum addition being 8 and 5% for calcium and magnesium respectively (Fig. 4). An inverse relationship between calcium and magnesium is probably indicative of ion-exchange reaction between calcium in the clays of riverine origin and magnesium in the water when river water encounters sea water. Fresh water clay minerals normally have Ca^{2+} ions occupying majority of ion-exchange sites which can be replaced by Mg^{2+}, Na^{+} and K^{+} when the clay encounters sea water. It was

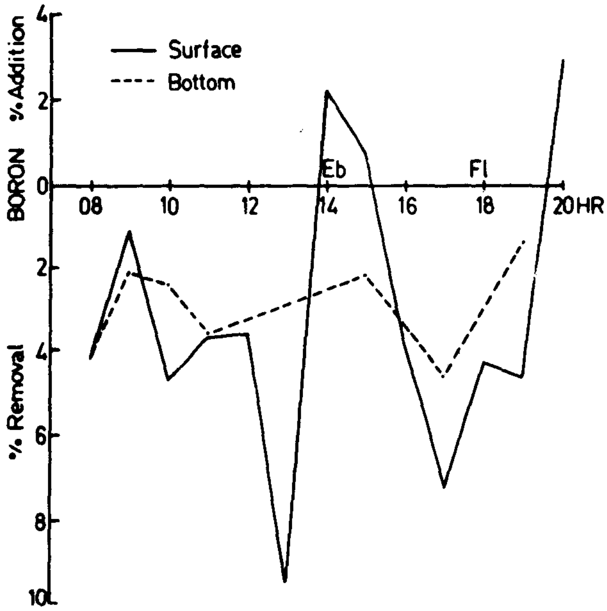

Fig. 3—Per cent addition/removal of boron with time at st 1

shown[13] that the total uptake of Mg^{2+}, Na^{+} and K^{+} by the clays of Rio Ameca River, Mexico, was balanced by the loss of Ca^{2+}.

Although the discussion in this paper is based only on limited data, similar observations[7] for nearby Purna and Ambika Rivers indicated that such processes were predominant at least in these three rivers of South Gujarat.

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References

1 Aston S R, in *Chemical oceanography*, Vol. VII, edited by J.P. Riley & R. Chester (Academic Press, London) 1978, 361.

2 Liss P S & Pointon M J, *Geochim Cosmochim Acta*, **37** (1973) 1493.

3 Hosokawa I, Ohshima R & Kondo N, *J Oceanogr Soc Japan*, **26** (1970) 1.

4 Warner T B, *J Geophys Res*, **77** (1972) 2728.

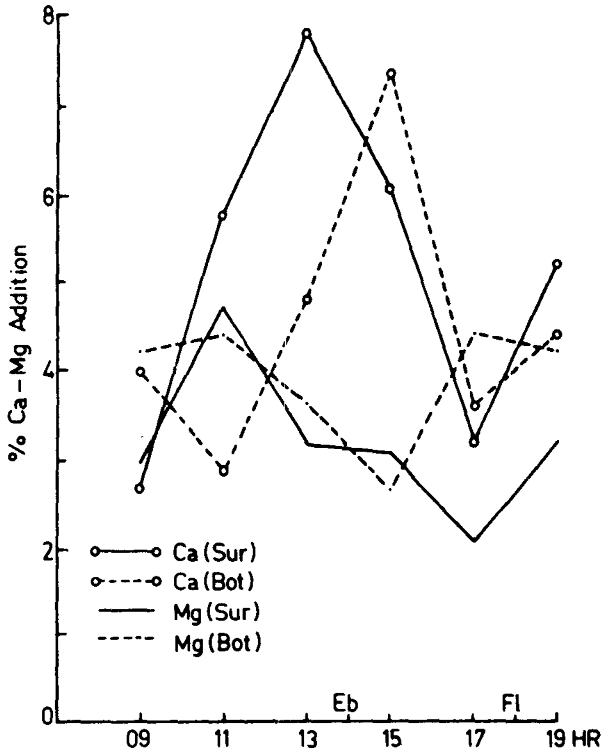

Fig. 4—Per cent addition of calcium and magnesium with time at st 1

5 Hulthe P, Uppstrom L & Ostling G, *Anal Chim Acta*, **51** (1970) 31.

6 Uppstrom L, *Anal Chim Acta*, **43** (1968) 475.

7 Narvekar P V, *Study of boron in marine environment with special reference to boron chlorinity ratio*, M.Sc Thesis, Univ. of Bombay, 1979.

8 Grasshoff K, in *Methods of sea water analysis*, edited by K. Grasshoff (Verlag Chemie) 1976.

9 Culkin F & Cox R A, *Deep Sea Res*, **13** (1966) 789.

10 Sen Gupta R, Naik S & Singbal S Y S, *Mar Chem*, **6** (1978) 125.

11 *Pollution and hydrographic survey of Auranga, Ambika, and Mindola Rivers (South Gujarat)*, (Report submitted to the Gujarat Water Pollution Control Board. NIO, Regional Centre, Bombay) 1980.

12 Livingstone D A, *US Geol Surv Prof Pap* 440-G, 1963.

13 Russell K L, *Geochim Cosmochim Acta*, **34** (1970) 893.