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DISTRIBUTION AND BEHAVIOUR OF BORON AND FLUORIDE IN RUSHIKULYA ESTUARY (SOUTH COAST OF ORISSA)

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ABSTRACT

Chlorinity varied from 1.063 to 14.486% in the estuarine water. The chlorinity showed positive correlation with boron and fluoride, which indicated similar source origin of the elements to the estuary. Boron and fluoride varied from 0.122 to 0.198 g/L and from 0.25 to 0.99 g/L respectively. The B/Cl and F/Cl ratio showed variation from 0.0640 to 0.1288 and from 0.0683 to 0.2446 respectively. The elements (boron and fluoride) to chlorinity ratio showed maximum value during monsoon, whereas minimum during summer. The more fresh water influx into the estuary during monsoon is responsible for higher values of B/Cl and F/Cl. Boron showed non conservative behavior during monsoon, postmonsoon and winter, whereas semi conservative behavior during premonsoon and winter. There were net removals of boron and fluoride during the study period. The PA/PR of born was positively correlated with chlorinity, whereas the correlation between chlorinity and PA/PR of fluoride did not show any significant value.

INTRODUCTION

Behaviour of many elements in estuarine mixing zones often differ considerably from their well known conservative nature in seawater due to interactions between solid solution components, adsorption, ion exchange and

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variation in ionic strength (Liss and Pointon, 1973). Factors controlling the behaviour of an element in the mixing zone of one estuary may differ from those of another and could result in its differential behaviour in different estuaries. The levels of major constituents generally do not exhibit appreciable changes in the oceanic and in coastal water. They bear a relatively constant ratio with chlorinity. The concept of constant ratio in estuarine environment is a misnomer. 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 after the level of some important biogeo-chemical elements (Barnes and Green, 1979).

Boron is an essential plant micronutrient and occurs in seawater to the extent of 4.5 mg/kg at salinity 35% (Wilson, 1975). According the Levinson and Ludwick (1966) boron is differentially adsorbed and deposited on suspended matter during estuarine mixing. Harris (1969) has attributed the removal of boron from waters to adsorption on detrital clays. Similar observations have been made by Liss and Pointon (1973) in their studies in Alde estuary, England. Like wise similar studies on removal mechanism and behaviour of boron have been made by several workers in different estuaries (Hosokawa *et al.*, (1970) in Chikugogawa river, Narvekar *et al.*, (1981)in Mindola river estuary, Narvekar et al., (1983) in Ambica estuary, Narvekar and Zingde (1987) in Auranga estuary. Ghosh and Jana (1993) in Hooghly estuary and Padmavathi and Satyanarayana (1999) in Godavari estuary). Fluoride has long been considered as an acute pollutant to natural environment because of the ability of plants and marine organism to accumulate it and because of its detrimental effects upon aquatic biota, which can be affected by concentrations as low as 1.5 mg/L (Wright and Davison, 1975). Several workers reported the behaviour and removal of fluoride in different estuarine environments (De Souza and Sen Gupta 1988) in Mandovi and Zuari estuary, Zingde and Mandalia (1988) in Auranaga river estuary, Sarma *et al.* (1993) in Gouthami Godavari estuary and Padmavathi and Satyanarayana (1999) in Godavari estuary). But there is no such report on the distribution and behaviour of boron and fluoride in Rushikulya estuary. The present investigations have been undertaken in the said estuary to understand the distribution and behaviour of these two chemical constituents during estuarine mixing in different seasons.

MATERIALS AND METHODS

Basing on the meteorological condition of Rushikulya estuary (lat 190 22′-19024′N and long 85002′-85004′E), five different seasons namely monsoon (July- Sept), postmonsoon, (Oct-Nov), winter (Dec -Jan), premonsoon (Feb-Apr.) and summer (May-June) are experiences . The sampling was undertaken during these seasons in 1999-2000 at seven selected stations (Fig-1), which cover the entire estuary. The surface water samples were collected using polythene bucket, while bottom water samples were collected 1.5 m below the surface using shallow water sampler. The samples were collected

1.5 m below the surface using shallow water sampler. The samples were filtered through Whatman GF/C filter papers. Before filling, the acid cleaned polythene bottles were rinsed 2/3 times with the respective station water. These filled polythene bottles with leak proof stoppers were preserved in a refrigerator till analyses, which was completed within a month from the date of collection. Generally, samples preserved in refrigerator give no change in result even after 1 month storage.

Chlorinity determinations were made using argentometric titration pro-

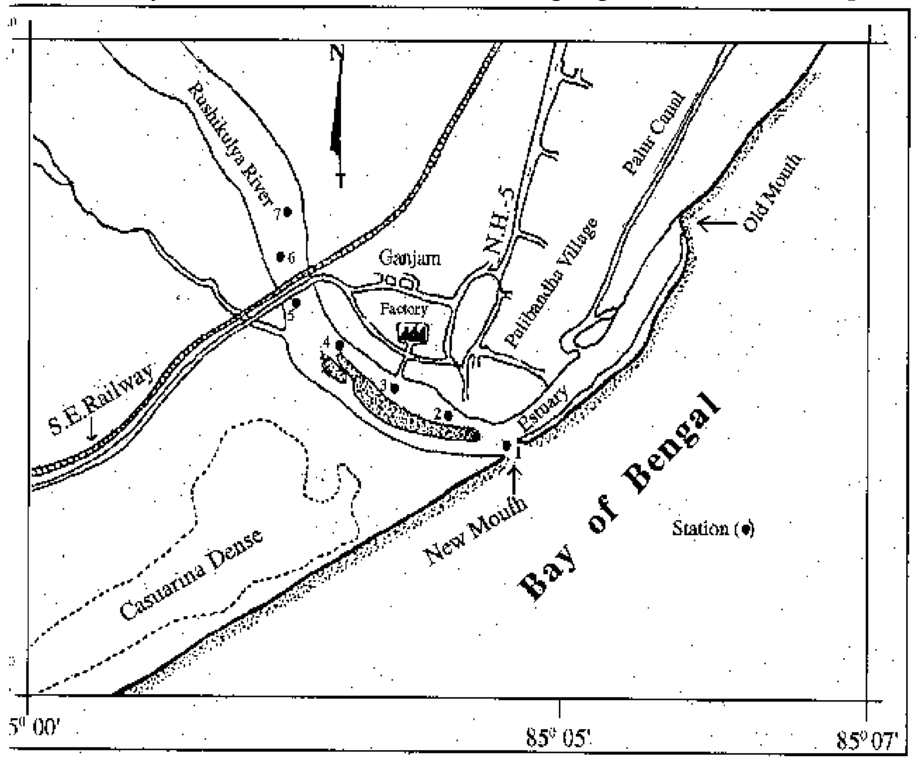

Fig. 1- Location map of Rushikulya estuary showing sampling stations

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cedure (Grasshoff, 1976). The procedure developed by Hulthe et al., was modified and applied for the determination of boron. Propionic anhydride and oxalyl chloride available locally gave erroneous results. Hence, these were replaced by acetic anhydride and hydrochloric acid respectively. Acetone was also replaced by acetic anhydride and hydrochloric acid respectively. Acetone was also replaced by methyl isobutyl ketone to avoid uncertainties due to evaporation of acetone. Fluoride was measured spectrophotometrically (Greenhalgh and Riley, 1961). The ANOVA test was done by MS Office- 2000, Excel Package. When a chemical constituent is removed from or added to the water, the points would lie wither below or above the TDL depending on removal or addition of the constituents under study. Theoretical concentrations (pth) were directly obtained from the equations derived for TDL (Table-1) and the percentage of addition (PA) or removal (PR) was obtained from the

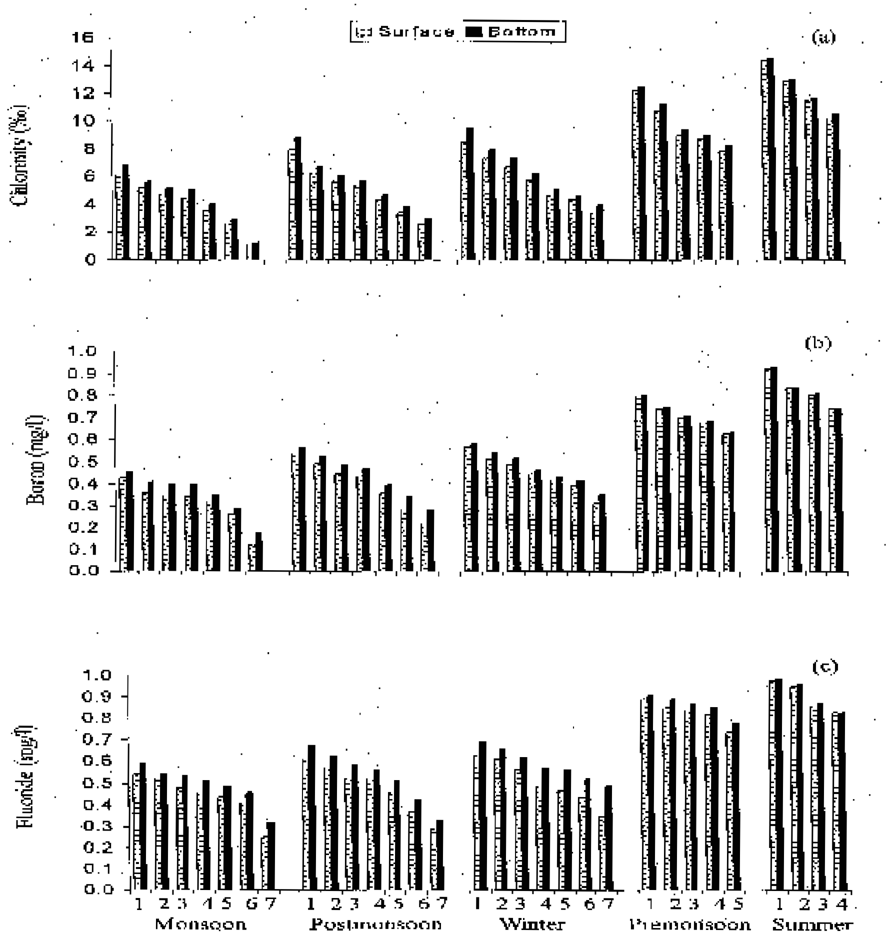

Fig. 2- Seasonal variations of chlorinity, boron and fluoride in Rushikulya estuary

knowledge of the measured concentration of dissolved property (Pm) by using the relation PA and PR =100 (Pm/Pth)-1)). The positive sign for the result would indicate addition and negative sign would indicate removal. Correlation coefficient between PA and PR of elements (B and F) and chlorinity were calculated after converting all negative PR values to positive by raising all values (PA and PR) converting all negative PR values to positive by raising all values (PA and PR) through certain positive number (Narvaker and Zingde, 1987).

RESULT AND DISCUSSION

Chlorinity

Chlorinity fluctuations in an estuarine milieu vary seasonally depending upon the admixing of high chlorinity seawater and riverine fresh water in

differing volumes (Choudhary and Panigrahy, 1991). It recorded relatively lower values during monsoon as compared with other seasons under study for surface and bottom water. The lower values during monsoon may be due to intense precipitation, freshwater influence and land drainage (Padmavathi and Satyanarayana, 1999). Higher values observed during premonsoon and summer indicated minimum influence of fresh water resulting in maximum interference of marine environment in the estuary (Das *etal.*, 1997). High surface evaporation and cessation of fresh water inflows during premonsoon and summer result higher value of chlorinity. The bottom water chlorinity concentrations were more than the surface ones (fig- 2a) at all the stations during the seasons under study. The difference in chlorinity concentrations between surface and bottom were very less during premonsoon and summer, whereas more during other seasons (winter, monsoon an postmonsoon) . Thus, the chlorinity distribution suggests slight stratification during winter, postmonsoon and monsoon, whereas well mixed conditions during premonsoon and summer. This can be attributed to fairly high river discharge during monsoon postmonsoon and winter resulting in this well mixed type of estuary. Similar observations were found in other estuaries (Upadhayay, 1988 and Mahapatro and Padhy, 2001).

The correlation coefficient of chlorinity with major elements (Born and Fluoride) showed highly positive correlation. From this it is conformed that, the sources of these major elements are similar to the chlorinity, in the estuary. The interstation comparison of surface and bottom water showed significant value at 0.01% level whereas the interseason comparison for the same showed significant value at 5% level (Table-2)

Boron

It showed an increasing trend from reiverine to estuarine (St. 7 to St. 1) during all the seasons. The bottom water concentrations showed higher values than the surface one at all the stations during the seasons under study (fig. 2b). It may be due to its utilization by phytoplankton. It may not also be the primary factor responsible for lower boron content at surface even though it is an essential micronutrient (Narvekar *et al.*, 1981). Some fraction is also removed from seawater during the formation of antigenic silicate and by adsorption onto siliceous oozes (Porrenga, 1967). The order of boron concentration during study period was summer> premonsoon>winter >postmonsoon>monsoon. Highest concentration was observed at station 1 during summer, whereas lowest at station 7 during monsoon. During monsoon. The estuary was flooded an almost throughout its course, it was predominant with freshwater. So, the concentration of boron was also considerably low during this season and reverse during summer due to scanty freshwater input to the estuary. According to Rajagopal *et al.*, (1981) low values during monsoon was due to high influx of fresh water from the river containing relatively low concentration of boron into the estuary. The boron showed highly significant positive correlation with fluoride and chlorinity. The interstation comparison of surface and bottom water showed significant value at 0.01% level. The interseason comparison of bottom water showed significant value at 5% level ,whereas the interseason

TABLE -1

Regression equations, percentage of addition (PA) and removal (PR) of B and F and B/Cl and F/Cl ratio.

	Equation for TDL	Range of B/Cl or	Range of addition	Range of Removal
For Boron	B (mg/l) = 0.0527 Cl (%) +0.1128	0.0683-01.288	0-7.130	0- -16.267
Monsoon	B (mg/l) = 0.0565 Cl (%) +0.1184	0.0663-0.0914	0-4.337	0- -9.955
Postmonsoon	B (mg/l) = 0.0422Cl (%) +0.2054	0.0640-0.0923	0-3.015	0- -7.712
Winter	B (mg/l) = 0.427Cl (%) +02864	0.0651-0.0827	0-3.424	0- -3.479
Summer	B (mg/l) = 0.0424Cl (%) +0.3078	0.0614-0.0720	0-1.828	0- -1.477
For Fluoride				
Monsoon	F (mg/l) = 0.0496Cl (%) +0.2604	0.0875-0.2446	0-8.644	0- -11.827
Postmonsoon	F (mg/l) = 0.0588Cl (%) +0.1923	0.0767-0.1138	0-6.681	0- -13.097
Winter	F (mg/l) = 0.0446Cl (%) +0.2773	0.0737-0.1158	0-4.550	0- -4.327
Premonsoon	F (mg/l) = 0.0412Cl (%) +0.4264	0.0732-0.1002	0-4.762	0- -5.984.
Summer	F (mg/l) = 0.0403Cl (%) +0.414	0.0683-0.0805	0-1.621	0—2.457

comparison of surface water did not show any significant value (table-2).

As regards to conservative behaviour of boron in seawater, the ration remains absouletly constant throughout ocean. The change in the ratio occurs moatly at nearshore regions under the influence of freshwater (Shirodkar and Singbal, 1992). There is annual discharge of 1800 million M^3 fresh water to the sea through Rushikulya estuary (Panigrahy *et al*., 1999), which alters the boron and chlorinity concentrations in the estuary. During the study period B/Cl ratio increased with decrease in chlorinity value. Freshwater of river is responsible for the higher ratio of B/Cl at riverine end than estuarine end (Rajagopal et al., 1981). For this reason highest values during monsoon, whereas lowest values during summer season (Table-1) were found. Highest value during monsoon may be due to drastic crop in chlorinrity associated with heavy fresh water influx. Lowest value during summer may be due to dominance of seawater over riverine water. It showed non conservative behaviour during monsoon, postmonsoon ad winter, which can be attributed to its uptake by sedimentary particles and phytoplankton (Rajagopal *et al.* , 1981). It showed semiconservative behaviour during premonsoon and summer. Similar observation was reported by Ghosh and Jana (1993). There was net removal of boron during the study period. The abiogenic processes include complexion 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

TABLE -2

Analysis of variance (ANOVA) of chlorinity, calcium and magnesium of degree of freedom, SOS- sum of the squares MSOS- mean of the squares, FS- Fischer constant)

Parameter	Position	Sources of variation	SOS	df	MSOS	Fs
		Between stations	316.08	6	52.679	8.4277[c]
	Surface	Between seasons	45.954	4	11.489	2.838[a]
		Residuals	150.02	24	6.2507	
Chlorinity		Between stations	342.49	6	57.081	9.0248[c]
	Bottom	Between seasons	37.825	4	9.4564	2.8951[a]
		Residuals	151.8	24	6.3249	
		Between stations	1.2733	6	0.2122	6.1894[c]
	Surface	Between seasons	0.1602	4	0.0401	2.1683[NS]
		Residuals	0.8229	24	0.0343	
Boron		Between stations	1.2458	6	0.2076	5.8497[c]
	Bottom	Between seasons	0.1013	4	0.0253	2.9134[a]
		Residuals	0.8518	24	0.0355	
	Surface	Between stations	1.5316	6	0.2552	5.7212[c]
		Between sesaons	0.0857	4	0.0214	2.48[NS]
Fluoride		Residuals	1.0708	24	0.0446	
		Between stations	1.491	6	0.2485	5.0649[b]
	Bottom	Between seasons	0.0715	4	0.0179	2.3641[NS]
		Residuals	1.1775	24	0.0491	

Note- a= Significance at 5% level, b= Significance at 1% level

C= Significance at 0.01% level, NS- Not significant.

deposits it in the sediments and the evaporation of boric acid from estuarine water (Shirodkar & Singbal 1991). In the estuarine water, intense turbulence and the churning action caused by winds resuspend the settled sediment, which has a great potential for boron removal by adsorption (Levinson and Ludwick, 1966 and Hosokawa *etal*., 1970). Bryne & Kester (1974), 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 the reason for which the low concentration of boron observed in estuarine water. Thus in the eutrophic zone boron is utilized by phytoplankton. In addition the biological process removes dissolved boron from seawater and estuarine water (Shirodkar & Singbal , 1992). The Pa/Pr of boron was positively correlated (0.79) with chlorinity.

Fluoride

Maximum fluoride concentration was observed during summer at station 1, whereas minimum monsoon at station 7. It showed a clear increasing trend from riverine to estuarine end. The surface water concentration was less than bottom one at every station during all the seasons of study (Fig. 2c) during premonsoon and summer the bottom and surface water concentrations showed very less or no difference. It may be due to the partial stratification of bottom water during these seasons. With the onset of monsoon its concentration dropped abruptly and remained low during the entire study period. Highest concentrations were noted in both surface and bottom waters during premonsoon and summer, which showed the regulation of fluoride, by highest salt water intrusion. Similar reports have been observed by several workers (De Sousa and Sen Gupta, 1998; Sarma *et. al*., 1993; Padmavathi and Satyanarayana, 1999 and Mahapatro and Padhy 2001). Its concentration during the study period showed the order of summer> premonsoon> winter> postmonsoon> monsoon. The postmonsoon and winter showed a recovery period when the fluoride concentration at any point in the estuary sowed gradual increase with time reaching its peak during premonsoon and summer. Highly significant positive correlation was found between fluoride and chlorinity. The positive correlations indicated the contribution of fluoride to the estuary from the same source as chlorinity. The intersation comparison (ANOVA) for the surface and bottom water showed significant value at 0.1% and 1% Respectively, whereas the interseason comparison for the surface and bottom water did not show any significant value (Table-2). Seasonal variation indicated the involvement of chlorinity in changing the ratio with element. High values were notices during postmonsoon and monsoon due to lower chlorinity and vice versa during summer season (Table-1). It may be due to the higher value of F/Cl ratio for fresh water than seawater, which indicated the very low chlorinity of river water not only brings down the value at estuarine points but also increases the F/Cl ratio. This was in agreement with the report of De Souza and Sen Gupta (1988). Semi conservative behaviour of fluoride was noticed during winter. Likewise non conservative behaviour was notices during premonsoon and summer, conservative behaviour was noticed during monsoon and postmonsoon. De Souza and Sen Gupta (1988) reported

conservative behaviour of fluoride during monsoon and postmonsoon, wheras non conservative behaviour during premonsoon resulting in its removal to an extent of 28% and 25% in Mandovi and Zuari estuaries respectively. This was attributed to several factors such a sadsorption on suspended particles, biological activity and evapoaration at he air water inerface. Non conservative behaviour of fluoride during premonsoon was also observed by Zingde and Mandalai (1988) in Minodola river and Sarma *et al*., (1993) in Gouthami Godavari estuary. The conservative behaviour of it during monsoon and postmonsoon may be due to its conentration in the estuarine waters, which his governed by physical processes of mixing and tidal variations. It is also not affected by any other geochemical factor. Similar observations wer found by several worers elsewhere (De souza aend Mandalai 1988; Sarma *et al*., 1993) and Padmavathi and Satyanarayana , 1999). On an overall, ther was net removal of fluoride during the study period (Table-1) the removal may be due to some biogeochemical mechanisms. Simialr results wer found by several workers (De Souza and Sen Gupta, 1988; Zindge and Mandalia, 1988; Sarma *et.al*. 1993 and Padamavati and satyanarayana, 1999). On an overall, there was net removal of fluoride during the study period (Table-1) the removal may be due to some biogeochemcal mechanism. Similar results wer found by several workers (De souza and Sen Gupta, 1988, Zingde and Mandalia, 1988; Sarma *et al*., 1993 and Padmavathi and Satyanarayana 1999). The other possible removal mechanisms are lost by evaporation at the air-water interface, loss by deposition as calcim carbonate, loss during precipitation as fluorpatite in shallow areas (Arrhenius, 1963), where saturation could be reached at low pH and loss due to biological activity. Some biological species having abundant growth may deplete the fluoride and relase it subsequently due to their death and decay. One or more of these mechanisms may be operaive in the removal fluoride. It may be pointed out that due to more suspended particles in monsoon, maximum removal of fluoride occurred in this estuary. The correlation between chlorinity and PA/PA of fluoride was not significantduring the study period.

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REFERENCE

Arrhenius, G. 1963. In : *The sea* vol. 3. Ed.by M.N. Hill (Inter Science, New York) p. 665.

Barnes, R.S.K. and Green, J. 1970. The estuarine environment. In : *Chemcial Processes in Estuaries*. John Philips (ed.), Applied Science Pub. Ltd. London.

Bryne, R.H. and Kester, D.R. 1974. *J. Mar. Res*. 32 : 119.

Choudhary, S.B. and Panigrahy, R.C. 1991. Seasonal distribution and behavouir of nutrients in the creek and coastal waters of Gopalpur, east coast of India. *Mahasagar - Bull Natn. Inst. Oceanogr*. 24 : 81-88.

Das, J., Das, S.N. and Sahoo, R.K. 1997. Semidiurnal variation of some physicochemical parameters in the Mahanadi estuary east coast of India. *Indian J. Mar. Sci.* 26 : 323-326.

De sousa, S.N. and Sen Gupta, R. 1988. Distribution and behaviour of fluoride in Mandovi and Zuari estuaries, central west coast of India. *Indian J. Mar. Sci.* 17 : 195 -201.

Ghosh S.K., and Jana, T.K. 1993. Boron-boric acid complexes in estuarine waers of River Hooghly, East coast of India. *Indian J. Mar. Sci.* 22 : 225-226.

Grasshoff, K. 1976. *Methdos of sea water analysis*. Verlag Chemie, Weinhein, pp- 260.

Greenhalgh, R., and Riley, J.P. 1961. Determiantion of fluoride in natural waters with particular reference to seawter. *Annal. Chim. Acta.* 25 : 179-186.

Harriss, R.C. 1969. Boron regulation in the oceans. Nature, 223 : 290-291.

Hosokawa, I., Ohshima, F. and Kondo, N. 1970. On the concentrations of the dissolved chemical elements in the estuarine waters of the Chikugogawa River. *J. Oceanogr Soc. Japan 26 :1-5.*

Hulthe, P., Uppstrom, L., and Ostling, G. 1970. *Anal Chim Acta*. 51 : 31.

Levinson, A.A. and Ludwick, J.C. 1966. Speculation on the incorporation of boron into orgillaceous sediments. *Geohim. Cosmochim. Acta.* 30 : 855-861.

Liss, P.S. and Pointon, M.J. 1973. Removal of dissolved boron and siliconduring estuarine mixing of sea and river waters. *Geochim. Cosmoshim. Acta*. 37 :1493-1498.

Mahapatro, T.R. and Padhy, S.N. 2001. Behaviour of fluoride in Rushikulya Estuary, Bay of Bengal. *Jr. of Env. Res.* 11(2) :141-144.

Narvekar, P.V. and Zingde, M.D. 1987. Behaviour of boron, calcium and magnesium in Purna and Auranga estuaries (Gujarat), east coast of India. *Indian J. Mar. Sci.,* 16 : 46-50.

Narvekar, P.V., Zingde, M.D. and Kamat, Dalal, V.N. 1981. Behaviour of boron, calcium and magnesium in Mindola estuary (Gujarat). *Indian J. Mar. Sci.* 10 : 90-92.

Narvekar, P.V., Zindge, M.D., and Kamat Dalal, V.N. 1983. Behaviour of boron, calcium and magnesium in polluted estuary. *Estuar. Coast. Shelf Sci.* 16 : 9-16.

Padmavathi, D. and Satyanarayana, D. 1999. Distribution of nutrients and major elements in riverine, estuarine and adjoining coastal waters of Godavari, Bay of Bengal. *Indian J. Mar. Sci,* 28 : 345-354.

Panigrahy, P.K., Das, J., Das, S.N., and Sahoo, R. 1999. Evaluation of the influence of various physico-chemical parameers on coastal water quality, around Orissa, by factor analysis, *Indian J. Mar. Sci.* 28 : 360-364.

Porrenga, D.H. 1967. Influence of grinding and heating of layer silicates on boron adsorption, *Geochim Coschim Acta*. 32 : 309-312.

Rajagopal, M.D., Rajendran, A. and Reddy, C.V.G. 1981. Distribution of dissolved boron in the waters of the Zuari (Goa). *Indian J. Mar. Sci.* 10 : 20-23.

Sarma, V.V., Sudhakar, U. and Varaprasad, S.J.D. 1993. Behaviour of fluoride and dissolved silicon in Gauthami Godavari estuarine environment. *Mahasagar- Bull. Natn. Inst. Oceanogr.* 26 : 105-113.

Shirodkar, P.V. and Singbal, S.Y.S. 1992. Boron chlorinity in relation to its variations in eastern Arabian sea. *Indian J. Mar. Sci.* 21 : 178-182.

Upadhayay, S. 1988. Physico-chemical characteristics of the Mahanadi estuarine ecosystem, East coast of India. *Indian J. Mar. Sci.* 17 :19-23.

Wilson, T.R.S. 1975. Salinity and the major elements of seawater. In : *Chemcial Ocenography.* Vol. I. J.P. Riley and G. Skirrow (Eds.), Academic Press, London, 365-413.

Wright, D.A. and Davison, A.W. 1975. The accumulation of fluoride by marine and intertidal animals. *Env. Poll.* 8 : 1-13.

Zingde, M.D. and Mandalia, A.N. 1988. Study of fluoride in polluted and unpolluted estuarine environment. *Estuar. Coast. Shelf Sci.* 27 : 707-712.