

BEHAVIOUR OF FLUORIDE AND DISSOLVED SILICON IN GOUTHAMI GODAVARI ESTUARINE ENVIRONMENT

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ABSTRACT

The concentrations of fluoride and dissolved silicon in Gouthami-Godavari estuarine region have been measured as a function of chlorinity during different seasons. Fluoride and dissolved silicon behave conservatively during post-monsoon season. However, during premonsoon season, removal of approximately 16% in case of fluoride and 41% in case of dissolved silicon was found during mixing of sea and river waters. The possible mechanisms for removal of both the elements have been explained. The net annual flux of dissolved silicon has been calculated to be 4.70×10^5 tons/yr from Godavari river into the Bay of Bengal.

Key-words : Fluoride, silicon, Gouthami- Godavari estuary.

INTRODUCTION

The behaviour of a few elements have been studied to know the extent of dissolved constituents removal from/addition to the water during mixing processes in an estuary. The most widely studied element is dissolved silicon. The nature and relative magnitude of the processes that control the distribution of dissolved silicon have been investigated (Burton and Liss, 1968; Calvert, 1968; Burton, Liss and Venugopalan, 1970). Fluoride has long been considered as an acute pollutant to natural environment because of the ability of plants and marine animals to accumulate it and because of its detrimental effects upon marine biota which can be affected by concentration as low as 1.5 mg.l^{-1} . Most of the investigations (Windom, 1971; Warner, 1972; Hosokawa and Ohshima, 1970) on fluoride revealed its conservative behaviour during estuarine mixing. Though extensive work has been reported on the geochemical studies of major ions in the river-estuary systems of Mahanadi (Ray, Mohanti and Somayajulu, 1984) and Krishna-Godavari (Sarin, Rao, Bhattacharya, Ramesh and Somayajulu, 1985) information available on the behaviour of fluoride and dissolved silicon during mixing in Gouthami-Godavari estuarine region is meager. The present investigations have been undertaken in Gouthami-Godavari estuarine region to understand the behaviour of these two chemical constituents during estuarine mixing in different seasons.

MATERIAL AND METHODS

Water samples (surface and bottom) at seven stations along a 40 km stretch (Fig.1) were collected at monthly interval for a period of 6 months from November 1989 to April 1990. All the samples were filtered using Whatmann GF/C filter papers and fluoride in water was estimated using the alizarine complexone procedure of Greenhalgh and Riley (1961), while dissolved silicon was estimated by the molybdenum blue method (Grasshoff, 1976). Chlorinity was estimated by argentometric method. Because of practical difficulties we could not collect number of samples within the low chlorinity ranges ($0 - 5 \times 10^{-3}$) as the depth of the water column in the river was less than 2 m.

General Hydrography

Godavari river ($16^{\circ}-83^{\circ}3'E$) starts from Nasik district near the western ghats and traverses across the Indian Peninsular shield. It covers an area of 3.1×10^5 sq km in the central and southern parts of Indian subcontinent. It branches into two major distributaries, namely, the Gouthami-Godavari and Vasishta-Godavari (Fig.1). The Gouthami-Godavari estuary covers a distance of 44 km and it is tidal. The tide is semi-diurnal and its range as recorded from the annual tide tables in the vicinity of the estuarine region was 1.9 - 4.0 m.

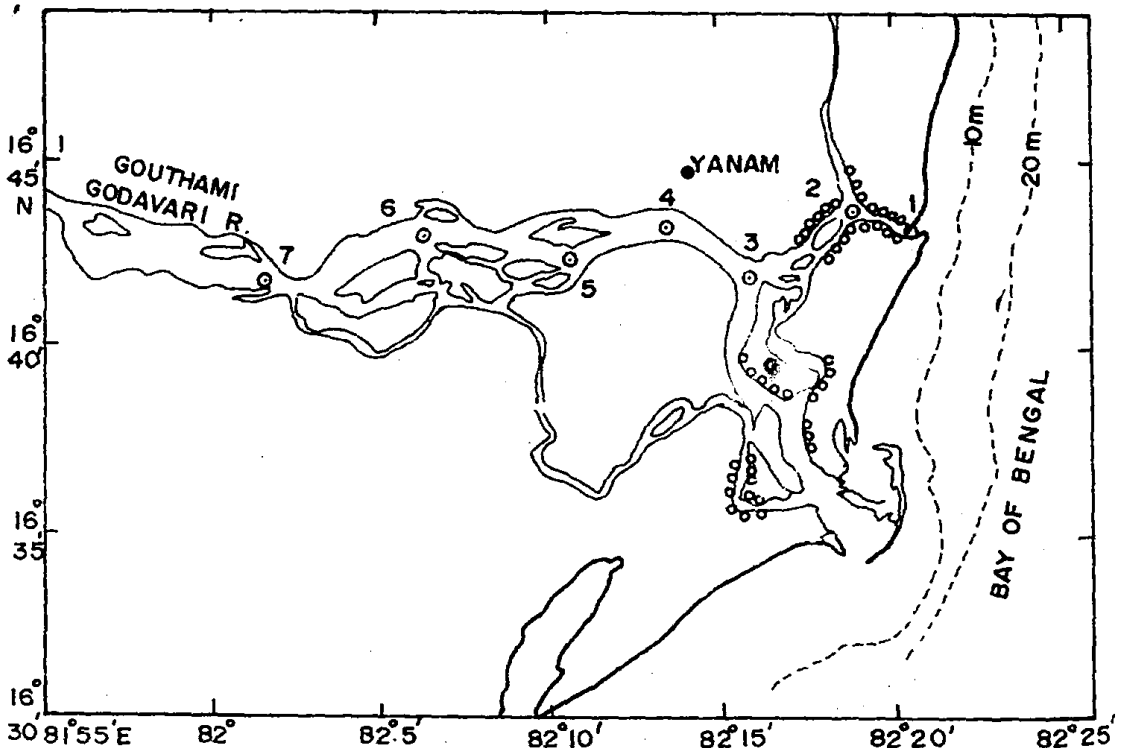


Fig. 1. Station location map.

RESULTS AND DISCUSSION

The fluoride content of the Gouthami-Godavari estuarine region varied between 0.20 and 1.33 mg. kg⁻¹. At any station it increased from November to January, and thereafter uniform concentration levels were observed till April. In the post- monsoon season, average bottom concentrations of fluoride at the sea end stations 1 to 3 (1.058 mg.kg⁻¹) and at river end stations 4 to 7 (0.757 mg.kg⁻¹) are higher when compared with their respective average surface concentrations at the sea end (0.926 mg.kg⁻¹) and river end (0.670 mg.kg⁻¹) stations, showing partially stratified estuarine conditions. However in premonsoon season, small difference between the surface to bottom concentrations (average = 0.55 mg.kg⁻¹) in the sea end stations 1-3 indicates the well mixed conditions in the estuary. Highest average concentrations noticed in surface (1.133 mg.kg⁻¹) and bottom (1.188 mg.kg⁻¹) waters during premonsoon season shows the regulation of fluoride by highest saltwater intrusion. Further the difference between surface to bottom concentrations in the river end stations (4 to 7) in premonsoon season was also marginal (0.03 mg.kg⁻¹). This seasonal variation of fluoride is similar to that in Mandovi and Zuari estuaries (De Souza and Sen Gupta, 1988). Monsoon collections could not be made systematically due to heavy floods but the surface concentrations of fluoride in July, 1990 ranged from 0.08 - 0.28 mg.kg⁻¹ in the entire study region. The *t*-test shows that the mean values of fluoride in post- and premonsoon seasons are not significant and hence considered as two data sets for further analytical purpose.

Fluoride - chlorinity relationship

The regression analysis shows highly significant positive correlations ($r=0.88$ and 0.82) in postmonsoon and premonsoon seasons respectively. A Theoretical Dilution Line (TDL) was drawn (Fig. 2) joining the concentration of fluoride at zero chlorinity with that in coastal seawater. It was observed that fluoride behaves conservatively during postmonsoon season and this linear relationship shows that its concentration is governed by mixing of seawater and river water alone. But during premonsoon season, a significant deviation from the TDL is noticed at higher chlorinity ranges (Fig. 2b) indicating a removal mechanism. The extent of removal of fluoride has been calculated to be 15.71% (± 8.1) which is comparable to the earlier reported values viz., 25 to 28% in Mandovi and Zuari estuaries (De Souza and Sen Gupta, 1988) and 17-30% in Baltic and other rivers flowing into it (Kullenberg and Sen Gupta, 1973). In the estuary, the ionic strength changes rapidly and turbulent mixing produces higher concentrations of suspended sediment that found in the sea or in river. Such conditions should be conducive to rapid reaction between dissolved species and solids in suspension. Thus fluoride may be absorbed on the solid phases as the first step in removal process. Further, the seasonal distribution of fluoride and silicon (as described in the foregoing section) in the present investigations was

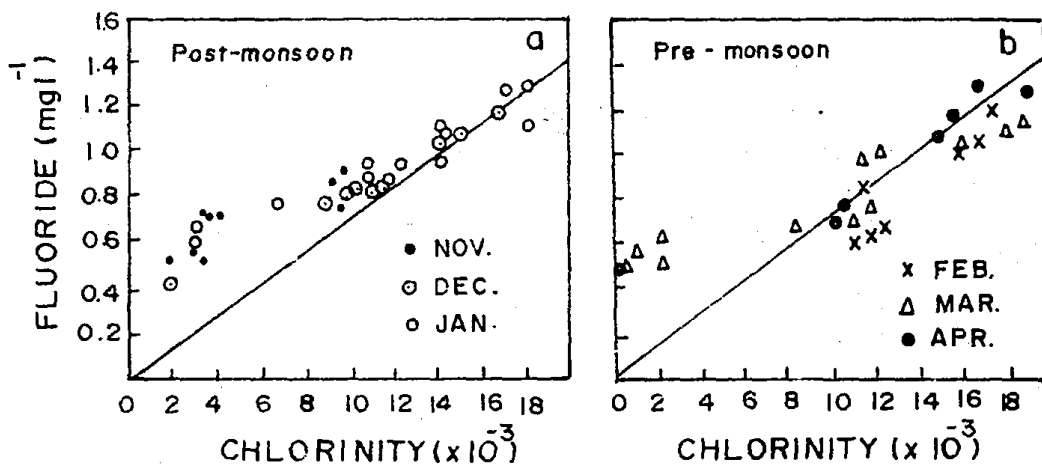


Fig. 2. Variation of fluoride with chlorinity during (a) postmonsoon and (b) premonsoon.

completely different and as such silicon is believed to be the well known biolimiting element, the removal mechanism for fluoride is possibly due to the geochemical processes as reported earlier (Carpenter, 1969; Kullenberg, and Sen Gupta, 1973). However, it is interesting to note that at low chlorinities ($<5 \times 10^{-3}$) the fluoride values falling above the TDL in both seasons indicating addition of fluoride from an external source. Gouthami-Godavari estuary is fresh water dominated beyond 30 km, *i.e.*, from sea end in the present investigations. Further, there are several industries like fertilisers, paper mills, gas based thermal plant, aluminium, ceramic and small scale chemical industries situated on the banks of upstream of Godavari in the vicinity of Rajahmundry and nearby regions (around 30 km from station 7). Eventhough, the data on effluent discharges are not available, because of the existing industries like fertilisers, inorganic chemicals and gas based thermal power station, fluoride is likely to be released and hence the possible source of excess fluoride in lower salinity range.

Table I presents the range and mean of fluoride and fluoride to chlorinity ratio in different chlorinity ranges. These values are in close agreement with reported values of fluoride to chlorinity ratio for ocean water (Riley, 1965; Brewer, Spencer and Wilkniss, 1970).

Concentration of dissolved silicon varied between 0.23 and 15.8 mg kg^{-1} and the increase was from sea end to river end. During postmonsoon season surface concentration of dissolved silicon in the river end stations 4 to 7 (8.392 mg.kg^{-1}) and sea end stations 1 to 3 (4.869 mg.kg^{-1}) were higher than their respective bottom concentrations in the river end (7.865 mg.kg^{-1}) and sea end (3.634 mg.kg^{-1}) stations, showing the surface flow of fresh water rich in silicon. During premonsoon season, the difference between average surface and bottom concentrations was marginal and also low concentrations of silicon were noticed in stations 1 to 3 (average surface con-

Table I – Variation of fluoride/chlorinity in postmonsoon and premonsoon in Gouthami-Godavari estuarine region.

Chlorinity $\times 10^{-3}$	Postmonsoon				Premonsoon			
	Range		Mean (SD)		Range		Mean (SD)	
	(F ⁻) mg. kg ⁻¹	Fluoride/ Chlorinity $\times 10^{-5}$	(F ⁻) mg. kg ⁻¹	Fluoride/ Chlorinity $\times 10^{-5}$	(F ⁻) mg. kg ⁻¹	Fluoride/ Chlorinity $\times 10^{-5}$	(F ⁻) mg. kg ⁻¹	Fluoride/ Chlorinity $\times 10^{-5}$
0.5 - 1.0	0.29 - 0.51	102 - 58	0.40 (± 0.11)	80.0 (± 22.0)	0.20 - 0.53	249 - 92.70	0.31 (± 0.13)	165.11 (± 61.7)
1.0 - 1.5	0.29 - 0.75	27.93 - 12.16	0.56 (± 0.13)	10.85 (± 4.29)	0.54 - 0.63	60.80 - 24.98	0.50 (± 0.03)	40.41 (± 16.60)
5.0 - 10.0	0.55 - 0.86	10.89 - 7.99	0.82 (± 0.06)	9.18 (± 0.99)	0.52 - 1.02	14.50 - 7.37	0.72 (± 0.22)	10.94 (± 2.88)
10.0 - 15.0	0.83 - 1.25	9.54 - 6.70	0.96 (± 0.13)	8.00 (± 0.75)	0.59 - 1.23	10.22 - 5.15	0.86 (± 0.22)	7.24 (± 1.86)
15.0 - 18.0	0.96 - 1.33	8.30 - 9.38	1.19 (± 0.12)	7.29 (± 0.67)	1.04 - 1.23	7.84 - 6.12	1.13 (± 0.09)	6.81 (± 0.58)

centration 1.563 mg.kg⁻¹ and bottom concentration 1.386 mg.kg⁻¹). The low concentrations of silicon in premonsoon season compared to postmonsoon season may be due to its involvement in the biological processes of the estuary. Further, the difference between average surface to bottom concentration of stations 4 to 7 was also marginal (average surface concentration 6.283 mg.kg⁻¹ and bottom concentration 6.525 mg.kg⁻¹) indicating well mixed conditions in the estuary.

Dissolved silicon - chlorinity relationship

Highly significant inverse correlation was obtained in postmonsoon season ($r = -0.92$), between silicon and chlorinity (Fig. 3a and b). The results were in close agreement with distribution of silicon in Cochin estuary (Anirudhan and Nambisan, 1990). A TDL was drawn joining the end member concentrations. Silicon behaves conservatively in postmonsoon season where all points fall in the vicinity of TDL (Fig. 3a), suggesting that the dilution of riverine silicon by surface seawater is the major process.

During premonsoon season, even though significant inverse correlation ($r = -0.84$) is obtained between dissolved silicon and chlorinity, some of the points lie below TDL in the higher chlorinity ranges. Thus, the distribution of silicon is not only controlled by simple mixing but also by some other processes in the estuarine region. The depletion in concentrations of silicon during premonsoon season indicates its involvement in biogeochemical cycles of the estuary. Earlier investigation on silicon

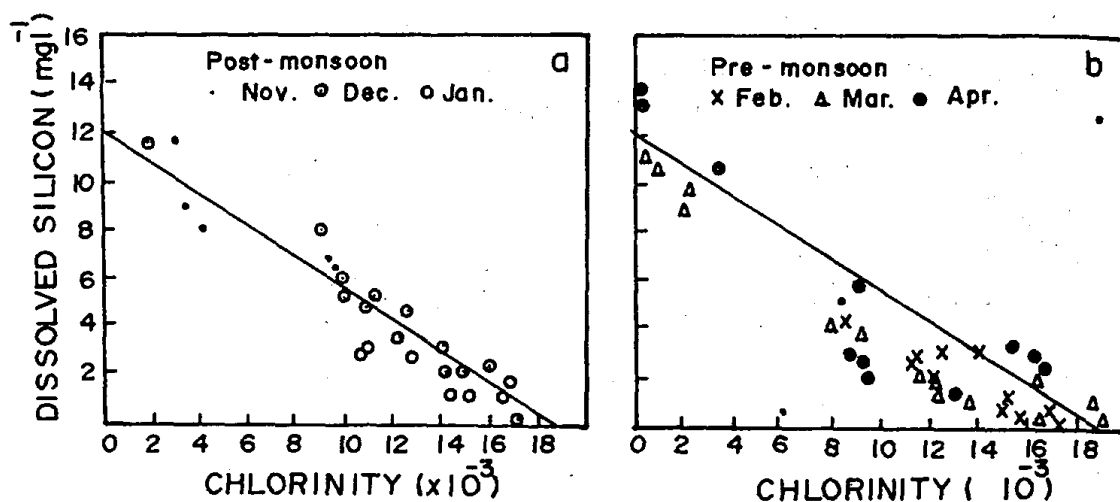


Fig. 3. Variation of dissolved silicon with chlorinity during (a) postmonsoon and (b) premonsoon.

in Godavari estuarine region by Borole, Krishnaswamy and Somayajulu (1977), had shown that the nonconservative behaviour of silicon in Godavari estuary is not due to its removal by sedimentary particles. Further, the diurnal changes in the physico-chemical conditions during tidal cycles in Gouthami-Godavari estuary (Rama Sarma, 1970) reflect the same type of distribution pattern obtained in the present study indicating the depletion of silicon to be likely due to diatom formation. Similar non-conservative behaviour of silicon has been reported by several other workers for different estuaries (Wollast, and De Broeu, 1971; Purushothaman and Venugopalan, 1972). The extent of removal of silicon in the estuarine region during premonsoon is calculated to be 41.39% (± 18.7). However, earlier investigations in Godavari estuary (Sarin, Rao, Bhattacharya, Ramesh and Somayajulu, 1985) showed that there is only 15% removal during May-June. The high percent removal observed during the present observations may be because of high biological productivity during February - April rather than May - June. Also the depletion percentage of silicon in present investigation was comparable with that of Mahanadi estuary (Ray, Mohanti and Somayajulu, 1984) in the East Coast of India and Cochin backwaters and Periyar estuary (Sankaranarayanan, Joseph, Jayalaxmi and Balachandran, 1984) in the West Coast of India.

A knowledge of soluble inputs from rivers to the ocean is essential for calculating material balances for various elements and to find out their possible sinks and sources (Borole, Krishnaswamy and Somayajulu, 1982). In this connection an attempt has been made to calculate the net annual flux of silicon to the Bay of Bengal from Godavari river by utilising the average river concentrations derived from the regression equations ($11.72 \pm 0.99 \text{ mg.kg}^{-1}$) and the annual discharges of Godavari into the

Bay of Bengal 1.05×10^{14} l ('UNESCO', 1971; Borole, 1980). It was reported that out of the estimated annual discharge of 1.05×10^{14} l only 12.3% was non-monsoonal discharge (1.3×10^{13} l/yr) from Godavari into the Bay of Bengal (Sarin, Rao, Bhattacharya, Ramesh and Somayajulu, 1985). Thus the non-monsoonal flux, calculated from the zero chlorinity value of silicon and non monsoonal discharge was 1.52×10^{11} g/yr or 1.52×10^5 tons/yr. As there is 41% removal of dissolved silicon in Godavari, silicon flux is reduced to 9.0×10^{10} g/yr, which is considered to be an insignificant chemical mass transfer. By utilising the annual discharge of 9.2×10^{13} l during monsoon season and the average concentration of silicon ($4.17 \text{ mg} \cdot \text{kg}^{-1}$) obtained from July 1990 data, the monsoonal flux was estimated. It should be mentioned here that the concentration of silicon in the monsoon season is low as reported earlier for the major ion concentrations in Indian river waters (Borole, 1980). The monsoonal flux of silicon was calculated to be 3.8×10^{11} g/yr and the total annual flux (monsoon + non monsoon) of silicon into the Bay of Bengal was now estimated to be 4.70×10^{11} g/yr or 4.70×10^5 tons/yr. Thus, the estimated total silicon flux from Godavari to the Bay of Bengal was less than the combined input of dissolved silicon into the Bay of Bengal from the Ganges, Brahmaputra and Irrawady (Raju, 1988) which indicates the high amounts of chemical and suspended loads and high rates of denudation from these rivers compared to Godavari (Subramanian, 1979).

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