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STUDY ON FLUORIDE IN THE MANDOVI-ZUARI RIVER SYSTEM (GOA)

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ABSTRACT

An assessment has been made of effects of mixing processes on distribution of fluoride in Mandovi and Zuari estuaries (Goa). Percentage of seawater and freshwater in the estuaries has been calculated on the basis of fluoride levels in water; these values agree with those obtained from determinations of water salinity. The data obtained are in accordance with the nature of fluoride as a conservative constituent of seawater.

Key-words : Fluoride, estuary, Mandovi estuary, Zuari estuary, Goa.

INTRODUCTION

Fluoride is present at an average concentration of 1.3 mg/kg in seawater of salinity 35‰, the F/Cl ratio being 6.7×10^{-5} (Greenhalgh and Riley, 1963). The conservative nature of fluoride in the marine environment is retained in estuaries as is evident from the investigations of Windom (1971) and Warner (1972) in American waters.

In the present work (carried out during 1981-82), water samples from the marine, estuarine and freshwater zones of Mandovi and Zuari rivers (Goa) have been analysed for chlorinity and fluoride content with a view to study the effects of mixing processes on the chemistry of the waters.

MATERIALS AND METHODS

Water samples were collected from fifteen stations (M_1–M_5 in Mandovi, Z_1–Z_6 in Zuari, C_1–C_8 in sea and station C_x in Cumbarjua Canal which connects the Mandovi with the Zuari) (Fig. 1). Stations M_5 and Z_6 in the freshwater zones served for reference as river controls. The depths at the estuarine stations M_1–M_5 and Z_1–Z_6 varied from 6 to 12 m and samples were collected from surface, mid-depth and bottom. Fluoride was estimated through its reaction with the wine red lanthanum chelate of alizarin complexone. A correction was made for interference due to magnesium (Greenhalgh and Riley, 1961). Chlorinity was determined by argentometric titration (Grasshoff, 1976).

DESCRIPTION OF THE AREA UNDER STUDY

The river Mandovi rises from the Parwa Ghat of the Sahyadri hills and after flowing a stretch of about 70 km, joins the Arabian Sea through the Aguada Bay. It is 3.2 km wide at the mouth and narrows down to 0.25 km

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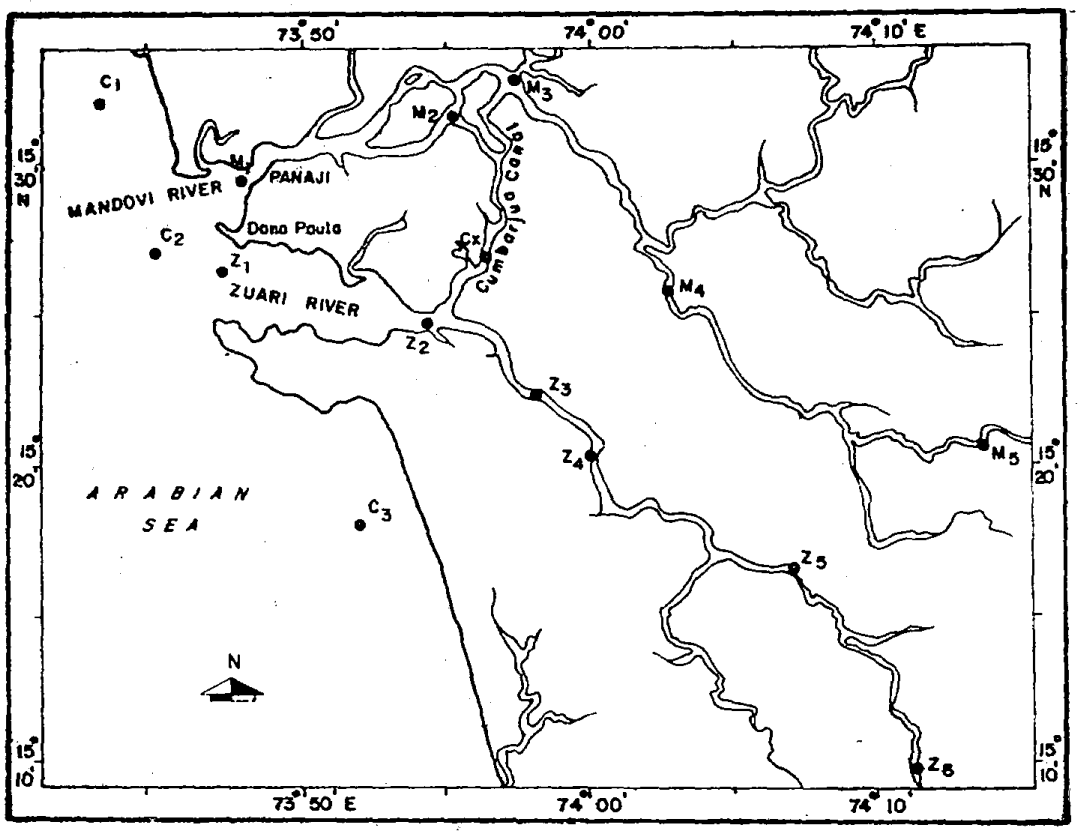

Fig. 1. Mandovi–Zuari river system.

upstream. The Zuari river originates in the Dighi Ghat and on flowing through 67 km meets the sea at Dona Paula. It is 5.5 km wide at the mouth and less than 0.5 km upstream (Anon., 1979). Both rivers are influenced by semi-diurnal tides with a maximum amplitude of 2 m. They are dominated by freshwater during the southwest monsoon season (June-September) and a weak stratification develops in both the rivers resulting in the formation of a salt-wedge due to penetration of the estuaries by seawater (Qasim and Sen Gupta, 1981). Taking 0.5‰ chlorinity as the index of seawater penetration, it has been observed that the distance varies from the maximum of about 65 km in both the rivers during May to a minimum of about 20 km in Zuari in June (Fig. 2).

RESULTS AND DISCUSSION

The experimental data on chlorinity and fluoride content of the waters have been analysed seasonwise: monsoon (June–Sept.), postmonsoon (Oct.–Jan.) and premonsoon (Feb–May). In Fig. 3 longitudinal variations of chlorinity have been represented as functions of distances from mouths of rivers. Monthly variations in fluoride content of water are given in Fig. 4. Ranges of fluoride concentrations in Mandovi and Zuari estuaries are depicted in Fig. 5.

Calculations of percentages of freshwater and seawater in estuaries

(1) Based on salinity of water: Percent freshwater (F) in an estuary is given by

$$\frac{(S_2 - S_1) \times 100}{S_2} \quad \ldots\ldots \text{(Yentsch, 1975)}$$

where S_1 is salinity of mixture and S_2 is salinity of the oceans neighbouring the estuary.

This relationship has been used in calculating percentages of freshwater in the Mandovi and Zuari estuaries (Table I). The freshwater percentage varied between 3 and 8 in pre-monsoon, 66 and 99 in monsoon and 9 and 24 in post-monsoon. For calculating averages for monsoon season, data from stations Z_1 and Z_2 have been pooled as also data from stations M_1 and M_2. Seawater averages were obtained by pooling data from stations C_1, C_2 and C_3 (Sen Gupta and Naik, 1981).

(2) Based on fluoride content of water: Equations (i) and (ii) have been applied to calculate seasonal variations in percentage freshwater in Mandovi and Zuari estuaries (Table II).

$$A_1/A_2 = F/(1-F) \quad .. \qquad .. \quad \text{(i)}$$

where $F = (X - X_2)/(X_1 - X_2)$ and $F < 1$ .. .. (ii)

X_1: conc. of fluoride in seawater, X_2: conc. of fluoride in river water, X: conc.

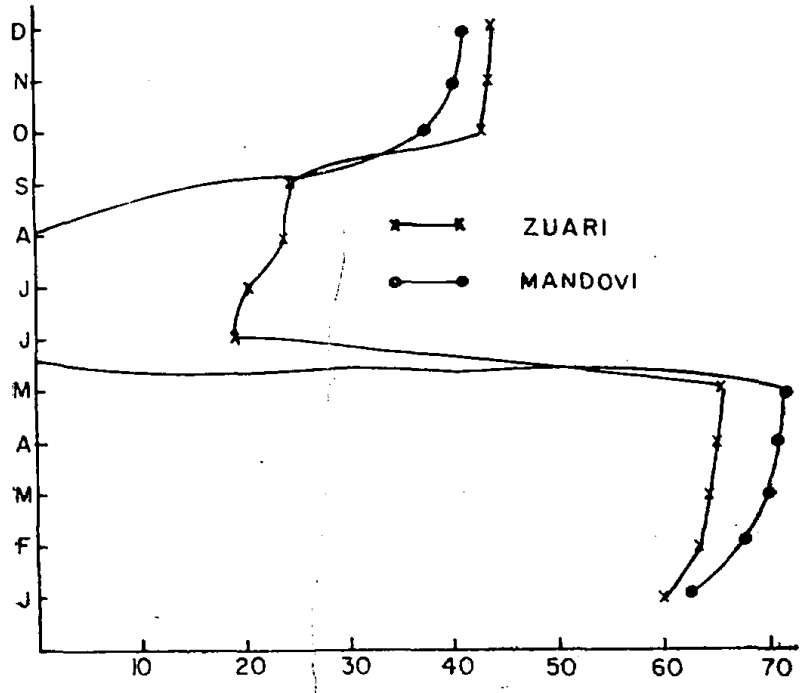

Fig. 2. Variations in distances of monthwise penetration of 0.5‰ chlorinity water.

of fluoride in the sample, A_1: amount of seawater in the sample, A_2: amount of river water in the sample and F: a constant.

The dilution constants for the three seasons are in the ranges of 0.01–0.34 (monsoon), 0.76–0.91 (postmonsoon) and 0.92–0.97 (premonsoon). and agree well with the values obtained from data on salinity of water, viz., 0.01–0.34 (monsoon), 0.76–0.91 (postmonsoon) and 0.92–0.97 (premonsoon).

Fluoride–chlorinity relationships

Carpenter, Bradford and Grant (1975) have derived the following equation interrelating fluoride and chlorinity in estuaries

$$X_{sample} = X_{river} + \frac{X_{sw} - X_r}{Cl_{sw}} Cl_{sample} \quad .. \quad .. \quad (iii)$$

where X_{sample} : conc. of fluoride in the sample, X_r : conc. of fluoride in the

Table I. Seasonal variations in percentage freshwater in Mandovi and Zuari estuaries (Based on salinity of water).

Sea	Salinity ‰		Freshwater % **	
S_2	Mandovi	Zuari	Mandovi	Zuari
	S_1			
		Postmonsoon		
35.20	32.25	34.19	8	3
		Monsoon		
31.77*	0.386	10.74	99	66
		Premonsoon		
34.40	26.45	31.31	24	9

*Observation during September only.

**Freshwater % $= \left(\frac{S_2 - S_1}{S_2}\right) \times 100$

Table II. Seasonal variations in percentage freshwater in Mandovi and Zuari estuaries (Based on fluoride content of water).

Sea	Mandovi estuary	Mandovi river	Zuari estuary	Zuari river	F: seasonal	onstant	A_1/A_2 *		Freshwater %	
	Fluoride conc. mg/kg				Mandovi	Zuari	Mandovi	Zuari	Mandovi	Zuari
					Postmonsoon					
1.26	1.19	0.126	1.25	0.14	0.94	0.99	15.66	99	6	1
					Monsoon					
1.11	0.118	0.092	0.314	0.098	0.02	0.21	0.02	0.26	98	79
					Premonsoon					
1.19	1.02	0.12	1.15	0.112	0.83	0.96	4.88	24	17	4

* $A_1/A_2 = F/(1-F)$.

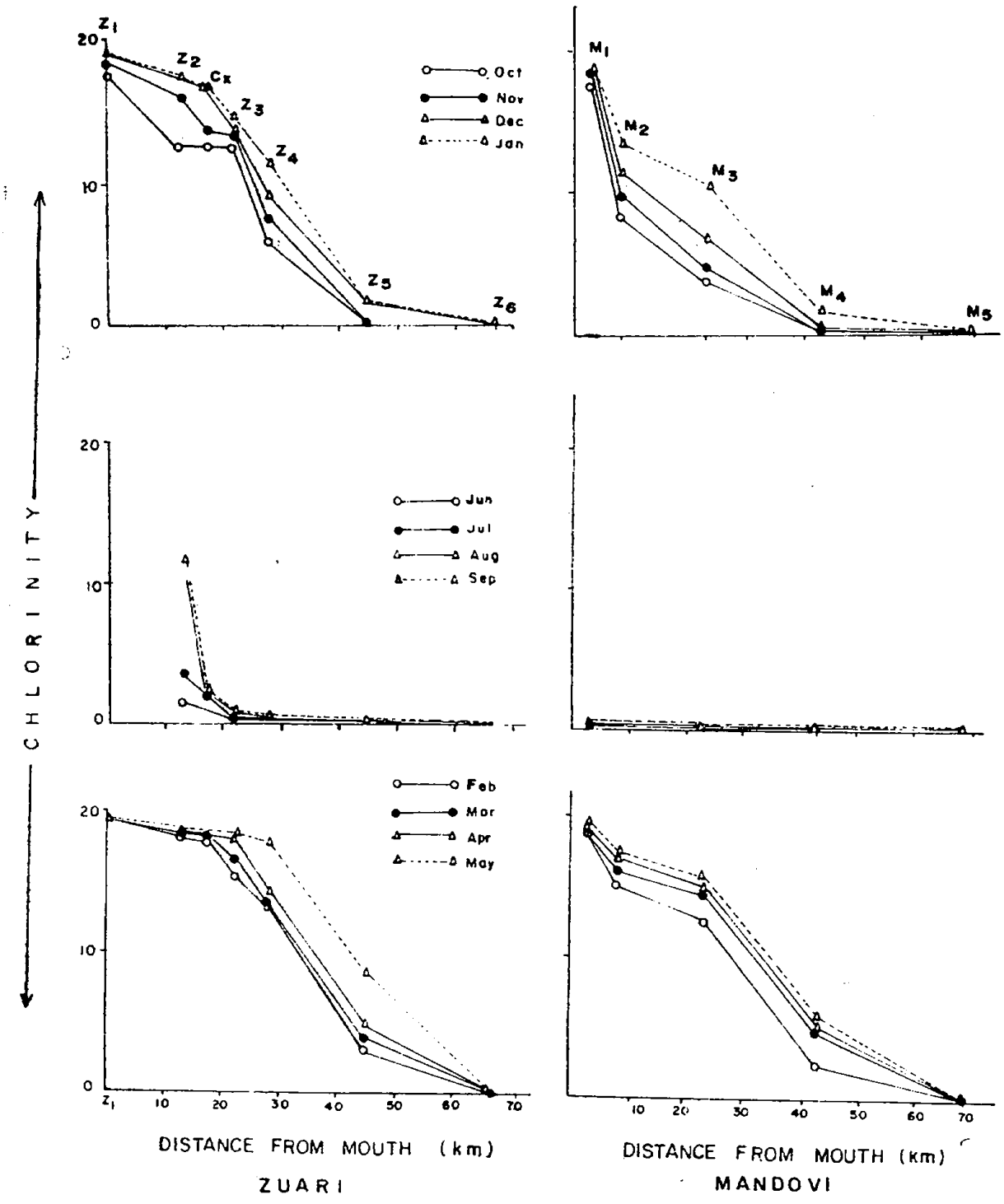

Fig. 3. Variations in chlorinity with distance from the mouth of rivers Zuari and Mandovi.

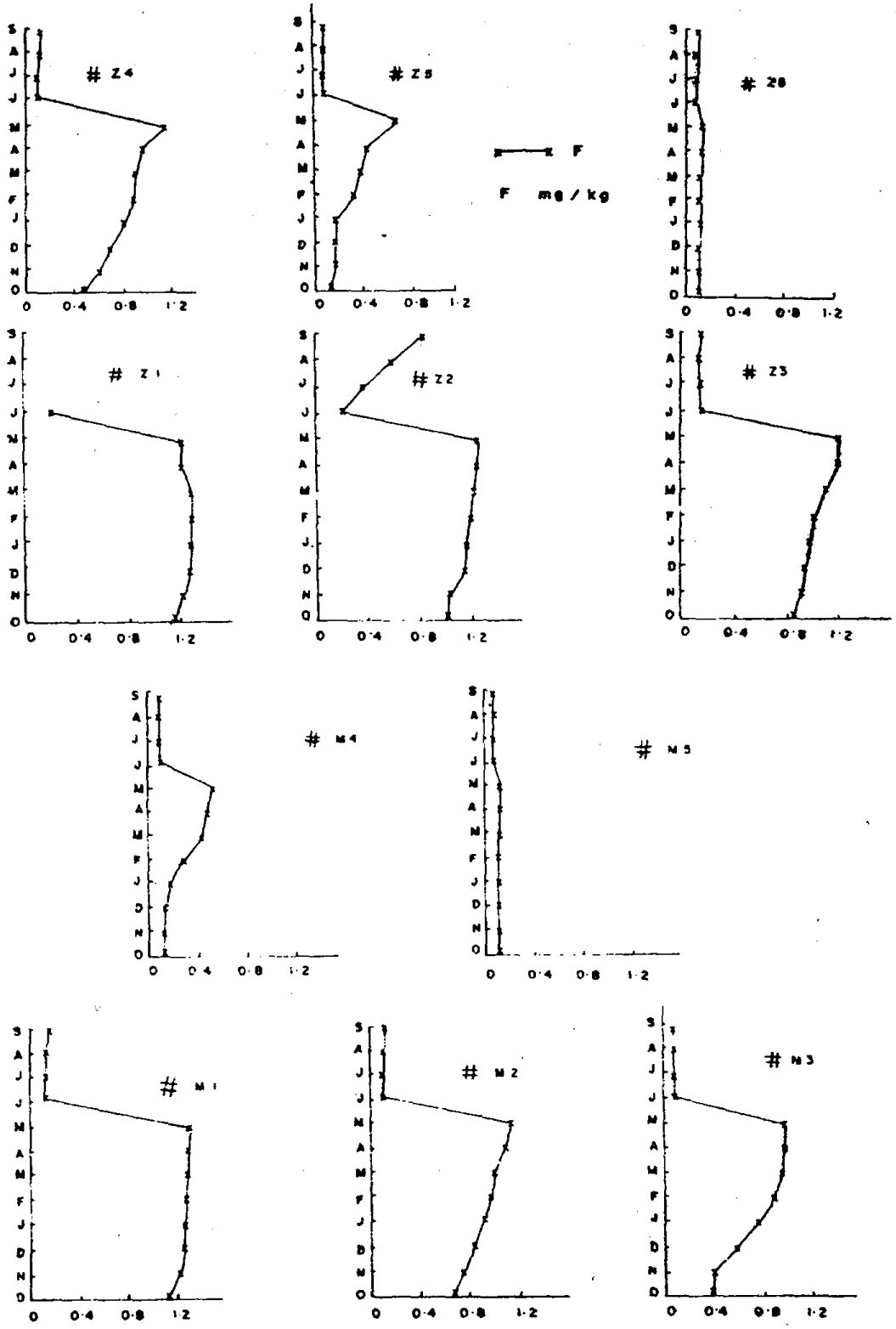

Fig. 4. Monthly variations of fluoride of all stations in Mandovi and Zuari rivers.

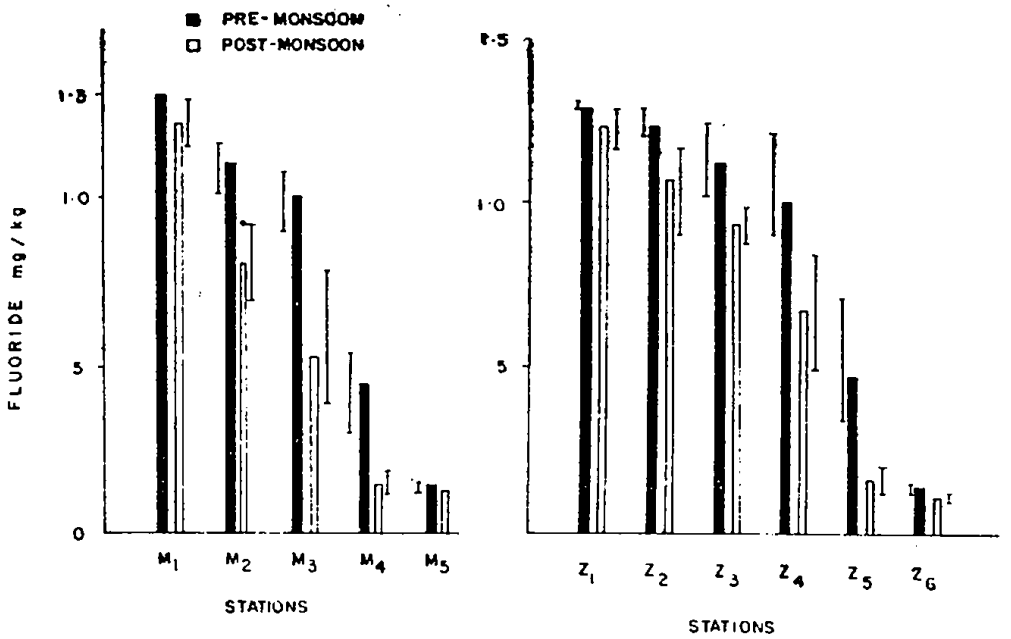

Fig. 5. Average fluoride concentrations (mg/kg) in premonsoon and postmonsoon seasons in Mandovi and Zuari. (Vertical line shows range of values.)

river water, X_{sw} : conc. of fluoride in the seawater, Cl_{sw} : chlorinity of seawater and Cl_{sample} : chlorinity of the sample.

Using equation (iii), fluoride values were computed for various months in the year in respect of waters of Mandovi and Zuari estuaries (Table III). Here the stations M_1 to M_3 as also at Z_1 to Z_4 are averaged. At the mouth of the rivers the ranges of variation are 1.28–1.31 mg/kg (premonsoon), 0.12–1.16 mg/kg (monsoon) and 1.13–1.28 mg/kg (postmonsoon). Maximum differences between observed and calculated values of fluoride were seen during

Table III. Fluoride and chlorinity in waters of Mandovi and Zuari.

Months	Cl ‰	Mandovi estuary			Cl‰	Zuari estuary		
		F mg/kg		$F_{calc} - F_{obs}$		F mg/kg		$F_{calc} - F_{obs}$
		Obs	Calc			Obs	Calc	
Premonsoon								
Feb.	15.56	1.06	1.02	–0.01	16.65	1.12	1.08	–0.04
to	to	to	to	to	to	to	to	to
May	17.7	1.17	1.18	+0.01	18.53	1.23	1.22	–0.01
Monsoon								
June	0.10	0.116	0.097	–0.019	0.63	0.15	0.136	–0.014
to	to	to	to	to	to	to	to	to
Sept.	0.423	0.124	0.125	+0.001	4.19	0.429	0.348	–0.081
Postmonsoon								
Oct.	9.91	0.847	0.653	–0.194	11.94	0.85	0.76	–0.09
to	to	to	to	to	to	to	to	to
Jan.	14.3	0.990	0.94	–0.049	16.00	1.08	1.04	–0.04

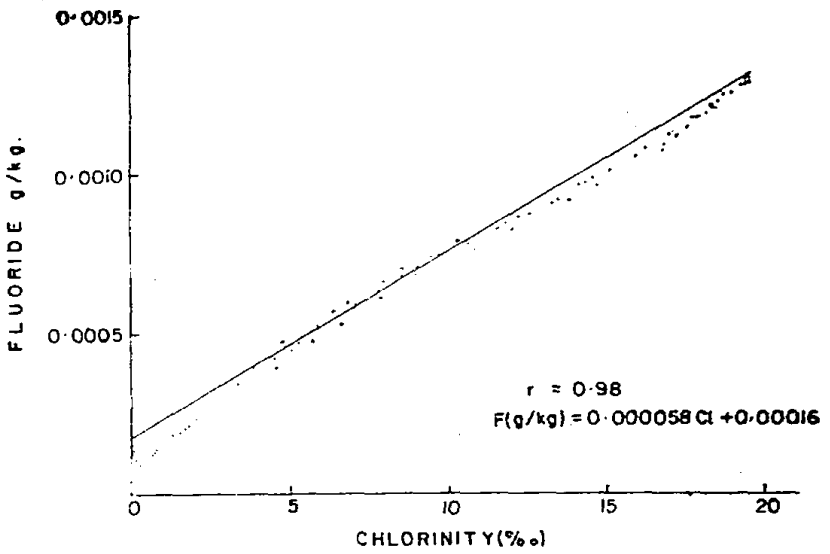

Fig. 6. Relationship between chlorinity and fluoride for all seasons.

monsoon seasons indicating significant dilution effects of precipitation. These differences are presumably geochemical in nature since fluoride is known not to participate in biological cycles (Sen Gupta, Naik and Singbal, 1978).

In order to examine overall relationships, data on fluoride have been plotted against chlorinity (Fig. 6). The linear least-square fit gave a slope of 5.8×10^{-5} and an intercept of 0.16 mg/kg with a correlation of 98%. This excellent relation would indicate an overall F/Cl ratio of 5.8×10^{-5}, with a fluoride concentration of 0.16 mg/kg at zero chlorinity. A mean fluoride concentration of 0.12 mg/kg in the freshwater zones of both the rivers is observed, which is in good agreement with the intercept in the figure. The overall F/Cl ratio is somewhat lower than the expected seawater value of 6.7×10^{-5}, because of inclusion of low values obtained during the monsoon months.

Fluoride in river inputs

The fluoride content of the average river input can be calculated at any point in the mixed system by measuring the actual fluoride content X_{sample} and chlorinity, and rearranging equation (iii) to give

$$X_{river} = \frac{X_{sample}Cl_{sw} - X_{sw}Cl_{sample}}{Cl_{sw} - Cl_{sample}} \quad \ldots \quad (iv)$$

These variations in river inputs can be reliably inferred from measurements in the body of the estuary far from the source. If a conservative substance enters freshwater at a uniform rate then the downstream distribution will follow the curve describing the fresh-water seawater distribution.

At the river stations M_5 and Z_6, fluoride concentrations varied from 0.08 to 0.14 mg/kg and 0.09 to 0.15 mg/kg. The average value for fluoride

in these freshwaters was 0.12 mg/kg. The global average value for fluoride in river water is 0.1–0.2 mg/kg (Livingstone, 1963).

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REFERENCES

Anon., 1979. Master Plan for Pollution Control of the Rivers Mandovi and Zuari. *NIO Technical Report 02/79, Part 1,* NIO, Goa, India : 8 pp.

Carpenter, J.H., W.I. Bradford and V. Grant, 1975. Processes affecting the composition of estuarine waters. In: *Estuarine Research*, edited by L.E. Cronin, Academic Press, Inc New York, **1:** 188–214.

Grasshoff, K., 1976. Determination of salinity. In : *Methods of Sea Water Analysis*, edited by K. Grasshoff, Verlag Chemie, Weinheim, 31–41.

Greenhalgh, R. and J.P. Riley, 1961. The determination of fluoride in natural waters with particular reference to sea water. *Analytica Chimica Acta*, **25:** 179–188.

Greenhalgh, R. and J.P. Riley, 1963. Occurrence of abnormally high fluoride concentration in the North Atlantic. *Nature*, **197:** 371–372.

Livingstone, D.A., 1963. Chemical composition of rivers and lakes. *United States Geological Survey Professional Paper 440–G,* 64 pp.

Qasim, S.Z. and R. Sen Gupta, 1981. Environmental characteristics of the Mandovi-Zuari estuarine system in Goa. *Estuarine, Coastal and Shelf Science*, **13:** 557–578.

Sen Gupta, R., S. Naik and S.Y.S. Singbal, 1978. A study of fluoride calcium and magnesium in the Northern Indian Ocean. *Marine Chemistry*, **9:** 125–140.

Sen Gupta, R. and S. Naik, 1981. Studies on calcium, magnesium and sulphate in the Mandovi and Zuari river systems (Goa). *Indian Journal of Marine Sciences*, **10:** 24–34.

Warner, T.B., 1972. Mixing model prediction of fluoride distribution in Chesapeake Bay. *Journal of Geophysical Research*, **77:** 2728–2732.

Windom H.L., 1971. Fluoride concentration in coastal and estuarine waters of Georgia. *Limnology and Oceanography*, **16:** 806–810.

Yentsch, C.S., 1975. New England waters — An Infinite Estuary. In : *Marine Chemistry in the Coastal Environment*, edited by T.M. Church, American Chemical Society, Washington D.C., 608–617.