

Distribution & Behaviour of Fluoride in Mandovi & Zuari Estuaries, Central West Coast of India

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Fluoride concentrations in Mandovi and Zuari estuaries are regulated largely by salt water intrusion. Highest concentrations are observed during the premonsoon season, when the salt water intrusion is also the highest, the concentration increasing from fresh water-end to the sea-end. During monsoon, however, fluoride concentrations are the lowest and the estuaries show freshwater characteristics at the surface while at the bottom higher fluoride concentrations are observed near the mouth as a result of salt wedge formation. Postmonsoon season shows a recovery period when the fluoride concentration has values lying between those during premonsoon and monsoon. F-Cl relationship is linear during monsoon and postmonsoon indicating that fluoride behaves conservatively during these 2 seasons. During the premonsoon, however, the F-Cl relationship is not linear but exponential of the type $Y = ab^x$ which is curve concave to the fluoride-axis indicating that fluoride is lost in estuaries in this season (28 and 25% in Mandovi and Zuari respectively).

Fluoride is considered as a major element being present in seawater at concentrations $> 1 \text{ mg.kg}^{-1}$. The average fluoride concentration in seawater is 1.3 mg.kg^{-1} at salinity 35×10^{-3} . However, since it lies on the borderline between major and minor elements, its behaviour, conservative or non-conservative, is yet to be fully understood. Average fluoride concentration in river water^{1,2} is given as 0.1 mg.kg^{-1} . It is, however, reported³ that rivers such as the Amazon, which are not appreciably affected by man's activities, have dissolved fluoride content slightly $> 0.1 \text{ mg.kg}^{-1}$.

The study of fluoride in river water, specially in the freshwater zone, which is used as source of raw water for public water supply, is of great importance. Optimum concentration of fluoride in natural waters required for the prevention of tooth decay⁴ is 1 mg.kg^{-1} while fluoride concentrations in excess of 4 mg.kg^{-1} may cause mottled or stained teeth and fluorosis.

Materials and Methods

Four stations $M_1 - M_4$ and $Z_1 - Z_4$ were fixed in Mandovi and Zuari rivers respectively (Fig. 1), covering the marine, estuarine and freshwater regions. In order to study the monthly variations of fluoride, surface and bottom water samples were collected from the 4 stations in Mandovi once a month from February 1980 to March 1981. Since both Mandovi and Zuari have almost similar topographies, it was expected that both the rivers would show similar variations in fluoride concentration.

Hence, in Zuari observations were made during few months only representing all the 3 seasons. Niskin water samplers were used to collect the surface and bottom water samples. In order to study the behaviour of fluoride during estuarine mixing a series of surface water samples covering the salinity range from 0 to 35×10^{-3} were collected from both Mandovi and Zuari once in each season. All the samples were filtered through Whatman GF/C filter papers and analysed for chlorinity and fluoride as follows: The chlorinity was measured by titrating the samples with AgNO_3 solution using K_2CrO_4 solution as

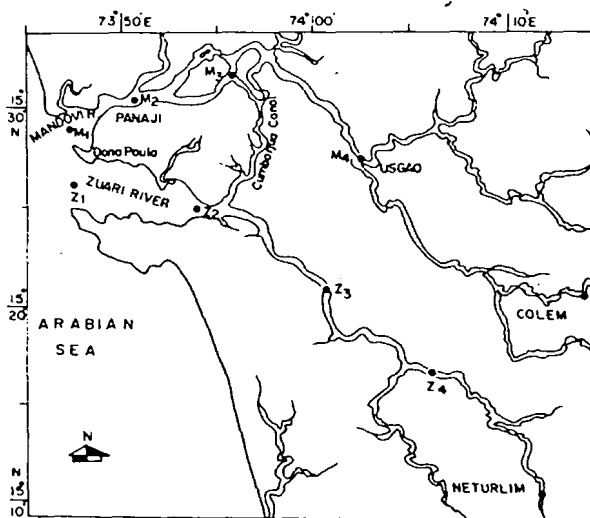


Fig. 1—Station positions

indicator, while fluoride was measured spectrophotometrically⁵.

Results and Discussion

The cycle of meteorological events in the west coast of India is fairly regular making the year divisible into 3 distinct seasons of 4 months each, viz. premonsoon (February to May), monsoon (June to September) and post monsoon which is a transition period (October to January).

Chlorinity—Fig. 2 shows the seasonal distribution of chlorinity at surface and bottom in Mandovi. The highest chlorinity values are observed during premonsoon reaching a maximum of 19×10^{-3} in May just before the onset of the monsoon. During this season both the rainfall and the freshwater discharge are insignificant. Consequently the estuaries are entirely dominated by semi-diurnal tides with seawater penetrating deep upstream. During monsoon, however, the chlorinity values are greatly reduced with surface water having very low chlorinity throughout the entire length while the bottom water shows decreasing chlorinity from the mouth upstream. Beyond a distance of about 13 km upstream the chlorinity is uniform at 0.5×10^{-3} . The very low

chlorinity at the surface is due to the fresh water discharge caused by heavy rainfall occurring during this season while the higher chlorinity of bottom water near the mouth is caused by the formation of a salt wedge⁶. During the postmonsoon chlorinity values increase caused by the decreasing amount of freshwater discharge resulting in increasing penetration of seawater upstream. It is to be noted that high values of chlorinities $> 20 \times 10^{-3}$ are observed near the mouth in December. One of the reasons for this is the discharge of brine from the salt pans which are located around this place.

Table 1 shows the variations of chlorinity in Zuari during the year. A comparison of Fig. 2 with Table 1 shows that chlorinity variations in both the rivers are similar with high concentrations occurring during premonsoon months, the lowest during monsoon with the postmonsoon indicating the recovery period. As in Mandovi, salt wedge formation extending up to about 12 km from the mouth upstream has been reported in Zuari also⁶.

Fluoride—Fig. 3 shows the monthly variations of fluoride at the surface and bottom in Mandovi. A comparison between Fig. 3 and Fig. 2 would indicate that the fluoride isopleths agree fairly well with

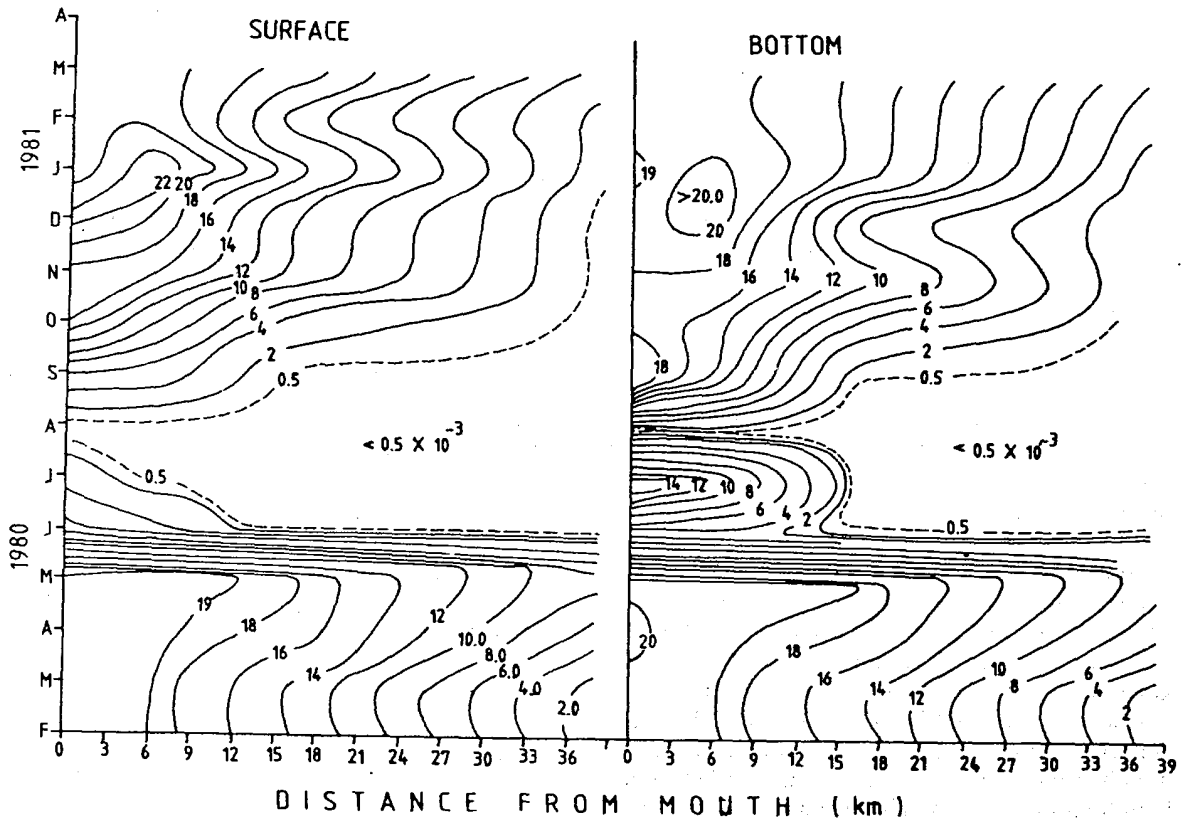


Fig. 2—Seasonal distribution of chlorinity in Mandovi

the isohalines. This would amount to the regulation of fluoride in the Mandovi largely by salt water incursion. The same is true for Zuari also (Table 1 compared with Table 2). Fig. 3 shows fluoride concentrations ranging from 0.2 at freshwater-end to 1.4 mg.kg⁻¹ at the mouth during premonsoon. In this season both surface and bottom waters show almost the same fluoride concentrations indicating vertical homogeneity of the water column. With the onset of monsoon, fluoride concentration drops abruptly and remains low during the entire season. In this season the estuary shows freshwater charac-

teristics with very low fluoride concentrations (< 0.1 mg.kg⁻¹) at surface and bottom from 15 km from the mouth upstream. Downstream the estuary shows stratification with surface water showing low (< 0.1 mg.kg⁻¹) fluoride concentration and the bottom water showing comparatively higher concentration (0.1 - 0.8 mg.kg⁻¹) which increases gradually towards the mouth. The postmonsoon season shows a recovery period when the fluoride concentration at any point in the estuary shows gradual increase with time reaching its peak in premonsoon. In this season the estuary gets partially stratified with bot-

Table 1—Variations of Chlorinity (Cl × 10⁻³) in Zuari

St		1980 Feb.	March	May	Aug.	Sept.	Oct.	Dec.
Z1	S	—	19.04	—	9.06	16.70	19.17	17.74
	B	—	19.60	—	18.82	19.72	19.56	19.12
Z2	S	18.79	19.17	20.39	7.13	15.31	15.13	18.13
	B	19.40	19.23	20.20	10.67	17.02	15.58	17.62
Z3	S	15.39	13.72	17.67	0.15	3.95	5.77	11.74
	B	15.48	12.81	17.67	0.29	5.95	7.70	10.84
Z4	S	4.90	2.21	8.29	0.04	—	0.09	0.26
	B	5.47	2.21	8.69	0.03	—	0.07	0.15

S = surface; B = bottom

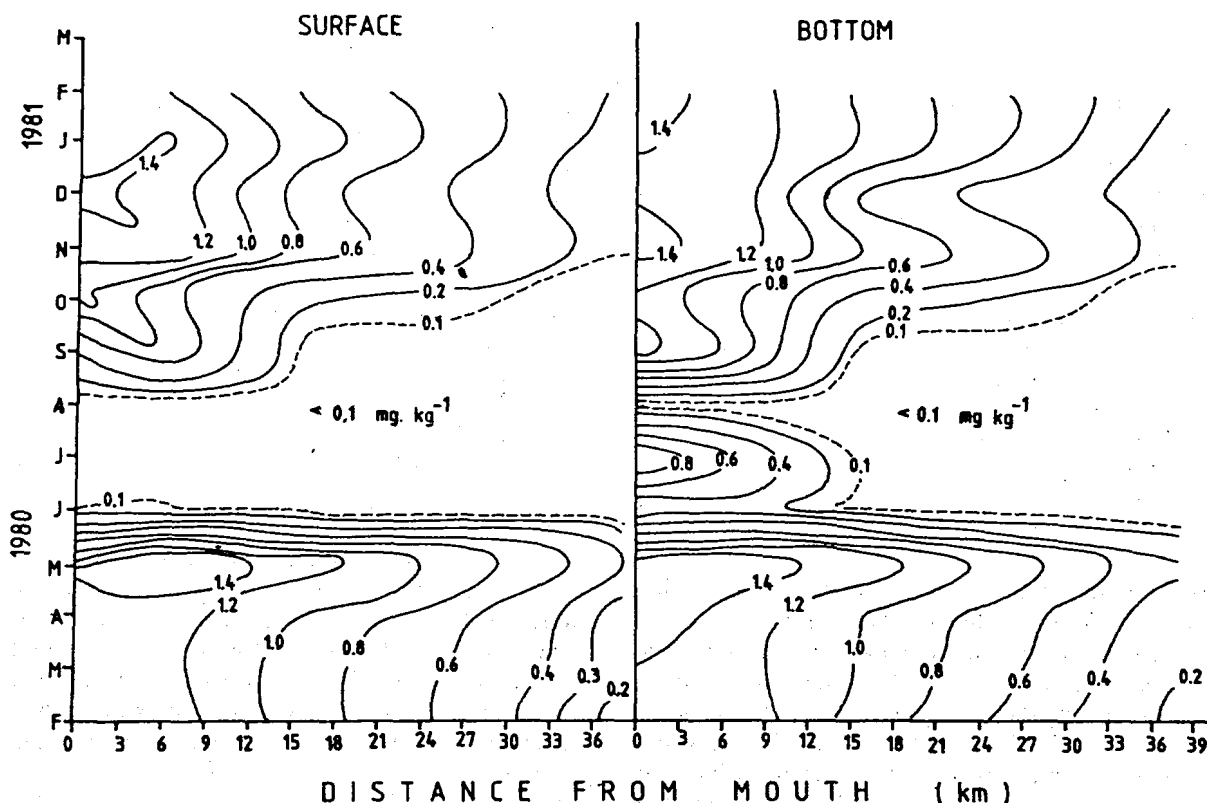


Fig. 3—Seasonal distribution of fluoride in Mandovi

Table 2—Variations of Fluoride (mg.kg⁻¹) in Zuari

St		1980 Feb.	March	May	Aug.	Sept.	Oct.	Dec.
Z1	S	—	1.36	—	0.65	1.06	1.15	1.29
	B	—	1.40	—	1.11	1.26	1.07	1.37
Z2	S	1.18	1.35	1.16	0.45	0.98	0.95	1.30
	B	1.23	1.36	0.91	0.80	1.07	0.92	1.28
Z3	S	0.97	0.93	0.89	0.03	0.32	0.37	0.97
	B	0.97	0.99	0.93	0.14	0.40	0.42	0.97
Z4	S	0.32	0.32	0.30	0.02	ND	ND	0.23
	B	0.36	0.31	0.26	0.14	ND	ND	0.24

ND - not detectable; S = surface; B = bottom

tom water showing slightly higher fluoride concentrations as compared to the surface.

Variations of fluoride in the Zuari (Table 2) also follow the same trend as in the Mandovi with premonsoon showing the highest concentrations and monsoon the lowest. The postmonsoon shows intermediate values. High concentrations of fluoride (> 1.4 mg.kg⁻¹) were observed at surface and bottom at M₂, a few kilometers from the mouth in the Mandovi in December, 1981. This is associated with the occurrence of high chlorinities (Fig. 2) and can be attributed to the discharge of salt pan brines into Mandovi. The salt industry which suspends its activities during monsoon, starts preparing the salt pans in early December.

Fluoride-chlorinity relationship—F (mg.kg⁻¹) - Cl(× 10⁻³) relationship for Mandovi and Zuari during monsoon, is linear given by

$$F = 0.060 Cl + 0.043 \quad \dots (1)$$

Correlation coefficient $r = 0.95$

$$F = 0.062 Cl + 0.022 \quad \dots (2)$$

$r = 0.99$

for Mandovi and Zuari respectively.

Linear relation between fluoride and chlorinity is also observed for Mandovi and Zuari during postmonsoon season.

$$F = 0.060 Cl + 0.039 \quad \dots (3)$$

$r = 0.98$

$$F = 0.062 Cl + 0.076 \quad \dots (4)$$

$r = 0.98$

for Mandovi and Zuari respectively. It is thus clear that fluoride bears a linear relationship with chlorinity during monsoon and postmonsoon with $r = 0.98$. The slope of the regression line which may be taken as representing the average F/Cl ratio in a particular season is 6×10^{-5} and 6.2×10^{-5} for Mandovi and Zuari respectively, while the intercept on fluoride-axis gives the concentration of fluoride at zero chlorinity i.e. in river water, which is nearly the same

for Mandovi in the 2 seasons (0.039-0.043) while it varies widely in the Zuari (0.022-0.076).

During premonsoon, however, the fluoride-chlorinity relation is not linear (Fig. 4) but forms a curve which is concave towards the fluoride-axis. However, on plotting the same data on a semilogarithmic scale with fluoride on the logarithmic axis and chlorinity on the linear axis, a linear relation can be obtained. This indicates the suitability of the equation of the type $Y = ab^X$ to represent the relation in Fig. 4. Writing the above equation in logarithmic form results in

$$\log Y = \log a + X \log b \quad \dots (5)$$

which is an equation of a straight line in terms of X and log Y, a and b being constants. The values of constants a and b in Eq. 5 can be obtained by solving the normal Eqs (6) and (7) below⁷.

$$\sum \log Y = N \log a + \log b \sum X \quad \dots (6)$$

$$\sum X \log Y = \log a \sum X + \log b \sum X^2 \quad \dots (7)$$

where N is the number of observations. Solving Eqs 6 and 7 the following relations are obtained between fluoride and chlorinity.

$$\log F = 0.0651 Cl - 1.017 \quad \dots (8)$$

and

$$\log F = 0.0494 Cl - 0.867 \quad \dots (9)$$

for Mandovi and Zuari respectively. The corresponding exponential equations representing Fig. 4 are given by

$$F = 0.0962 \times 1.15^{Cl} \quad \dots (10)$$

and

$$F = 0.1358 \times 1.12^{Cl} \quad \dots (11)$$

Fig. 5 gives the overall picture of fluoride in Mandovi and Zuari for the whole year. In this figure all the fluoride values of these 2 estuaries were pooled together and plotted against chlorinity. The resultant plots are not linear (Fig. 5) but are curves concave to fluoride-axis whose equations, derived by adopting the same method as used above, are exponential, given by

$$F = 0.073 \times 1.176^{Cl} \quad \dots (12)$$

and

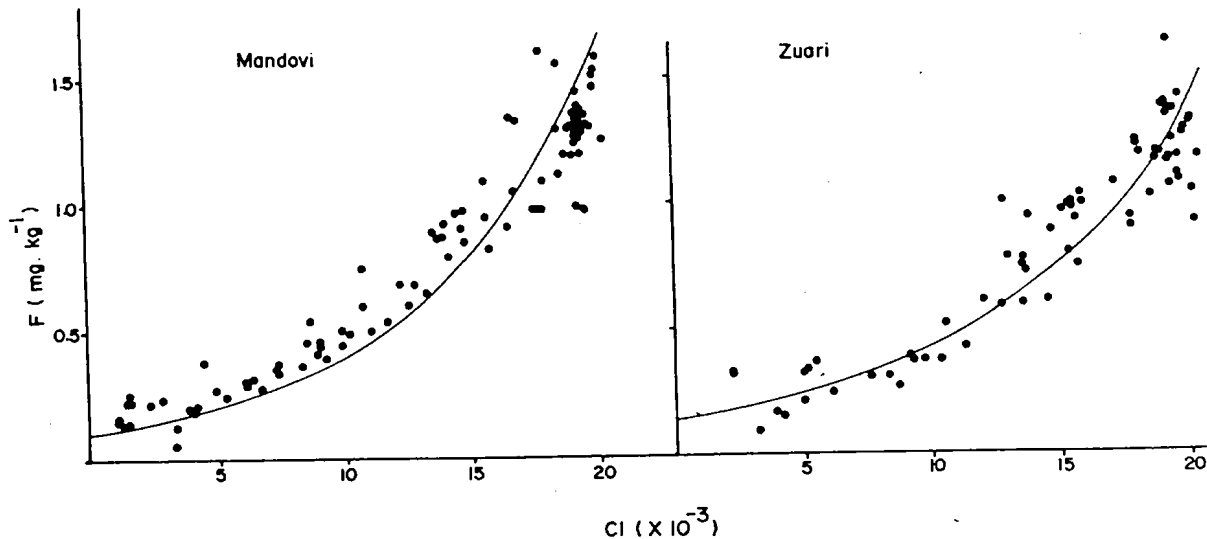


Fig. 4—Fluoride-chlorinity relationship during premonsoon

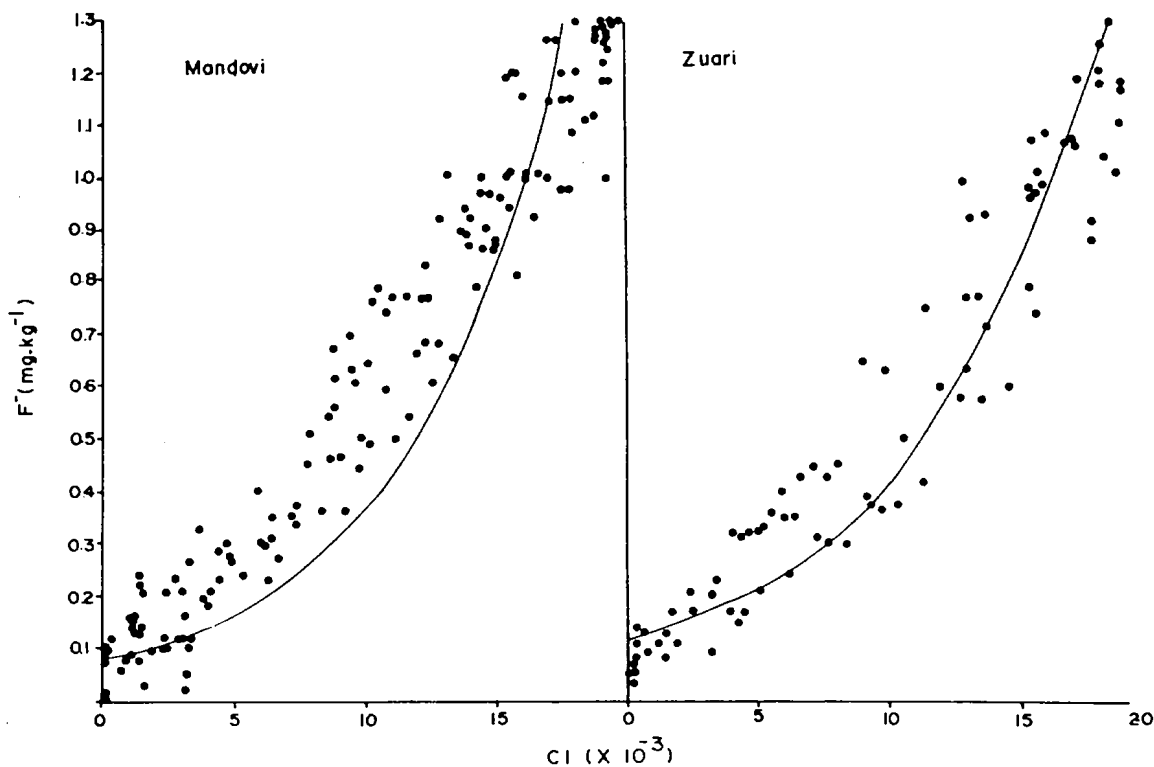


Fig. 5—Overall fluoride - chlorinity relationship

$$F = 0.109 \times 1.145^{Cl} \quad \dots (13)$$

for Mandovi and Zuari respectively.

Thus Eqs 12 and 13 give the overall relationships between fluoride and chlorinity in the 2 estuaries giving average fluoride concentration in river water as 0.073 mg.kg⁻¹ in Mandovi and 0.109 mg.kg⁻¹ in Zuari. These values are comparable to the global av-

erage fluoride concentration in river water^{1,2}. However, they are lower than 0.166 mg.kg⁻¹ which is reported for the Scandinavian rivers⁸.

From Fig. 4 it is apparent that fluoride is lost in the estuaries during premonsoon. In order to determine the extent of fluoride removal, the exact salinity/chlorinity region where it is removed the maxi-

imum and to avoid the scatter of points due to tidal variations, a set of observations was carried out in both the rivers in March 1981 during low tide. Starting from the freshwater-end stations Colem and Nertulim (Fig. 1) in Mandovi and Zuari respectively, a series of surface water samples were collected at increasing salinities from river-end to sea-end and analysed for fluoride. The observed fluoride concentrations were plotted against chlorinity (Fig. 6), which shows that the points lie on a curve which is concave to fluoride-axis suggesting removal of fluoride during mixing. The above figure also shows the 'Theoretical Dilution Line' (TDL) joining the end-members of mixing series and which represents the trend fluoride would follow had it not been removed during mixing. A rough estimate shows that during premonsoon about 28% fluoride is lost in Mandovi estuary while the loss in Zuari estuary is slightly lower (about 25%), the maximum loss occurring at Cl around 10.

The linear relationship of fluoride with chlorinity during monsoon and postmonsoon shows that fluoride behaves conservatively during these seasons and that its concentration in the estuarine waters is governed by physical processes of mixing and tidal variations and is not affected by any other geochemical factor. A conservative behaviour of fluoride during mixing was observed by Warner⁹ in Chesapeake Bay water. The coastal and estuarine waters of Georgia also showed similar behaviour of fluoride¹⁰. The F/Cl ratios 6×10^{-5} and 6.2×10^{-5} observed for Mandovi and Zuari respectively during these seasons are lower than the ratio 6.7×10^{-5} reported by Riley¹¹ and much lower than 6.9×10^{-5} reported by Brewer *et al.*¹² for ocean water. This

low F/Cl ratio may be due to the fact that the fluoride concentration in river waters, draining from the Indian subcontinent is lower than the average river water concentration of 0.1 mg.kg^{-1} observed elsewhere. Sen Gupta *et al.*¹³ suggested that the Indian Ocean rivers have lower fluoride content as compared to 0.166 mg.kg^{-1} observed by Kullenberg and Sen Gupta⁸ for the Scandinavian rivers. Present values, however, compare well with the suggested value¹³ of about 0.08 mg.l^{-1} . According to Carpenter³ about 80-90% of fluoride in river water is cyclic derived from sea salts transported through rain. He also suggested that the contribution of dissolved fluoride by weathering and leaching of rocks is very small since most of the fluoride mobilized during weathering is carried in suspension still bound in detrital minerals.

During premonsoon, the fluoride-chlorinity relationship is not linear but exponential of the type $Y=ab^X$ which is a curve concave to fluoride-axis suggesting that during this season the fluoride concentration in the estuaries is not governed by physical process of mixing alone but by some other biogeochemical processes also. The dilution curve in Fig. 6 shows that the observed fluoride is well below TDL. The removal may be due to some biogeochemical mechanism. The above values of percentage loss are higher than the losses 10 - 20% calculated by Carpenter³. Kullenberg and Sen Gupta⁸ reported 17-30% loss of fluoride in the Baltic and suggested that particles in suspension settling at the confrontation of river water with saline water may be responsible for this removal. The other possible removal mechanisms are loss by evaporation at the air-water interface, loss by deposition as calcium

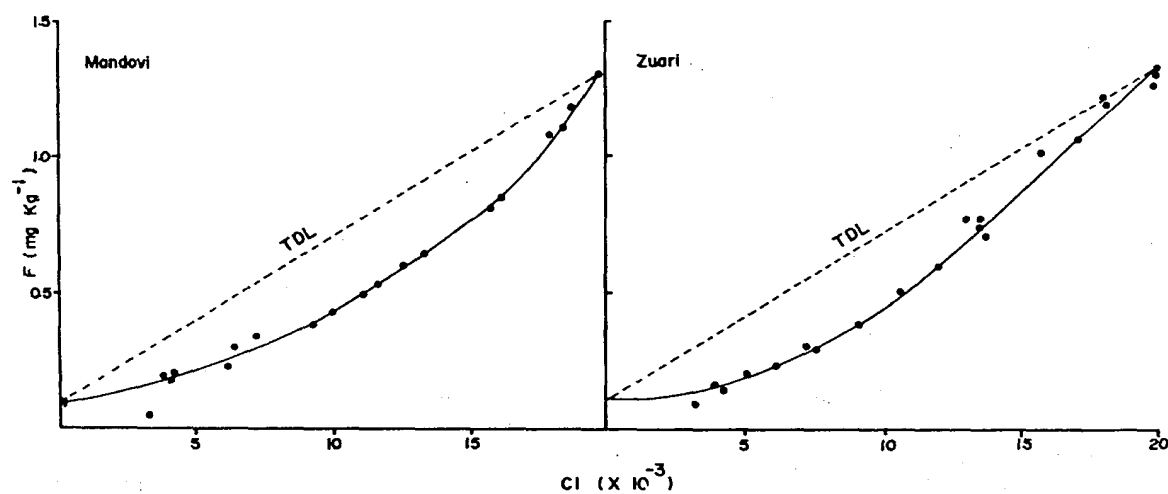


Fig. 6—Fluoride dilution curve

carbonate³, loss during precipitation as fluorapatite in shallow areas¹⁴ where saturation could be reached at low pH and loss due to biological activity. Some biological species having abundant growth in this season may deplete the fluoride and release it subsequently due to their death and decay. One or more of these mechanisms may be operative in the removal of fluoride. It may be pointed out that if suspended particles are the major factor in removing fluoride in these estuaries then the highest removal would have occurred during the monsoon when the suspended sediment load is the maximum. Evaporation, on the other hand, is maximum during premonsoon since the temperature of water and air is highest in this season, added to this is the high amount of water spray caused by the high speed winds. So one may expect maximum loss of fluoride by evaporation during this season.

Comparing the values of fluoride and chlorinity in these estuaries with the tolerance limits for these elements set by the Indian Standard Institution (IS: 2296 - 1974) it can be deduced that the river water upstream of about 33 km from the mouth is safe for use as raw water for public water supply and bathing as far as fluoride and chlorides are concerned.

Acknowledgement

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