

Notes and Discussions

Study of Fluoride in Polluted and Unpolluted Estuarine Environments

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Mindhola River estuary, which receives industrial waste containing high concentrations of fluoride, and Purna River estuary, which is free from fluoride contamination, have been investigated. While fluoride behaved conservatively in Purna River estuary, significant deviation from the theoretical dilution line (TDL) in the chlorinity range 0.5–8‰ was observed in Mindhola River estuary due to the externally added fluoride which largely remained in solution. The excess of fluoride over the theoretically calculated value was at a maximum around a chlorinity of 3‰. High natural fluoride content of the river waters resulted in F/Cl ratios exceeding 300×10^{-5} at low chlorinities. The ratio decreased rapidly with increasing chlorinity and the value near to that of seawater was observed at chlorinities above 14‰.

Introduction

The relationship between fluoride and chlorinity in estuarine mixing zones has been examined by several workers. Windom (1971) found an almost linear relationship for estuarine and coastal areas of Georgia. Warner (1972) came to a similar conclusion from a study of the Chesapeake Bay. Conservative behaviour has also been reported for the Chikugogawa Estuary (Hosokawa *et al.*, 1970). The only work which suggests the non-conservative behaviour of fluoride during the mixing of fresh and saline water is a study of the Baltic and the rivers flowing into it (Kullenberg & Sen Gupta, 1973). Information on the fate of fluoride added through waste-water discharges to coastal marine environments is, however, lacking. The present study in Mindhola and Purna River estuaries was undertaken in order to determine the influence of externally added fluoride on the fluoride–chlorinity relationship. The behaviour of boron, calcium and magnesium in the Mindhola River estuary has been studied. Boron was found to be removed over the entire tidal cycle, while magnesium and calcium were preferentially added, though to a small extent (Narvekar *et al.*, 1983).

Materials and methods

Flood- and ebb-tide samples at six locations along a 30-km stretch (Figure 1) in the Purna and Mindhola River estuaries were collected during September–October 1979. Sampling

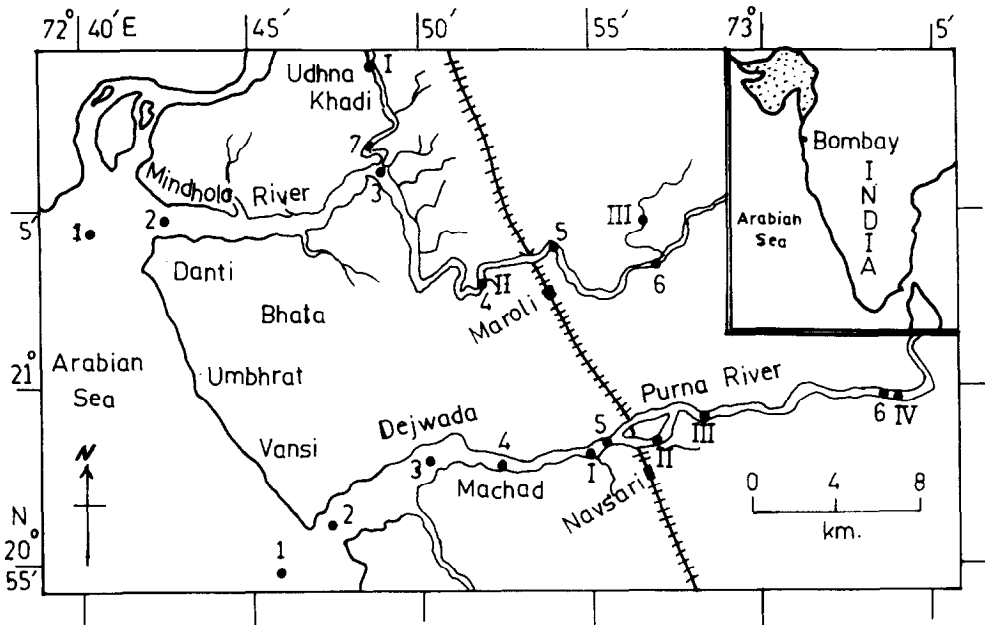


Figure 1. Map showing the sampling locations. The shaded area represents Gujarat State.

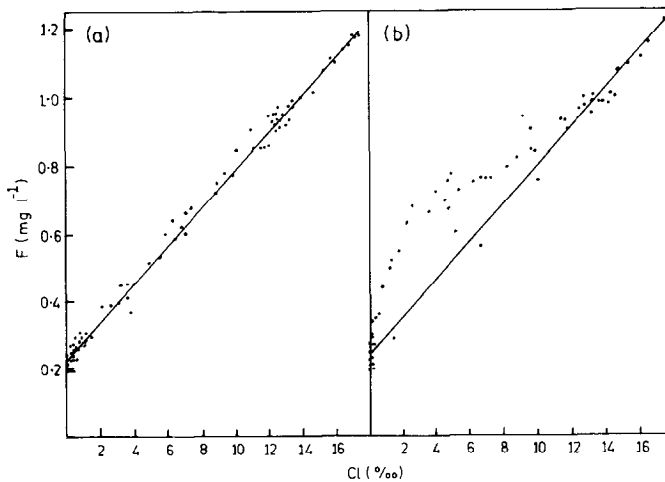


Figure 2. Variation of fluoride with chlorinity in the (a) Purna and (b) Mindhola River estuaries.

of freshwater was done at a location about 45-km inland (not shown in Figure 1) which was beyond the influence of seawater penetration. Time-series studies over complete tidal cycles were also undertaken at stations 2, 4 and 6 during both spring and neap tides. The waste water streams sampled at locations I, II, III and IV marked in Figure 1 were analysed using standard procedures (APHA, 1975). Fluoride in water was estimated

using the alizarine complexone procedure of Greenhalgh and Riley (1961). Correction was made for interference due to magnesium. Replicate analyses of samples having a fluoride content of 1.06 mg l^{-1} (av) gave a standard deviation of $\pm 1.0\%$. Chlorinity was determined by the argentometric titration procedure (Grasshoff, 1976).

Results and discussion

General hydrography

The estuaries in Gujarat State are influenced by strong semidiurnal tides with the spring tidal amplitude exceeding 5 m at the mouth regions. The rivers experience a pronounced cycle of freshwater discharge associated with the monsoonal drainage during July–August. The flow diminishes considerably during the post-monsoon period and is at a minimum during May–June. High seawater influx, strong tidal currents and the small low-tide volume render the Mindhola and Purna River estuaries generally well mixed with good flushing characteristics (NIO, 1980). A flushing time of about one tidal cycle obtained from the application of the tidal prism method was found to be markedly lower than that calculated (6.2–8.0 tidal cycles) from the application of the fraction of freshwater method. The maximum intrusion of saline water during spring tides was up to 25 km inland for both estuaries, although the tidal influence was observed much further inland.

Waste water discharges

The Mindhola River estuary receives waste water from textile, fertilizer, rayon, paper and pulp, chemical and pharmaceutical industries through tidal tributaries at I, II and III with the bulk of the load arriving through Udhna Khadi. It has been estimated (NIO, 1980) that a combined waste water flow of $95 \times 10^6 \text{ l day}^{-1}$ (av) through Udhna Khadi adds $12\,900 \text{ kg day}^{-1}$ of BOD into the estuary, while the combined BOD entering the Purna River estuary at I, II, III and IV is only of the order of 1000 kg day^{-1} . Other pollutants rarely exceeded the permissible limits.

All waste water streams in each estuary were periodically analyzed for fluoride. Except at Station I (Udhna Khadi), the levels of fluoride were below 0.3 mg l^{-1} . The effluent sampled at Station I (Udhna Khadi) showed variable levels of fluoride in the range 0.8 – 2.8 mg l^{-1} , with an average of 1.6 mg l^{-1} . The source of this fluoride was traced to an industry manufacturing bulk fluoride chemicals, which released $3.6 \times 10^6 \text{ l day}^{-1}$ of waste water containing 30 – 80 mg l^{-1} fluoride into Udhna Khadi.

The fluoride content of freshwater (river water) which varied between 0.2 – 0.25 mg l^{-1} , with an average of 0.23 mg l^{-1} and 0.24 mg l^{-1} for Purna and Mindhola River estuaries, respectively, is relatively higher than the average fluoride content (0.1 mg l^{-1}) of the world rivers (Burton, 1976). However, a high level of fluoride in natural waters is not uncommon. Powder River has been reported (Faust & Aly, 1981) to contain 0.4 mg l^{-1} fluoride, while a fluoride content of 32 mg l^{-1} is known to occur in a groundwater in Arizona. A water from the Union of South Africa has been reported to have a fluoride content of 67 mg l^{-1} (Faust & Aly, 1981).

Figure 2 shows the results of fluoride analysis plotted against chlorinity. For straightforward mixing of sea and river water without any loss due to biological or abiological removal or addition, all points in a plot of element concentration against chlorinity would lie on the theoretical dilution line (TDL) joining the end members of the estuarine mixing series, i.e. river water at one end and seawater at the other (Liss, 1976). When a chemical constituent is removed from or added to the water, the points will lie below or above the

TABLE 1. Variation of fluoride-chlorinity ratios in the Purna and Mindhola River estuaries

Chlorinity (%)	Purna		Mindhola		Udhna	
	F (mg l ⁻¹)	F/Cl (× 10 ⁻⁵)	F (mg l ⁻¹)	F/Cl (× 10 ⁻⁵)	F (mg l ⁻¹)	F/Cl (× 10 ⁻⁵)
0.03-0.08	0.18-0.25	600-400	0.18-0.26	600-330	0.41-0.52	650-460
0.1-1	0.23-0.31	119-29	0.21-0.44	250-57	0.39-0.62	325-72
1-5	0.28-0.45	26-9.7	0.5-0.78	37-15	0.52-0.81	180-17
5-10	0.6-0.91	10-7.7	0.56-0.95	13-8.4	0.72-0.81	11-10
10-14	0.85-1.08	8.5-7.0	0.9-1.04	8.1-7.1	0.84-0.98	9.2-7.9
14-17	1.06-1.19	7.2-6.9	1.07-1.23	7.3-6.9	—	—

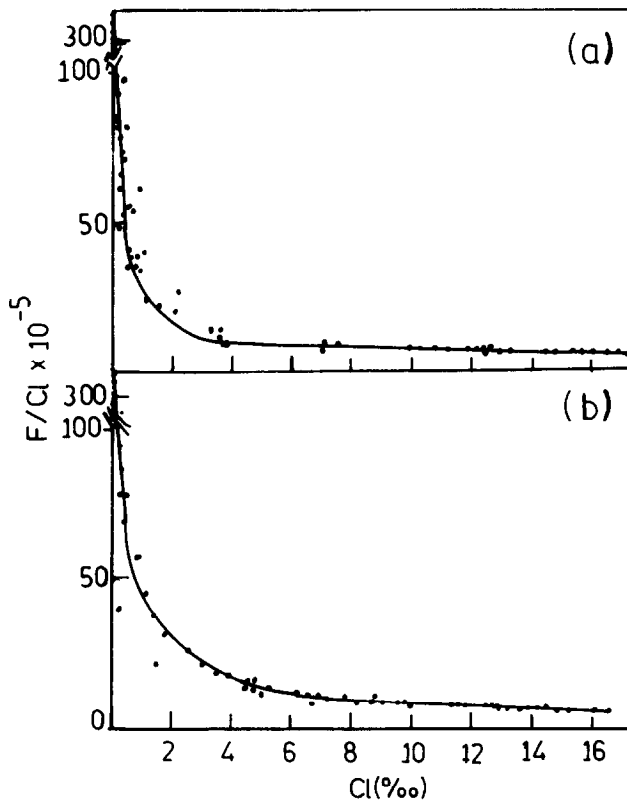


Figure 3. Variation of the fluoride-chlorinity ratio with chlorinity in the (a) Purna and (b) Mindhola River estuaries.

TDL indicating removal or addition, respectively. The following equations were derived for TDL to calculate the theoretical concentrations (in g l⁻¹) of fluoride:

$$[F] = 0.0000552 \text{ Cl}(\text{‰}) + 0.00023 \text{ (Purna),}$$

$$[F] = 0.0000553 \text{ Cl}(\text{‰}) + 0.00024 \text{ (Mindhola).}$$

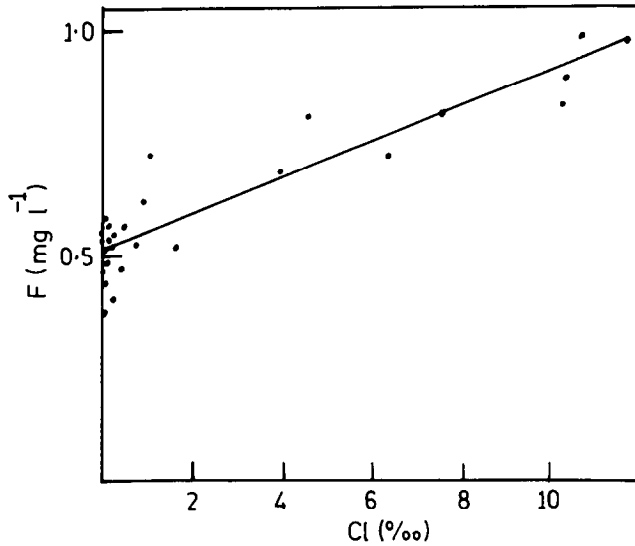


Figure 4. Variation of fluoride with chlorinity at station 7 in Udhna Khadi.

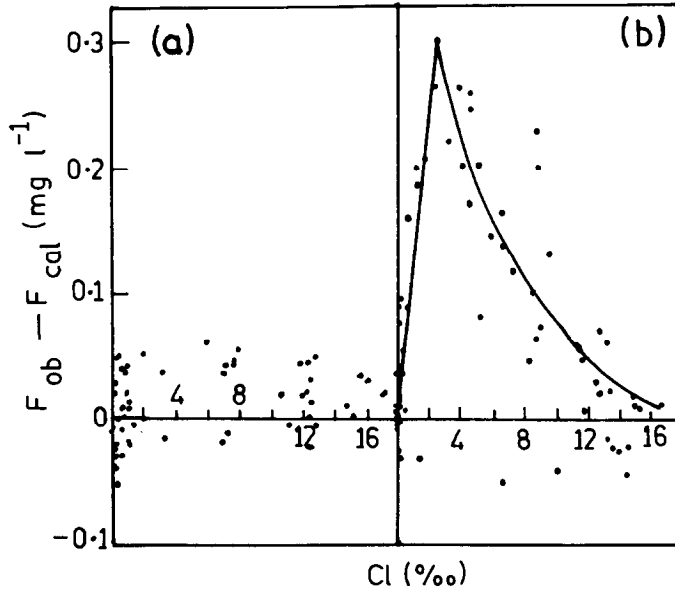


Figure 5. The difference between observed and calculated fluoride concentrations plotted against chlorinity.

The conservative behaviour of fluoride is evident from Figure 2 for the Purna River estuary with all the points falling close to the TDL. The high F/Cl freshwater ratio (Table 1) decreased rapidly with increasing chlorinity and reached a value of 50×10^{-5} at a chlorinity of 0.5‰ , increasing further to 10×10^{-5} at a chlorinity of 4‰ . A ratio near to the seawater value was observed at chlorinities exceeding 14‰ (Figure 3).

Significant deviation from the TDL is, however, evident for the Mindhola River estuary in the chlorinity range 0.5–8‰ (Figure 2), with 90% of the fluoride values falling above the TDL, indicating addition of fluoride from an external source. Any appreciable transfer of fluoride from the solution to the solid state and *vice versa* in marine waters is unlikely (Carpenter, 1969) in view of the similar fluoride content of the clay minerals in aeolian dust, riverborne suspended solids and marine sediments (both in the deep sea and close to estuary mouths). The source of this excess fluoride appears to be the high concentration of fluoride in the contaminated water of the Udhna Khadi. The estuary was freshwater dominated beyond 15 km from the mouth and the majority of the abnormal values were observed in the lower estuary. Diurnal studies undertaken at station 7 (the results of which are represented graphically in Figure 4), clearly indicate the influence of externally added fluoride on the F/Cl ratio. Although the behaviour was more or less conservative (Figure 4), the F/Cl ratios were high at this location, especially in the low chlorinity ranges (Table 1).

Using the equations derived for the TDL, the difference between the calculated and the observed values for fluoride was obtained and is shown in Figure 5 for both estuaries. The maximum deviation from the calculated value for the Mindhola River estuary ($+0.3 \text{ mg l}^{-1}$) is significantly higher than that observed ($+0.05 \text{ mg l}^{-1}$) for the Purna River estuary. The excess fluoride was particularly evident in the chlorinity range 2–6‰ and decreased with an increase in chlorinity beyond 6‰ for the Mindhola River estuary. The difference was in the range observed for the Purna River estuary above 10‰ and below 0.5‰. It may therefore be considered that the fluoride entering the estuarine system remains in solution to a large extent, influencing the fluoride–chlorinity relationship.

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References

- APHA, 1975 *Standard methods for the examination of water and wastewater*, 14th edition. Washington, DC: American Public Health Association.
- Burton, J. D. 1976 Basic properties and processes in estuarine chemistry. In *Estuarine Chemistry* (Burton, J. D. & Liss, P. S., eds). London: Academic Press, pp. 1–31.
- Carpenter, R. 1969 Factors controlling the marine geochemistry of fluoride. *Geochimica et Cosmochimica Acta* 33, 1153–1167.
- Faust, S. D. & Aly, O. M. 1981 *Chemistry of Natural Waters*. Michigan: Ann Arbor Science Publishers, Inc.
- Grasshoff, K. 1976 Determination of salinity. In *Methods of Sea Water Analysis* (Grasshoff, K., ed.). Weinheim: Verlag Chemie, pp. 31–41.
- Greenhalgh, R. & Riley, J. P. 1961 Determination of fluoride in natural water with particular reference to sea water. *Analytica Chimica Acta* 25, 179–186.
- Hosokawa, I., Ohshima, F. & Kondo, N. 1970 On the concentrations of the dissolved chemical elements in the estuary of the Chikugogawa River. *Journal of the Oceanographic Society of Japan* 26, 1–5.
- Kullenberg, B. & Sen Gupta, R. 1973 Fluoride in the Baltic. *Geochimica et Cosmochimica Acta* 37, 1326–1337.
- Liss, P. S. 1976 Conservative and non-conservative behaviour of dissolved constituents during estuarine mixing. In *Estuarine Chemistry* (Burton, J. D. & Liss, P. S., eds). London: Academic Press, pp. 93–130.
- Narvekar, P. V., Zingde, M. D. Kamat Dalal, V. N. 1983 Behaviour of boron, calcium and magnesium in a polluted estuary. *Estuarine, Coastal and Shelf Science* 16, 9–16.
- NIO, 1980 Pollution and hydrographic survey of Auranga, Ambika, Purna and Mindhola rivers (South Gujarat). (Project Report.) Bombay: National Institute of Oceanography, Regional Centre.
- 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.