Dissolved fluoride in the Lower Ganges-Brahmaputra-Meghna River system in the Bengal Basin, Bangladesh

D.K. Datta · L.P. Gupta · V. Subramanian

Abstract The dissolved fluoride (F^-) in the Lower Ganges-Brahmaputra-Meghna (GBM) river system, Bengal basin, Bangladesh, was studied during 1991–1993 to determine its distribution and source in the basin, and its annual flux to the Bay of Bengal. The concentration of dissolved F^- varied between 2 and 11 μmol l^{-1} with statistically significant variations both spatially and temporally in the basin. Such variations are attributable to the geology of the individual subbasins (Ganges, Brahmaputra and Meghna), dilution by rainwater during monsoon and groundwater contribution to the river systems during dry season. Correlation coefficients among F^- and major cations and anions suggest diverse inorganic processes responsible for regulating the concentration of F^- in these river systems. However, fluorite seems to be one of the major sources of dissolved F^-. The concentration of F^- in the Lower GBM river system is low compared to the rivers draining Deccan Plateau and arid regions of the subcontinent, for example, Yamuna and its tributaries. However, it is within the range of most of the other Peninsular and Himalayan rivers. The GBM system contributes about 115×10^3 tonnes year^{-1} of dissolved F^- into the Bay of Bengal, and thus accounts for about 3% of the global F^- flux to the oceans annually.

Key words Dissolved fluoride · GBM river system · Bengal basin · Bangladesh

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Introduction

Fluorine is physiologically important, and it is the most reactive element in nature. It is relatively abundant in the earth's crust (relative abundance 13). The dominant source of fluoride in the aquatic system is mineral fluorite (CaF_2). Other minerals such as topaz, fluorapatite, micas, cryolite, etc., having fluorine as an essential component, are accessory minerals, and are sparingly soluble in water; therefore fluoride contribution from them is minimal. Fluoride ions (F^-) in drinking water (about 1 ppm or 52.6 μmol l^{-1}) greatly reduce dental caries. It makes tooth enamel much harder by converting hydroxyapatite [$3(Ca_3\ (PO_4)_2\ Ca\ (OH)_2$] into fluorapatite on the tooth surface. However, F^- concentration above 2 ppm causes discoloration of teeth and even higher concentrations are harmful and cause fluorosis – making bones fragile (Lee 1991).

The Bengal basin, Bangladesh is situated at the confluence of the Ganges-Brahmaputra-Meghna (GBM) river system – the largest sediment-dispersal system in the world (Kuehl and others 1989), and offers the passage of an estimated amount of 1330 km^3 of water to the Bay of Bengal annually (Milliman and others 1995). More than 86% of the basin is composed of recent floodplain deposits of medium to fine sand, silt and clay composed dominantly of quartz, feldspars, illite and kaolinite (Datta and Subramanian 1997a). The population density of the basin is one of the highest in the world (on average 755 people per km^2 in 1991; Anonymous 1998), and ranges from 400 to 1200 people per km^2 (Milliman and others 1989). Industrialization is very low, but extensive agricultural activities are peculiar to this region.

The GBM system constitutes one of the major pathways transferring dissolved solute to the world oceans (152×10^6 tonnes year^{-1}; representing about 5% of the total solute flux from land to oceans globally; Datta and Subramanian 1997b). The major ion chemistry of the GBM river system has been updated from time to time

(Abbas and Subramanian 1984; Ittekkot and others 1986; Subramanian and others 1987; Sarin and others 1989; Datta and Subramanian 1997b). However, dissolved fluoride in the Lower GBM system has not yet attracted the attention of the researchers. The present study deals with the distribution and controlling factors of dissolved F^- in the Bengal basin, Bangladesh and its flux into the Bay of Bengal.

Methodology

River water samples were collected systematically during December–January 1991–1992, August–September 1992 and April–May 1993 from sites uniformly located all over the basin, avoiding sites of tributary effect and point-source pollution (Fig. 1). The water was collected in 1 litre polythene bottles from about mid-channel at a depth between 50 and 100 cm from the water surface, and was stored at 1–4 °C in a cold room. The pH and alkalinity were measured on-site and fluoride was measured at the laboratory within 2 weeks of sample collection (see Datta and Subramanian 1997b). Dissolved fluoride was measured by Radiometer ION85 ion analyzer and OMEGA fluoride ion electrode following the instrument manual. The analytical precision was ±5% of the reported values. Single-factor ANOVA was performed to compute statistical significance of differences in parameter among individual river basins.

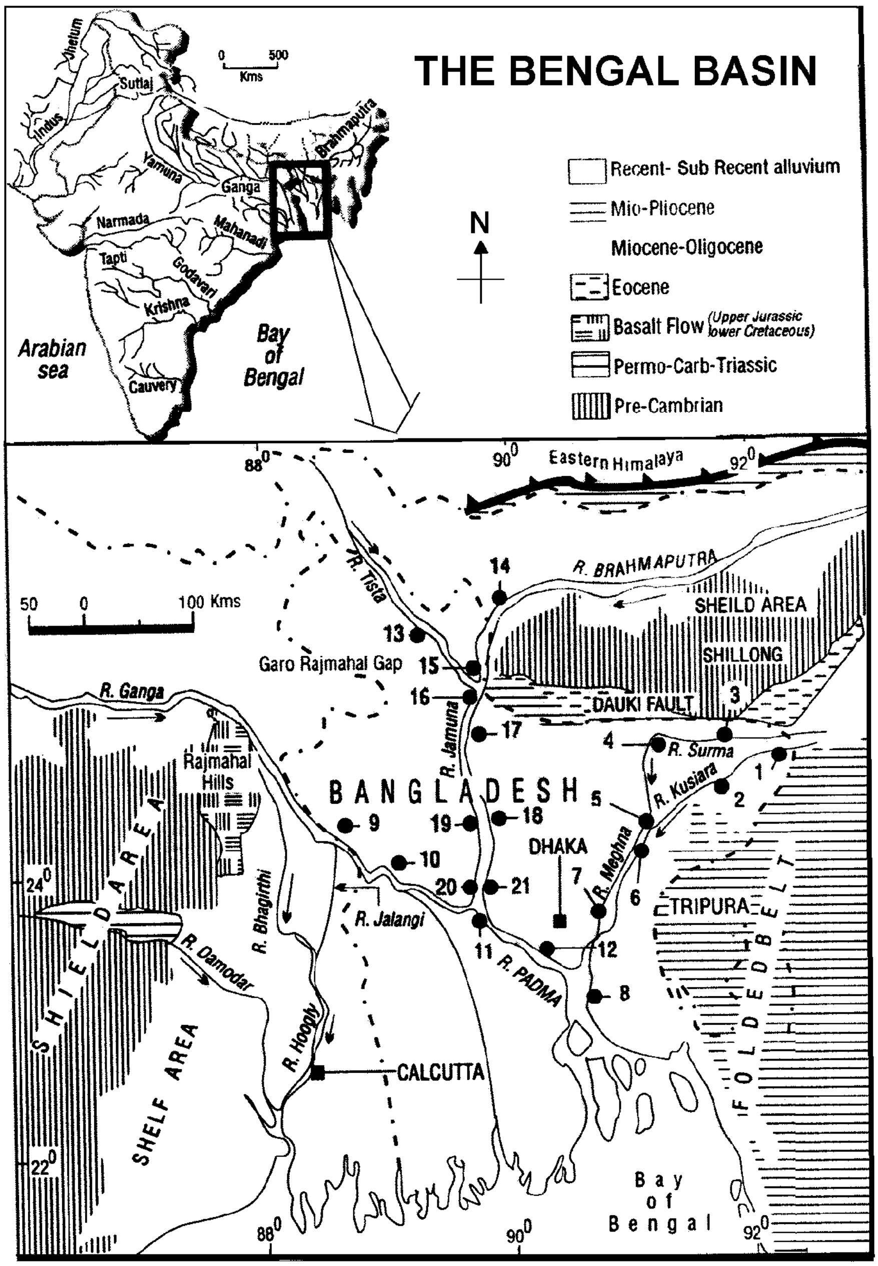

Fig. 1
Geological features and sampling locations in the Bengal Basin, Bangladesh

Results and discussion

The concentration of dissolved fluoride (F^-) in the GBM drainage basin, Bangladesh, is presented in Table 1. Dissolved F^- concentration in the Bengal basin, Bangladesh, ranges between 2 and 11 μmol l^{-1}. However, statistically significant spatial (P value = 0.008) and temporal (P value = 0.0001) variations in the F^- concentration among individual river basins could be observed in the GBM basin (Fig. 2). The Ganges River shows the highest concentration (average 8.2 ± 3.6 μmol l^{-1}), while the Meghna River shows the lowest (average 3.5 ± 1.8 μmol l^{-1}). The Brahmaputra River shows an intermediate concentration (average 6.3 ± 3.1 μmol l^{-1}) relative to the Ganges and Meghna. The dry season is marked by higher concentration of F^- (average 7.6 ± 1.9 μmol l^{-1}) compared to monsoon and pre-monsoon (average 3.3 ± 2.8 μmol l^{-1}). The drainage regime of most of the Peninsular tributaries of the Ganges includes known deposits of fluorite (CaF_2; Wadia 1975). Contributions from these tributaries are responsible for higher F^- concentration in the Ganges. The factors responsible for temporal variations in F^- concentration in the rivers also include (1) contribution of F^- from groundwater, (2) evaporation during dry season and (3) dilution by rainwater during the monsoon. Dissolved F^- in the Lower GBM system shows excellent correlation with most of the cations and other anions (Table 2); thereby suggesting diverse rock/mineral sources of F^- in the river water. A major source of F^- in aquatic systems is the weathering of fluorite (CaF_2), although minerals such as fluorapatite, apatite, micas,

Table 1
Dissolved fluoride (F^-) in the Lower Ganges-Brahmaputra-Meghna (GBM) river system, Bengal Basin, Bangladesh. Station numbers correspond with those in the Fig. 1

Station	Site	Sampling date	F^- (μmol l^{-1})
Meghna and tributaries			
01	Sheola	Dec 1991	5.8
		Apr 1993	1.6
02	Sherpur	Apr 1993	1.8
03	Sylhet	Apr 1993	2.1
04	Sunamganj	Dec 1991	5.5
06	Bhairab Bazer	Jan 1992	5.1
		May 1993	2.1
07	Meghna Ghat	Jan 1992	5.9
		Sep 1992	3.7
		May 1993	2.1
08	Chandpur	May 1993	2.1
Brahmaputra (Jamuna) and tributaries			
13	Tista Bridge	Dec 1991	9.4
15	Chilmari	Dec 1991	6.3
16	Phulchari	Dec 1991	8.1
17	Bahadurabad Ghat	Dec 1991	9.3
		May 1993	2.1
19	Sirajganj	Dec 1991	7.7
		Aug 1992	2.1
20	Nagarbari	Dec 1991	7.7
21	Aricha	Jan 1992	8.0
		May 1993	1.8
Ganges (Padma)			
09	Rajshahi	May 1993	9.2
10	Hardinge Bridge	Dec 1991	11.1
		Aug 1992	10.0
11	Daulatdia Ghat	Jan 1992	8.9
12	Maoa	Aug 1992	2.1

Fig. 2
Temporal and spatial variations of dissolved fluoride in the GBM basin

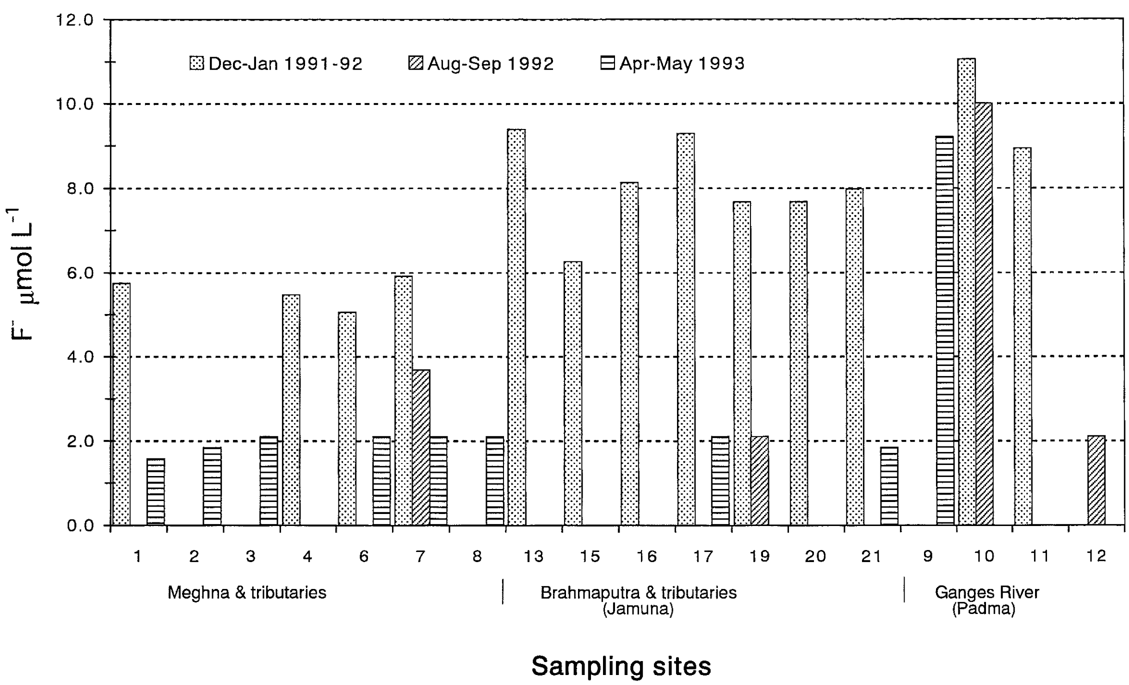

Table 2
Correlation coefficient (*r*) of fluoride (F^-) with major cations, anions and silica in the Lower GBM river system

Parameter	*r* with F^- ($n=26$)
Ca^{2+}	0.78
Mg^{2+}	0.78
Na^+	0.64
K^+	0.60
Cl^-	0.42
SO_4^{2-}	0.58
HCO_3^-	0.80
PO_4^{3-}	−0.18
SiO_2	0.89

amphiboles, clays (illite, chlorite, smectites) and villiaumite, etc. have hydrogeochemical effects on the aqueous concentration of F^- (Pickering 1985; Apambire and others 1997). The limit of saturation of these minerals in river water plays a role in determining F^- concentration (Pickering 1985; Gaciri and Davies 1993; Ramamohana Rao and others 1993; Apambire and others 1997).
The concentration of Ca^{2+} is important in determining the level of dissolved F^- (Gaciri and Davies 1993). Fluorine is incorporated into a calcium carbonate structure and removed from solution when the latter precipitates (Carpenter 1969, as mentioned in Gaciri and Davies 1993). Thus calcite saturation, with respect to that of fluorite, controls F^- concentration in water. Following Stallard and Edmond (1987), saturation indices (SI) of fluorite and calcite can be expressed as given below:

Fluorite:
$$SI_F = \log(a_{Ca} \times a_F^2 / K_{sp\ fluorite}) \quad (1)$$

Calcite:
$$SI_C = \log(a_{Ca} \times a_{CO_3} / K_{sp\ calcite}) \quad (2)$$

where a is the activity (or mole concentration) term and K_{sp} is the solubility product (a constant; 3.2×10^{-11} for fluorite and $10^{-8.3}$ for calcite at room temperature of 20–25 °C; Moore 1999).
Using Eqs. (1) and (2) and the data from Datta and Subramanian (1997b), SI_F and SI_C for all the samples were calculated. When SI_F is plotted against SI_C (Fig. 3), a majority of the samples represent undersaturation with respect to both calcite and fluorite (except at sites 10 and 21 where calcite shows supersaturation), which suggests that the Ca^{2+} concentration is not above the limit of fluorite saturation and is therefore not responsible for the suppression of the dissolution of fluorite. In accordance with this inference, the excellent correlation between F^- and Ca^{2+} ($r=0.78$; $n=26$; Table 2) suggests that fluorite is a significant source of F^- in the Lower GBM system.
The excellent positive correlation between F^- and HCO_3^- ($r=0.80$, n = 26) can be explained by the following mass law equation relating calcite and fluorite when both the minerals are in contact with water (Handa 1975):

$$CaCO_{3\ solid} + H^+ + 2F^- = CaF_{2\ solid} + HCO_3^-$$

In this case,

$$K_{CaF_2} = \frac{a_{HCO_3^-}}{a_{H^+} \times (a_{F^-})^2} \quad (3)$$

Thus, at reasonably constant K_{CaF_2} and pH, a positive correlation is established between F^- and HCO_3^-.
A relatively high concentration of Na^+ increases the solubility of fluorite by base exchange (Ca and Mg for Na; Apambire and others 1997) in the relatively alkaline water of the Lower GBM system (Datta and Subramanian 1997b). Also, the positive correlation between F^- and Na^+ ($r=0.64$; $n=26$) suggests villiaumite (NaF) – a water-soluble fluoride mineral – as a source of F^- in the river water. F^- also exhibits very good correlation with SiO_2, Mg^{2+}, K^+ and SO_4^{2-}. Minerals such as amphiboles, micas, clay minerals (illite, chlorite and smectites) sellaite (MgF_2), which could be possible sources of F^-, have very low solubility products and their ready decomposition is doubtful (Nanyaro and others 1984). However, both carbonate and silicate weathering are equally significant in the Lower GBM drainage basin and the river system exhibits one of the highest denudation rates in the world, representing enormous weathering and erosion in the denudation regime (Datta and Subramanian 1997b). Thus chemical weathering of silicate minerals could be a significant source of fluoride in the Bengal Basin. However, additional data are needed to ascertain contribution from these minerals.
The discharge weighted mean concentration of dissolved F^- and its annual flux to the Bay of Bengal is presented in Table 3. The estimation procedure has been described in detail elsewhere (Datta and Subramanian 1997b). In

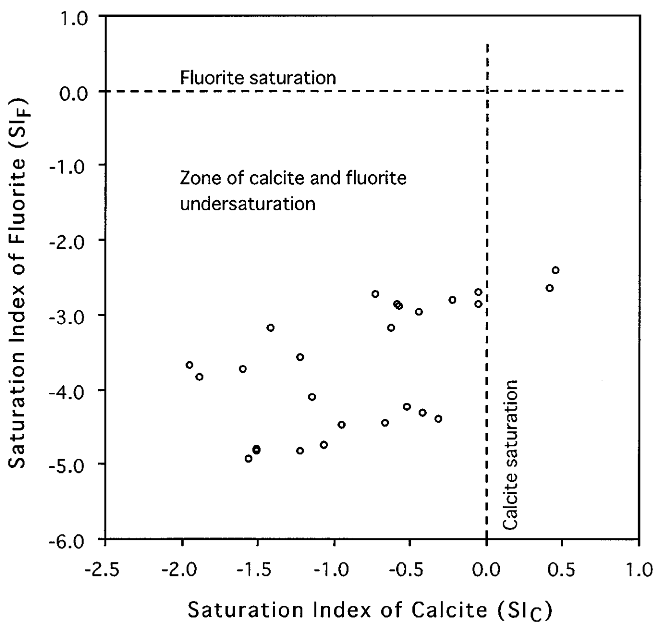

Fig. 3
Plot of calcite saturation index (SI_C) vs. fluorite saturation index (SI_F)

Table 3
Discharge weighted mean concentration of dissolved fluoride (F^-) in the Lower GBM river system, and its flux to the Bay of Bengal

Rivers	Discharge (km^3 $year^{-1}$)	F^- ($\mu mol\ l^{-1}$)	Total flux ($\times 10^3$ tonnes $year^{-1}$)
Lower Ganges (Padma)	350.5	10.15	68
Lower Brahmaputra (Jamuna)	654.5	2.92	36
Meghna	151.5	3.73	11
Global average	26,000[a]	8.00[b]	4,000

[a] Calculated from Milliman and others (1995)
[b] Livingstone (1963)

brief, the discharge weighted mean concentrations of F^- in the Ganges (Padma) at Station 10, Brahmaputra (Jamuna) at station 17 and Meghna at Station 06 were calculated using the following equations:

For Ganges:
$$C = 0.847\ C_A + 0.153\ C_D \quad (4)$$

For Brahmaputra:
$$C = 0.766\ C_A + 0.115\ C_D + 0.119\ C_M \quad (5)$$

For Meghna:
$$C = 0.721\ C_S + 0.183\ C_M + 0.096\ C_D \quad (6)$$

where C is the discharge weighted concentration, and C_A, C_D, C_M, and C_S are the concentrations of F^- during the months of August, December, March and September, respectively. Various factors (e.g. 0.847, 0.153, 0.766, etc.) were calculated from average monthly water discharges recorded at the respective stations. The Ganges shows a higher discharge weighted mean concentration of F^- by a factor of 2.5–3 as compared to that of the Brahmaputra and Meghna. However, it is close to the global average value of 8.0 $\mu mol\ l^{-1}$ (Table 3). The GBM system contributes about 115×10^3 tonnes $year^{-1}$ of dissolved F^- into the Bay of Bengal, and thus accounts for ~3% of the total global F^- flux to the world oceans annually.
The range of F^- concentration in the Bengal basin, Bangladesh, is similar to that of most of the Himalayan and the Peninsular rivers of the Indian subcontinent, except for the Sai, Yamuna, Chambal, Betwa and Ken Rivers (Table 4). The denudation regimes of the latter rivers are located in the southern slope of the Vindhyan mountain which has known fluorite deposits (Wadia 1975). The relatively higher concentration of F^- in these rivers could be related to bed-rock geology and climatic condition over their denudation regimes. Similar reasoning has also been invoked for the relatively higher concentration of F^- in some of the tributaries of the Krishna River – one of the largest rivers in peninsular India (Ramamohana Rao and others 1993).

Table 4
Dissolved fluoride (F^-) concentrations in the major South Asian Rivers

Rivers	F^- ($\mu mol\ l^{-1}$)	Reference
Ganges-Brahmaputra-Meghna river system		
Bhagirathi	5 – 39	Author
Middle Ganges	5–11	Abbas and Subramanian (1984)
Lower Ganges	2–11	This study
Brahmaputra in Assam	5–11	Mahanta (1995)
Lower Brahmaputra	2–8	This study
Meghna	2–6	This study
Surma	2–5	This study
Kushiara	2–6	This study
Tista	9	This study
Gomti	13–17	Gupta and Subramanian (1994)
Sai	17–21	Author
Yamuna	17–43	Author
Chambal	13	Author
Betwa	50	Author
Ken	28	Author
Peninsular Rivers		
Mahanadi	0.5–1	Chakrapani and Subramanian (1990)
Godavari	Trace	Biksham and Subramanian (1988)
Krishna	11–32	Ramesh and Subramanian (1988)
Cauvery	4–16	Ramanathan and others (1994)
Global Average	5–11	Livingstone (1963)

Bangladesh – one of the most densely populated countries in the world – is dominated by an agrarian society accounting for more than 85% of the total population in the country (Anonymous 1991). The land area of the country is crisscrossed by more than 250 major tributaries and distributaries of the Lower GBM river system. River water plays a most essential role in the agricultural and household activities in such a society. The optimum safe limit of F^- in drinking water is between 37 and 63 $\mu mol\ l^{-1}$ (Saether and others 1995), and up to 526 $\mu mol\ l^{-1}$ for all types of crop plants (Leone and others 1948, as mentioned in Singh and others 1987). These concentration limits and the data generated in the present study lead us to conclude that the river water in the Bengal basin is low in F^- content and does not pose a threat to crops, livestock or man. Instead, fluoridation of potable water needs to be considered for better dental health of the people in this region.

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