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Geochemical pathways of fluoride and boron in the alluvial aquifer of the Dwarka river basin, India

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Dwarka river basin, situated in the Birbhum district of West Bengal, India is endemic to fluorosis as groundwater contains fluoride as high as 14 mg/L (permissible limit 1.5 mg/L). Co-existence of boron (B) and fluoride (F^{-1}) in groundwater, sometimes acts as a tool to predict the source of fluoride. This research was carried out with an objective to identify the geochemical relationship of these two elements and to find out their source(s) in groundwater. pH of groundwater of the study area was mostly neutral to alkaline, F^- generally ranged from 0.1 to 10.6 mg/L and boron ranged from 0.01 to 0.5 mg/L. Fluoride and boron showed a strong positive correlation indicating similar source. Fluorapatite observed in sediment samples was considered to be the main source of fluoride. Clay minerals found in the sediment sample were considered to be the most probable source of boron.

IN groundwater, occurrence of fluorine (F^-) and boron (B) together has attracted attention because of their effects on human health. Fluoride (F^{-1}) bearing minerals such as fluorite, cryolite and fluorapatite are commonly found in granitic rocks[1,2] which can contaminate groundwater with F^- through water–rock interaction. Occurrence of F^- has also been reported in secondary rocks such as argillaceous carbonate rocks[3], loess deposits[4], flood plain deposits[5,6]. Occurrence of F^- bearing minerals in hard rock terrains is well known, but F^- dynamics in alluvial terrains is less documented[7,8]. Natural sources of B include both igneous rocks and sedimentary deposits. The main process for the origin of B in groundwater is water–rock interaction in carbonate rocks, bentonites and evaporites, and ion exchange phenomenon of aquifer materials. In soil, B, associated with organically bound clay and mineral-fixed fractions commonly occurs as borates of sodium (Na) and calcium (Ca). In the earth's crust, average concentration of B is generally 10 ppm; its concentration in rocks ranges from 5 ppm in basalts to 100 ppm in shales[9]. Dwarka river basin (DRB) in Birbhum district

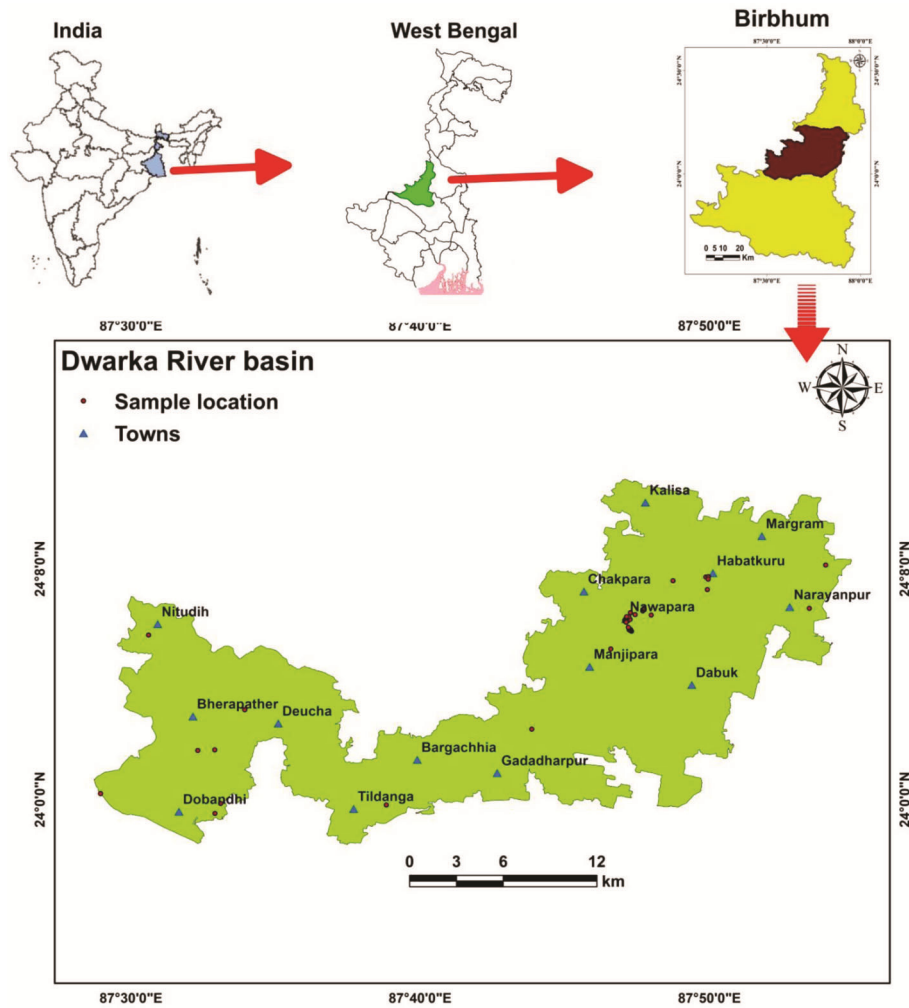*For correspondence. (e-mail: srimantagupta@yahoo.co.in)

Figure 1. Location map of the study area.

encompasses an area of about 857.773 sq. km with geographical coordinates lying within 23°58′10″N–24°14′12″N lat. and 87°28′52″E–24°14′12″E long. Spread of the DRB is about 858 sq. km (Survey of India toposheet nos 72P/08, 72P/12, 72P/16, 73M/05, 73M/09 and 73M/13) (Figure 1). The study area is endemic to fluorosis. The main basement rock formation of the basin is the Chottanagpur Gneissic Complex comprising pink granite, granite gneiss with veins of pegmatite and quartz and epidote granite. The Rajmahal Formation occurring in the western part of the study area comprises intertrappean sedimentary rocks and a succession of basaltic flows with the presence of megacrysts of feldspar at the bottom parts. In the eastern part of the basin, hard clay with impregnated caliche nodules (Rampurhat Formation) occurs whereas the central part is mainly covered by laterites extending from north to south[10,11]. Recent sediments occur along the Dwarka river channel. In the southwestern part of the area, from Mollarpur, semi-consolidated Gondwana rocks are known. The subsurface disposition of bedrock and the aquifers in the study area indicate that

hard consolidated rocks occur at shallow depth in the western part of the study area and the depth to the bedrock increases from west to east. In the DRB, F^- contamination in groundwater has been reported earlier, but its source and mobilization mechanism has not been addressed so far in the perspective of associated B. The aim of this paper is to highlight the sources of F^- and B anomalies in an alluvial aquifer along with their release mechanisms in groundwater, based on the geochemical study.

In the study area, 40 water samples were collected from 21 villages, namely Phullaipur, Kumardih, Rampur, Sehera, Shrikantapur, Bhagabandh, Kujopara, Kamdebpur, Bilaspur, Murulidanga, Junidpur, Nawapara, Chaktola, Kalidaha, Diyara, Phulidanga, Kalkapur, Habatkuru, Tejhari, Srirampur and Pachanpur (Table 1). pH was measured at the site of collection with a portable pH meter. Fluoride was measured with ion-selective electrode method and B was measured by inductively coupled plasma-mass spectrophotometry (ICP-MS). Three different sites were selected based on the availability of high F^- in

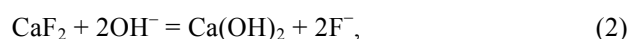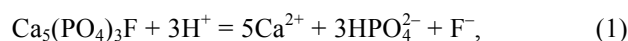**Table 1.** Details results of water sample analysis in the study area

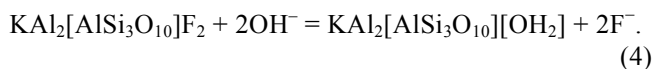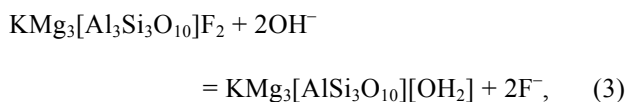| Sample	Name of village	Latitude	Longitude	pH	EC	F	B
1	Phullaipur	23.99766	87.55172	7.0	–11.0	0.3	1.7
2	Kumardih	24.00334	87.48254	7.4	–31.0	0.1	28.3
3	Rampur	24.02864	87.54834	7.4	–33.0	1.7	10.7
4	Sehera	23.99189	87.54844	7.6	–42.0	1.5	3.7
5	Shrikantapur	24.0283	87.53857	7.5	–41.0	0.8	19.5
6	Bhagabandh	24.09502	87.51021	7.2	–24.0	0.4	0.1
7	Kujopara	24.12643	87.81244	8.0	–64.0	1.7	45.4
8	Kamdebpur	24.10895	87.79497	7.5	–40.0	1.7	17.1
9	Kamdebpur	24.1097	87.79582	7.8	–57.0	2.7	15.5
10	Kamdebpur	24.11045	87.79582	7.7	–52.0	2.7	0.1
11	Bilaspur	24.08696	87.77661	8.1	–74.0	3.5	277.7
12	Murulidanga	24.04062	87.73105	7.5	–42.0	0.3	15.6
13	Junidpur	24.09721	87.78854	8.4	–92.0	0.7	47.6
14	Junidpur	24.09766	87.78793	8.3	–82.0	2.1	111.8
15	Junidpur	24.09827	87.78793	8.5	–91.0	1.7	91.5
16	Junidpur	24.09807	87.78717	8.5	–95.0	3.4	118.9
17	Junidpur	24.09887	87.78703	8.5	–95.0	1.9	95.4
18	Junidpur	24.09948	87.78673	8.4	–91.0	1.0	39.4
19	Nawapara	24.10358	87.78461	8.4	–89.0	2.3	421.0
20	Nawapara	24.10435	87.7852	8.4	–91.0	7.3	245.1
21	Nawapara	24.10456	87.78707	8.5	–94.0	6.8	277.5
22	Nawapara	24.10462	87.78639	8.3	–84.0	2.4	131.5
23	Nawapara	24.10367	87.78624	8.5	–94.0	10.0	494.9
24	Nawapara	24.10397	87.78568	8.6	–98.0	9.8	415.4
25	Nawapara	24.10278	87.78511	8.3	–85.0	4.0	151.8
26	Nawapara	24.10239	87.78544	8.5	–95.0	9.4	414.4
27	Nawapara	24.10408	87.78773	8.5	–97.0	10.6	350.7
28	Nawapara	24.10551	87.78699	8.1	–77.0	1.8	83.0
29	Nawapara	24.1056	87.78571	8.5	–92.0	9.8	339.8
30	Chaktola	24.10792	87.78791	8.2	–79.0	2.0	322.7
31	Kalidaha	24.13548	87.90041	8.0	–67.0	1.8	43.7
32	Diyara	24.11043	87.89101	7.8	–56.0	0.5	21.9
33	Phulidanga	24.10659	87.79989	7.7	–53.0	0.6	20.8
34	Kalkapur	24.12132	87.83225	7.6	–47.0	0.4	17.1
35	Habatkuru	24.12857	87.83131	7.9	–63.0	1.1	111.9
36	Habatkuru	24.12876	87.83274	8.1	–71.0	2.2	157.6
37	Habatkuru	24.12729	87.8327	8.2	–75.0	4.4	159.7
38	Tejhari	24.1068	87.79065	7.9	–61.0	1.2	76.1
39	Srirampur	23.99675	87.64722	8.0	–70.0	0.3	22.0
40	Pachanpur	24.05184	87.56565	7.5	–42.0	0.2	5.8

groundwater and depth-wise sediment samples were collected. Field-emission scanning electron microscopy and energy-dispersive X-ray analysis (EPMA, FESEM-EDX and XRD) were performed on the collected sediment samples.

The pH of the groundwater of the study area was generally alkaline (range 7–8.56; mean 8.02). Approximately, 7.5% of the total number of samples had pH outside the range permissible for drinking water (6.5 to 8.5; WHO, 2011). The F^- concentration in the groundwater ranged from 0.1 to 10.6 mg/L, and approximately 37.5% of water samples had $F^- < 1.5$ mg/L, a permissible limit for drinking water. Boron in groundwater ranged from 0.01 to 0.5 mg/L. Pearson's correlation indicated a strong positive correlation between F^- with B ($r = 0.70$) (Figure 2 a) and moderate positive correlation of F^- with pH ($r = 0.41$) (Figure 2 b).

Wide variation of F^- content in the same alluvium is mainly attributed to the presence or absence of clay layer intercalations within the aquifer. It was noticed that most of the high F^- aquifers were intercalated with clay layer having total F^- in the range of 70 mg/kg to 1008 mg/kg whereas, low F^- aquifer within the same alluvium was predominantly made up of thick sand layer.

In alkaline groundwater, the F^- present in the fluoride-bearing minerals such as fluorapatite, biotite, fluorite, muscovite and soil can be replaced by OH^- resulting in higher F^- concentrations in groundwater. The most probable mechanisms involved in this are represented in eqs (1–4)

$$Ca_5(PO_4)_3F + 3H^+ = 5Ca^{2+} + 3HPO_4^{2-} + F^-, \tag{1}$$

$$CaF_2 + 2OH^- = Ca(OH)_2 + 2F^-, \tag{2}$$

$$KMg_3[Al_3Si_3O_{10}]F_2 + 2OH^-$$

$$= KMg_3[AlSi_3O_{10}][OH_2] + 2F^-, \quad (3)$$

$$KAl_2[AlSi_3O_{10}]F_2 + 2OH^- = KAl_2[AlSi_3O_{10}][OH_2] + 2F^-. \quad (4)$$

Total F^- in sediments, collected from the study area ranged from 70 mg/kg to 1008 mg/kg. Clayey sediments were found to have elevated concentration of F^-. The results of sequential extraction indicate that the residual form of F is the most important fraction compared to other forms studied, where, about 80% of total F is in residual form. Thus the results of the sequential extraction of F of sediment samples collected from the three different sites showed that the residual form was the most dominant and the decreasing sequence of availability are as follows: residual form > water-soluble > Fe–Mn form > organic bounded > carbonate form > exchangeable form.

High Fe_2O_3 (4%), MnO (1%) and organic matter content of the clay layers also support the crucial role of Fe–Mn in releasing F^- in groundwater. Boron is strongly absorbed onto natural organic matter which is released into groundwater during microbial decomposition of organic matter. Competitive sorption of HCO_3 from the

surface of ferric oxyhydroxide or clay minerals facilitates desorption of B (ref. 12).

X-ray diffraction (XRD) analysis showed the presence of intercalated zeolitic clay in the sediment samples and was considered to be the most probable source of F^- in the study area aquifer[13]. EPMA analysis of the sediment sample revealed the presence of fluorapatite with F^- content as high as 5 wt%. Cations such as Ca, Na, K are loosely bound to the framework of zeolites and do not fill the cavities, hence, they can easily replace each other. In aquifer system, B undergoes several interactions which involve processes such as its adsorption and desorption onto clay mineral surfaces which play a crucial role in the mobilization of B[14]. The zeolitic clay could have been derived from tuffs interbedded with Rajmahal Traps. Apart from geogenic sources, the concentration of F^- and B in groundwater is also influenced by several other factors such as rock–water interaction, residence time of groundwater, pH, etc.[15].

In the present study, a moderately strong positive correlation ($R^2 = 0.7$) was observed between F^- and B. Similar observations have also been reported by other researchers[15].

Boron primarily exists as undissociated boric acid along with some borate ions in natural waters. Since boric acid is a weak acid (pKa of 9.15), it usually exists as undissociated boric acid [$B(OH)_3$] at neutral to acidic pH (i.e. pH < 7) conditions in aqueous solution[16]. With increase in alkalinity of the solution (i.e. pH > 10), the availability of metaborate anion $B(OH)_4$ increases and becomes the main species in the solution.

Clay minerals are considered to get remarkably bound with F^- and B through ion-exchange and adsorption processes[14,17]. Clay mineral in the aquifer system prolong the residence time of groundwater and changes the water type from $Ca-HCO_3$ to $Na-HCO_3$ type and increases the pH value. Hence the formed alkaline condition favours the leaching of F^- and B in groundwater[14]. Increase in F^- concentration is associated with enhanced B concentration, since these two ions can form stable boron–fluoride ortho-oxy compounds such as $BF_3(OH)$, and on interaction with Na rich alkaline water, NaF will become available in groundwater along with B in the form of boric acid[14]. The probable mechanism involved here is

$$2BF_3(OH)^- + 4OH^- + 6Na^+ \rightarrow 6NaF + 2H_3BO_3 \quad (5)$$
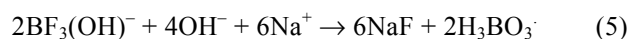
Additionally, F^- in groundwater can form several complexes with iron, i.e. FeF^+ (bivalent) and FeF_2 (trivalent), aluminium (AlF_n^{3-n}), certain organic complexes, etc.[13,18]. From the present study, following observations can be highlighted: (a) About 62.5% of water samples have F^- beyond the permissible limits for drinking water; B in groundwater ranges from 0.01 to 0.5 mg/L. (b) Strong positive correlation of F^- with B ($R^2 = 0.70$). (c) Sequence of F^- availability in sediment sample is: residual
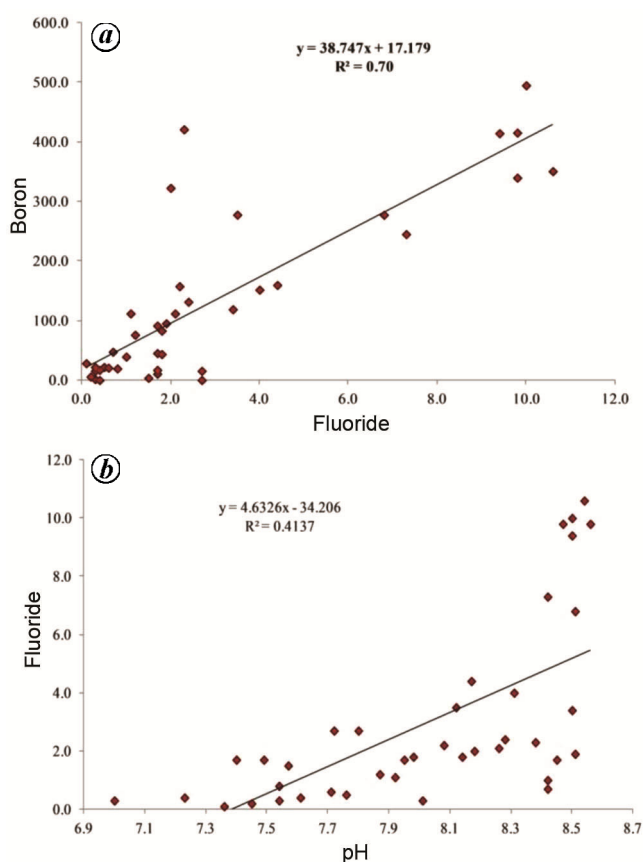

Figure 2. Scatter plot (*a*) fluoride versus boron (*b*) fluoride versus pH.

form > water-soluble > Fe–Mn form > organic bounded > carbonate form > exchangeable form. (d) Fe–Mn plays a crucial role in releasing F^- in groundwater. (e) Intercalated zeolitic clay in sediment samples could be the main source of F and B.

Finally, collaborative approaches between government, local NGOs and local people will play a vital role towards successfully implementing water management strategies in the DRB. As majority of the water sources in the study area are affected with F^- concentration, an alternative source of water, such as pipeline from uncontaminated surface water resources, rainwater harvesting, watershed management, artificial groundwater recharge, etc. should be considered.

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Financialization and its impact on the nature of knowledge production in bioeconomy

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The growth of medical biotechnology (MBT) globally over the last few decades has brought to light several significant changes in various aspects of society. The most prominent impacts were witnessed in the organization of industrial activity, and the nature of knowledge production. With innovation occupying the centre stage in the creatively destructive economies, financial actors and institutions became important in fuelling innovations. Such dominance of financialization has in turn led to the constitution of several new relationships among various actors and the emergence of a new business culture. This constitution of the 'new' is also a result of the active involvement of the state through a favourable policy environment. In all

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