

Water Security for Sustainable Development

Theme: Water Resources - Quantity and Quality

Release of Geogenic Fluoride from Contaminated Soils of Rajasthan, India: Experiments and Geochemical Modeling

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Abstract

Management of groundwater contaminants that are primarily of geogenic origin, such as fluoride, is a major public health concern. Worldwide, around 200 million people are dependent on drinking water resources that contain elevated levels of fluoride that exceeds WHO's drinking water threshold limit of 1.5 mg/L. According to the Ministry of Drinking Water and Sanitation of India, about 11.7 million people, mostly in the Rajasthan state, are exposed to high fluoride risk. It is important to understand the soil-water interaction mechanisms to properly assess the fluoride contamination of geogenic origins prevalent in the region. In this study, batch desorption experiments were performed with soils obtained from varied depths at two sites in Rajasthan that has high fluoride levels in groundwater. The fluoride release kinetics followed a pseudo first-order kinetic model. The results of the batch experiments indicate higher release of fluoride from lower soil layers when compared to the upper layers. Further, the release of fluoride was dependent on pH wherein higher release was noticed under basic pH. Since the natural pH of the

28 soils from this region is ca. pH 8 it is expected to play a vital role in continued release of fluoride
29 to the groundwater system. Furthermore, a simplified geochemical model, incorporating general
30 composite approach, has been used to simulate the experimental results that include dissolved Al
31 and Al-F surface complexes. The model was able to capture the observed experimental results
32 for various soils within reasonable RMSE of 11.74%. The results of this study not only further
33 the existing understanding of the fate and transport mechanisms of fluoride in the contaminated
34 subsurface but also would aid in designing remedial strategies to ensure future water security in
35 this region.

36 *Keywords:* Fluoride pollution, Desorption kinetics, Geochemical modelling, Surface
37 complexation, Rajasthan.

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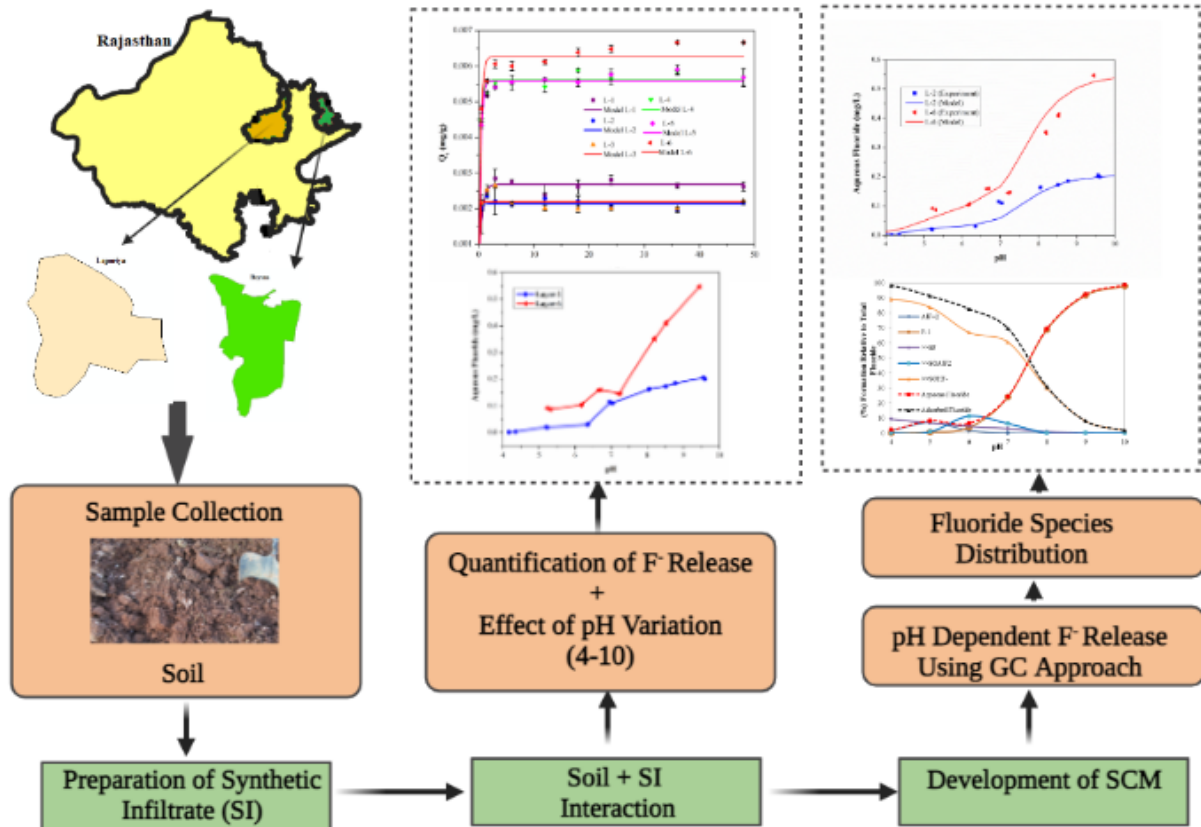
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Graphical Abstract



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Highlights

51 1) Quantification of fluoride release from contaminated soils of Rajasthan using batch
 52 studies at field-relevant conditions.

53 2) Evaluation of time dependent release of fluoride using the pseudo-first order kinetic
 54 model.

55 3) Development of surface complexation model to capture pH dependent release of fluoride
 56 using a general composite approach.

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58

59 **1. Introduction**

60 Groundwater has become the most preferred water resource supporting India's drinking water
61 needs and also providing agricultural security. In the past few decades, overexploitation and
62 contamination of groundwater resources have resulted in adverse impact to both human health
63 and the environment (Prabhu et al. 2023). The contamination of groundwater is primarily
64 attributed to anthropogenic as well as geogenic factors which limit its accessibility per capita in
65 many countries (Li et al. 2021). According to World Health Organisation (WHO), one of the
66 groundwater contaminants of global concern is dissolved fluoride. It is estimated that worldwide
67 over 200 million people rely on well water having fluoride concentration exceeding safety
68 guidelines (Ayoob and Gupta, 2006). The presence of fluoride in water can be beneficial or
69 deleterious to human health depending on its concentration level and the duration of continuous
70 uptake (Jha et al. 2013). It is well known that prolonged consumption of fluoride with high
71 concentration (>1.5 mg/L) cause endemic fluorosis (Wu et al. 2022). On the contrary, small
72 amount of fluoride (0.5 mg/L to 1.5 mg/L) is essential for dental caries and bone development
73 (WHO, 2002).

74 In India, presence of around 12 million of the 85 million global fluoride deposits of earth's crust
75 have been reported leading to high chance of endemic fluorosis in many states (Teotia and
76 Teotia, 1984). According to NHP set up by Ministry of Health and Family Welfare, India is one
77 among the fluoride endemic nation, where high fluoride concentration was reported in 230
78 districts of 20 states that has affected 11.7 million population. Rajasthan, a north-western state in
79 India, has an area of 342,239 lakh km² which is 10.41 % of the India's total geographical area
80 (CGWB, 2012). The state has extreme climatic condition of arid to semi-arid type and suffers
81 from water related problems both in terms of quantity and quality (CGWB, 2021). All the 33

82 districts of Rajasthan have been declared as fluorosis prone areas as a consequence of geogenic
83 origin of fluoride due to natural underground weathering processes (Choubisa, 2012). In the rural
84 Rajasthan, water from almost all the groundwater sources (bore wells, hand pumps and deep dug
85 wells) are polluted with high levels of fluoride wherein a maximum of 37 mg/L has been
86 reported in groundwater sources (Jha et al. 2013).

87 Fluoride enrichment in subsurface environment is a well discussed topic in Indian as well as
88 global context. Unlike other halides, Fluoride, a highly electronegative ion is chemically reactive
89 due to its ionic size (Edmunds and Smedley, 2012). The concentration of fluoride in the earth's
90 crust is abundant i.e. approx. 625 mg/kg that exists in water as the negatively charged fluoride
91 ion (F^-) (Edmunds and Smedley, 2012). The fluoride-rich groundwater is mostly geologic and is
92 associated with presence of various fluorine-bearing minerals such as fluorite, cryolite,
93 amphiboles (hornblende), fluorapatite, micas (biotite and vermiculite), sellaite, villiamite, topaz
94 and certain clays etc. that are ubiquitous in igneous, sedimentary and metamorphic rocks (Singh
95 et al. 2018). Some of the important hydrogeochemical processes that are responsible for the
96 prevalence of fluoride in the subsurface environment are chemical weathering,
97 precipitation/dissolution of fluoride bearing minerals, evapotranspiration, ion exchange,
98 adsorption-desorption and hydrolysis (Kimambo et al. 2019). The factors which are likely to
99 affect these processes are rock composition, groundwater chemistry, temperature, salinity,
100 presence of precipitating or complexing ions, residence time of rock-water interaction with the
101 source minerals, anion exchange capacity of aquifer materials, microbial activity, particle size
102 distribution etc. (Gao et al. 2019; Kumar et al. 2020). Especially, the water quality parameters
103 viz. pH, ionic strength, alkalinity, and other dissolved ions play an important role on fluoride

104 mobilization in the subsurface (Kimambo et al. 2019). Hence, fluoride mitigation solutions
105 require a comprehensive understanding of subsurface fluoride mobilisation mechanisms.

106 Reports have indicated that high fluoride concentration in groundwater mainly circumscribed to
107 arid and semi-arid regions with high pH, low calcium content, high evaporation rates, calcite
108 precipitation and Na-HCO₃-type waters (Hossain and Patra, 2020). Apart from these geogenic
109 sources, several anthropogenic activities such as industrial waste discharge, application of
110 phosphate fertilizer, agricultural irrigation, glass manufacturing, iron and steel manufacturing
111 and coal combustion (Prabhu et al. 2023) as well as managed aquifer recharge (MAR) (Schafer
112 et al. 2020) could lead to an increase in high fluoride level in subsurface. Although fluoride
113 release in MAR system has received significantly less attention compared to toxic metal(loid)s
114 elevated fluoride concentration in subsurface has been observed with the application of MAR
115 (Stone et al. 2016, Brindha et al. 2016). Since no major studies were conducted with a focus on
116 soil-water interaction leading to fluoride release during aquifer recharge with rainwater in the
117 study area of Rajasthan, the present study seek to understand the mechanism for subsurface
118 fluoride mobilisation in this area.

119 The contamination of groundwater with fluoride is of rising concern due to the release of soluble
120 fluoride from shallow soils that can migrate downward with the potential to contaminate deeper
121 aquifers (Shi et al. 2019). Though much work has been reported on the hydrogeochemical
122 characteristics of fluoride-rich groundwater in many countries (Kimambo et al. 2019) studies are
123 sparse with regard to understanding of soil-water interaction and fate and transport of fluoride in
124 the subsurface. In soil-water system, fluoride is in the chemical equilibrium of two geochemical
125 processes i.e. enrichment and release that reflect the adsorption and desorption of F⁻ between the
126 soil and groundwater (Liu et al. 2014). A study by Dehbandi et al. (2018) reported that the soil

127 characteristics play an important role than country rocks in releasing fluoride (F^-) into the
128 groundwater. Among other factors, it has been reported that pH of soil solution is one of the
129 major factors that could control the enrichment and leaching of fluoride in soil (Prabhu et al.
130 2023). In subsurface environment aluminium (Al) is also considered to play a key role in
131 regulating the movement of F^- by forming Al-F complexes (Deng et al. 2011). In solutions
132 containing Al, fluoride speciation is pH-dependent, that could significantly affect the fluoride
133 adsorption on the soil surface (Padhi and Tokunaga, 2018). In this case, surface complexation
134 model (SCM) could play an important role in describing the dominant chemical species along
135 with the associated aqueous/surface chemical reactions. Based on SCMs, previous studies have
136 probed the behaviour of fluoride with respect to pH on clay minerals viz. kaolinite, laterite and
137 bauxite (Weerasooriya et al. 1998; Vithanage et al. 2012; Craig et al. 2015), Gibbsite
138 nanoparticles (GNPs) (Vithanage et al. 2014) and on granitic soils (Padhi and Tokunaga, 2018).
139 However, to our knowledge, the application of SCMs to describe fluoride release from natural
140 soil in the presence of complexing agents has not been reported. Therefore, understanding the
141 interaction between fluoride and soil will help in predicting the soil's desorption capacity that
142 will further provide an accurate description of fluoride release in the environment. Hence, the
143 overarching objective of this study is to investigate the fluoride release processes through a series
144 of batch experiments on soils obtained from two different districts of Rajasthan, India where
145 high levels of fluoride had been observed in the groundwater. Knowledge on soil-water
146 interaction and the changing geochemical conditions that can have effect on the release of
147 fluoride from soil to groundwater in this region are not fully understood. Hence, the major
148 objectives of the study include:

- 149 (i) To quantify the release of fluoride from various layers of soils obtained from two
150 different contaminated sites of Rajasthan using batch experiments at field relevant
151 geochemical conditions,
- 152 (ii) To investigate the role of pH on fluoride release from the soils, and
- 153 (iii) To describe the experimental results using a surface complexation model.

154 **2. Material and Methods**

155 **2.1 Study Area**

156 The study area i.e. Laporiya village and Bayana town are located in the Jaipur and Bharatpur
157 district of Rajasthan, India (Fig.1). The study area belongs to a semi-arid region and is
158 characterized by very hot summers wherein the maximum temperature reach upto 48°C for
159 Laporiya and 47°C for Bayana (CGWB, 2017a,b). The state receives approximately 90% of total
160 rainfall in the monsoon season that occurs during June to September is the primary source for
161 recharging groundwater. The average yearly rainfall in Jaipur and Bharatpur district is about
162 575.7 mm and 664.4 mm, respectively (CGWB, 2017a,b).

163 The geology of study area i.e. Laporiya village is characterized by quaternary fluvial and aeolian
164 deposits while Bayana region is characterized by quaternary alluvium and Vindhyan Sandstone
165 (CGWB, 2017a,b). In the region of Laporiya the top soil (<1 m) mainly comprised of sandy loam
166 (Yadav et al. 2022) and loam soils followed by weathered gneiss for 1 m to 20 m. Further, the
167 deeper region (i.e. 20 m - 40 m) is dominated by schist mixed with mica, quartz, and feldspar
168 pieces (CGWB, 2017a). According to CGWB report, the main aquifer system of Laporiya village
169 consists of hard rocks of the Bhilwara Super Group having granulitic gneisses, quartz mica
170 schist, phyllite as well as granite pegmatite intrusive (CGWB, 2017a). Whereas, aquifer of

171 Bayana region is occupied by alluvium (75%) formation followed by hard rocks and hard
172 formation of sandstone (25%) (CGWB, 2017b).

173 2.2 Collection of Samples

174 Soils for the experiments were collected from two different locations of Rajasthan, India as
175 shown in Fig. 1. Lajoriya village of Jaipur district and Bayana town in Bharatpur district were
176 selected as these regions have reported high levels of fluoride concentration in surface and
177 groundwater sources. The soil samples were collected at six different depths (L1: 0 cm - 30 cm,
178 L2:30 cm - 60 cm, L3:60 cm - 90 cm, L4:90 cm - 120 cm and L5:120 cm - 150 cm and L6: 150
179 cm - 180 cm) from Lajoriya site and five different depths (L1: 0 cm – 30 cm, L2: 30 cm – 60
180 cm, L3: 60 cm -90 cm, L4: 90 cm – 120 cm and L5:120 cm – 150 cm) from Bayana site. After
181 collection, the soil samples were transported to the laboratory and stored in polyethylene bags for
182 further analysis. The basic physiochemical properties of the soils are given in Table 1.

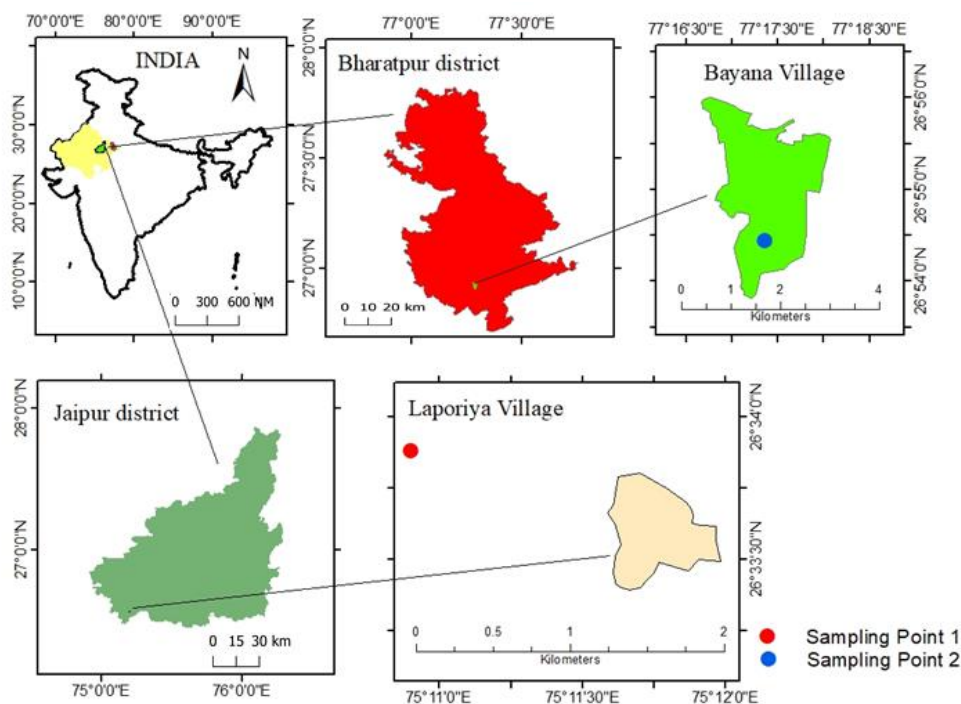


Fig.1 Study area maps indicating sites of sample collection

Table 1 Physiochemical properties of soil

Parameter	Laporiya Soil						Bayana Soil				
	L1**	L2	L3	L4	L5	L6	L1	L2	L3	L4	L5
% Gravel (>4.75mm)	13	7.2	12.1	9.9	15.9	19.2	44.6	35.6	43.7	22.85	44.6
% Sand (4.75mm-0.075mm)	78.55	83.3	79.2	85.2	80.1	76.8	53	45.15	50.55	68.4	53
% Fine (<0.075mm)	8.45	9.5	8.7	4.9	4	4	2.4	19.25	5.75	8.75	2.84
* pH in (DIW)	7.27	7.28	7.32	7.41	7.57	7.63	7.72	8.22	8.14	8.06	7.73
* pH in (CaCl ₂)	7.04	6.91	7.03	7.19	7.28	7.34	7.23	7.45	7.38	7.29	7.28

186 * The accuracy of pH is ± 0.1 unit.

187 ** L1: Layer-1

188

189

190 **2.3 Chemicals and Analysis**

191 Synthetic infiltrate mimicking the chemistry of surface ponded-water was prepared using
 192 analytical reagent grade chemicals procured from Sigma Aldrich[®], India and deionised water.
 193 Fluoride analysis was performed using Ion Chromatography (Metrohm India Ltd.) technique
 194 wherein anion (Metrosep A Supp 5: 4.0 x 250 mm) column was used.

195 **2.4 Soil Characterisation (X-Ray Diffraction)**

196 The mineralogy of the study area was identified and quantified using Panalytical X'Pert Pro
 197 (MPD) which is equipped with a Cu K α_1 radiation source at 45 kV voltages, 40 mA current.
 198 Diffraction patterns were collected in the 2θ range of 2° - 90° at a scan speed of $0.5^\circ \text{ min}^{-1}$ and a
 199 step size of 0.02° . Goniometer radius was maintained at 240 mm. Identification of minerals in the
 200 samples that are finely grounded with a mortar was obtained by using X'pert High Score Plus
 201 software with search and match of the reference mineral database.

202

203 **2.5 Batch Kinetics Experiment**

204 Batch kinetic experiments were carried out to quantify the release of fluoride from soils obtained
205 from different depths. In the batch experiment, soil fraction less than 2 mm and synthetic
206 infiltrate (Table S1 and S2) were taken and mixed at a soil to solution ratio of 50 g/L. The
207 background solution i.e. synthetic infiltrate has an ionic strength of 0.013 M for Laporiya site
208 and 0.0073 M for Bayana site, respectively. The experiments were carried out for 48 hours at a
209 constant temperature of 25°C and samples were taken out at desired intervals by sacrificing the
210 test tubes. After mixing the test tubes for the desired time interval they were centrifuged for 20
211 minutes at 6000 g. Fluoride in the supernatant solution was then measured using ion
212 chromatograph after filtration of the samples through 0.45 µm acrodisc filters. Quality control
213 measures for fluoride investigation included duplicate samples for each sampling interval and
214 reference quality control test tubes (no soil).

215 **2.6 Desorption Kinetic Model**

216 In the present study, desorption rate of fluoride from natural soil is investigated by using pseudo-
217 first order kinetic model. The desorption process is modeled using the non-linearized form of
218 pseudo-first-order (PFO) reaction (equation 1). This is accomplished by plotting q_t versus t and
219 through nonlinear regression the kinetic parameters have been estimated (Lagergren, 1898).

$$220 \quad q_t = q_e (1 - \exp^{-k_1 t}) \quad (1)$$

221 where q_e (mg/g) and q_t (mg/g) are the fluoride desorption at equilibrium and at any time t (h),
222 respectively; K_1 is the pseudo-first order rate constant (h^{-1}).

223 **2.7 pH Edges Experiment**

224 The pH experiments were performed on soils fractions less than 2 mm from Layers-2 and 6 of
225 Laporiya site and Layers-2 and 4 of Bayana site. The experiments were conducted using
226 synthetic infiltrate of the respective site at a soil to solution ratio of 50 g/L. The experiments
227 were performed over a range of pH from pH 4 to pH 10 by adding required amount of acid (HCl)
228 or base (NaOH). Based on the kinetic studies, an equilibrium time of about 36 hours for Laporiya
229 site and 24 hours for Bayana site was chosen for the experiments. After mixing the test tubes for
230 the desired time interval they were centrifuged for 20 minutes at 6000 g. Fluoride in the
231 supernatant solution was then measured using ion chromatograph after filtration of the samples
232 through 0.45 μm acrodisc filters. Quality control measures included duplicate samples for each
233 pH and reference quality control test tubes (no soil).

234 **2.8 Geochemical Modelling**

235 In this study, to predict the results from batch experiment, a surface complexation model was
236 developed and used in a predictive mode to model the experimental data using Visual Minteq
237 (version 3.1). A 2-pk Double-Layer Model (DLM) was used to simulate the release of fluoride
238 from soil with respect to pH. Past research has suggested that the adsorption and release of
239 fluoride in near surface environment is primarily controlled by pH of the soil among other
240 geochemical parameters like ionic strength, presence of ions such as Ca^{2+} , Al^{3+} , HCO_3^- etc
241 (Prabhu et al. 2023). A surface complexation model developed by (Padhi and Tokunaga, 2018)
242 incorporating general composite (GC) approach which described the pH dependent fluoride
243 sorption isotherms on granitic soils. In this mode, to describe the fluoride sorption edges in soil,
244 the generalised two layer model (Dzombak and Morel, 1991) was considered assuming that all
245 the surface complexes are inner sphere complexes. The GC model approach has been proven to

246 be successful at simulating fluoride sorption by soil. The model was used to simulate the
 247 experimental results by including the dissolved Al and Al-F complexes.

248 The surface complexation reactions of the model and their corresponding stability constants were
 249 taken directly from (Padhi and Tokunaga, 2018) and are listed in Table 2. The surface site
 250 density of 7 sites nm⁻² which is within the range of 2-8 sites nm⁻² as reported by (Davis and Kent,
 251 1990) for natural assemblages was found to be the optimum to describe our experimental results.
 252 The possible surface complexation reactions (Table 2) are represented by protonation,
 253 deprotonation, and fluoride adsorption reactions. To simulate the experimental results, dissolved
 254 Al and Al-F surface complexes are incorporated in the model calculation. The difference
 255 between the model predictions and the experimental data was quantified using the root mean
 256 square error (RMSE) given in equation (2) (Loganathan et al. 2009):

$$257 \quad \text{RMSE} = \left(\frac{1}{n_d - n_p} \sum_{i=1}^{n_d} \left(\frac{C_i - \hat{C}_i}{C_0} \right)^2 \right)^{1/2} \quad (2)$$

258 where n_d is the number of data points, n_p is the number of adjustable parameters (zero in this case
 259 as the model was used in a purely predictive mode), i is an index, C and \hat{C} are the measured and
 260 predicted aqueous fluoride concentration at equilibrium (mg L⁻¹), C₀ is the total fluoride
 261 concentration (mg L⁻¹), respectively.

262 **Table 2 List of surface complexation reactions and model parameters**

Reaction	Parameters	Reference
1. Surface and Solution Parameters		
Surface Site Density (sites nm ⁻²)	7	This study
Solid Concentration (g/L)	50	This study
Temperature (°C)	25	This study

Ionic Strength (M)		
(For Laporiya site)	0.0073	This study
(For Bayana site)	0.013	This study
Aluminium (mmol/L)	0.00757	This study
2. Surface Complexation Reaction	log k	
$>SOH + H^+ \Rightarrow SOH_2^+$	3.8	(Padhi and Tokunaga., 2018)
$>SOH \Rightarrow SO^- + H^+$	-6.9	-do-
$>SOH + F^- + H^+ \Rightarrow SF + H_2O$	8.4	-do-
$>SOH + F^- \Rightarrow SOHF^-$	4.2	-do-
$>SOH + 2F^- + Al^{3+} \Rightarrow SOAlF_2 + H^+$	10.3	-do-

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264 3. Results and Discussion

265 3.1 X-Ray Diffraction Analysis

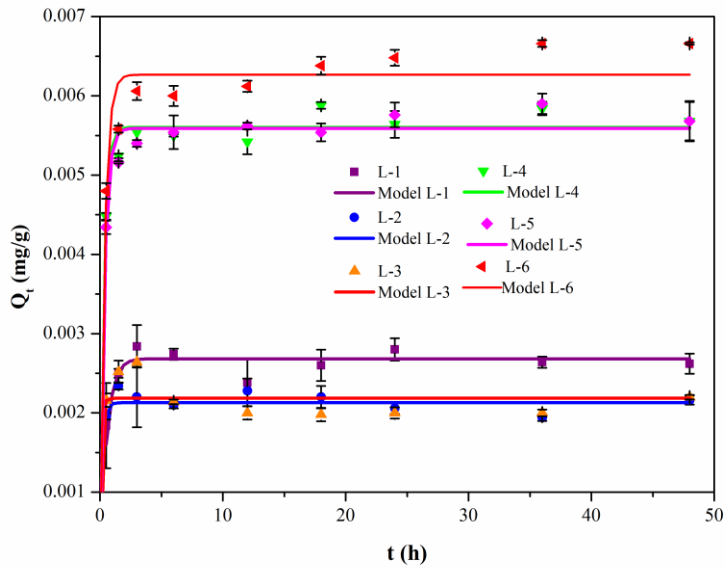
266 The X-ray diffraction was carried out on powdered soil samples obtained from various depths.
267 The investigation revealed that in the Laporiya soil minerals viz. Ferruccite ($NaBF_4$) and Fluorite
268 (Ca_4F_8) were identified as major fluoride bearing minerals. Whereas in the Bayana soil
269 Zinnwaldite ($K (Al Fe Li) (Si_3 Al) O_{10}OH F$) were identified as major fluoride bearing minerals
270 in the top 1.5m. Along with these minerals Baratovite ($Li_2KC a_8Ti_2Si_{12}O_{37}F$) in Laporiya soil and
271 Chukhrovite ($Ca_{32}Si_8 Al_8S_8O_{128}F_{104}H_{192}$) and Afghanite ($Si_{24}Al_{24} O_9Ca_{10} C_{15.80} F_{0.20} K_{4.72} Na_{17.28}$
272 S_6Os_{24}) in Bayana soils were also present. The mineralogical analysis indicates the
273 predominance of fluorite, ferruccite and zinnwaldite in soil samples of study area. Among
274 primary minerals fluoride content found to be higher in fluorite and may contribute to ~ 49 wt%
275 of F^- (Speer, 1984). One such study reported by Liu et al. 2015 observed that the sediment
276 fluoride in the form of fluorite had an average content of 780 mg/kg being the primary source of
277 groundwater fluoride. The groundwater with elevated pH when react with rocks containing

278 fluoride bearing minerals such as fluorite may leads to mobilization of fluoride along with
279 precipitation of calcium carbonate (Kimambo et al. 2019).

280 The mineralogical investigation also revealed the predominance of zinnwaldite in the present
281 sample. Zinnwaldite is a silicate mineral in the mica group may contain upto 6.5 wt% of fluoride
282 content (Tischendorf, 1997). As reported by Toupal et al. 2022, high fluoride level had been
283 observed in stream water samples as a result of dissolution of zinnwaldite and fluorite. Likewise,
284 chukhrovite is the Ca-dominant species of the chukhrovite mineral group, is a colourless to white
285 cubo-octahedral crystals having diameter up to 100–150 μm . This new calcium alumina fluoride
286 contains upto 36.61 wt% of fluoride content (Vignola et al. 2012).

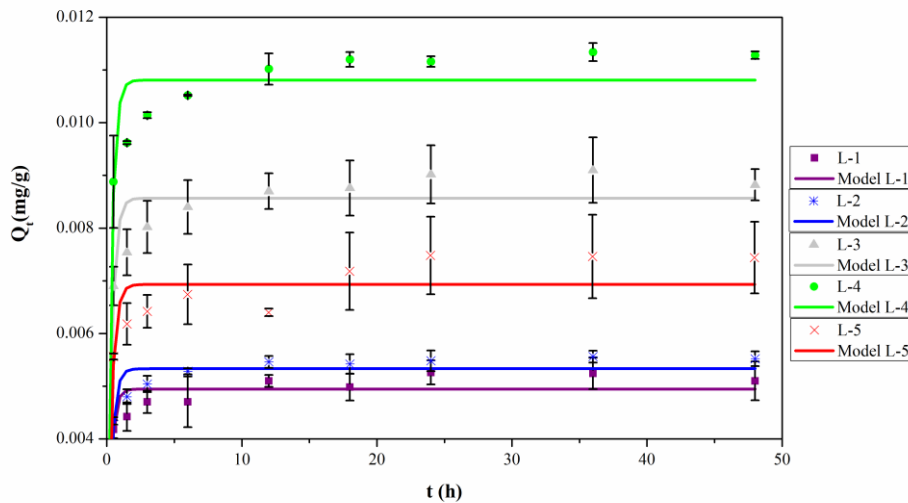
287 **3.2 Batch Kinetic Experiments**

288 The results of kinetic experiments indicate that the fluoride desorption capacity at different
289 depths of Laporiya site and Bayana site varies between (0.007 mg/g to 0.002 mg/g) and (0.0113
290 mg/g to 0.0042 mg/g), respectively. The fluoride release for different experimental time periods
291 is shown in Figs. 2 and 3. The results for Laporiya site indicates an instantaneous release of
292 fluoride followed by gradual plateauing at around 36 hours of soil water interaction (Fig.2).
293 Likewise, soils from Bayana site showed two step release behaviours - an instantaneous release,
294 which occurs during the first three hour followed by a gradually plateauing around 24 hours
295 (Fig.3).



296

297 **Fig.2 Time dependent release of fluoride release from various layers of Laporiya soil along**
 298 **with Pseudo-first order kinetic model. L1 to L6 represent soil obtained from layers 1 to 6 of**
 299 **Laporiya site. [Error bars on kinetic data represent the standard deviation of the mean for**
 300 **duplicate measurements].**



301

Fig.3 Time

302 **dependent release of fluoride release from various layers of Bayana soil along with Pseudo-**
 303 **first order kinetic model. L1 to L5 represent soils obtained from Layers 1 to 5 of Bayana**

304 site. [Error bars on kinetic data represent the standard deviation of the mean for duplicate
305 measurements].

306 In Laporiya soils, the capacity of soil to release fluoride was found to be relatively low ca.0.002
307 mg/g near surface layers i.e. 90 cm (Layer-1, 2 and 3). On the contrary, the higher fluoride
308 release ca.0.0067 mg/g beyond 90 cm (Layer-3, 4 and 5) is likely due to the native origin. The
309 increase in soil fluoride with increasing depth may possibly due to the long-term downward
310 movement of fluoride through soil profile. The soil column leaching experiment performed by
311 Shi et al. 2019 indicated that the fluoride concentration in leachate from the upper soils
312 decreased continuously in soil column while that of the leachate from the lower soils increased.
313 Similarly, for Bayana soils, fluoride release increases with depth and it was found to be in high
314 concentration for Layer- 4 as shown in Fig.3. However, in the bottom most layer (i.e.layer-5) the
315 release of fluoride was lesser than layer-4. The reduction in fluoride concentration could
316 represent the variation in the mineralogy at the site.

317 In the state of Rajasthan high fluoride level (0.2 mg/L – 37 mg/L, Jha et al. 2013) had been
318 reported whereas, within the present study area the fluoride levels in Laporiya (0.2 mg/L – 12.3
319 mg/L, Carriere, 2018) and in Bayana (0.33 mg/L – 7 mg/L, CGWB, 2021) had been observed in
320 the groundwater. In contrast, the labile fluoride content of soil samples were found to be below
321 safety levels. Thus the difference between fluoride level that was observed in groundwater of
322 study area and release from soil samples in the experiments suggests the variation in the
323 mineralogy below sampling depth (i.e. below 2 m) at the site. Therefore, it can be concluded that
324 the proper geochemical and mineralogical analysis needed to done below 2 m depth in the study
325 area in order to find the pathways and the mechanism that are responsible for high fluoride
326 levels in the subsurface.

327 The desorption rate constant (K_1) and equilibrium desorption capacities (Q_e) were estimated
 328 using nonlinear regression analysis for pseudo-first order kinetics model (Figs. 2 and 3). The
 329 coefficient of determination close to 1 indicates that the model is able to describe the release of
 330 fluoride from soils (Table 3).

331 **Table 3 Pseudo first-order kinetic model parameters for fluoride release from soils**

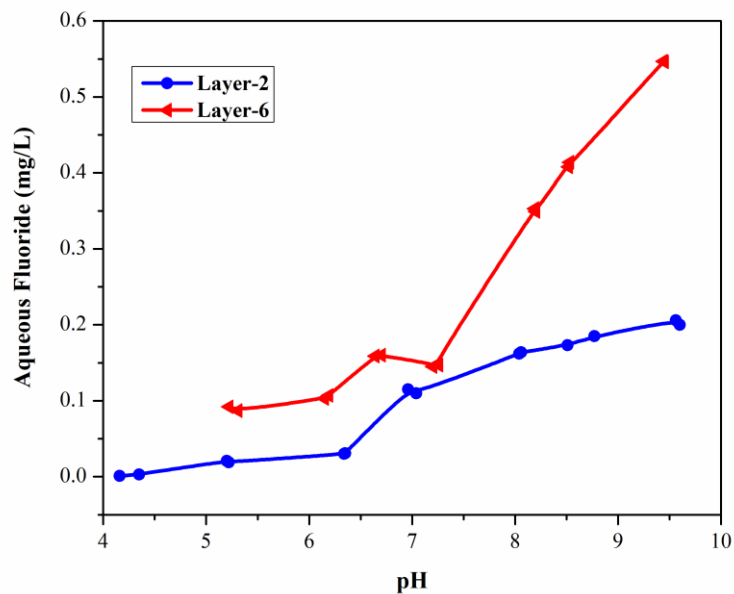
Laporiya Site				Bayana Site			
Layers	Q_e	K_1	R^2	Layers	Q_e	K_1	R^2
1	0.0027	2.3243	0.97455	1	0.0049	3.6309	0.96924
2	0.0022	4.8072	0.97027	2	0.0053	3.2518	0.97968
3	0.0022	8.9527	0.88965	3	0.0086	3.1263	0.96909
4	0.0056	3.1432	0.98858	4	0.0108	3.3262	0.97242
5	0.0056	2.9016	0.98783	5	0.0069	3.1100	0.95081
6	0.0063	2.7556	0.97324				

332

333 3.3 pH Edges Experiment

334 The fluoride release plots with respect to pH for Layer-2 and Layer-6 of Laporiya site are shown
 335 in Fig. 4a. The amount of fluoride release from soil increased gradually as the pH increased. At
 336 pH <7, Layer-2 shows less amount of fluoride desorbed when compared to Layer-6. In contrast,
 337 increasing the pH beyond 7 resulted in higher fluoride release for both the layers. The
 338 experimental results indicate that the fluoride release is highly dependent on solution pH,
 339 especially, beyond circumneutral pH. The results show that the alkaline pH of all soil samples
 340 would favour soil-F mobilization in the study area. This finding supports the recent research
 341 study (i.e. Paikaray and Mahajan, 2023) that observed the maximum release of soil-F under
 342 alkaline condition (i.e.pH-9) compared to acidic condition (i.e.pH-5). Likewise, Vithanage and

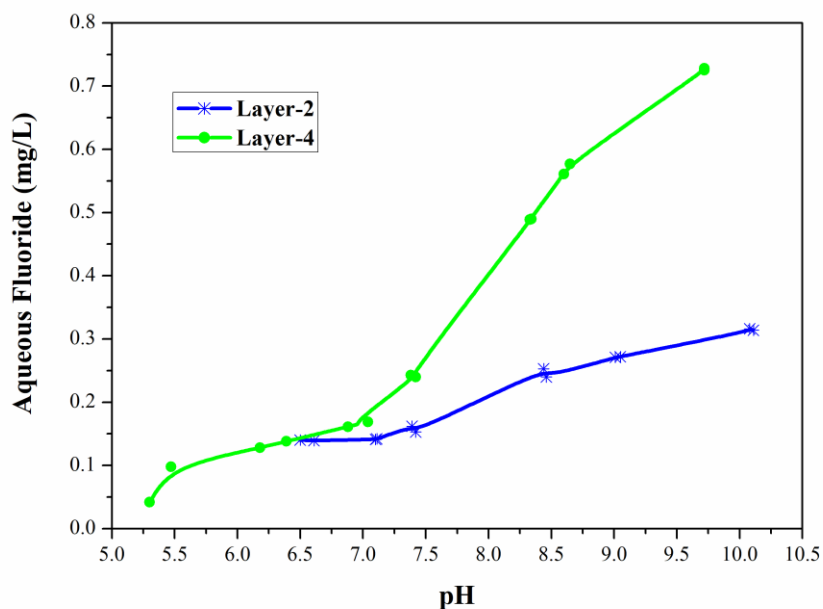
343 [Bhattacharya, 2015](#) also reported high fluoride adsorption at low pHs whereas soils with high pH
344 shows high fluoride release to groundwater.
345 The regression meta-analysis of fluoride with physical factor like pH that was carried out by
346 [Islam and Mostafa, 2021](#) indicated that fluoride desorption is positively correlated to pH and
347 followed a linear model. It has been observed that under acidic condition fluoride complexes
348 with cation such as Ca^{2+} , Fe^{3+} and Al^{3+} in soil solution resulting in small amount of free fluoride
349 ions in solution. This was also supported in an earlier study by [Vithanage and Bhattacharya,](#)
350 [2015](#) where it was observed that under acidic condition fluoride form complexes with Al^{3+} and
351 Fe^{3+} in soil. On the other hand, at high pH, an increase in free fluoride concentration is observed
352 in soil solution as hydroxide ions cause the cations to precipitate preventing the formation of
353 fluoride complexes.



354

355

(a)



(b)

Fig.4 Release of fluoride with respect to pH in soils from (a) Laporiya site (b) Bayana site

356
 357
 358
 359
 360 The fluoride desorption at varied pH for Layer-2 and Layer-4 of Bayana site is shown in Fig .4b.
 361 It has been observed that for both layers the amount of fluoride released from the soil increased
 362 gradually as pH increases (pH>7), implying that under alkaline condition, comparable ionic
 363 radius of OH⁻ (1.37–1.40 Å) and F⁻ (1.23–1.36 Å) facilitate the ion exchange process i.e.
 364 displacement of sorbed fluoride by the increased concentration of hydroxide ions in the soil
 365 solution (Islam and Mostafa, 2021; Paikaray and Mahajan, 2023). The above phenomenon could
 366 be better explained through fluoride surface and aqueous species distribution. The present study
 367 also suggests that the release of fluoride is desorption based rather than dissolution-driven,

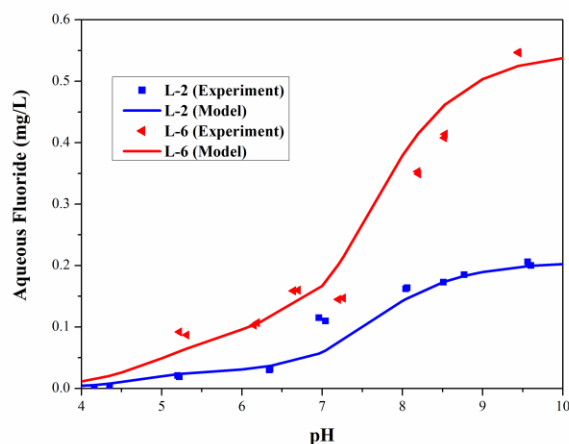
368 otherwise it would have resulted in a reverse trend, i.e., more release at pH < 6 (Borgnino et al.
369 2013).

370 It is also noted that soil from layer-2 of Bayana site shows greater pH buffering capacity under
371 acidic condition (pH < 6) which could be due to more percentage of finer (Table 1) as compared
372 to soils of other layers. This indicates that soil of this layer will retain more fluoride ions because
373 of fine-textured and thus the release of fluoride from these soils will be limited. Past studies have
374 also shown the retention of fluoride by fine-textured soil particularly those associated with clay
375 component (Wang et al. 2002).

376 **3.4 Geochemical Modelling**

377 A surface complexation model developed by (Padhi and Tokunaga, 2018) incorporating general
378 composite (GC) approach is used in a predictive mode to model the experimental data. The
379 possible surface complexation reactions that included protonation, deprotonation, ligand
380 exchange have been incorporated to study the fluoride release from soils (Table 2). The
381 geochemical model was run assuming 100% release of fluoride at basic pH (ca. pH 10). This has
382 been verified by performing base extraction, using 0.1N sodium hydroxide, on selected samples
383 of batch kinetic experiments. Maximum release of labile fluoride at basic pH has been
384 established in previous studies as well (Kim et al. 2012; Kumar et al. 2016; Wambu and Kurui,
385 2018). There have been studies that have attempted fluoride interaction with single mineral
386 phases i.e. clay minerals, Gibbsite nanoparticles (GNPs) and granitic soils (Vithanage et al.
387 2012; Vithanage et al. 2014; Craig et al. 2015; Padhi and Tokunaga, 2018) but the surface
388 complexation modelling of fluoride release from natural soil in the presence of complexing agent
389 have not been reported in detail. The simulation results indicate that the model was able to

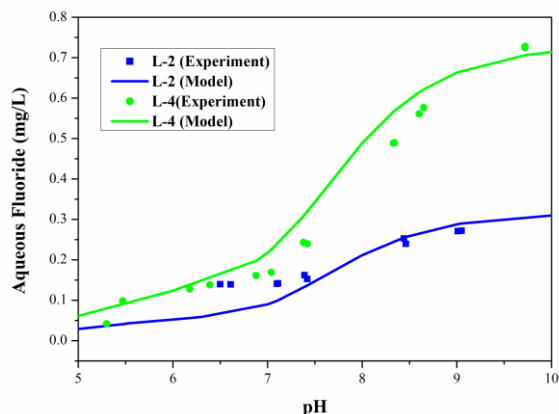
390 reasonably predict the experimentally observed variation of fluoride release with respect to pH
391 for layer-2 of Laporiya soil with in an RMSE of 10.47% (Fig. 5a). In the case of layer-6 (Fig.
392 5a), though the model could predict the trend of fluoride release, significant difference between
393 experimental data and model prediction could be observed in the pH range 7-8.5. It shall be
394 noted that these simulations were performed under the assumptions that soil-water interaction of
395 fluoride with co-solutes viz. Fe, Ca etc. are negligible which could affect the release of fluoride
396 in soils.



397

398

(a)



(b)

Fig. 5 Surface complexation model predications on fluoride release with respect to pH in soils of (a) Laporiya site (b) Bayana site

Similar to the results of Laporiya site, the model for Bayana site (Fig. 5b) shows better prediction at low fluoride release (layer-2) with in an RMSE of 6.86% when compared to higher fluoride release scenarios (layer-4). Relatively higher variation between experimental data and model prediction could be observed in the pH range 7-8.5. Despite the variation at high pH, the model was able to predict the overall pH dependent fluoride release in both soils within a reasonable RMSE of 11.74%.

To better understand the fluoride release processes, surface and aqueous species distribution plots for soils of Laporiya and Bayana have been presented. Figures S3 and S4 provide the surface species distribution for bottom and top layers of Laporiya and Bayana soil. In the case of Laporiya soils (Figs. S3 a and b), the surface species distribution for bottom and top layers indicates that at higher pH, fluoride exists mainly as free fluoride ions (F^-). On increasing the pH, the fraction of ionic fluoride increases whereas the fraction of sorbed fluoride decreases. Around

415 pH 5, a small increase in aluminium fluoride complex (i.e. AlF^{+2}) can be noticed. Along with
416 these species other aqueous fluoride species like NaF, CaF and HF are also present under
417 alkaline condition but in very low concentration (<1%). It is also observed that with increase in
418 pH the $>\text{SOHF}^-$ complex decreases. At pH less than 6, more than 80% of the total adsorbed F^-
419 was in the form of $>\text{SOHF}^-$, wherein $>\text{SF}$ and $>\text{SOAlF}_2$ contribute to less than 10% of total
420 adsorbed fluoride.

421 Similarly, for Bayana soil (Figs. S4 a and b), free fluoride (F^-) is the predominant aqueous
422 species at higher pH values whereas under acidic condition (i.e. around pH-5) AlF^{+2} complexes
423 contribute to less than 10% of the total aqueous fluoride. Hence, it can be concluded that at low
424 pH the decrease in fluoride release could be associated with ligand exchange (i.e. replacement of
425 $-\text{OH}/\text{H}_2\text{O}$ groups bound to surficial Al by F^- ion) whereas in alkaline condition the higher
426 fluoride release is associated with the presence of fluoride in free ionic fluoride (F^-) form. This
427 further suggests that fluoride speciation is strongly pH-dependent (Figs. S1 and S2, where
428 simulations are done without considering Al-F complex). Our results reaffirm the results of
429 earlier studies that delved on the pH dependent fluoride speciation and reported that in most
430 natural waters, free F^- is by far the predominant form or complexed with cations like Ca^{2+} , Mg^{2+}
431 and Na^+ , while under acidic conditions, fluoride form complex with Al^{3+} and H^+ (Deng et al.
432 2011).

433 4. Conclusion

434 In the present study, experiments were performed to understand the release of fluoride from soils
435 of Rajasthan, India where high fluoride levels had been observed in groundwater. The fluoride
436 release kinetic experiments performed using soils obtained from different depths of Laporiya and

437 Bayana sites under variable pH in the solution matrix. Experimental results indicated that in both
438 the sites, the release of fluoride was found to be more in the bottom layers when compared to the
439 top layers that are likely due to the infiltration facilitating long-term downward movement of
440 fluoride through soil profile. The difference in fluoride concentration observed in the field and
441 that released from soils suggests variation in the mineralogy below sampling depth (i.e. below
442 2m) at the site. The result of kinetic experiments followed Pseudo-first order model that well
443 represents the fluoride desorption processes indicating desorption-based fluoride mobilization
444 rather than dissolution-driven mobility. Further, the results of the geochemical model indicated
445 that under acidic conditions the reduction in fluoride release could be explained by ligand
446 exchange while under alkaline condition fluoride release is in the form of free ionic fluoride (F).
447 Furthermore, the release of fluoride with respect to pH indicates a sigmoidal trend with higher
448 release of fluoride at higher pH. The experimental results were fairly predicted using a
449 simplified surface complexation model that used a generalized composite approach along with
450 Al-F complexes. In future studies, the geochemical model could be coupled with transport model
451 to simulate the subsurface mobilisation of fluoride in these contaminated regions. The results of
452 this study are envisaged to provide a better comprehension of the fluoride contamination
453 scenario in Rajasthan which is a prerequisite for developing efficient remedial strategies.

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Release of geogenic fluoride from contaminated soils of Rajasthan, India: experiments and geochemical modeling

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