

# 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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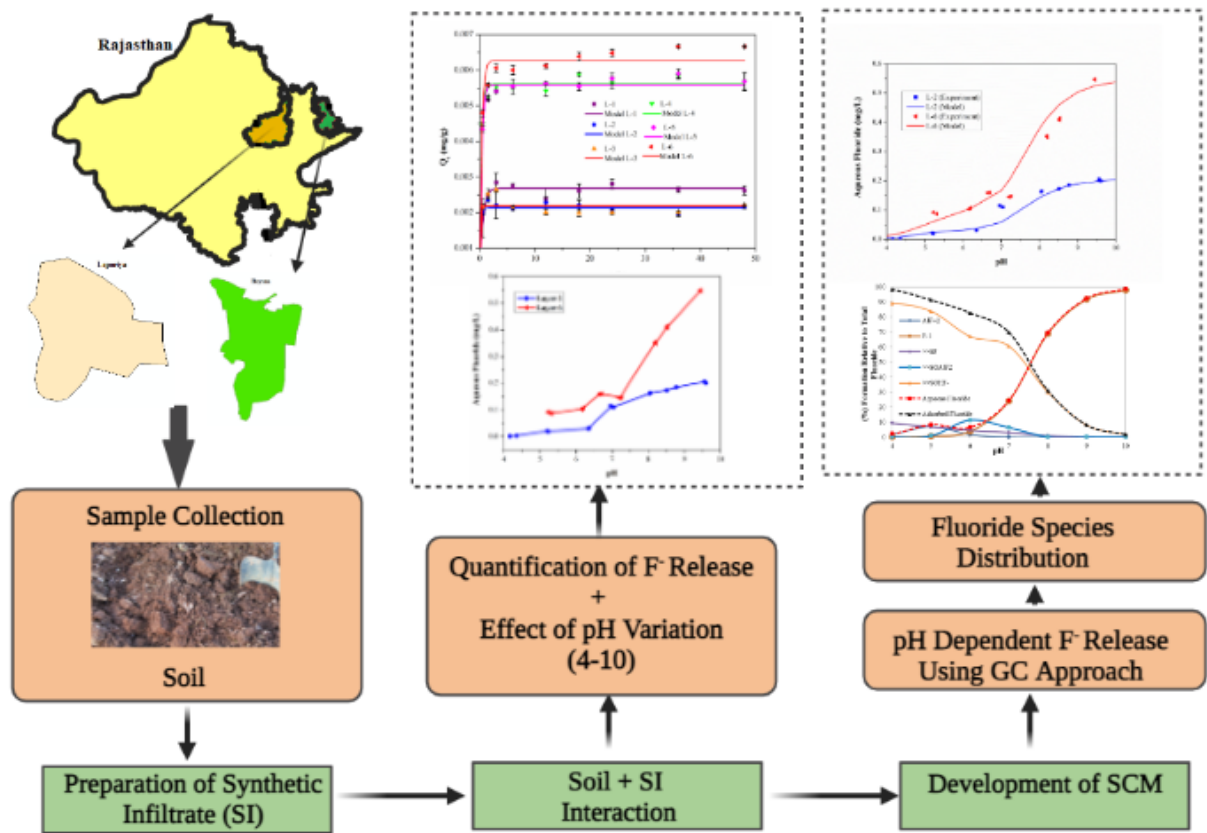
## Abstract

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

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

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

Graphical Abstract



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Highlights

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

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

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

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## 1. Introduction

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

In India, presence of around 12 million of the 85 million global fluoride deposits of earth's crust have been reported leading to high chance of endemic fluorosis in many states (Teotia and Teotia, 1984). According to NHP set up by Ministry of Health and Family Welfare, India is one among the fluoride endemic nation, where high fluoride concentration was reported in 230 districts of 20 states that has affected 11.7 million population. Rajasthan, a north-western state in India, has an area of 342,239 lakh km<sup>2</sup> which is 10.41 % of the India's total geographical area (CGWB, 2012). The state has extreme climatic condition of arid to semi-arid type and suffers from water related problems both in terms of quantity and quality (CGWB, 2021). All the 33

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

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

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

Reports have indicated that high fluoride concentration in groundwater mainly circumscribed to arid and semi-arid regions with high pH, low calcium content, high evaporation rates, calcite precipitation and Na-HCO<sub>3</sub>-type waters (Hossain and Patra, 2020). Apart from these geogenic sources, several anthropogenic activities such as industrial waste discharge, application of phosphate fertilizer, agricultural irrigation, glass manufacturing, iron and steel manufacturing and coal combustion (Prabhu et al. 2023) as well as managed aquifer recharge (MAR) (Schafer et al. 2020) could lead to an increase in high fluoride level in subsurface. Although fluoride release in MAR system has received significantly less attention compared to toxic metal(loid)s elevated fluoride concentration in subsurface has been observed with the application of MAR (Stone et al. 2016, Brindha et al. 2016). Since no major studies were conducted with a focus on soil-water interaction leading to fluoride release during aquifer recharge with rainwater in the study area of Rajasthan, the present study seek to understand the mechanism for subsurface fluoride mobilisation in this area.

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

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

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

## **2. Material and Methods**

### **2.1 Study Area**

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

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

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

## 2.2 Collection of Samples

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

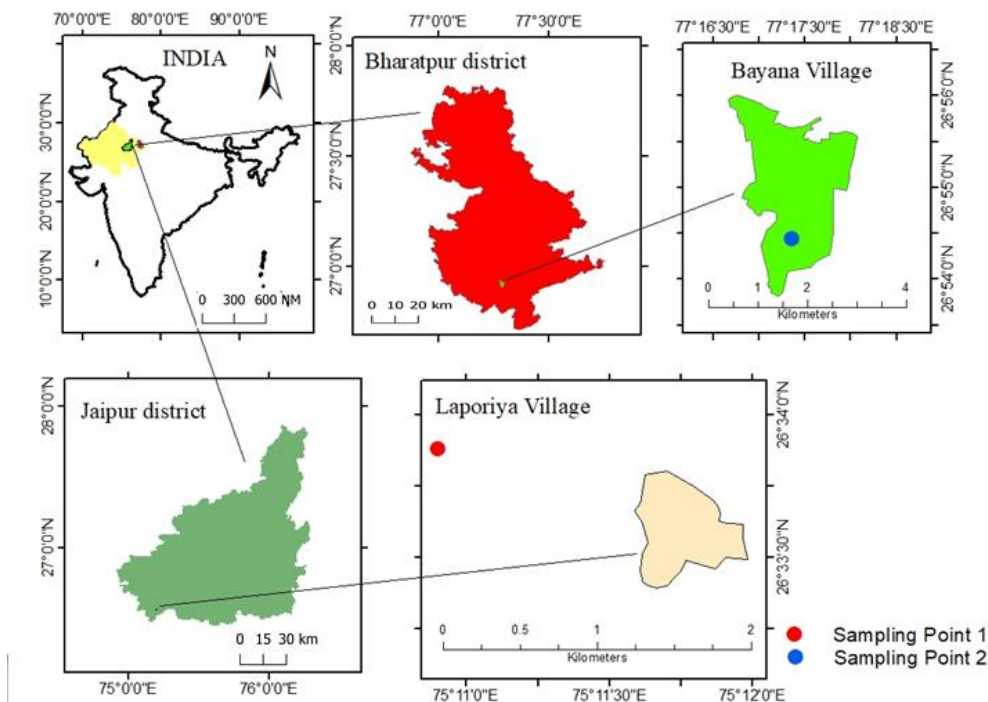


**Fig.1 Study area maps indicating sites of sample collection**

**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 <sub>2</sub> ) | 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  $\pm 0.1$  unit.

187 \*\* L1: Layer-1

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## 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 $\alpha_1$  radiation source at 45 kV voltages, 40 mA current.  
 198 Diffraction patterns were collected in the 2 $\theta$  range of 2° - 90° at a scan speed of 0.5° min<sup>-1</sup> 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.

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## 2.5 Batch Kinetics Experiment

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

## 2.6 Desorption Kinetic Model

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

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

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

## 2.7 pH Edges Experiment

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

## 2.8 Geochemical Modelling

In this study, to predict the results from batch experiment, a surface complexation model was developed and used in a predictive mode to model the experimental data using Visual Minteq (version 3.1). A 2-pk Double-Layer Model (DLM) was used to simulate the release of fluoride from soil with respect to pH. Past research has suggested that the adsorption and release of fluoride in near surface environment is primarily controlled by pH of the soil among other geochemical parameters like ionic strength, presence of ions such as  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{HCO}_3^-$  etc (Prabhu et al. 2023). A surface complexation model developed by (Padhi and Tokunaga, 2018) incorporating general composite (GC) approach which described the pH dependent fluoride sorption isotherms on granitic soils. In this mode, to describe the fluoride sorption edges in soil, the generalised two layer model (Dzombak and Morel, 1991) was considered assuming that all the surface complexes are inner sphere complexes. The GC model approach has been proven to

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

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

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

where  $n_d$  is the number of data points,  $n_p$  is the number of adjustable parameters (zero in this case as the model was used in a purely predictive mode),  $i$  is an index,  $C$  and  $\hat{C}$  are the measured and predicted aqueous fluoride concentration at equilibrium (mg L<sup>-1</sup>),  $C_0$  is the total fluoride concentration (mg L<sup>-1</sup>), respectively.

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

| Reaction                                       | Parameters | Reference  |
|------------------------------------------------|------------|------------|
| 1. Surface and Solution Parameters             |            |            |
| Surface Site Density (sites nm <sup>-2</sup> ) | 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   |                             |
| $>\text{SOH} + \text{H}^+ \Rightarrow \text{SOH}_2^+$                                | 3.8     | (Padhi and Tokunaga., 2018) |
| $>\text{SOH} \Rightarrow \text{SO}^- + \text{H}^+$                                   | -6.9    | -do-                        |
| $>\text{SOH} + \text{F}^- + \text{H}^+ \Rightarrow \text{SF} + \text{H}_2\text{O}$   | 8.4     | -do-                        |
| $>\text{SOH} + \text{F}^- \Rightarrow \text{SOHF}^-$                                 | 4.2     | -do-                        |
| $>\text{SOH} + 2\text{F}^- + \text{Al}^{3+} \Rightarrow \text{SOAlF}_2 + \text{H}^+$ | 10.3    | -do-                        |

### 3. Results and Discussion

#### 3.1 X-Ray Diffraction Analysis

The X-ray diffraction was carried out on powdered soil samples obtained from various depths. The investigation revealed that in the Laporiya soil minerals viz. Ferruccite ( $\text{NaBF}_4$ ) and Fluorite ( $\text{Ca}_4\text{F}_8$ ) were identified as major fluoride bearing minerals. Whereas in the Bayana soil Zinnwaldite ( $\text{K}(\text{Al Fe Li})(\text{Si}_3\text{Al})\text{O}_{10}\text{OH F}$ ) were identified as major fluoride bearing minerals in the top 1.5m. Along with these minerals Baratovite ( $\text{Li}_2\text{KCa}_8\text{Ti}_2\text{Si}_{12}\text{O}_{37}\text{F}$ ) in Laporiya soil and Chukhrovite ( $\text{Ca}_{32}\text{Si}_8\text{Al}_8\text{S}_8\text{O}_{128}\text{F}_{104}\text{H}_{192}$ ) and Afghanite ( $\text{Si}_{24}\text{Al}_{24}\text{O}_{96}\text{Ca}_{10}\text{C}_{15.80}\text{F}_{0.20}\text{K}_{4.72}\text{Na}_{17.28}\text{S}_6\text{Os}_{24}$ ) in Bayana soils were also present. The mineralogical analysis indicates the predominance of fluorite, ferruccite and zinnwaldite in soil samples of study area. Among primary minerals fluoride content found to be higher in fluorite and may contribute to ~ 49 wt% of  $\text{F}^-$  (Speer, 1984). One such study reported by Liu et al. 2015 observed that the sediment fluoride in the form of fluorite had an average content of 780 mg/kg being the primary source of groundwater fluoride. The groundwater with elevated pH when react with rocks containing

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

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

### 3.2 Batch Kinetic Experiments

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

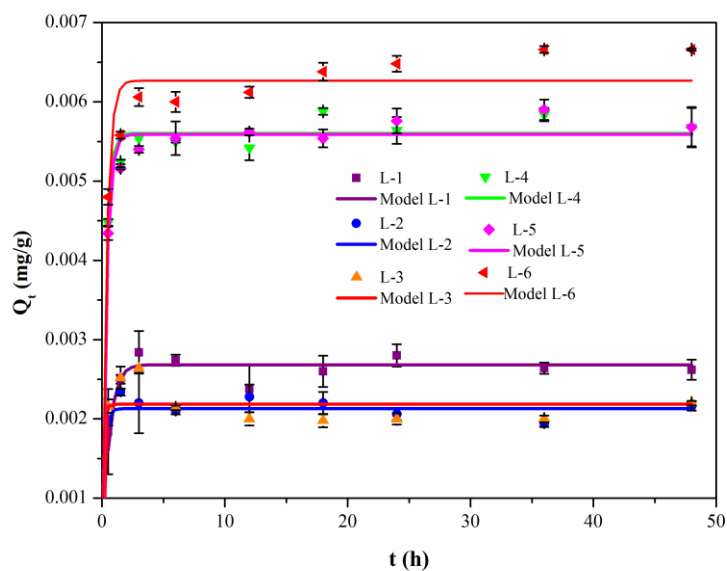


**Fig.2 Time dependent release of fluoride release from various layers of Laporiya soil along with Pesudo-first order kinetic model. L1 to L6 represent soil obtained from layers 1 to 6 of Laporiya site. [Error bars on kinetic data represent the standard deviation of the mean for duplicate measurements].**

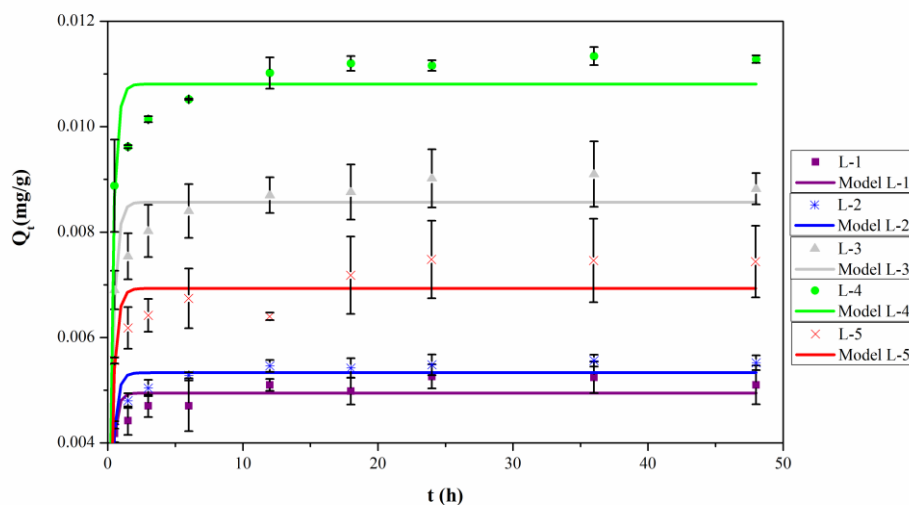


**Fig.3 Time dependent release of fluoride release from various layers of Bayana soil along with Pesudo-first order kinetic model. L1 to L5 represent soils obtained from Layers 1 to 5 of Bayana**

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

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

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

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

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

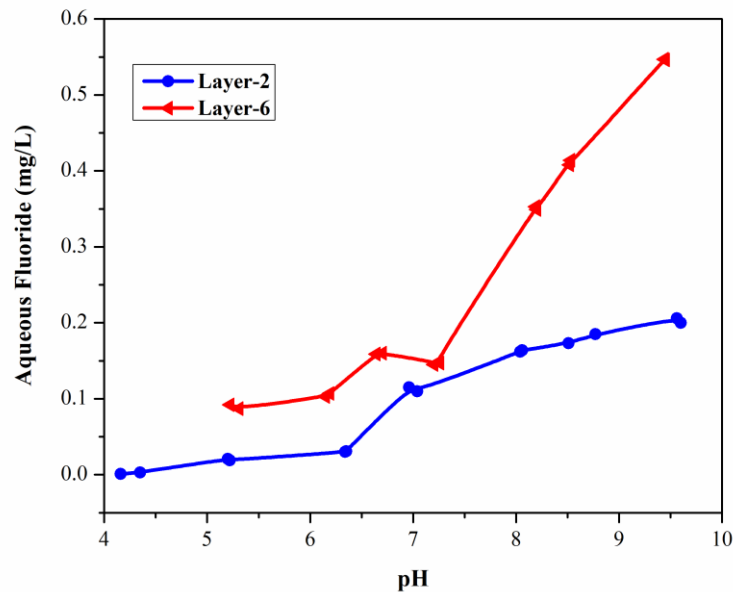
| Laporiya Site |        |        |         | Bayana Site |        |        |         |
|---------------|--------|--------|---------|-------------|--------|--------|---------|
| Layers        | $Q_e$  | $K_1$  | $R^2$   | Layers      | $Q_e$  | $K_1$  | $R^2$   |
| 1             | 0.0027 | 2.3243 | 0.97455 | 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 |             |        |        |         |

### 3.3 pH Edges Experiment

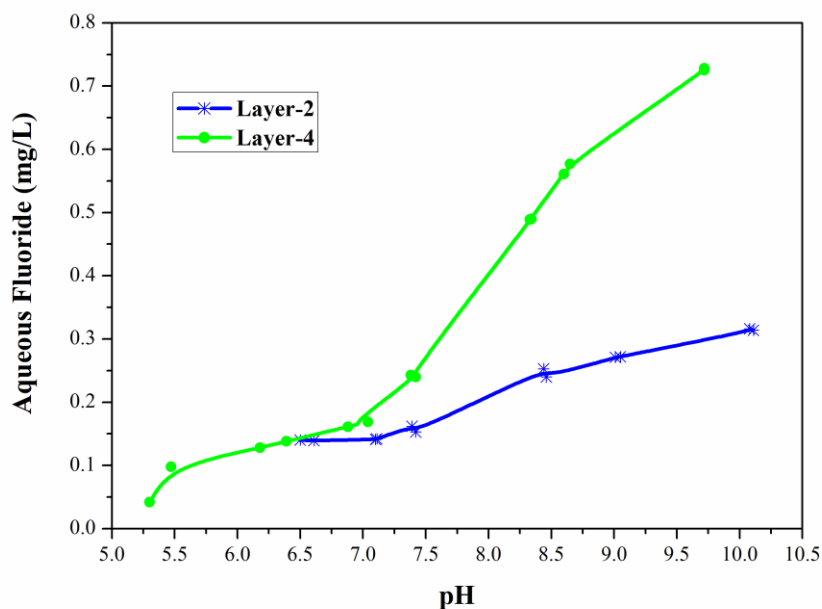
The fluoride release plots with respect to pH for Layer-2 and Layer-6 of Laporiya site are shown in Fig. 4a. The amount of fluoride release from soil increased gradually as the pH increased. At pH <7, Layer-2 shows less amount of fluoride desorbed when compared to Layer-6. In contrast, increasing the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

Bhattacharya, 2015 also reported high fluoride adsorption at low pHs whereas soils with high pH shows high fluoride release to groundwater.

The regression meta-analysis of fluoride with physical factor like pH that was carried out by Islam and Mostafa, 2021 indicated that fluoride desorption is positively correlated to pH and followed a linear model. It has been observed that under acidic condition fluoride complexes with cation such as  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  in soil solution resulting in small amount of free fluoride ions in solution. This was also supported in an earlier study by Vithanage and Bhattacharya, 2015 where it was observed that under acidic condition fluoride form complexes with  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  in soil. On the other hand, at high pH, an increase in free fluoride concentration is observed in soil solution as hydroxide ions cause the cations to precipitate preventing the formation of fluoride complexes.



(a)



(b)

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

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

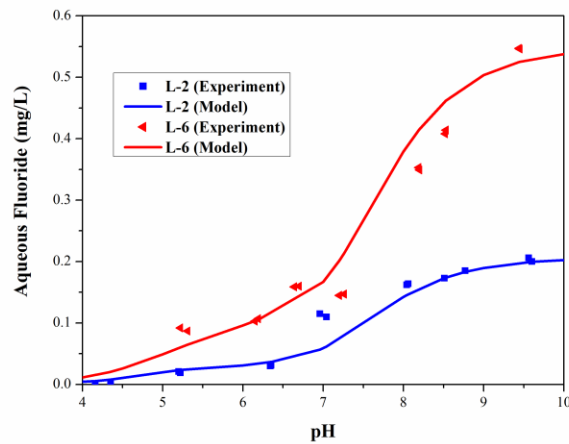
otherwise it would have resulted in a reverse trend, i.e., more release at  $\text{pH} < 6$  (Borgnino et al. 2013).

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

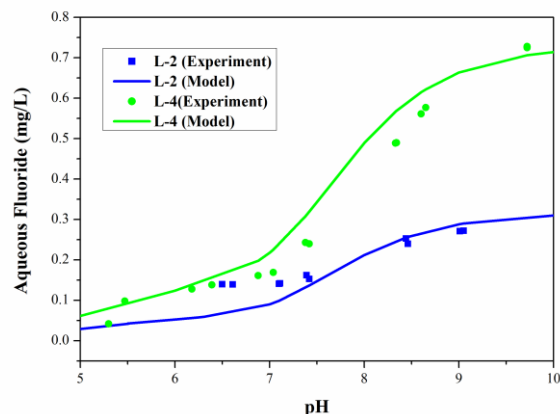
### 3.4 Geochemical Modelling

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

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



(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

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

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

#### 4. Conclusion

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

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