Surface Complexation Modeling of Fluoride Adsorption by Soil and the Role of Dissolved Aluminum on Adsorption

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The adsorption processes of F− on a natural soil as a function of varying pH and F− concentration were evaluated by applying a surface complexation model (SCM) based on a single surface functional group with monodentate binding sites. A granitic soil from Tsukuba, Japan, was chosen as an example, and the SCM was developed to explain the pH dependency of F− sorption isotherms on the soil. Four possible surface complexation reactions were postulated with and without including dissolved Al. Optimized constants for F− surface complexation, and those for protonation and deprotonation, were used for the simulations. The SCM including dissolved Al and the adsorption of Al–F complex can simulate the experimental results, the decreasing trend of F− adsorption with the increase in pH, quite successfully. Also, including dissolved Al and the adsorption of Al–F complex to the model explained the change in solution pH after F− adsorption. Therefore, incorporation of dissolved Al and Al–F complex in model calculations of a soil–F system is an important improvement to predict F− concentrations of soil solutions.

Fluorine is a minor element representing about 0.3 g kg−1 of the Earth’s crust and exists as fluorides in a number of minerals (World Health Organization, 2004). These minerals, e.g., fluorite, biotite, topaz, and their corresponding host rocks such as granite, syenite, and shale, can release F− into groundwater (Edmunds and Smedley, 2005; Apambire et al., 1997). On a local scale, a considerable amount of F− can be introduced into the environment from anthropogenic sources such as phosphate-containing fertilizers used in agricultural fields and aluminum smelters (Arnesen and Krogstad, 1998). In many Asian and African countries, F− contamination of groundwater and surface water has been reported, and more than 200 million people are exposed to groundwater with F− concentrations exceeding the safe drinking water limit (1.5 mg L−1, set by the World Health Organization, 2004) (Amini et al., 2008). The reported maximum dissolved F− levels in groundwater are: Rajasthan, India (69.7 mg L−1), Kuitan, China (21.5 mg L−1), Tanzania (12 mg L−1), South Africa (13 mg L−1) (Ayoob et al., 2008), and Kenya (55 mg L−1) (Gitonga et al., 1984). Because groundwater is used for drinking by >50% of the world’s population (World Health Organization, 2004), drinking water is often the main source of F− intake by humans. In addition, other modes of F− intake via food (Susheela, 2003) and air (Ando et al., 2001) have also been reported.

Although it has been shown that F− is beneficial for the prevention of dental caries, its essentiality has not been demonstrated unequivocally (World Health Organization, 2011). In fact, adverse effects of the long-term ingestion of F− (>1.5 mg L−1) is well documented (Ayoob and Gupta, 2006). Dental and skeletal fluorosis are the most common health effects of F− consumption. Besides this, excessive consumption of F− may affect various organ systems, including the immune system, circulatory system, liver and kidneys, reproductive system, brain, and skin (Liu et al., 2008b).
Contamination of soil by F⁻ is of growing concern because soluble F⁻ present in soil can migrate to surface water and groundwater in some circumstances (Wang et al., 2002; Pickering, 1985), and the increase of soluble F⁻ can enhance F⁻ uptake by plants (Gautam et al., 2010; Amalraj and Pius, 2013). Moreover, the adsorption and availability of F⁻ is mostly affected by the pH of the soil among other factors, and residues and effluents applied to the soil may contain specific chemicals in solution that may affect the soil pH and F⁻ adsorption. The release of Al (referring to all the dissolved Al species considered in this study) from soil contaminated with F⁻ is another environmental concern (Polomski et al., 1982), although some studies suggest that F⁻ complexation alleviates Al toxicity (Takmaz-Nisancioglu and Davison, 1988; McLean et al., 1992).

Therefore, it is necessary to study the fate and transport of F⁻ in soil to understand and predict F⁻ concentrations in both surface water and groundwater. Published information is sparse regarding the fate of F⁻ in the subsurface. One such study by Bégin et al. (2003) used the distribution coefficient (constant $K_d$) approach in the reactive transport model to describe F⁻ transport behavior in a soil column. However, the constant $K_d$ model introduces significant uncertainty in the calculation of ion sorption due to spatial or temporal variations in water chemistry (Bethke and Brady, 2000). In contrast, surface complexation models (SCMs) provide a more robust and realistic description of ion sorption than the $K_d$ approach (Kohler et al., 1996). There have been studies of the pH-dependent adsorption behavior of F⁻ with respect to a single mineral constituent, such as kaolinite (Weerasooriya et al., 1998; Weerasooriya and Wickramaratne, 1999), laterite (Vithanage et al., 2012), and laterite and bauxite (Craig et al., 2015) based on SCMs; however, to our knowledge, there are no previous reports on the application of SCMs to describe F⁻ adsorption to natural soil in the presence of complexing agents.

In subsurface systems, Al is considered to be important in governing the mobility of F⁻ because F⁻ induces Al release by forming Al–F complexes (Manoharan et al., 2007; Berger et al., 2015). The importance of F⁻ in Al speciation and vice versa have been critically discussed in the literature (e.g., Berger et al., 2015). The speciation of F⁻ in solution in the presence of Al is pH dependent (Gago et al., 2002), which can greatly influence the adsorption of F⁻ on the soil surface. Despite that, the interactions between F⁻ and Al, and their effects on F⁻ adsorption in soil, are not fully understood.

Hence, the main objective of this study was to improve the understanding of F⁻ adsorption behavior on soil as a function of various solution properties such as the initial F⁻ concentration, ionic strength, and pH and to model the pH dependence of F⁻ adsorption on soil. Our major goal was also to examine the effect of Al on F⁻ adsorption and the related implications in predicting F⁻ adsorption in porous media. In this study, we chose a natural granitic soil from Tsukuba, Japan, as an example. A series of batch experiments were conducted to produce the F⁻ sorption isotherms or envelopes. We deliberately chose to work at low F⁻ concentrations (maximum of 0.526 mM) both to avoid precipitation of F-bearing mineral phases and to choose the F⁻ concentration range commonly observed in groundwater. An SCM was developed to model F⁻ adsorption under our experimental conditions. Information on the micropore distribution in the soil was also used to support an F⁻ adsorption mechanism.

Materials and Methods

Sampling Site and Soil Characterization

A granitic soil from Tsukuba, Japan, was selected to study F⁻ adsorption behavior. The sampling site (36.2122° N, 140.1066° E) is located near the Tsukuba Shrine at the foot of the southern face of the Tsukuba Mountain. Soil samples were collected at the site by removing the upper layer to avoid roots and litter, and they were then characterized for physicochemical properties. In this study, a granitic soil was chosen because groundwater and soil F⁻ contamination has quite often been reported from granitic terrains due to the relative abundance of F-bearing minerals such as biotite, amphibole, apatite, and fluorite in granites (Edmunds and Smedley, 2005; Apambire et al., 1997).

Micropore Distribution

The specific surface area, micropore surface area, and micropore volume were determined by N₂ gas adsorption and desorption processes using a surface area and pore size analyzer (NOVA 2200c, Quantachrome). The 10-point Brunauer, Emmett, Teller (BET) method was used to determine the specific surface area (Brunauer et al., 1938). A t-plot was created from the adsorption–desorption data by plotting the quantity of gas adsorbed as a function of the calculated film thickness to determine the microporosity (Gregg and Sing, 1982). The statistical film thickness was calculated using the Harkins–Jura equation (de Boer et al., 1966):

$$t(A^0) = \sqrt{\frac{13.99}{0.034 - \log(p/p^0)}}$$  \[1\]

where $t(A^0)$ is the statistical film thickness and $p/p^0$ is the relative pressure. Micropore surface area and micropore volume were determined from the curve fits to the linear portion of the plot (Gregg and Sing, 1982; Hay et al., 2011; Craig et al., 2015).

Chemical Analysis

Soil pH (1:2 solid/solution ratio with aqueous solution, pH$_{aq}$ and 0.01 M CaCl$_2$ solution, pH$_{CaCl_2}$) was measured by a Sentix 81 pH electrode combined with an inoLab pH 7310 pH meter. Leachable ions (1:10 solid/solution ratio with aqueous solution), such as F⁻, SO$_4^{2-}$, NO$_3^-$, Cl⁻, Ca$^{2+}$, Mg$^{2+}$, Na$^+$, and K$^+$ were analyzed by ion chromatography (IC). Leachable and exchangeable Al (extraction with 1.0 M KCl), and leachable Fe were analyzed by inductively coupled plasma mass spectrometry (ICP–MS; ICPM-8500, Shimadzu). All the samples for dissolved ion, Al, and Fe analysis were filtered with a 0.45-µm syringe filter. Colloids of
Al can pass through the 0.45-μm filter, and hence, the measured Al concentration may include dissolved and colloidal Al. In this study, for the Al speciation calculation, Al phases were allowed to precipitate according to the database in Visual Minteq 3.2 (see the discussion in the Supplemental Material, Section S3).

Part of the filtered sample was acidified to pH < 2 with concentrated HNO₃ and was refrigerated for the analysis of cations, Al, and Fe. The samples were brought to room temperature before analysis. Total organic C of the sample was measured by dry combustion method. The dissolved organic C in the soil leachate was measured by a total organic C analyzer (TOC-L, Shimadzu). The different forms of F⁻ in the soil, which can be classified as water-soluble F⁻, exchangeable F⁻, F⁻ bound to Fe and Mn oxides, F⁻ bound to organic matter, and residual F⁻, were quantified by the method suggested by Wu et al. (2002).

Mineralogy and Amorphous Phase Identification

The soil sample was oven dried and sieved through a 2-mm mesh prior to characterization and adsorption studies. Grain size was determined by a sieve test. The mineralogical composition of the bulk powdered soil sample (<2 mm, air dried, and finely ground with a mortar) was identified by X-ray diffractometry (XRD). The XRD patterns were also obtained for the clay fraction and ethylene glycol solvated clay fraction mounted on a glass slide. The major elements in the bulk sample were quantified by X-ray fluorescence. The spreadsheet program MINSQ (Herrmann and Berry, 2002) was used to semi-quantitatively estimate the mineral constituents of the soil from the mineralogical information and elemental data.

Amorphous mineral phases in the soil such as allophane or imogolite were analyzed by the chemical extraction method and solid-state nuclear magnetic resonance spectra of ²⁹Si and ²⁷Al (details are described in the Supplemental Material, Section S1).

Zeta Potential

Electrokinetic measurements are helpful to assess the interfacial electrical characteristics of a substrate at the solid–solution interface (Fuerstenau and Pradip, 2005). A Zetasizer Nano Z equipped with an autotitrator (Malvern) was used to determine the zeta potential of the soil under varying pH conditions by potentiometric titration. Soil suspensions at a 1:1000 solid/solution ratio were injected into the zeta potential analyzer. No supporting electrolyte was used, and the pH was controlled by adding NaOH and HCl. The zeta potential was measured in the pH range of 2 to 13.

Adsorption Experiments

All chemicals used in the adsorption experiments and soil characterization were analytical reagent grade (Kanto Chemical Co., Inc.) and were used without further purification. Milli-Q water was used to prepare the solutions. Fluoride solutions were prepared by dissolving an appropriate amount of analytical reagent grade NaF (Wako Pure Chemicals Industries, Ltd.). The desired F⁻ concentration solutions were prepared from the stock solution by dilution. The soil sample used in the batch experiments was the one sieved to <250 μm, unless otherwise stated (this fraction was chosen because F⁻ adsorption was much lower for the larger fraction, as explained below). The batch experiments were conducted in clean, acid-washed polyethylene bottles, and the temperature was kept constant at 25 ± 0.5°C. Batch experiments without any soil sample were also conducted to check F⁻ adsorption by the polyethylene bottles, which showed no F⁻ adsorption on the bottles. The shaker bath was set to an agitation speed of 60 ± 2 rotations per minute.

Sorption Isotherm

Fluoride sorption isotherms were obtained to characterize F⁻ uptake by soil as a function of the initial F⁻ concentration at a pH range of 4 to 9. To the experiment bottles, 0.5 g of soil was weighed, and 0.5 mL of deionized water was added to it. The bottles were then capped and left overnight for the soils to equilibrate with the solution. Appropriate amount of 5.26 mM F⁻ solution was added to produce a total F⁻ concentration ranging from 0.131 to 0.526 mM in 50 mL of solution. The ionic strength of the solution was kept constant by adding 2.5 M KNO₃ solution. The pH of the solution was measured and adjusted to the desired pH by adding 0.01 M KOH or 0.01 M HNO₃. The total volume was adjusted to 50 mL, and the bottles were capped and placed in the shaker bath for 24 h (the equilibration time was decided from the results of kinetic batch experiments [Supplemental Material, Section S2]). After the experiment, the solutions were analyzed for pH, filtered with 0.45-μm syringe filter, and stored for analysis of dissolved ions and total Al and Fe (the procedure for sample storage and analysis were as described above). The concentration of adsorbed F⁻ was calculated as the difference between the amount added and that remaining in solution after equilibrium.

Adsorption at Various Ionic Strengths, Solid/Solution Ratios, and Grain Sizes

The effect of soil mass loading on F⁻ adsorption was investigated by varying the solid/solution ratio from 5 to 30 g L⁻¹. Fluoride adsorption on the soil was also tested at various ionic strengths (0 [no electrolyte addition], 0.001, and 0.01 M) and different grain sizes (>425, >250, >106, and <106 μm). The experimental procedure and reaction time were the same as that described for the batch pH-dependent isotherm experiments.

Analytical Methods

The pH of the solutions was measured using a Horiba pH meter (Horiba D54 pHCond meter) and sensor (Horiba 9625–10D), calibrated using commercial pH 4.0, 7.0, and 10.0 buffers. Filtered solutions from the adsorption experiments were analyzed for major anions including F⁻ by IC (Dionex DX120, with Dionex IonPac Column, AS18, 4 by 250 mm) with an eluent of 23 mM KOH and a flow rate of 1 mL min⁻¹. However, except for the filtrates from the kinetic experiment and the experiments where the electrolyte was not added, the IC results were erroneous because...
of a high concentration of NO$_3^-$, as dissolved KNO$_3$ was used as a background electrolyte in the experiments. Hence, the samples were reanalyzed for F$^-$ with the SPADNS method using a Hach 890 colorimeter. The filtered and acidified sample was analyzed for total Al and Fe concentrations by ICP–MS.

**Surface Complexation Modeling**

It should be noted that empirical models, such as the Freundlich and Langmuir models, are valid only for the conditions under which the experiment is conducted (Goldberg et al., 2007a). For example, adsorption isotherm datasets are typically developed for a single pH value. Hence, most adsorption isotherm models are valid only at the pH at which it was developed and are difficult to use to predict adsorption behavior involving pH variations.

Surface complexation models are able to describe surface species, mass balance, and chemical reactions and have been used to model the effect of pH variation on adsorption (Davis and Kent, 1990; Dzombak and Morel, 1990). Application of an SCM to single mineral phases is well known (e.g., FeO [Dzombak and Morel, 1990] and gibbsite [Karamalidis and Dzombak, 2010]), whereas application of an SCM to a mineral assemblage (or soil) is not straightforward (Goldberg et al., 2007a). Two kinds of approaches have been suggested for the application of an SCM to a mineral assemblage (or soil), i.e., the component additive (CA) and the general composite (GC) approaches (Davis et al., 1998).

The assumptions, approaches, and the details of these methods were presented by Davis et al. (1998). The advantages and limitations of using the CA and GC approaches were illustrated well by Davis et al. (1998), Davis et al. (2004), and the references therein. Application of both CA and GC approaches to explain metal and oxy(an)ion adsorption to a complex mineral assemblage and soil were reported. For example, the CA approach was used to explain Pb and Cd adsorption onto soil (Serrano et al., 2009), and the GC approach was used to explain U(VI) adsorption to natural sediments at laboratory and field scales (Davis et al., 2004; Liu et al., 2008a; Ma et al., 2010; among others). Based on the discussion on both approaches, and considering the uncertainties in quantifying mineral phases and mineral coatings in soil, the GC approach was found to be appropriate in application of an SCM to soil (Davis et al., 1998), hence the GC approach was chosen to describe the sorption behavior of F$^-$ in this study.

In this study, the generalized two-layer model (Dzombak and Morel, 1990) was used to describe the F$^-$ sorption edges in soil and to optimize the reaction constants because it is simple, requires fewer input parameters, is applicable to different solution conditions, is capable of handling several surface sites simultaneously, and uses the Gouy–Chapman theory to describe the relation between surface charge and surface potential. The Gouy–Chapman theory describes electric double layers very well and is appropriate for the approximation of the electrostatic potential at the surface for all solutions of monovalent salts at concentrations smaller than 0.2 M.

Furthermore, the necessary aspects of developing an SCM were to determine the total number of surface sites, to define the mass action and mass balance equations that describe the equilibrium of surface reactions, to determine the conditional equilibrium constants for surface species, and to develop an approach to quantify the Coulombic correction factors (Davis et al., 1998). An SCM was developed in this study as follows.

**Total Number of Surface Sites Determination for Natural Soil**

Determination of the total site density of single mineral phases can be achieved by a variety of methods (Davis and Kent, 1990). For a complex mineral assemblage, according to the GC approach, the most used method was determining the specific surface area of the assemblage and then calculating the total reactive surface sites from the recommended surface site density for a mineral assemblage or soil (2.31 sites nm$^{-2}$; Davis and Kent, 1990). However, a range of surface site densities can be found for complex systems such as soil (2–8 sites nm$^{-2}$; Davis and Kent, 1990), and uncertainty in the measurement of the specific surface area by the BET method can be introduced by the presence of poorly crystalline solids. The BET surface area determination may underestimate the actual reactive surface area in the presence of sufficiently small micropores, which prevents access for N$_2$ adsorption. Furthermore, Villalobos et al. (2003) discussed the variability of goethite surface site density with surface area for different adsorbents. Hence, in this study, the surface site concentration per liter of solution (i.e., surface site density multiplied by the specific surface area and solid concentration) was chosen as a fitting parameter in the model.

**Surface Complexation Reactions**

The reactive surface hydroxyl groups in soils are represented by a generic surface site (>SOH) in the GC approach. Hence, the surface complexation reactions are written in terms of >SOH. The generalized two-layer model (Dzombak and Morel, 1990) considered in this study assumed that all the surface complexes are inner sphere complexes. Moreover, although it is possible that F$^-$ can form monodentate, multidentate, inner sphere, and outer sphere complexes (Vithanage et al., 2012), we neglected multidentate and outer sphere complexes considering that the maximum F$^-$ concentration in our study was 0.526 mM, not the high concentration needed to introduce a multidentate complex, and ionic strength has a negligible effect on F$^-$ sorption under our experimental conditions (see above).

**Parameter Optimization**

The software PEST (Doherty, 2004) coupled with PHREEQC (Parkhurst and Appelo, 1999) was used to estimate surface and adsorption constants and the site density parameter from the experimental data. PEST has been commonly used for groundwater flow and transport modeling (Doherty, 2004), and coupling PHREEQC with PEST to optimize surface complexation constants has also been reported (Bachma and Merkel, 2011; Se et al., 2008). The main advantages of using the PHREEQC–PEST approach were that (i) a built-in thermodynamic database and activity coefficient model in PHREEQC can be used, and...
(ii) by using PEST, any number and type of parameters can be optimized as long as the number of parameters to be estimated is less than or equal to the number of observations (Doherty, 2004), which can avoid the non-convergence problem often encountered by other models while fitting multiple model parameters.

Results

Physical and Chemical Properties of Soil

Physical Characteristics

The BET $c$ parameter calculated from the N$_2$ gas adsorption–desorption isotherm for the sample (<2 mm) was 167 (Table 1), suggesting the dominance of mesopores in the sample (Davis and Kent, 1990). The $t$-plot surface area was almost equal to the surface area calculated by the BET method (Table 1), and the micropore volume was 0.18 mm$^3$ g$^{-1}$. The BET surface area increased with a decrease in grain size of the soil fraction (Table 1), as expected.

Chemical Properties

The soil (<2 mm) is silica rich, with 15% Al$_2$O$_3$ and 2.8% Fe$_2$O$_3$ (Table 2). From the XRD analysis, minerals identified in the bulk sample were quartz, feldspar, kaolinite, chlorite, and biotite (Table 2). Mineral phase quantification for the <2-mm sample by MINSQ (Herrmann and Berry, 2002) resulted in 29% quartz, 42% feldspar, 17% clay minerals (kaolinite and chlorite), and 2% biotite (Table 2).

Table 3 shows that oxalate-extractable Al is less than pyrophosphate-extractable Al. Quantification of noncrystalline phases from the chemical extraction method (Supplemental Material, Section S1) suggested that noncrystalline phases such as allophane or imogolite in the soil are negligible. From the solid-state nuclear magnetic resonance spectra of $^{29}$Si and $^{27}$Al of the bulk sample (<2 mm) (Supplemental Fig. S1a and S1b), the presence of allophane or imogolite could not be confirmed (no peak at −78 ppm in the $^{29}$Si spectra), whereas the peak at −90 ppm confirmed layered silicates. The results are in agreement with the results of the chemical extraction analysis.

The soil was acidic, with a pH$_{aq}$ of 4.4 and pH$_{CaCl_2}$ of 4.01 (Table 3). Leachable F$^-$ for this soil is negligible. Different forms of F$^-$ in the soil are in the order residual F$^-$ > F$^-$ bound to Fe and Mn oxides > F$^-$ bound to organic matter > exchangeable F$^-$ > water-soluble F$^-$ (Table 3). Fluoride bound to Fe and Mn oxides includes F$^-$ adsorbed or co-precipitated on oxides, hydroxides, and hydrous oxides of Fe and Mn (Wu et al., 2002). The fractions of water-soluble, exchangeable, and organically bound F$^-$ together were considered environmentally available F$^-$. It should be noted here that the sequential extraction procedure for F$^-$ (Wu et al., 2002) needs to be validated in terms of complete selective extraction and dissolution of the target component and total recovery of dissolved target components without resorption or precipitation. Thus, the phase association of F$^-$ in the soil was treated qualitatively in this study.

The organic C content of the studied sample was low (total organic C 0.7% and dissolved organic C 3.7 mg L$^{-1}$ in the 1:10 soil/aqueous extract) (Table 3). Speciation modeling results (for details, see the Supplemental Material, Section S3) showed that at in the pH range of 4.6 to 6.1, Al–F complexes dominated the Al speciation, whereas F$^-$ speciation was dominated by F$^-$ and Al–F complexes (Supplemental Table S1). The AI–FA complex (Al bound to fulvic acid) was negligible at all the pH values studied (Supplemental Table S1).

Zeta Potential

The pH-dependent surface charge of soil is an important property for discussion of ion adsorption at the solid–solution interface.

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Table 1. The BET surface area, BET $c$ parameter, and the $t$-plot surface area, micropore volume, and micropore area of the sample (<2-mm) fraction used in this study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (BET), m$^2$ g$^{-1}$</td>
<td>7.67</td>
</tr>
<tr>
<td>Bulk</td>
<td>7.67</td>
</tr>
<tr>
<td>&gt;425-μm fraction</td>
<td>3.4</td>
</tr>
<tr>
<td>&gt;250-μm fraction</td>
<td>7.3</td>
</tr>
<tr>
<td>&gt;106-μm fraction</td>
<td>9.7</td>
</tr>
<tr>
<td>&lt;106-μm fraction</td>
<td>13.7</td>
</tr>
<tr>
<td>BET $c$ parameter</td>
<td>167</td>
</tr>
<tr>
<td>From $t$-plot analysis</td>
<td></td>
</tr>
<tr>
<td>External surface area, m$^2$ g$^{-1}$</td>
<td>7.24</td>
</tr>
<tr>
<td>Micropore volume, mm$^3$ g$^{-1}$</td>
<td>0.18</td>
</tr>
<tr>
<td>Micropore area, m$^2$ g$^{-1}$</td>
<td>0.422</td>
</tr>
<tr>
<td>Micropore area/surface area, %</td>
<td>5.5</td>
</tr>
<tr>
<td>Micropore volume/pore volume, %</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Table 2. Elemental composition and mineralogical properties of the studied soil (<2-mm fraction).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental composition, %†</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>64.4</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>15.5</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.8</td>
</tr>
<tr>
<td>MgO</td>
<td>0.52</td>
</tr>
<tr>
<td>CaO</td>
<td>1.1</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>2.1</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>3.3</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.25</td>
</tr>
<tr>
<td>MnO</td>
<td>0.09</td>
</tr>
<tr>
<td>Mineral phase quantification, %‡</td>
<td></td>
</tr>
<tr>
<td>quartz</td>
<td>29.3</td>
</tr>
<tr>
<td>feldspar</td>
<td>42.1</td>
</tr>
<tr>
<td>chlorite</td>
<td>0.7</td>
</tr>
<tr>
<td>kaolinite</td>
<td>16.0</td>
</tr>
<tr>
<td>biotite</td>
<td>1.6</td>
</tr>
</tbody>
</table>

† Element contents of the sample as measured by X-ray fluorescence spectroscopy.
‡ Mineralogy was determined by X-ray diffraction. Mineral phase quantification was done according to Herrmann and Berry (2002).
The zeta potentials ($\zeta$) of the soil measured under various pH conditions are presented in Fig. 1. The isoelectric point (IEP) of the studied soil, as measured by electrophoretic techniques, corresponding to $\zeta = 0$ is 3.9.

## Adsorption Experiments

### pH-Dependent Fluoride Adsorption

The pH-dependent $F^-$ sorption isotherms for initial $F^-$ concentrations of 0.131 to 0.526 mM are shown in Fig. 2. Although the amount of $F^-$ removed increased with the increase in initial $F^-$ concentration, the percentage of $F^-$ removal decreased, e.g., at pH 4.6, the percentage of $F^-$ removed was 66.7% for an initial $F^-$ concentration of 0.131 mM, while it was 62.5% at pH 4.75 for an initial $F^-$ concentration of 0.263 mM. The data showed a decrease in $F^-$ adsorption with an increase in pH, similar to the trend observed for $F^-$ adsorption on kaolinite (Weerasooriya et al., 1998) and laterite (Craig et al., 2015; Vithanage et al., 2012). The pH dependence of $F^-$ adsorption was less pronounced at lower $F^-$ concentration, especially at a $F^-$ concentration of 0.131 mM. The effects of solid concentration, background electrolyte concentration, and grain size on $F^-$ adsorption onto soil are presented in Fig. 3. Fluoride adsorption increased with an increase in mass loading in the range of solid concentrations tested (5–30 g L$^{-1}$) (Fig. 3a) because of the increase in available surface sites. Grain size also had a similar effect on $F^-$ adsorption—a decrease in adsorption with an increase in grain size (Fig. 3b)—because the surface area decreased with the increase in grain size (Table 1). Figure 3c shows that ionic strength variation in the range of 0 to 100 mM had insignificant effects on $F^-$ removal, although an increase in ionic strength increases charge screening and reduces the electrostatic repulsion on the surface (Yang et al., 2007). This effect of electrolyte also indicates that outer sphere electrostatic interactions had a negligible role in $F^-$ adsorption on this soil in our pH range of interest, consistent with other studies for $F^-$ adsorption on different materials, e.g., laterite (Vithanage et al., 2012), where $F^-$ adsorption was primarily described by inner sphere complexation.

## Surface Complexation Modeling

In this study, $F^-$ adsorption reactions were chosen based on previous studies (Hao and Huang, 1986; Karamalidis and Dzombak, 2010) for $F^-$ adsorption onto hydrous alumina. Multidentate complexes of $F^-$ were not considered in the model. Even though a $F^-$ bidentate complex ($>\text{FeF}_2^0$) on goethite (Hiemstra and Van Riemsdijk, 2000) and goethite and
lepidocrocite (Ding et al., 2012) has been proposed at high F⁻ loading, at low F⁻ loading as in this study, F⁻ preferably exchanges with singly coordinated sites (Hiemstra and Van Riemsdijk, 2000; Ding et al., 2012). The possible surface complexation reactions for F⁻ adsorption to soil could be represented by Reactions [2–5], where Reactions [2] and [3] represent protonation and deprotonation reactions and Reactions [4] and [5] represent F⁻ adsorption reactions:

\[ \text{>SOH} + \text{H}^+ \rightarrow \text{>SOH}^+ \]  
\[ \text{>SOH + F}^- + \text{H}^+ \rightarrow \text{>SF} + \text{H}_2\text{O} \]  
\[ \text{>SOH + F}^- \rightarrow \text{>SOHF}^- \]  

The rationale for considering F⁻ adsorption reactions, Reactions [4] and [5] in this study, is as follows. Reaction [4] represents ligand exchange processes between F⁻ in solution and OH⁻ at the surface, which could explain the increase in the pH of the solution after adsorption. Protonated hydroxyl sites can also adsorb F⁻, however; in that case, adsorption will be mainly electrostatic. Based on the fact that F⁻ adsorbs onto the net negative surface in the pH range studied (considering that the point of zero charge [PZC] of this soil is close to an IEP of 3.9), we considered that adsorption is not driven by electrostatic interactions. Here, the net electrostatic repulsion between the soil surface and F⁻ is overcome by some sort of specific interaction forming inner sphere surface complexes. Also, in our study, the pH of the equilibrated solution slightly increased in the acidic and neutral pH range (Fig. 4); hence, the ligand exchange Reaction [4], where F⁻ ions are exchanged for OH⁻ ions on the uncharged surface species (Hiemstra and Van Riemsdijk, 2000; Hao and Huang, 1986), was included in the model. Also, under the alkaline conditions, the ligand exchange processes should almost cease because of greater competition between OH⁻ in solution and F⁻. Our experimental data suggested that F⁻ adsorbed...
even at higher pH values (Fig. 2); hence other processes, such as surface complexation, were needed to explain F⁻ adsorption. Reaction [5] represents F⁻ adsorption processes, where an inner sphere surface complex without ligand exchange has been invoked. We consider this complex as an inner sphere complex without ligand exchange, where F⁻ is bonded to the central atom. This complex is similar to the one proposed by Nordin et al. (1999) at the edge and kink sites of bayrite (Nordin et al., 1999, Fig. 6).

In addition, F⁻ can effectively facilitate Al dissolution from Al-containing minerals (Haidouti, 1995; Harrington et al., 2003; Zhu et al., 2004). In this study, Al release was enhanced by adding F⁻ at the pH ranges considered; however, a further increase in F⁻ concentration did not affect Al release to a greater extent (Fig. 5), although Harrington et al. (2003) observed an increase in Al release with F⁻ concentration (0–15 mM). The amount of Al released strongly depended on the change in pH, i.e., the decrease in released Al with the increase in pH. Nevertheless, Al release even at pH 7.08 was about 10 times greater than that of the exchangeable Al obtained by KCl extraction (6.28 mg kg⁻¹) (Table 3). Supplemental Table S1 lists the speciation results of Al and F⁻ in solution at pH 4.6 to 6.1 for initial F⁻ concentrations of 0.131 and 0.526 mM. Aluminum and F⁻ speciations were mostly dominated by AlF₂⁺ and AlF₃(aq) species throughout the pH range. At other intermediate F⁻ concentrations, the speciation results were also dominated by AlF₂⁺ and AlF₃(aq) species at the studied pH range. Hence, the possibility of F⁻ adsorption as AlF₂⁺ cannot be ruled out [we considered that other Al–F complexes are negligible in comparison to AlF₂⁺ and AlF₃(aq) and adsorption of AlF₂⁺ is more favorable than that of the uncharged AlF₃(aq) species]. In a study of F⁻ sorption to Al(OH)₃, Haraguchi et al. (2011) found that F⁻ was primarily sorbed as F⁻ when the initial molar ratio of F/Al was <3, whereas, when the F/Al molar ratio was >3, Al–F complexes such as AlF⁺², AlF₂⁺, AlF₃⁻, and AlF₄⁻ were adsorbed. Therefore, model calculations were conducted by including AlF₂⁺ (the charged species) adsorption. The surface complexation reaction considering AlF₂⁺ adsorption could be written as

\[ >\text{SOH} + 2\text{F}^- + \text{Al}^{3+} \rightleftharpoons >\text{SOAlF}_2 + \text{H}^+ \]  

The intrinsic equilibrium constants considered for the aforementioned reactions (Reactions [2–6]) are represented by Eq. [7–11], respectively:

\[ K_+ (\text{int}) = \frac{[\text{SOH}^+] [\text{H}^+]}{[\text{SOH}]} \exp \left( \frac{F \psi_0}{RT} \right) \]  

\[ K_- (\text{int}) = \frac{[\text{SO}^-] [\text{H}^+]}{[\text{SOH}]} \exp \left( \frac{-F \psi_0}{RT} \right) \]  

\[ K_F^1 (\text{int}) = \frac{[\text{SF}]}{[\text{SOH}] [\text{F}^-] [\text{H}^+]} \]  

\[ K_F^2 (\text{int}) = \frac{[\text{SOHF}^-]}{[\text{SOH}] [\text{F}^-] \exp \left( \frac{-F \psi_0}{RT} \right)} \]  

\[ K_F^5 (\text{int}) = \frac{[\text{SOAlF}_2]}{[\text{SOH}] [\text{F}^-]^2 [\text{Al}^{3+}]} \]  

where \( F \) is the Faraday constant (C mol⁻¹), \( R \) is the molar gas constant (J mol⁻¹ K⁻¹), \( \text{int} \) indicates intrinsic, \( T \) is the absolute temperature (K), and square brackets indicate concentrations (mol L⁻¹). The exponential terms account for the solid-phase activity coefficients that also correct for charge on the surface complexes (e.g., Goldberg, 1992).

The mass balance of the surface functional group \( >\text{SOH} \) ([SOH]ₜ) considering surface protonation, deprotonation, and F⁻ adsorption reactions (Reactions [2–5]) is

\[ [\text{SOH}]_T = [\text{SOH}] + [\text{SOH}_2^+] + [\text{SOH}^-] + [\text{SF}] + [\text{SOHF}^-] + [\text{SOAlF}_2] \]
Parameter Optimization and Forward Modeling

The nonlinear optimization program PEST (Doherty, 2004) was run in combination with PHREEQC (Parkhurst and Appelo, 1999) to obtain the optimized parameters by minimizing the weighted least square difference between the observed data and model calculations. The thermodynamic data for the inorganic ions, such as $F^-$, $SO_4^{2-}$, $NO_3^-$, $Cl^-$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, and $Al^{3+}$, were from the default thermodynamic database of PHREEQC. Aluminum can form various monomeric and polymeric complexes; however, the polymeric complexes were not included in the model. The database in PHREEQC does not contain the data for $F^-$ adsorption to soil or mixed oxides. Hence, the database was created in the PHREEQC format for $F^-$ adsorption to soil using a generic surface site. The model was calibrated by using all the experimental $F^-$ adsorption isotherm data.

The PHREEQC and PEST calculations were first completed to check which single surface reaction would provide a best fit to the experimental data. To check the importance of including Al species in the model, the optimization processes set in PEST and PHREEQC were run for three different cases: Case 1, without adding dissolved Al and Al–F complex adsorption to the model; Case 2, including dissolved Al but without Al–F complex adsorption; and Case 3, including dissolved Al and Al–F complex adsorption. Dissolved organic C (DOC) was not included in the model because of the small amount of DOC in the soil leachate (see Supplemental Material, Section S3, for the effect of DOC on $F^-$). The composition of the initial soil solution considered in the model was that of the soil leachate (Table 3). The initial $F^-$ concentration was the total of water-soluble $F^-$ and exchangeable $F^-$, and initially adsorbed $F^-$ was not included in the model because of the very small amount of adsorbed $F^-$ as described above. The measured Al concentration at each pH for the corresponding $F^-$ concentration was used as the initial Al concentration because we assumed that this is the maximum Al concentration that could be released under the prevailing environmental conditions.

The initial guesses for the protonation constant (Reaction [2]) and deprotonation constant (Reaction [3]) were 7.23 and $-10.05$, respectively, which were the averaged values of the protonation and deprotonation constants for amorphous Fe oxide (Dzombak and Morel, 1990) and gibbsite (Karamalidis and Dzombak, 2010) for the generalized two-layer model. For Reactions [4] and [5], the initial guesses for the equilibrium constants were taken from Karamalidis and Dzombak (2010), and that for Reaction [6] was chosen by trial and error considering the program convergence with the set of parameters. The initial guess for the surface site density per liter of solution was calculated from the measured surface area ($9.7 \text{ m}^2 \text{ g}^{-1}$) (Table 1) and the surface site density, 2.31 sites nm$^{-2}$, which was suggested by Davis and Kent (1990).

The optimized model parameters (Table 4) were carried to the forward simulation set in PHREEQC using the generalized two-layer model. The results for all three cases are shown in Fig. 6. The modeled results for Cases 2 and 3 for pH-dependent $F^-$ adsorption apparently reproduced the experimental data, whereas the model with Case 1 did not explain the pH dependence of $F^-$ adsorption well. To better evaluate the model calculation results, the surface species distribution for all the model cases are presented in Fig. 7.

The weighted mean square errors (WMSE) normalized by the model values were calculated for different cases of $F^-$ adsorption simulation and were used to choose the best fit model:

$$WMSE = \frac{1}{n} \sum_{i=1}^{n} \left( \frac{x_i - y_i}{y_i} \right)^2$$

where $n$ is the number of data points, $x_i$ is the amount of adsorbed $F^-$ calculated, and $y_i$ is the amount of adsorbed $F^-$ observed in our experiments. Table 5 shows the calculated WMSE for model Cases 1 through 3.

Table 4. Surface complexation reactions for protonation, deprotonation, and $F$ sorption along with initial guesses for intrinsic surface complexation reactions [$logK$([int])] and model parameters.

<table>
<thead>
<tr>
<th>Reaction no.</th>
<th>Surface complexation reactions</th>
<th>Initial guess</th>
<th>logK$\dagger$ Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$\text{SOH} + H^+ = \text{SOH}_2^+$</td>
<td>7.23$\dagger$</td>
<td>6.0</td>
<td>9.5</td>
<td>3.8</td>
</tr>
<tr>
<td>3</td>
<td>$\text{SOH} = \text{SO}^+ + H^+$</td>
<td>$-10.05$</td>
<td>-9.0</td>
<td>-5.0</td>
<td>-6.9</td>
</tr>
<tr>
<td>4</td>
<td>$\text{SO}^+ + F^- + H^+ = \text{SF} + \text{H}_2\text{O}$</td>
<td>8.78$\dagger$</td>
<td>10.1</td>
<td>12.7</td>
<td>8.4</td>
</tr>
<tr>
<td>5</td>
<td>$\text{SOH} + F^- = \text{SOH}^- + H^+ + H_2O$</td>
<td>2.88$\dagger$</td>
<td>4.7</td>
<td>3.1</td>
<td>4.2</td>
</tr>
<tr>
<td>6</td>
<td>$\text{SO}^+ + 2F^- + Al^{3+} = \text{SOAlF}_2 + H^+$</td>
<td>10.00$\dagger$</td>
<td>-</td>
<td>00.0</td>
<td>10.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No. of surface sites, mmol L$^{-1}$</th>
<th>Surface area, m$^2$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.371</td>
<td>9.68</td>
</tr>
</tbody>
</table>

$\dagger$ Initial guesses for logK and surface site density values taken from averaged values of amorphous Fe oxide (Dzombak and Morel, 1990) and gibbsite (Karamalidis and Dzombak, 2010).

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$\dagger$ Initial guesses by this study.

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Discussion

Physical and Chemical Properties That Affect Fluoride Adsorption

Surface Area and Porosity

The analysis of micropore size distribution by $t$-plot method provided valuable information regarding sorption processes. The surface area calculated by $t$-plot was almost identical to the BET surface area, suggesting a smaller number of micropores. The micropore volume and micropore area (0.9% of the total volume and 5.6% of the total surface area) was small (Table 1), suggesting that diffusion to the intragranular region for this soil might not significantly affect sorption processes.

Chemical Properties, Zeta Potential, and Fluoride Adsorption

Fluoride sorption to soil is known to be negatively correlated with soil pH and Ca content but positively correlated with Al, Fe, and organic matter content (Wang et al., 2002). Considering the chemical properties (Table 2), $F^-$ sorption is favored for the soil sample concerned. Noncrystalline phases are considered not to be

Fig. 6. Amounts of $F^-$ sorbed for different $F^-$ concentration (dots) and the results of the forward modeling (lines): (a) model calculations with Case 1, without dissolved Al and Al–F complex sorption; (b) model calculations with Case 2, with dissolved Al but without Al–F complex sorption; and (c) model calculations with Case 3, with dissolved Al and Al–F complex sorption.

Fig. 7. Fluoride surface species distribution for an initial $F^-$ concentration of 0.394 mM as calculated with the generalized two-layer model, with model parameters given in Table 4, for (a) Case 1, without dissolved Al and Al–F complex sorption; (b) Case 2, with dissolved Al but without Al–F complex sorption; and (c) Case 3, with dissolved Al and Al–F complex sorption.
Table 5. Weighted mean square error by considering different sets of F⁻ sorption reactions for different F⁻ concentrations.

<table>
<thead>
<tr>
<th>Initial F⁻ conc. (mM)</th>
<th>Weighted mean square error†</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.131</td>
<td></td>
<td>0.17</td>
<td>0.005</td>
<td>0.009</td>
</tr>
<tr>
<td>0.262</td>
<td></td>
<td>0.08</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>0.394</td>
<td></td>
<td>0.09</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>0.526</td>
<td></td>
<td>0.03</td>
<td>0.12</td>
<td>0.03</td>
</tr>
<tr>
<td>All data</td>
<td></td>
<td>0.37</td>
<td>0.18</td>
<td>0.08</td>
</tr>
</tbody>
</table>

† Conditions for Model Cases 1 through 3 shown in Table 4.

major contributor to F⁻ sorption, considering that these phases are negligible in this soil (see above). The semi-quantitative mineralogical estimation showed that the soil consisted of 29% silica, mostly quartz, which is a very poor sorbent for F⁻ (Fan et al., 2003), and the major clay minerals are kaolinite and chlorite, which can adsorb F⁻.

The IEP of the soil calculated from zeta potential measurements is 3.9 (Fig. 1), which corresponds to zero electrophoretic mobility. When H⁺ and OH⁻ are the only potential-determining ions and no other ions adsorb specifically at the solid surface, the IEP corresponds to the PZC (Stumm and Morgan, 1981). However, for soil, the IEP is a composite value because (i) inferring the PZC from the IEP for phyllosilicates is complicated, as it may give different IEP values depending on whether the measurement is made on the face or edge of the minerals (Fuerstenau and Pradip, 2005), and (ii) IEP and PZC values are reported to be quite variable for clay minerals and oxides (Osei et al., 2016). Low PZC values for silica and clay minerals including kaolinite, chlorite, and biotite have also been reported (Osei et al., 2016), and the presence of these minerals could be one of the reasons for the lower PZC of the granitic soil in this study.

A change in ionic strength does not affect F⁻ adsorption considerably, suggesting a strong chemical interaction rather than a weaker electrostatic attraction. Fluoride adsorption by soil is pH dependent, with the increase in adsorption with the decrease in pH in general (Fig. 2) due to the negative surface charge of the surface at higher pH ranges, which prevents adsorption of negatively charged F⁻. Similar F⁻ adsorption behavior, i.e., increase in adsorption with a decrease in pH, was also observed for Namoo laterite (Craig et al., 2015) and chemically treated laterite (Maiti et al., 2011), although the rate of F⁻ adsorption by chemically treated laterite (Maiti et al., 2011) was higher than that by Namoo laterite (Craig et al., 2015) and the value reported in this study for granitic soil.

**Surface Complexation Modeling**

Considering the generalized two-layer model, the average values for the protonation and deprotonation constants for amorphous Fe oxide and gibbsite were 7.23 and −10.05, respectively (Dzombak and Morel, 1990; Karamalidis and Dzombak, 2010). It is usually assumed that the PZC of soil is related to the protonation and deprotonation constants as: $\text{pH}_{\text{PZC}} = 0.5(\log K_+ + \log K_-)$ (James and Parks, 1982). The IEP of the soil is 3.9 (Fig. 1), which does not correspond to the assumed PZC value of the soil by these assumptions. It should be noted here that the IEP of soil is a composite value and the protonation–dissociation constant should not be directly related to the IEP as it is for pure minerals. Furthermore, the associated uncertainty in the approach for estimating site density and surface area and the interdependence among model parameters require estimating the set of parameters that best describe F⁻ adsorption to soil under the experimental conditions considered. Hence, in our modeling approach, constants for surface protonation and deprotonation, those for F⁻ surface complexation, and surface site density parameters were optimized.

Our modeling results showed that both Cases 2 and 3 (Table 4; Fig. 6b and 6c) can explain quite fairly the observed F⁻ adsorption at all pH values compared with Case 1 (Fig. 6a). Case 3 resulted in a low protonation constant ($\log K_+ = 3.8$). Low protonation constants for clay minerals and soil (with and without high organic C) have been reported in other studies (Sverjensky and Sahai, 1996; Schroth and Sposito, 1998; Peacock and Sherman, 2005; Goldberg et al., 2007b).

Also, changes in solution pH were observed by comparing the solution before and after the batch experiments (Fig. 4). At acidic pH, the solution pH increased, whereas at alkaline pH, the solution pH decreased after equilibrium. An increase in solution pH due to ligand exchange processes could be explained by both Cases 2 and 3, whereas the decrease in pH of the solution after equilibrium under alkaline conditions could be explained by Case 3 with the formation of a >SOAlF₂ surface complex (Reaction [6]).

The surface species distribution for each case was examined to better understand the modeled results and F⁻ adsorption processes. Figure 7 provides surface species distribution at an F⁻ concentration of 0.395 mM. In Case 1, >SF complex decreases with the increase in pH, whereas >SOHF⁻ complex increases with the increase in pH (Fig. 7a). However, at low F⁻ concentration (0.131 mM F⁻), F⁻ sorption was dominated by >SF complex (not shown). Considering Case 2, F⁻ sorption was almost represented by >SF complex only (>99%) at all the F⁻ concentrations studied (Fig. 7b). Thus, with Case 2, adsorption processes were explained by ligand exchange only within the pH range considered. In Case 3, both the >SF and >SOHF⁻ complex decreased with the increase in pH, and >SOAlF₂ contributed at all the pH values (Fig. 7c). At pH 4.9, 30.8% of the total adsorbed F⁻ was >SF and 66.1% of that was >SOHF⁻, with only 3.1% being >SOAlF₂ complex. Similarly, at pH 6.7, >SF complex contributed 9% of the total adsorbed F⁻, whereas >SOHF⁻ and >SOAlF₂ contributed 74.4 and 16.5%, respectively. The neutral >SF complex was not favored at higher pH ranges, where the surface becomes more negatively charged. It can therefore be safely said that in Case 3, both ligand exchange and surface complexation dominated F⁻ adsorption at lower pH, and F⁻ adsorption was explained by surface complexation including Al–F complex sorption at neutral and alkaline conditions.
pH (Fig. 7c). The pH change was better explained in the case of Case 3, where the increase in equilibrium pH after $F^-$ adsorption at an initial acidic pH could be explained by ligand exchange processes, whereas the decrease in pH after $F^-$ adsorption under alkaline conditions was explained by the increase in $\text{SOAIF}_2$ surface complex (Fig. 7c). Lowering of the equilibrium pH after $F^-$ adsorption could also be possible because of concomitant Al release from the solid phase and OH$^-$ consumption via amorphous Al(OH)$_3$ precipitation, which will result in increased $F^-$ adsorption on the newly formed amorphous Al(OH)$_3$ surface (Zhu et al., 2006). Nevertheless, in the initial F$^-$ concentration range of 0.131 to 0.526 mM in this study, Al release was pH dependent, rather than F$^-$ concentration dependent, and no increase in F$^-$ adsorption was observed that would indicate F$^-$ adsorption on amorphous Al(OH)$_3$.

Table 5 indicates that the WMSE values for Case 1 are larger than those for Cases 2 and 3. Hence, model calculations with Case 1 are considered to not be appropriate to implement in the F–soil system studied. Including dissolved Al and Al–F complex sorption in the model yielded the best results, which showed the effect of Al on F speciation and sorption on soil, which is also evidenced from the WMSE values (Table 5).

This study demonstrated that pH and Al are potentially important parameters governing F$^-$ adsorption, and the GC modeling approach was successful at simulating F$^-$ adsorption by soil. Although the surface complexation reactions and the related stability constants are valid only for the studied soil, the same modeling approach could be adapted to predict F$^-$ adsorption by different soil or mineral assemblages and in the presence of interfering ions or humic substances by adding sorption reactions associated with the interfering ions or humic substances and by calibrating the sorption model across a wider pH range. Moreover, spectroscopic investigation of F$^-$ adsorption processes will supplement the model calculations, which can be a future study.

**Conclusions and Environmental Implications**

The results of this study illustrate the applicability of surface complexation modeling for F$^-$ adsorption to soil with the GC approach and, more specifically, the effect of Al on the model results. The experimental results were well explained by introducing dissolved Al and Al–F complex sorption, while the results were quite different when dissolved Al was not included in the model, suggesting the importance of the dissolved Al on F sorption to soil. This study introduced the importance of including dissolved Al and Al–F complex sorption to the model to explain F$^-$ sorption behavior, which is the first of its kind. Although it is not possible to define a unique set of model parameters because of the independence among the parameters, other surface properties such as zeta potential measurements can be used to compare some of the model parameters, for example the surface protonation and deprotonation constants. The results also reveal that F$^-$ may be released into the environment under neutral to alkaline conditions because of the weak binding and no precipitation, although an acidic pH may help in binding F$^-$ in soil.

The SCM developed in this study with the GC approach can be incorporated into transport models with less uncertainty than that of the constant $K_a$ approach, which should be the next step to be studied. However, in the presence of strongly interacting ligands, the extrapolation of batch-measured adsorption characteristics of F$^-$ to field conditions should be done with caution.

**Supplemental Material**

Amorphous phase identification, kinetic uptake experiments, and speciation modeling can be found in the supplemental material.

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**References**


