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Predicting sulphate adsorption/desorption in forest soils: evaluation of an extended Freundlich equation

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ABSTRACT

Sulphate adsorption and desorption can delay the response in soil acidity against changes in acid input. Here we evaluate the use of an extended Freundlich equation for predictions of pH-dependent SO₄ adsorption and desorption in low-ionic strength soil systems. Five B horizons from Spodosols were subjected to batch equilibrations at low ionic strength at different pHs and dissolved SO₄ concentrations. The proton coadsorption stoichiometry (η), i.e. the number of H⁺ ions co-adsorbed for every adsorbed SO₄²⁻ ion, was close to 2 in four of

five soils. This enabled the use of a Freundlich equation that involved only two adjustable parameters (the Freundlich coefficient K_F and the non-ideality parameter m). With this model a satisfactory fit was obtained when only two data points were used for calibration. The root-mean square errors of log adsorbed SO_4 ranged from 0.006 to 0.052. The model improves the possibility to consider SO_4 adsorption/desorption processes correctly in dynamic soil chemistry models.

Keywords: sulphate adsorption, Spodosols, acidification, Freundlich, pH

1. Introduction

Sulphate adsorption is a process typically associated with the effects of acid deposition on ecosystems. In the 1980s it was established that SO_4^{2-} could be adsorbed to iron and aluminium hydrous oxides in soils (Johnson and Todd, 1983; Singh, 1984; Fuller et al., 1985), thus delaying acidification effects in soil and water ecosystems. The major reason for the delayed effect was found to be co-adsorption of H^+ during the SO_4 adsorption process, a phenomenon described by Hingston et al. (1972). Because the ratio of H^+ to SO_4^{2-} (usually referred to as the proton co-adsorption stoichiometry, η) is higher during SO_4 adsorption than it is in the soil solution, SO_4 adsorption and desorption greatly affects the response time of ecosystems towards changes in acid deposition (Eriksson, 1988; Eriksson and Karlton, 1994). More recently, it has been shown that SO_4 adsorption plays a role not only in mediating the effects of anthropogenic S emissions. For example, Moldan et al. (2012) showed that SO_4 adsorption and desorption is important in buffering soil systems against extreme climatic events such as ‘sea salt’ episodes. For these reasons, correct understanding of SO_4 adsorption and desorption remains an important scope for geochemical research.

SO₄ adsorption in soils involves surface complexation to Fe and Al hydrous oxides as well as poorly crystalline aluminosilicates (imogolite-type materials) (Johnson and Todd, 1983; Gustafsson et al., 1995). Rietra et al. (2001) concluded that for goethite, the mechanism probably involved both inner-sphere and outer-sphere complexes. They constrained the CD-MUSIC surface complexation model of Hiemstra and van Riemsdijk (1996) by use of the following general complexation reaction:

Alone this reaction implies that $\eta = 1$; however, for electrostatic reasons the surface will resist to accommodate this change in charge (-1), especially at low ionic strength; hence some surface groups (FeOH^{1/2-}) will protonate (to FeOH₂^{1/2+}) causing η to be higher. Recent structural evidence supports the idea that SO₄²⁻ adsorption on ferrihydrite involves both inner-sphere and outer-sphere complexes (Zhu et al., 2014).

Surface complexation models are, however, still difficult to integrate in dynamic models for soil chemistry, not least because they require full knowledge of the system including reactions for all possible competing and interacting ions on the surface. For this reason, simpler relationships consisting of only one or two equations are normally used for predicting the extent of SO₄ (and associated H⁺) adsorption.

Some dynamic models (e.g. MAGIC; Cosby et al., 1986 and SMART; Kämäri et al., 1995) use Langmuir equations without explicit consideration of the pH effect. Eriksson (1988), in a rarely cited but pioneering book chapter, suggested a modified Langmuir equation in which each SO₄²⁻ ion was accompanied by two co-adsorbed H⁺ ions (i.e. $\eta = 2$). This equation was applied to understand the downward migration of acid in Swedish Spodosols in response to acid deposition (Eriksson et al., 1992) and to provide the basis for a dynamic transport model (Eriksson and Karlton, 1994). A similar SO₄ adsorption model, which instead used the Temkin equation as a basis, was suggested by Gustafsson (1995). Fumoto and Sverdrup

(2000, 2001) suggested the use of an extended Freundlich equation with both sulphate and hydrogen ion activities as terms. The model was able to satisfactorily describe pH-dependent SO₄ adsorption in an allophanic Andisol. This equation was later modified and included in the dynamic soil model ForSAFE (Wallman et al., 2005) by Martinson and colleagues (Martinson et al., 2003; Martinson and Alveteg, 2004; Martinson et al., 2005).

A problem with these empirical equations is, however, that they contain a large number of parameters that have to be optimized. The objective of this paper was to evaluate the use of the extended Freundlich equation using laboratory data from five B horizons from Swedish Spodosols, in which pH and dissolved SO₄ concentrations were varied systematically. In particular we tested whether a modified Freundlich equation employing a common value of $\eta = 2$ would allow calibration with a minimum of laboratory data and still be able to satisfactorily describe SO₄ adsorption.

2. Materials and methods

2.1 Soil samples

Selected characteristics of the investigated soils are listed in Table 1 and Table 2. All sites were located in coniferous forest, with mostly *Pinus sylvestris* L. The Tärnsjö soil was sandy whereas the other soils were developed in glacial till with a low (< 5 %) clay content. All soils were classified as Typic Haplocryods. Samples were taken from the uppermost spodic B horizon at all sites except for the Kloten site, at which the investigated sample was from a Bs horizon underlying a thin Bhs horizon that had a larger organic C content.

After collection, samples were homogenized and sieved through a 4 mm sieve. They were then kept in doubly sealed plastic bags at 5°C. A small part of the sample was air-dried. The

dry weight of both field-moist and air-dried samples was determined using conventional methods (105°C for 24 h) to facilitate recalculations to dry-weight basis.

2.2 Laboratory procedures

To obtain sulphate adsorption data for calibration of the model, samples were subjected to batch experiments in which 2 g field-moist soil was suspended in 32 cm³ solution of various composition as follows:

- A background electrolyte of 0.1 mM MgCl₂ was present in all samples. This composition was selected to simulate the ionic strength conditions in typical Scandinavian forest soils.
- Various additions of MgSO₄ (0, 27, 54, 107, 214, 321, and 535 μmol L⁻¹) were made to different samples to produce SO₄ adsorption isotherm data.
- To produce additional data extending to lower pH values, stock solutions of MgSO₄ was mixed with H₂SO₄ in equivalent proportions to produce a second set of isotherm data (additions of 13.5+13.5, 27+27, 54+54, 107+107, 160+160, and 268+268 μmol SO₄²⁻ L⁻¹). Such additions were not made for the Risfallet B sample, however, as this sample was already quite acid.
- Some additional MgSO₄/H₂SO₄ mixtures were prepared and added to the Kloten Bs and Tärnsjö Bs samples to further increase the range of pH values of the data.

All equilibrations were performed in duplicate. The batch equilibrations were carried out using 40 cm³ polypropylene centrifuge tubes, and the suspensions were shaken for 24 h in room temperature. The suspensions were then centrifuged. The pH of the supernatant was measured with a Radiometer combination glass electrode. The remaining supernatant solution

was filtered through a 0.2 µm single-use filter (Acrodisc PF) prior to the analysis of SO₄ by ion chromatography (IC) using a Dionex 2000i instrument.

To obtain values for initially adsorbed SO₄ (Q_{ini}), dihydrogen phosphate extraction will quantify the amount of adsorbed SO₄ that is in equilibrium with the soil solution (Karlun, 1994). Thus, 3.00 g field-moist sample was suspended in 30 cm³ 20 mM NaH₂PO₄ and extracted for 2 h. The extracts were then filtered and subjected to IC analysis as above, after dilution 5 times.

To reduce analytical uncertainty, we made frequent use of internal standards both for the IC analysis and for the pH measurement. We estimate the analytical precision to be < 5 % for the IC analysis of SO₄, and less than 0.03 units for the pH measurement.

Oxalate- and pyrophosphate-extractable Fe and Al were determined according to the procedure of van Reeuwijk (1995), and determined by ICP-OES using a Perkin-Elmer Optima 3300 DV instrument. The organic C content of the soils were determined using a LECO CHN-932 analyzer.

2.3 Model development

The model was based on the equation of Martinson et al. (2003), which can be regarded as an extended Freundlich equation. Its mass-action expression can be written as follows:

$$Q = K_F \cdot [SO_4]^m \cdot \{H^+\}^n \quad (2)$$

where Q is the amount of adsorbed SO₄ (mol kg⁻¹ dry soil), [SO₄] is the total dissolved concentration of SO₄ (mol L⁻¹), whereas K_F , m and n are adjustable parameters; K_F is usually termed the Freundlich coefficient, whereas m and n are non-ideality parameters, where m may range between 0 and 1. In a dynamic model there is also a mass-balance equation that governs

the flux of chemical components between dissolved and sorbed phases. The model of Martinson et al. (2003) applied the following mass-balance equation:

$$[\text{SO}_4^{2-}] = 0.85 \cdot [\text{H}^+] + 0.15 \cdot [\text{BC}^{n+}] \quad (3)$$

where the concentration terms are written on an equivalent basis and $[\text{BC}^{n+}]$ denotes base cations (Ca^{2+} , Mg^{2+} , K^+). Equation 2 means that every SO_4^{2-} ion is accompanied by 1.7 H^+ ions during adsorption and desorption (i.e. $\eta = 1.7$), a value taken from Karlun (1997), who determined η in a soil suspension at 0.001 M NaNO_3 .

The major disadvantage with this model is the three adjustable parameters K_F , m and n , which make proper optimization difficult unless there is a large variation in pH and $[\text{SO}_4^{2-}]$ in the data. If not, different combinations of K_F , m and n can lead to equally good fits. Hence large amounts of data need to be collected from one site to sufficiently well constrain the model.

In this work, we redefined the mass-action equation (equation 2) so that, instead of viewing H^+ and SO_4^{2-} as separate components with an own non-ideality parameter m and n , we assumed that the relationship between their non-ideality parameters was constrained by the value of η , according to:

$$m = n \cdot \eta \quad (4)$$

This results in the following modified extended Freundlich equation:

$$Q = K_F \cdot ([\text{SO}_4^{2-}] \cdot \{\text{H}^+\}^\eta)^m \quad (5)$$

After taking the logarithm of both sides, and substituting $\log\{\text{H}^+\}$ for pH, we obtain:

$$\log Q = \log K_F + m \cdot (\log[\text{SO}_4^{2-}] - \eta \cdot \text{pH}) \quad (6)$$

Equation 6 implies that a plot of $\log Q$ vs. $\log[\text{SO}_4^{2-}] - \eta \cdot \text{pH}$ should lead to a straight line with the slope m and the intercept K_F . Although this equation still has three adjustable parameters, it can be brought down to two if a common value of η is employed. In this work, we

hypothesized that the value of η in forest soils can be set to 2. This would also provide a direct link between the mass-action and mass-balance equations and therefore simplify the mass-balance equation (equation 3), since co-adsorbing base cations would no longer need to be considered:

$$[\text{SO}_4^{2-}] = [\text{H}^+] \quad (7)$$

where, to be consistent with equation 3, the concentration terms are written on an equivalent basis.

To obtain additional evidence for the value of η , we (i) optimized the value of η for the batch experiment data of this study (c.f. below), and (ii) set up a simulation using the CD-MUSIC model for ferrihydrite at pH 5. The model was based on the work of Rietra et al. (2001) who investigated the use of the CD-MUSIC model for SO_4 adsorption onto goethite (see equation 1). The model was calibrated for ferrihydrite using the SO_4 adsorption data of Davis (1977), Swedlund and Webster (2001) and Fukushima et al. (2013) and by using parameters for surface charging estimated by Tiberg et al. (2013), see the Supplementary Content for details. This model was defined in Visual MINTEQ (Gustafsson, 2013) and used to calculate the η value at pH 5 and at different ionic strengths ranging from 0.4 mM (the conditions of the batch experiment of this study) to 10 mM. Because η is sensitive to the presence of competing ions in the system, we included also PO_4 and Si at environmentally “realistic” concentrations, c.f. Supplementary Content. The results show that the η value was approximately 1.95 at low ionic strength (Fig. 1) and remained above 1.9 also at an ionic strength of 0.001 M (Fig. 1). The result agrees with the results of Ishiguro et al. (2006), who obtained an η value close to 2.0 at low ionic strength for an allophanic Andisol.

To calibrate the model for the soils under study, we used three different optimization strategies:

1. Unconstrained fit. All three adjustable parameters (K_F , m and η) of equation 6 were fitted using linear regression of $\log Q$ vs. $\log[\text{SO}_4^{2-}] - \eta \cdot \text{pH}$ with the trendline tool in Microsoft Excel. The value of Q was calculated as the sum of initially adsorbed SO_4 as determined by phosphate extraction (Q_{ini}) and SO_4 sorbed during the experiment.
2. Constrained fit. Fitting was made as described above for the unconstrained fit, except that the η value was fixed at 2.
3. 2-point calibration (2PC) fit. Mean results from only two samples were used during optimization. These samples should be sufficiently different in terms of pH and $[\text{SO}_4^{2-}]$ to produce well-constrained values of K_F and m . We used (i) the sample to which only 0.1 mM MgCl_2 had been added (with relatively high pH and low $[\text{SO}_4^{2-}]$) and (ii) the sample to which 0.1 mM MgCl_2 , 0.27 mM MgSO_4 and 0.27 mM H_2SO_4 had been added (relatively low pH and high $[\text{SO}_4^{2-}]$). For the Risfallet sample, the latter sample was not available; instead the second sample used was the one to which 0.1 mM MgCl_2 + 0.535 mM MgSO_4 had been added.

To compare the goodness-of-fit, the RMSE (root-mean square errors) of the simulated values of $\log Q$ were determined, using the measured $\log Q$ values as the reference.

3. Results

The five B horizons investigated were different concerning their capability of retaining SO_4 , as could be deduced from the phosphate-extractable SO_4 values (Table 2). The Kloten and Risbergshöjden soils can be regarded as strongly SO_4 -adsorbing, whereas the three other soils contained rather low levels of initially adsorbed SO_4 . This is consistent with oxalate-extractable Fe and Al, which were highest in the Kloten and Risbergshöjden soils. When SO_4 was added, these soils sorbed the largest amounts (Fig. 2). In both soils, and also in the Tärnsjö B horizon, addition of MgSO_4 alone caused the pH to increase (Fig. 2), probably

because SO_4 adsorption caused co-adsorption of H^+ that was greater than the release of H^+ brought about by Mg^{2+} adsorption in the samples. Further, the SO_4 adsorption isotherms differed depending on whether SO_4 was added as MgSO_4 or as a mixture of MgSO_4 and H_2SO_4 . The latter solutions resulted in stronger SO_4 adsorption because of the lower pH obtained.

Concerning the extended Freundlich model, optimization using the unconstrained fitting method resulted in excellent fits for the Kloten and Risbergshöjden soils (Table 3, Fig. 3), whereas the fit was poorer particularly for the Risfallet soil. The optimized η value was close to 2 for all soils except for the Österström soil, for which η was found to be 3.83. The reason why η was high for the Österström soil could not be established; however, as was mentioned above the optimization of 3 parameters often leads to poorly constrained fits. It is also possible that some other process not accounted for by our simple model approach (e.g. precipitation as Al or Fe sulphate minerals at low pH) could be responsible. In the other four soils the finding that $\eta \approx 2$ is consistent with the assumption that the non-ideality parameters of H^+ and SO_4^{2-} are interrelated (equation 4).

As η was ≈ 2 in four of the five soils, the constrained fitting method (where η was fixed at 2) led to very similar fits (Fig. 3, Table 3). Also the 2PC method, for which only two samples were considered, led to good fits that in most cases were similar. The RMSE values (in terms of $\log Q$) ranged from 0.006 to 0.052. As concerns the fits of the 2PC approach, consistent deviation between model and measurements was found only for the Österström sample; this is probably related to the higher η for this sample (as mentioned above) for the unconstrained fit.

4. Discussion

The surface complexation modeling exercise suggests that the use of $\eta = 2$ for SO_4 adsorption should be possible in low-ionic strength systems such as acid forest soils, as $\eta > 1.9$ under

realistic conditions ($\text{pH} = 5$ and $I < 0.001 \text{ M}$). This is further supported by the evaluation of the unconstrained model fit, as the optimized η value was close to 2 for four out of five soils. This brings down the number of adjustable model parameters to two, which is important since it makes it easier to calibrate the Freundlich model. However, the result for the Österström sample (optimized $\eta = 3.83$) shows that this may not strictly hold true for all soils. Additional research is required to investigate whether this is due to the omission of some other process in the model (e.g. precipitation) or whether it may simply be caused by uncertainties or errors in one or more of the input parameters (measured pH, dissolved and adsorbed SO_4).

The results can be compared to earlier studies in which pH-dependent empirical adsorption equations have been evaluated. Both Eriksson (1988) and Gustafsson (1995) developed models in which it was assumed that $\eta \approx 2$, but they were based on the Langmuir and Temkin equations respectively. The former author did not present any experimental data in support of the Langmuir equation. Gustafsson (1995) used a sequential leaching procedure that produced data in support of the Temkin equation, according to which there should be a linear relationship between $\log[\text{SO}_4^{2-}] - 2 \cdot \text{pH}$ and Q . However, this model did not correctly reproduce the data of the present study (see Fig. S1). Our data are more consistent with the Freundlich equation, which assumes a relationship between $\log[\text{SO}_4^{2-}] - 2 \cdot \text{pH}$ and $\log Q$. This is in agreement with the conclusions of Fumoto and Sverdrup (2000). The reason why Gustafsson (1995) obtained a better fit with the Temkin equation may be due to the sequential leaching procedure used, which could have dissolved interacting ions, thus yielding incorrect results. The experimental method in the present study should be better suited for producing reliable results since only one equilibration was used; thus the dissolution of interacting ions was minimized.

The non-ideality parameter m for SO_4 ranged from 0.11 to 0.24 in this study; this can be compared to the results of Martinson et al. (2005) for 16 soils, according to which m ranged

from 0.0043 to 0.13. In addition, the non-ideality parameter for H^+ was similarly low in the study of Martinson et al. (2005) (range 0.017 to 0.11), whereas in the present study it ranged from 0.21 to 0.47. We believe that our results are more realistic, as the low parameter values reported by Martinson et al. (2005) predict substantial SO_4 adsorption even at $pH > 9$, which does not agree with results for pure Fe oxides (see, e.g. Fukushi et al. 2013). A possible reason to the different results is that dissolution of both interacting ions and sorbents may have occurred in the procedure used by Martinson et al. (2003, 2005), as this included collection of SO_4 adsorption data at very low pH (3.8 and 4). There may also be other possible reasons for the differences, relating e.g. to the numerical optimization methods used.

Accurate determination of the non-ideality parameters is important, as these determine to what extent the adsorbed SO_4 (and co-adsorbed H^+) pool changes in response to a change in influent H^+ and SO_4^{2-} concentrations. The low parameter values reported by Martinson et al. (2005) would imply that SO_4 adsorption/desorption is not very important for soil chemical dynamics, whereas the results of the present study suggest it to be much more significant.

An aspect not considered in the model is competition effects from, e.g. organic matter and phosphate. Indirectly the Freundlich model may account for the current state as concerns competition. If, however, the concentration of the competitors change over a long-term period, this will cause effects that cannot be described by the simple model presented here.

Although the suggested model is potentially useful to generate SO_4 adsorption parameters from a limited number of laboratory data, an additional limitation is that the method requires a wide range in dissolved SO_4 and/or pH to be successful. Hence, soils that initially are low in pH and high in dissolved SO_4 will be difficult to parameterize, as the sorption experiment method will not bring about substantial differences in chemical conditions. Ideally, it should be possible to calibrate the SO_4 adsorption model without any laboratory data at all, but instead using other measurements (e.g. organic C, extractable Fe+Al, total geochemistry)

made in soil inventories etc. An interesting observation in this regard is the relatively small variation in m , which may make it possible to use a generic m value and only use a relationship between soil properties and the K_F value. To address this issue, the SO_4 adsorption properties of a larger number of well-characterized soils need to be investigated using the model.

5. Conclusions

Sulphate adsorption could be described well by a modified pH-dependent Freundlich equation, in which the non-ideality parameters for the sulphate and hydrogen ion activities were interconnected by the η (proton co-adsorption stoichiometry) value. This enabled the number of fitted parameters to be reduced from 3 to 2 when using a fixed value for η . By use of the CD-MUSIC surface complexation model it was found that the η value in a competitive system on ferrihydrite was > 1.9 at low ionic strength, i.e. close to 2. This was supported by unconstrained fitting for the soils of this study, for which the optimized value of η for four out of five soils was close to 2. When using a fixed value of $\eta = 2$, it was possible to use a two-point calibration (2PC) method and still obtain satisfactory descriptions of SO_4 adsorption across a range of pH and dissolved SO_4 concentrations. These results may simplify the use of the extended Freundlich equation for SO_4 adsorption/desorption in dynamic soil chemistry models, both because only a small number of laboratory input data are required to calibrate the model, and because the mass balance equation for SO_4 adsorption can be simplified by only considering charge neutralization by H^+ .

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Fig. 1. Proton co-adsorption stoichiometry (η) for SO_4 adsorption on ferrihydrite as a function of ionic strength, at pH 5, as simulated by the CD-MUSIC model. Conditions are detailed in Appendix A.

Fig. 2. Adsorbed sulphate (Q) as a function of dissolved SO_4 in response to different additions of MgSO_4 or $\text{MgSO}_4 + \text{H}_2\text{SO}_4$ (see text). Points are observations and lines are model fits using the 2PC (two-point calibration) optimization. The figures shown are the pH values recorded after additions of 0 and 500 $\mu\text{mol L}^{-1}$ SO_4^{2-} .

Fig. 3. Plots of $\log Q$ vs. $\log[\text{SO}_4^{2-}] - \eta \cdot \text{pH}$ for the five soils (Kloten, Österström, Risbergshöjden, Risfallet and Tärnsjö) and linear regression results for the unconstrained fit (left column) and the constrained fit (right column).

Table 1

Location and properties of soils

Site	Location (Lat, Long)	Parent material	Horizon sampled	Sampling depth (cm)
Kloten	59.91°N 15.25°E	Glacial till	Bs	14-24
Österström	62.64°N 16.71°E	Glacial till	Bs	5-15
Risbergshöjden	59.72°N 15.05°E	Glacial till	Bs	4-13
Risfallet	60.34°N 16.21°E	Glacial till	Bs	7-15
Tärnsjö	60.14°N 16.92°E	Sand	Bs	2-16

Table 2

Chemical properties of the investigated soil samples

Sample	Organic C	pH(MgCl ₂) ^a	Fe _{ox} ^b	Fe _{pyr} ^b	Al _{ox} ^b	Al _{pyr} ^b	PSO ₄ ^c
	%		mmol kg ⁻¹				
Kloten	2.56	5.00	147	70	659	280	4.18
Österström	2.23	4.77	88	53	171	117	0.61
Risbergshöjden	2.58	4.78	124	29	554	175	4.55
Risfallet	2.30	4.96	155	86	265	168	1.29
Tärnsjö	0.72	5.38	46	15	120	65	0.78

^apH measured in the 0.10 mM MgCl₂ extract without SO₄ addition (see Methods section)^bSubscripts ox and pyr denote oxalate and pyrophosphate extracts, respectively^cPhosphate-extractable SO₄

Table 3

Best-fit results for the extended Freundlich model

Sample	Fit ^a	K_F	m	η^b	r^2	RMSE ^c
Kloten	Unconstr	1.74	0.179	1.98	0.996	0.006
	Constr	1.77	0.178	2	0.996	0.006
	2PC	2.09	0.184	2	-	0.010
Österström	Unconstr	1.72	0.148	3.83	0.977	0.025
	Constr	0.383	0.192	2	0.955	0.035
	2PC	0.536	0.201	2	-	0.045
Risbergshöjden	Unconstr	0.636	0.145	2.15	0.995	0.005
	Constr	0.554	0.148	2	0.995	0.005
	2PC	0.634	0.152	2	-	0.006
Risfallet	Unconstr	0.0719	0.108	2.35	0.959	0.015
	Constr	0.0505	0.111	2	0.959	0.015
	2PC	0.0445	0.107	2	-	0.016
Tärnsjö	Unconstr	4.18	0.236	1.97	0.970	0.034
	Constr	4.34	0.234	2	0.970	0.034
	2PC	4.43	0.237	2	-	0.052

^aUnconstrained, constrained and 2-point calibration (2PC) fits, respectively^bValues in italics were fixed during optimization^cRoot-mean square error of the simulated log Q values, as compared to the measured log Q .

Supplementary content

J.P. Gustafsson, M. Akram, C. Tiberg. Predicting sulfate adsorption/desorption in forest soils: evaluation of an extended Freundlich equation for use in a dynamic soil chemistry model

Table S1

Surface complexation reactions and constants used in the CD-MUSIC model for ferrihydrite.

Reaction	$(\Delta z_0, \Delta z_1, \Delta z_2)^a$	$\log K^b$	Data source(s)
$\text{FeOH}^{1/2-} + \text{H}^+ \leftrightarrow \text{FeOH}_2^{1/2+}$	(1,0,0)	8.1	Dzombak & Morel (1990)
$\text{Fe}_3\text{O}^{1/2-} + \text{H}^+ \leftrightarrow \text{Fe}_3\text{OH}^{1/2+}$	(1,0,0)	8.1	Assumed the same as above
$\text{FeOH}^{1/2-} + \text{Na}^+ \leftrightarrow \text{FeOHNa}^{1/2+}$	(0,1,0)	-0.6	Hiemstra & van Riemsdijk (2006)
$\text{Fe}_3\text{O}^{1/2-} + \text{Na}^+ \leftrightarrow \text{Fe}_3\text{ONa}^{1/2+}$	(0,1,0)	-0.6	”
$\text{FeOH}^{1/2-} + \text{H}^+ + \text{NO}_3^- \leftrightarrow \text{FeOH}_2\text{NO}_3^{1/2-}$	(1,-1,0)	7.42	”
$\text{Fe}_3\text{O}^{1/2-} + \text{H}^+ + \text{NO}_3^- \leftrightarrow \text{Fe}_3\text{OHNO}_3^{1/2-}$	(1,-1,0)	7.42	”
$\text{FeOH}^{1/2-} + \text{H}^+ + \text{Cl}^- \leftrightarrow \text{FeOH}_2\text{Cl}^{1/2-}$	(1,-1,0)	7.65	”
$\text{Fe}_3\text{O}^{1/2-} + \text{H}^+ + \text{Cl}^- \leftrightarrow \text{Fe}_3\text{OHCl}^{1/2-}$	(1,-1,0)	7.65	”
$2\text{FeOH}^{1/2-} + 2\text{H}^+ + \text{PO}_4^{3-} \leftrightarrow \text{Fe}_2\text{O}_2\text{PO}_2^{2-} + 2\text{H}_2\text{O}$	(0.46,-1.46,0)	27.59	Tiberg et al. (2013)
$2\text{FeOH}^{1/2-} + 3\text{H}^+ + \text{PO}_4^{3-} \leftrightarrow \text{Fe}_2\text{O}_2\text{POOH}^- + 2\text{H}_2\text{O}$	(0.63,-0.63,0)	32.89	”
$\text{FeOH}^{1/2-} + 3\text{H}^+ + \text{PO}_4^{3-} \leftrightarrow \text{FeOPO}_3\text{H}_2^{1/2-} + \text{H}_2\text{O}$	(0.5,-0.5,0)	30.23	”
$\text{FeOH}^{1/2-} + \text{H}^+ + \text{SO}_4^{2-} \leftrightarrow \text{FeOSO}_3^{1/2-} + \text{H}_2\text{O}$	(0.65,-1.65,0)	9.65	Rietra et al. (2001), this study
$2\text{FeOH}^{1/2-} + \text{H}_4\text{SiO}_4 \leftrightarrow \text{Fe}_2\text{O}_2\text{Si}(\text{OH})_2^- + 2\text{H}_2\text{O}$	(0.45,-0.45,0)	5.04	Gustafsson et al. (2009) ^c

^a The change of charge in the *o*-, *b*- and *d*-planes respectively.

^b Two or three numbers indicate binding to sites with different affinity, the percentages of which are within brackets (c.f. text).

^c This constant was updated using the more recent model of Tiberg et al. (2013)

Table S2

Data sets used for optimisation of sulfate surface complexation constants for ferrihydrite (Fh)

ID number	Source	Total SO ₄ (M)	Fh concentration (mM)	Equilibration time (h)	Background electrolyte
Fh-SO ₄ -01	Davis (1977)	1×10^{-5}	1	4	0.1 M NaNO ₃
Fh-SO ₄ -02	Swedlund and Webster (2001)	2.08×10^{-4}	0.96	”	”
Fh-SO ₄ -03	”	1.82×10^{-3}	”	”	”
Fh-SO ₄ -04	Fukushi et al. (2013)	2×10^{-4}	1.96	”	”
Fh-SO ₄ -05	“	2×10^{-4}	”	“	0.01 M NaNO ₃
Fh-SO ₄ -06	”	1×10^{-4}	”	”	0.1 M NaNO ₃
Fh-SO ₄ -07	”	1×10^{-4}	”	”	0.01 M NaNO ₃

Table S3

Intrinsic surface complexation constants for sulfate adsorption on ferrihydrite (standard deviations in parantheses). Weighted average equilibrium constants are shown, with the 95 % confidence interval (italics in parantheses).

Data set	$\log K_{\text{FeOSO}_3}$	V_Y^a
Fh-SO ₄ -01	9.97 (0.009)	5.7
Fh-SO ₄ -02	9.79 (0.014)	13.6
Fh-SO ₄ -03	9.68 (0.012)	2.0
Fh-SO ₄ -04	9.68 (0.007)	4.9
Fh-SO ₄ -05	9.38 (0.010)	6.3
Fh-SO ₄ -06	9.76 (0.007)	9.6
Fh-SO ₄ -07	9.32 (0.008)	25.2
Weighted averages	9.65 (9.57, 9.73)	

^aWeighted sum of squares, according to Herbelin and Westall (1999)

Table S4

Conditions assumed for the surface complexation modeling exercise on ferrihydrite to calculate η (proton coadsorption stoichiometry)

Parameter	Assumed value
Ferrihydrite concentration	0.89 g L ⁻¹ (= 10 mmol Fe L ⁻¹)
pH	5.0
Dissolved SO ₄ ^a	10 μmol L ⁻¹
Dissolved PO ₄ ^a	0.05 μmol L ⁻¹
Dissolved H ₄ SiO ₄ ^a	100 μmol L ⁻¹
Dissolved Mg ^{2+a}	100 μmol L ⁻¹
Dissolved Cl ^{-a}	100 μmol L ⁻¹
Dissolved Na ^a	0 μmol L ⁻¹

^aDissolved concentrations without any added SO₄ and at the lowest ionic strength (0.4 mM). By use of the “fixed total dissolved” option in Visual MINTEQ the total system concentrations of SO₄, PO₄ and H₄SiO₄ were determined and kept constant in all simulations. Ionic strengths were increased by adding equivalent amounts of Na⁺ and Cl⁻ to the solutions up to 10 mM. To calculate η , a further 0.1 mM SO₄ was added and the total H⁺ concentration of all surface species was calculated in the absence and presence of added SO₄, and divided with that of the calculated concentration of adsorbed SO₄.

Fig. S1. Plot of Q vs. $\log[\text{SO}_4^{2-}] - 2 \cdot \text{pH}$ for the Kloten soil (according to the Temkin model of Gustafsson, 1995) and linear regression results.

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