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5 Predicting sulphate adsorption/desorption in forest soils: 6 evaluation of an extended Freundlich equation

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17

18 ABSTRACT

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

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

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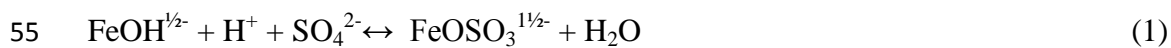
32 Keywords: sulphate adsorption, Spodosols, acidification, Freundlich, pH

33

34 **1. Introduction**

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

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



56 Alone this reaction implies that $\eta = 1$; however, for electrostatic reasons the surface will resist
57 to accommodate this change in charge (-1), especially at low ionic strength; hence some
58 surface groups ($\text{FeOH}^{1/2-}$) will protonate (to $\text{FeOH}_2^{1/2+}$) causing η to be higher. Recent structural
59 evidence supports the idea that SO_4^{2-} adsorption on ferrihydrite involves both inner-sphere and
60 outer-sphere complexes (Zhu et al., 2014).

61 Surface complexation models are, however, still difficult to integrate in dynamic models for
62 soil chemistry, not least because they require full knowledge of the system including reactions
63 for all possible competing and interacting ions on the surface. For this reason, simpler
64 relationships consisting of only one or two equations are normally used for predicting the
65 extent of SO_4 (and associated H^+) adsorption.

66 Some dynamic models (e.g. MAGIC; Cosby et al., 1986 and SMART; Kämäri et al., 1995)
67 use Langmuir equations without explicit consideration of the pH effect. Eriksson (1988), in a
68 rarely cited but pioneering book chapter, suggested a modified Langmuir equation in which
69 each SO_4^{2-} ion was accompanied by two co-adsorbed H^+ ions (i.e. $\eta = 2$). This equation was
70 applied to understand the downward migration of acid in Swedish Spodosols in response to
71 acid deposition (Eriksson et al., 1992) and to provide the basis for a dynamic transport model
72 (Eriksson and Karlton, 1994). A similar SO_4 adsorption model, which instead used the
73 Temkin equation as a basis, was suggested by Gustafsson (1995). Fumoto and Sverdrup

74 (2000, 2001) suggested the use of an extended Freundlich equation with both sulphate and
75 hydrogen ion activities as terms. The model was able to satisfactorily describe pH-dependent
76 SO₄ adsorption in an allophanic Andisol. This equation was later modified and included in the
77 dynamic soil model ForSAFE (Wallman et al., 2005) by Martinson and colleagues (Martinson
78 et al., 2003; Martinson and Alveteg, 2004; Martinson et al., 2005).

79 A problem with these empirical equations is, however, that they contain a large number of
80 parameters that have to be optimized. The objective of this paper was to evaluate the use of
81 the extended Freundlich equation using laboratory data from five B horizons from Swedish
82 Spodosols, in which pH and dissolved SO₄ concentrations were varied systematically. In
83 particular we tested whether a modified Freundlich equation employing a common value of η
84 = 2 would allow calibration with a minimum of laboratory data and still be able to
85 satisfactorily describe SO₄ adsorption.

86

87

88 **2. Materials and methods**

89 *2.1 Soil samples*

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

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

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

100

101

102 *2.2 Laboratory procedures*

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

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

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

122 was filtered through a 0.2 μm single-use filter (Acrodisc PF) prior to the analysis of SO_4 by
123 ion chromatography (IC) using a Dionex 2000i instrument.

124 To obtain values for initially adsorbed SO_4 (Q_{ini}), dihydrogen phosphate extraction will
125 quantify the amount of adsorbed SO_4 that is in equilibrium with the soil solution (Karlton,
126 1994). Thus, 3.00 g field-moist sample was suspended in 30 cm^3 20 mM NaH_2PO_4 and
127 extracted for 2 h. The extracts were then filtered and subjected to IC analysis as above, after
128 dilution 5 times.

129 To reduce analytical uncertainty, we made frequent use of internal standards both for the IC
130 analysis and for the pH measurement. We estimate the analytical precision to be $< 5\%$ for the
131 IC analysis of SO_4 , and less than 0.03 units for the pH measurement.

132 Oxalate- and pyrophosphate-extractable Fe and Al were determined according to the
133 procedure of van Reeuwijk (1995), and determined by ICP-OES using a Perkin-Elmer Optima
134 3300 DV instrument. The organic C content of the soils were determined using a LECO
135 CHN-932 analyzer.

136

137 *2.3 Model development*

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

$$140 \quad Q = K_F \cdot [\text{SO}_4]^m \cdot \{\text{H}^+\}^n \quad (2)$$

141 where Q is the amount of adsorbed SO_4 (mol kg^{-1} dry soil), $[\text{SO}_4]$ is the total dissolved
142 concentration of SO_4 (mol L^{-1}), whereas K_F , m and n are adjustable parameters; K_F is usually
143 termed the Freundlich coefficient, whereas m and n are non-ideality parameters, where m may
144 range between 0 and 1. In a dynamic model there is also a mass-balance equation that governs

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

$$147 \quad [\text{SO}_4^{2-}] = 0.85 \cdot [\text{H}^+] + 0.15 \cdot [\text{BC}^{n+}] \quad (3)$$

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

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

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

$$160 \quad m = n \cdot \eta \quad (4)$$

161 This results in the following modified extended Freundlich equation:

$$162 \quad Q = K_F \cdot ([\text{SO}_4^{2-}] \cdot \{\text{H}^+\}^\eta)^m \quad (5)$$

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

$$164 \quad \log Q = \log K_F + m \cdot (\log[\text{SO}_4^{2-}] - \eta \cdot \text{pH}) \quad (6)$$

165 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
166 the slope m and the intercept K_F . Although this equation still has three adjustable parameters,
167 it can be brought down to two if a common value of η is employed. In this work, we

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

$$172 \quad [\text{SO}_4^{2-}] = [\text{H}^+] \quad (7)$$

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

175 To obtain additional evidence for the value of η , we (i) optimized the value of η for the batch
176 experiment data of this study (c.f. below), and (ii) set up a simulation using the CD-MUSIC
177 model for ferrihydrite at pH 5. The model was based on the work of Rietra et al. (2001) who
178 investigated the use of the CD-MUSIC model for SO_4 adsorption onto goethite (see equation
179 1). The model was calibrated for ferrihydrite using the SO_4 adsorption data of Davis (1977),
180 Swedlund and Webster (2001) and Fukushi et al. (2013) and by using parameters for surface
181 charging estimated by Tiberg et al. (2013), see the Supplementary Content for details. This
182 model was defined in Visual MINTEQ (Gustafsson, 2013) and used to calculate the η value at
183 pH 5 and at different ionic strengths ranging from 0.4 mM (the conditions of the batch
184 experiment of this study) to 10 mM. Because η is sensitive to the presence of competing ions
185 in the system, we included also PO_4 and Si at environmentally “realistic” concentrations, c.f.
186 Supplementary Content. The results show that the η value was approximately 1.95 at low
187 ionic strength (Fig. 1) and remained above 1.9 also at an ionic strength of 0.001 M (Fig. 1).
188 The result agrees with the results of Ishiguro et al. (2006), who obtained an η value close to
189 2.0 at low ionic strength for an allophanic Andisol.

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

- 192 1. Unconstrained fit. All three adjustable parameters (K_F , m and η) of equation 6 were
193 fitted using linear regression of $\log Q$ vs. $\log[\text{SO}_4^{2-}] - \eta \cdot \text{pH}$ with the trendline tool in
194 Microsoft Excel. The value of Q was calculated as the sum of initially adsorbed SO_4
195 as determined by phosphate extraction (Q_{ini}) and SO_4 sorbed during the experiment.
- 196 2. Constrained fit. Fitting was made as described above for the unconstrained fit, except
197 that the η value was fixed at 2.
- 198 3. 2-point calibration (2PC) fit. Mean results from only two samples were used during
199 optimization. These samples should be sufficiently different in terms of pH and $[\text{SO}_4^{2-}]$
200] to produce well-constrained values of K_F and m . We used (i) the sample to which
201 only 0.1 mM MgCl_2 had been added (with relatively high pH and low $[\text{SO}_4^{2-}]$) and (ii)
202 the sample to which 0.1 mM MgCl_2 , 0.27 mM MgSO_4 and 0.27 mM H_2SO_4 had been
203 added (relatively low pH and high $[\text{SO}_4^{2-}]$). For the Risfallet sample, the latter sample
204 was not available; instead the second sample used was the one to which 0.1 mM
205 $\text{MgCl}_2 + 0.535$ mM MgSO_4 had been added.

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

208

209 3. Results

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

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

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

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

238

239 **4. Discussion**

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

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

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

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

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

276 Accurate determination of the non-ideality parameters is important, as these determine to
277 what extent the adsorbed SO_4 (and co-adsorbed H^+) pool changes in response to a change in
278 influent H^+ and SO_4^{2-} concentrations. The low parameter values reported by Martinson et al.
279 (2005) would imply that SO_4 adsorption/desorption is not very important for soil chemical
280 dynamics, whereas the results of the present study suggest it to be much more significant.

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

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

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

297

298 **5. Conclusions**

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

313

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318

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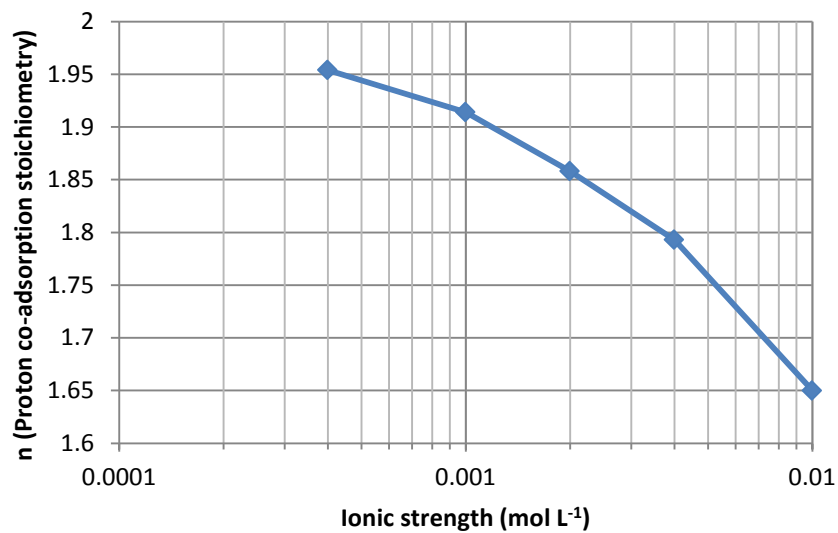
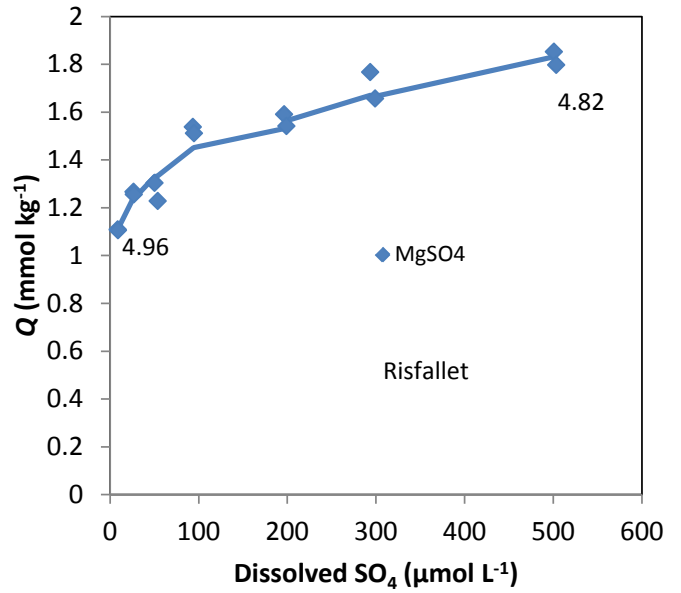
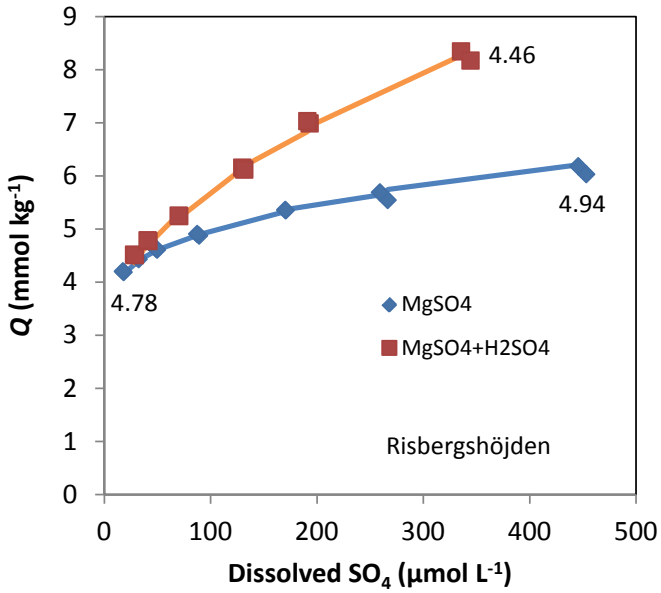
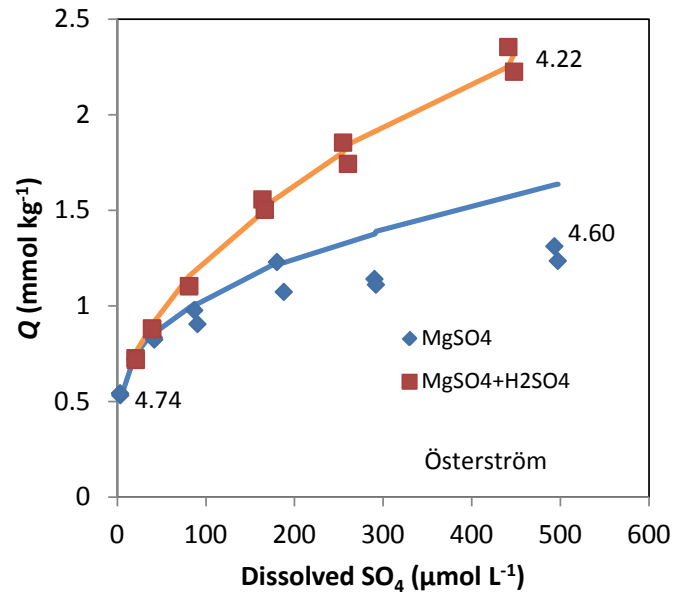
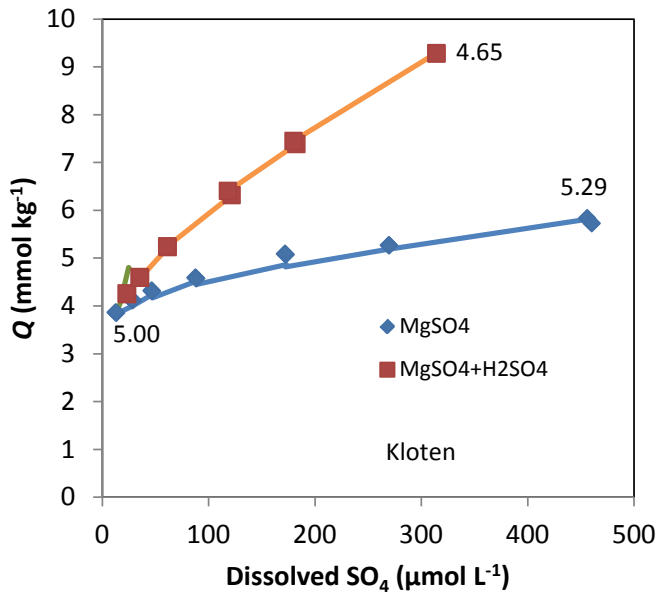


Fig. 1. Proton co-adsorption stoichiometry (η) for SO_4 adsorption on ferrihydrite as a function of ionic strength, at pH 5, as simulated by the CD-MUSIC model. Conditions are detailed in Appendix A.



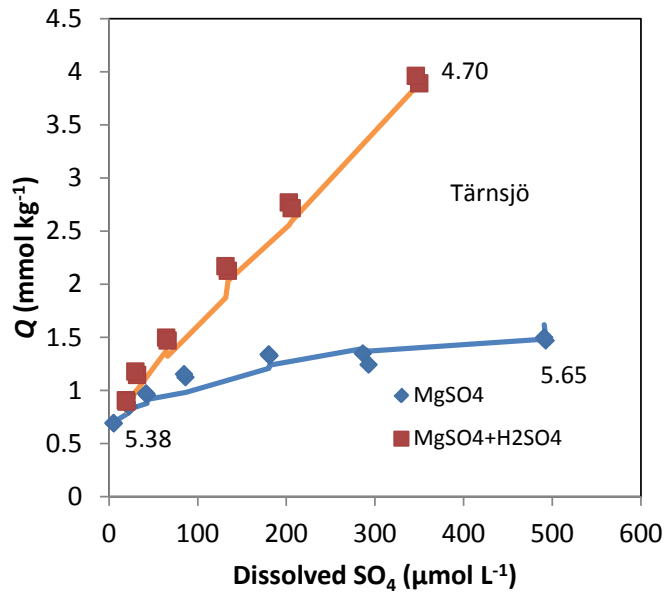
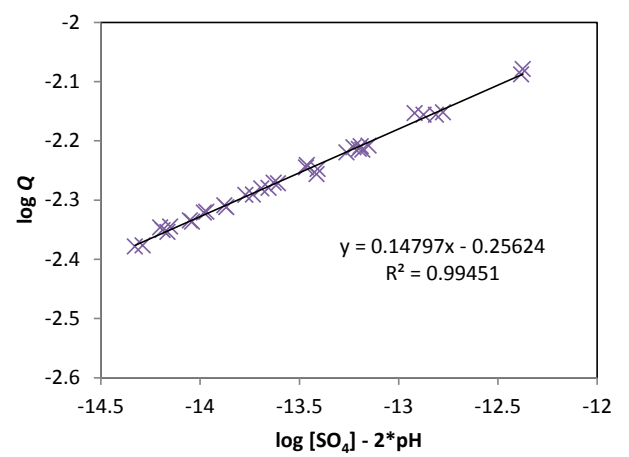
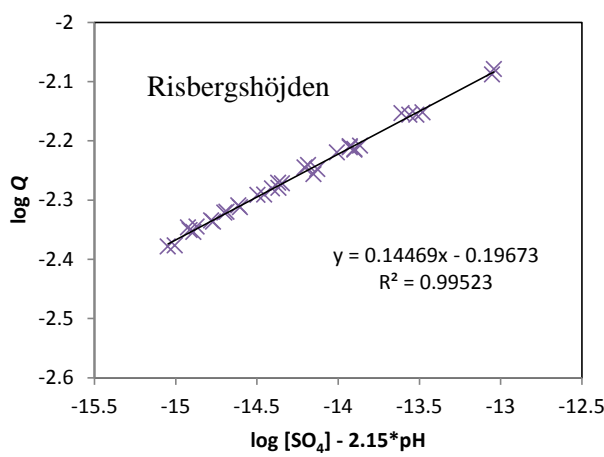
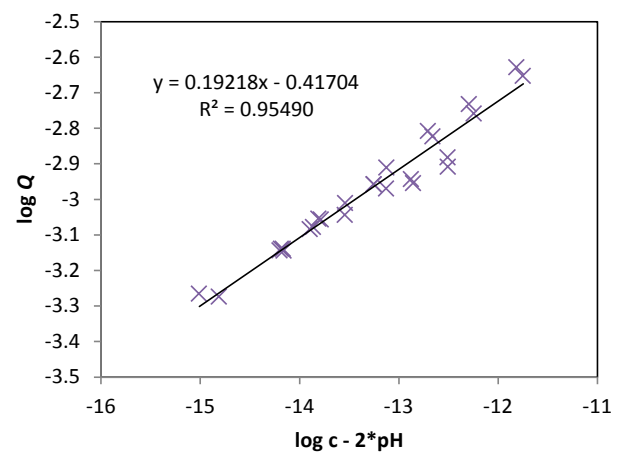
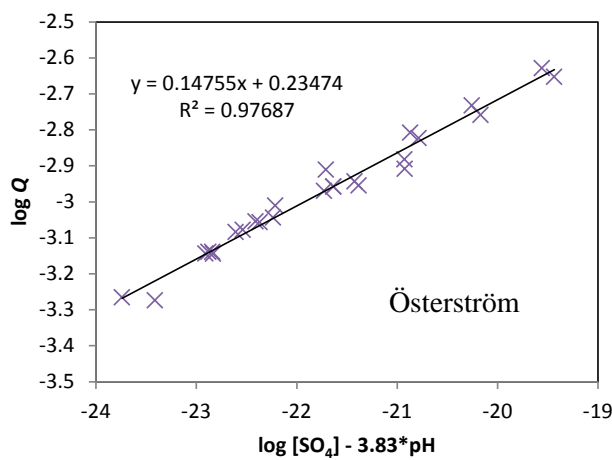
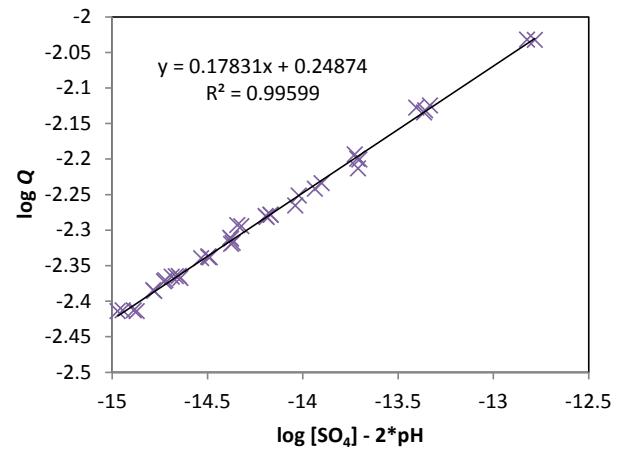
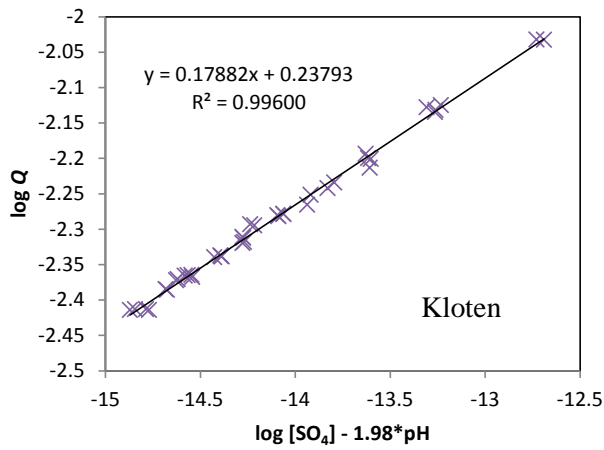


Fig. 2. Adsorbed sulphate (Q) as a function of dissolved SO_4 in response to different additions of MgSO_4 or $\text{MgSO}_4+\text{H}_2\text{SO}_4$ (see text). Points are observations and lines are model fits using the 2PC (two-point calibration) optimization. The figures shown are the pH values recorded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



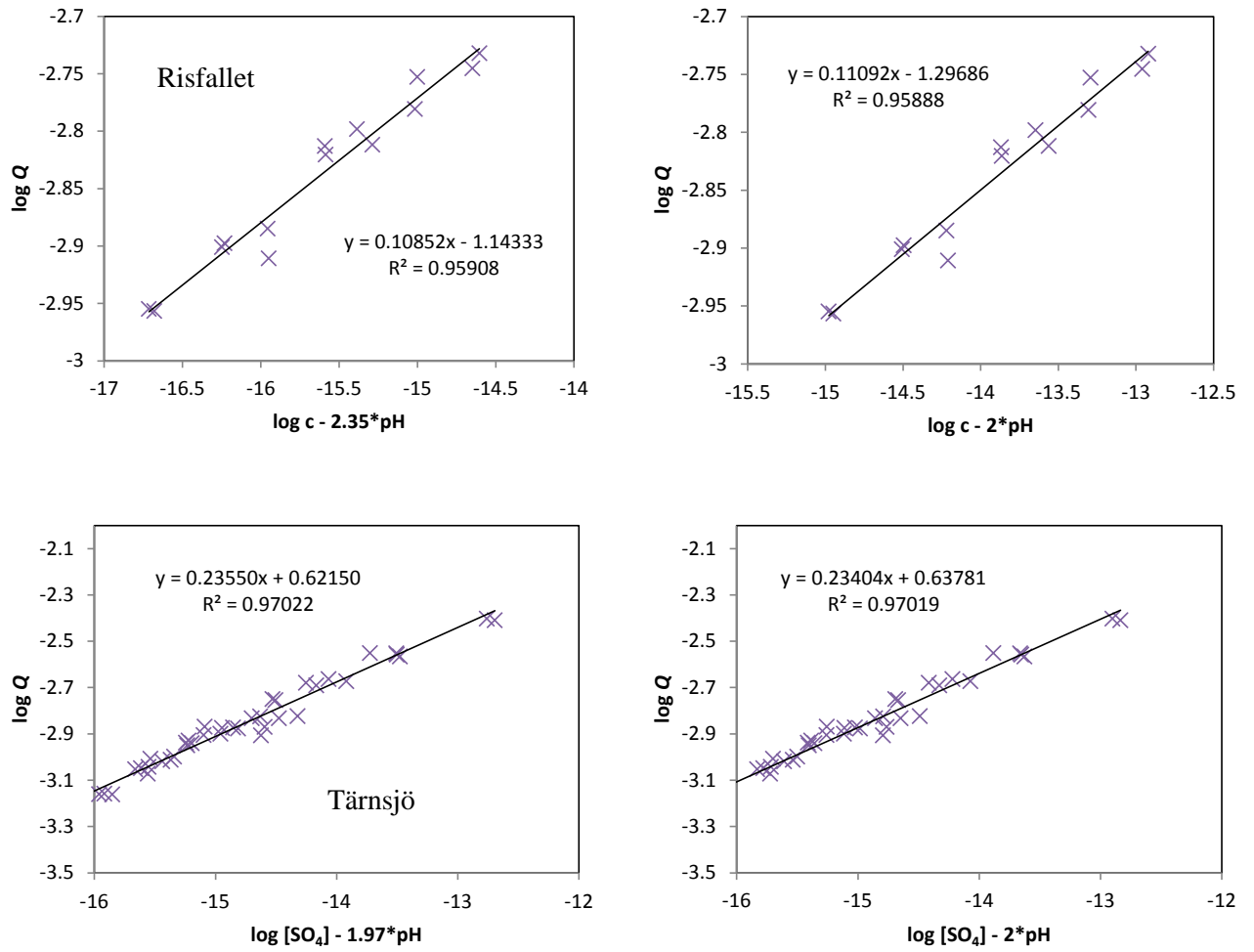


Fig. 3. Plots of $\log Q$ vs. $\log[\text{SO}_4^{2-}] - \eta \cdot \text{pH}$ for the five soils (Kloten, Österström, Risbergshöjden, Risfallet and Tärnsjö) and linear regression results for the unconstrained fit (left column) and the constrained fit (right column).

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.

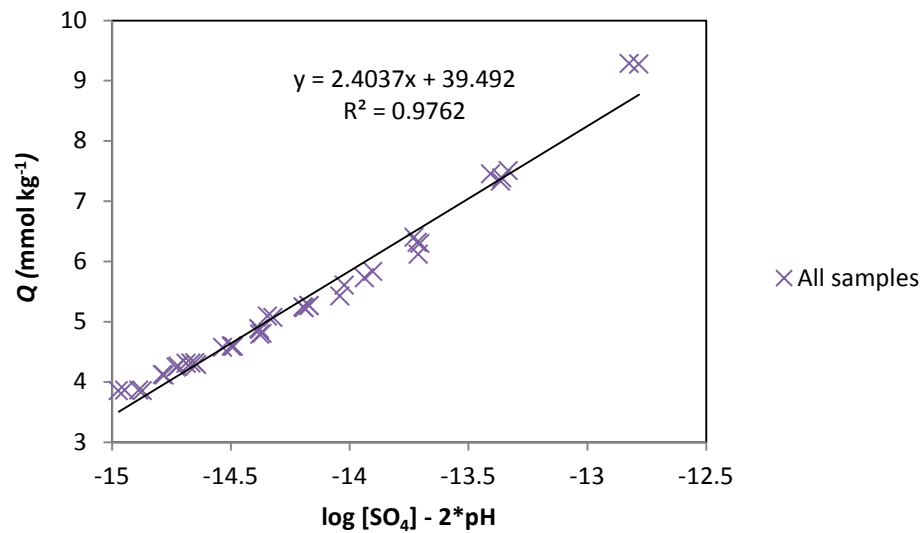


Fig. S1. Plot of Q vs. $\log[\text{SO}_4^{2-}] - 2 \cdot \text{pH}$ for the Kloten soil (according to the Temkin model of Gustafsson, 1995) and linear regression results.

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