

1 Predicting cadmium adsorption on soils using WHAM VI

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12 **Abstract**

13 Cadmium (Cd) adsorption on 14 non-calcareous New Jersey soils was investigated
14 with a batch method. Both adsorption edge and isotherm experiments were conducted
15 covering a wide range of soil composition, e.g. soil organic carbon (SOC) concentration
16 ranging from 0.18% to 7.15%, and varying Cd concentrations and solution pH. The SOC
17 and solution pH were the most important parameters controlling Cd partition equilibrium
18 between soils and solutions in our experimental conditions. The Windermere humic
19 aqueous model (WHAM) was used to calculate Cd adsorption on soils. The effect of
20 solution chemistry (various pH and Cd concentrations) on Cd adsorption can be well
21 accounted for by WHAM. For different soil compositions, SOC concentration is the most
22 important parameter for Cd binding. Only a fraction of SOC, the so-called active organic
23 carbon (AOC), is responsible for Cd binding. We found a linear relationship between
24 SOC and AOC based on the adsorption edge data. The linear relationship was validated
25 by the independent data sets: adsorption isotherm data, which presumably can be used to
26 predict Cd partition equilibrium across a wide range of soil compositions. The modeling
27 approach presented in this study helps to quantitatively predict Cd behavior in the
28 environment.

29 **Keywords:** cadmium, adsorption, WHAM, active organic matter, partition, modeling

30 **Introduction**

31 Adsorption of Cd on soils is an important process controlling Cd behavior in the
32 environment. Soils consist of different components including soil organic matter (SOM),
33 metal (hydro)oxides and clay minerals that are responsible for Cd binding. Different
34 components in soils may contribute to Cd adsorption to different extents. Due to the
35 limitations of experimental techniques (Zachara et al., 1992), it is very difficult to
36 experimentally identify the contribution of individual adsorbents to the control of trace
37 metal adsorption on soil particles. The partition coefficient K_p has been widely used to
38 characterize the equilibrium relationship of trace metals between solution and solid
39 phases. Empirical relationships have been derived by relating K_p to key soil and solution
40 parameters (e.g. total metal concentration, SOM content, pH, etc.) through multiple
41 regression analysis (Janssen et al., 1997; Impellitteri et al., 2002; McBride et al., 1997;
42 Sauvé et al., 2000, 2003). For example, the distribution of trace metals between solid and
43 solution phases could be calculated based on pH, total metal content and organic matter
44 (Sauvé et al., 2000).

45 Compared with traditional statistical regression models, more recently mechanistic
46 models have been used to describe metal partitioning between soils and solutions (Weng
47 et al., 2001; Gustafsson et al., 2003; Tipping et al., 2003; Lumsdon, 2004; Ponizovsky et
48 al., 2006), including the Windermere humic aqueous model (WHAM) (Tipping, 1994).
49 SOM has been reported to be the major component among soil components accounting
50 for metal binding. Furthermore, it has been reported that only a fraction of SOM, which is
51 called active organic matter (AOM), is responsible for metal binding (Tipping et al., 2003;
52 Gustafsson et al., 2003; Lumsdon, 2004). The AOM may be due to the difference

53 between the SOM and the generic humic substance to which the equilibrium models are
54 calibrated. SOM consists of non-humic substances such as amino acids, carbohydrates,
55 and lipids, as well as humic substance, a series of high-molecular-weight, brown to black
56 substances formed by secondary synthesis reactions (Stevenson, 1994). SOM may also
57 coat on mineral phase and thus some inner part of SOM may be not accessible due to
58 coating (Nachtegaal and Sparks, 2003). However, there are no well-established methods
59 to determine AOM.

60 Inorganic components, such as clay minerals and metal oxides/hydroxides, can also
61 be important in controlling Cd reactions in soils (Kabata-Pendias, 2001). The role of
62 different soil components for metal binding may be dependent on the experimental
63 conditions. For example, clay minerals are more important for metal adsorption at low
64 pH, low soil organic matter content and high metal loading (Weng et al., 2004).

65 In this paper, the Cd adsorption edge and adsorption isotherms data for 14 New
66 Jersey soils were analyzed using WHAM VI (Tipping 1998), the latest version of
67 WHAM. In WHAM VI, a number of parameters have been recognized as being
68 important for predicting metal partitioning including organic matter, and iron and
69 aluminum competition (Tipping, et al., 2003). In this study, we are seeking a unique set
70 of WHAM input parameters for Cd adsorption that are applicable for different soils at
71 various solution chemistry conditions. The competition effect of Al at different pH ranges
72 was tested.

73 **Materials and Methods**

74 The 14 New Jersey soils those were used to conduct adsorption experiments are
75 described in Table 1. The sample of Delaware River fill material that was included in the
76 original study (Lee et al., 1996) has not been included in the present analysis as it is not a
77 soil. All soils are non-calcareous soils with pH less than 7. These soils cover a variety of
78 soil properties. The soil organic carbon (SOC) concentration ranging from 0.18% to
79 7.15%, which was measured with a Variomax CN analyzer. The ammonium oxalate
80 extractable soil metal (hydro)oxides were presented in Lee et al. (1996). The
81 exchangeable Ca and Mg were extracted with the 0.1 M BaCl₂ for 24 h (Carter, 1993).
82 The Al was extracted with the 0.43 M HNO₃ for 24 h (Dijkstra et al., 2004).

83 1. Adsorption edge experiment

84 Batch equilibration studies were conducted with soil concentration = 1.00 ± 0.01 g
85 per 100 mL solution and ionic strength = 0.01M with NaNO₃. Cd nitrate concentrations =
86 1×10^{-5} and 1×10^{-4} M with pH = 3 to 9 and temperature = 25 ± 2 °C. Samples were
87 shaken at 150 rpm for 24 hours and filtered through 25 mm diameter, 0.45 µm membrane
88 filters.

89 2. Adsorption isotherm experiment

90 The soil samples, 1.0 gram of each, were immersed in 100 mL of 0.01 M NaNO₃.
91 The pH was adjusted in order to approach the desired pHs, 4.0, 5.5, and 7.0 and
92 temperature = 25 ± 2 °C. The initial Cd concentrations ranged from 1.0×10^{-6} to 5×10^{-3}
93 M, and the equilibration time was 24 hours. After 24 hours, the pH was readjusted to the
94 initial value and the samples were filtered through 0.45 µm membrane filters.

95 Cadmium concentrations in the filtered solutions were determined by atomic
96 absorption spectrometry as reported by Lee et al. (1996). The detailed information on
97 experimental procedures can be found in Lee et al. (1996).

98 **Modeling Method**

99 WHAM VI was used to calculate Cd adsorption equilibrium at different conditions.
100 WHAM is capable of calculating the equilibrium chemical speciation in surface and
101 ground waters, sediments, and soils, especially when the chemical speciation is
102 dominated by organic matter (Tipping, 1994; Tipping et al., 2003). WHAM uses Model
103 VI, a computer model, to describe the reactions of ions with humic substances, mainly
104 through complexation which is modified by electrostatic reactions. Previous modeling
105 results have demonstrated that, for most non-calcareous soils except for soils with very
106 low SOM concentrations, the SOM is the major adsorbent for trace metals (Tipping et al.,
107 2003; Ponizovsky et al., 2006). Preliminary WHAM calculations showed that metal
108 oxides have little effect on Cd adsorption for most of our soils, so only SOM and clay
109 fraction were used in WHAM calculations. The WHAM input parameters include
110 particulate humic acid (HA) and fulvic acid (FA) concentrations ([HA] and [FA]), the
111 clay concentration, pH, the CO₂ pressure (pCO₂), and solution cations and anions
112 concentrations or activities including [Na⁺], [Ca²⁺], {Al³⁺} or [Al³⁺], {Fe³⁺} and [NO₃⁻].
113 The pCO₂ was set at 10^{-3.5} atm. Ponizovsky et al. (2006) have demonstrated that the
114 variation of pCO₂ from 10⁻⁴ to 10⁻² atm had little effect in their model calculations. The
115 Mg concentrations were low which had little effect on Cd adsorption. For the solution
116 species, the concentrations were input as measured in the experiments. For the SOM,

117 only the active fraction, AOM, was used in WHAM VI calculations and the active
118 fraction was assumed to consist of 84% HA and 16% FA (Tipping et al., 2003).

119 Due to the high concentration of Cd in this study, preliminary model calculations
120 showed that the competition of Fe^{3+} was minimal. The competition of Al on Cd
121 adsorption could be different at different pH. The Al activity in the soil solution can be
122 estimated by assuming that the solution was equilibrated with Al hydroxides (Tipping et
123 al., 2003), as described by equation 1.

$$124 \quad \log\{ \text{Al}^{3+} \} = \log^* K_{s0} - 3\text{pH} \quad (1)$$

125 Tipping (2005) has further assessed how Al^{3+} activity was dependent on pH and whether
126 Al^{3+} activity was controlled by Al hydroxides or not. At low pH, solubility control of Al
127 hydroxides may overestimate the Al^{3+} activity and a linear regression equation was
128 proposed as described by equation 2.

$$129 \quad \log\{ \text{Al}^{3+} \} = -1.59\text{pH} + 2.22 \quad (2)$$

130 Other researchers used acid extraction to estimate the active Al accounting for Al
131 competition to metal binding (Dijkstra et al., 2004).

132 In our modeling for the Al competition effect, we started with the acid extractable Al.
133 The 0.43 M HNO_3 extractable Al was input as the total Al concentration in the WHAM
134 calculations for adsorption reactions. The model calculations showed that the Al^{3+}
135 activity calculated by acid extractable Al was too high, as it exceeds the solubility control
136 of Al hydroxides. Then we used the regression equation (equation 2) to calculate Al^{3+}
137 activity at low pH. At pH greater than 5, Al^{3+} activity controlled by $\text{Al}(\text{OH})_3$ solubility
138 with a $\log^* K_{s0}$ value of 8.5 can consistently describe the Cd adsorption. However, at pH
139 ≤ 5 , the regression equation provided too high Al^{3+} activity which resulted in much less

140 Cd adsorption on soils compared with the experimental values, as discussed later. So we
141 tried to estimate the active Al concentration by model fitting of experimental data at pH
142 ≤ 5 , which controls the Al competition for each soil at pH ≤ 5 .

143 For all 14 soils, the adsorption edge data at two initial Cd concentrations were
144 tabulated in Microsoft EXCEL 2000. A version of WHAM VI that can be executed in
145 EXCEL with specific input parameters described previously was used to fit the
146 adsorption edge data. The errors of the percentage of adsorption between WHAM VI
147 calculations and experimental results were calculated. Then the squares of the errors were
148 summed and minimized using the EXCEL 2000 SOLVER program by optimization of
149 model parameters, active organic carbon (AOC) and active Al. The AOC and active Al
150 were obtained separately. The AOC was converted to AOM by multiplying a factor of 1.8,
151 which was further calculated as HA and FA as described before. The data at pH > 5 was
152 used first to obtain the amount of AOC for each soil where the Al^{3+} activity was
153 controlled by the Al hydroxide. The amount of AOC was adjusted for each soil until the
154 sum of errors was minimized at pH > 5 . Then the data at pH ≤ 5 was used to obtain the
155 active Al which controls the Al competition at pH ≤ 5 . The AOC was used as obtained
156 from model fitting at pH > 5 . The total active Al concentration was adjusted until the sum
157 of errors was minimized at pH ≤ 5 . The total active Al concentrations for all soils are
158 low which precludes the formation of Al hydroxides. The parameters used for WHAM VI
159 calculations are summarized in Table 2.

160 After obtaining the amount of AOC, we developed a linear relationship between the
161 AOC and SOC. The linear relationship was applied to predict the adsorption isotherms,
162 which were validated by the experimental data.

163 **Results and Discussion**

164 The Cd adsorption changes dramatically from low pH to high pH, less than 10%
165 adsorption at $\text{pH} < 3$, and more than 90% adsorption at $\text{pH} > 8$ for most soils. Generally,
166 WHAM VI is able to account for the variation of Cd partitioning as a function of solution
167 pH and Cd concentrations for different soils, and the model fit is consistent with the
168 adsorption edge data. Figure 1 presents the results for three soils. The model curves show
169 discontinuities at pH 5 due to the different approaches for Al competition for pH below
170 or above 5. The model results support the assumption that SOM is the major sorbent for
171 Cd for most of soils in our study. Lee et al. (1996) also reported that SOM plays the most
172 important role in controlling Cd adsorption. By analyzing literature data of more than 70
173 studies, Sauvé et al. (2000) developed a regression equation for Cd partitioning between
174 soils and solutions based on pH, total Cd concentration and SOM concentration. Likewise,
175 the partitioning of Cd between soils and solutions can be predicted by the NICA-Donnan
176 model when the organic matter was considered as the major sorbent controlling Cd
177 binding (Benedetti et al., 1996; Lumsdon, 2004). Furthermore by using the regression
178 equation for low pH by Tipping (2005), the model calculated less Cd adsorption. The
179 regression equation was obtained from data at 10 °C and the Al^{3+} activity could vary
180 more than one order of magnitude for different soils (Tipping, 2005).

181 Overall, the amount of AOC for all 14 soils increases with the increase of SOC and
182 the quantity of AOC is linearly related to SOC, with $R^2 = 0.827$ (Figure 2). The linear
183 regression equation has a slope of 0.629 which results in about 63% AOC for all soils.
184 Gustafsson et al. (2003) tried to optimize the fraction of AOM for different soils to model
185 trace metals adsorption using their Stockholm humic model, but they did not find any

186 clear relationship between the optimized values and SOM. Tipping et al. (2003) did not
187 find a clear relationship between active humic substance and SOM in their study. In our
188 study, we focused on the mineral soils, which have much lower SOM than most of the
189 organic soils used by Tipping et al. (2003). The Cd concentrations used in this study are
190 also higher.

191 Different methods have been applied to quantify the reactive organic matter in soils.
192 The amount of AOC may vary depending on the methods used. Base extraction provides
193 a direct way to estimate the humic substances in soils as used by some researchers
194 (Dijkstra et al., 2004; Lumsdon, 2004). Dijkstra et al. (2004) reported that the percentage
195 of the base extractable SOM ranged from 25% to 67% for a variety of soils. To obtain the
196 reactive organic matter, Tipping et al. (2003) adjusted the amount of active humic
197 substances of the soil so that the WHAM calculated pH was the same as the observed
198 value. Weng et al. (2001) used another approach to calculate the AOM in their NICA-
199 Donnan model: adjusting the site density of SOM based on the cation exchange capacity
200 measurement of soils and the generic humic substance. Their results showed that the site
201 density of SOM varied between 46% and 16% of that of the generic humic substance,
202 with the average value of AOM for all soils being 31%. Similarly Cances et al. (2003)
203 assumed that 50% organic carbon in soils was reactive in their modeling study. The linear
204 regression equation obtained in this study is based on parameter optimization, which
205 provides a good approximation on reactive organic matter in soils for predicting Cd
206 adsorption on soils using WHAM VI. Whether this regression equation can be applied to
207 other trace metals needs to be further investigated.

208 Using the linear regression equation for AOC in Figure 2, WHAM VI was used to
209 predict both Cd adsorption edges and isotherms. The predictions for Cd adsorption edges
210 are self-calibrations for the linear regression equation since it is obtained from the
211 adsorption edge data (Figure 3). To further validate the linear regression equation for
212 AOC, WHAM VI predictions were compared with the independent data sets: Cd
213 adsorption isotherms. Figure 4 presents the WHAM VI predictions for the Cd adsorption
214 isotherms together with the experimental data at three different pHs for four typical soils.
215 The model predictions are consistent with the experimental results. The applicability of
216 AOC versus SOC linear relationship to independent data sets supports the validity of our
217 modeling approach.

218 Figure 5 presents a detailed comparison between WHAM VI predicted partition
219 coefficient K_p and experimental K_p in adsorption edge experiments. The results are
220 presented from low pH to high pH. At low pH (2 – 4), WHAM VI over-predicted K_p .
221 WHAM predictions are close to experimental values at intermediate pH (4 – 7). At high
222 pH (7 – 9), more scatter can be observed, indicating greater deviation between WHAM
223 predictions and experimental results. The deviations at high pH may be due to the
224 dissolution of SOM, which was not measured in the original experiment and thus not
225 considered in the modeling. Generally almost all deviations are within one order of
226 magnitude. The root mean square error (RMSE) of $\log K_p$ equals 0.41. The comparison
227 between WHAM VI predicted K_p and experimental K_p in adsorption isotherm
228 experiments are presented in Figure 6 for three pHs. The RMSEs were 0.33, 0.23 and
229 0.39 at pH 4.0, 5.5 and 7.0 respectively.

230 The Al competition varied at different pH ranges. It has been reported that, at low pH,
231 Al^{3+} activity may not be controlled by $Al(OH)_3$ but by adsorption/complexation reactions
232 (Tipping, 2005). Some researchers have used chemical extractions to quantify the active
233 Al (Gustafsson et al., 2003; Lumsdon, 2004). As pointed out by Gustafsson et al. (2003),
234 the total active Al concentrations are not well quantified by available extraction
235 procedures. Besides the extraction, different optimization methods have been used to
236 obtain the active Al. For example, Lumsdon (2004) used 0.1 M HCl extraction to
237 estimate the reactive Al and the fit of Cd adsorption curves was further improved by
238 optimizing the active Al. In our study, if the 0.43 M HNO_3 extractable Al was used as the
239 total Al controlling Al competition for Cd adsorption, the model calculations resulted in
240 higher Al^{3+} activity than that controlled by $Al(OH)_3$. Therefore, we obtained the active Al
241 by optimizing the cadmium adsorption data at low pH. The Al^{3+} activity controlled by
242 this active Al is lower than that controlled by $Al(OH)_3$. This approach provides good
243 model predictions as demonstrated in Figures 5 and 6, together with the solubility control
244 of Al^{3+} at higher pH. Nevertheless accurate measurement of Al^{3+} activity and
245 characterization of Al phases controlling Al^{3+} activity are desired in order to more
246 accurately predict metal partitioning.

247 The importance of mineral phases such as metal (hydro)oxides on Cd binding has
248 been reported by many studies (Tessier et al. 1985; Zachara, et al., 1992; Trivedi and Axe,
249 2000). In natural soils, with the competition of SOM for Cd binding, other sorbents
250 besides SOM may be less important with the increase of SOM concentration.
251 Furthermore, the dominant importance of SOM observed in this study is based on
252 laboratory adsorption experiments, which may be different from highly contaminated

253 field soils. The field contaminated soils may experience various contamination processes
254 and thus the metal speciation could differ significantly (Manceau et al., 1996; Roberts et
255 al., 2002).

256 **Conclusions**

257 WHAM VI has been successfully applied to describe Cd adsorption on different soils
258 with a wide range of soil compositions and different solution chemistry conditions.
259 WHAM VI is able to account for the effect of major solution and soil parameters that
260 control the Cd adsorption on soils. For most of soils in this study, SOC appears to be the
261 major soil component controlling Cd adsorption. Only a fraction of SOC, called AOC, is
262 responsible for Cd binding. The AOC concentration is linearly related to the SOC
263 concentration. Al competition effect should be considered differently at different pH
264 ranges. At low pH, the Al competition was controlled by an active fraction of soil Al
265 rather than the solubility of the Al hydroxides. With the model parameters presented in
266 this study, we can predict Cd adsorption behavior in soils using WHAM VI when SOC is
267 the dominant sorbent in soils.

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270 the Center for the Study of Metals in the Environment (CSME), University of Delaware.

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347 Figure captions

348 Figure 1. Adsorption of Cd on three soils at the initial Cd concentration of 0.1 mM. The
349 SOC concentrations are indicated in the figure. Solid lines are WHAM VI fit. The dash
350 line indicates the model fit with Tipping's regression equation for the highest SOC soil at
351 $\text{pH} \leq 5.0$.

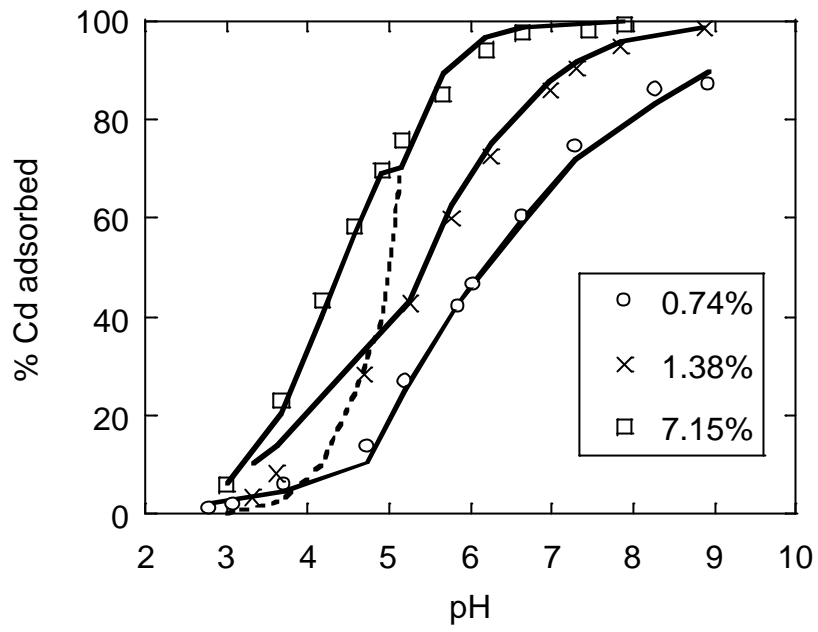
352 Figure 2. Linear regression of AOC concentration vs. SOC concentration for all 14 New
353 Jersey soils.

354 Figure 3. Adsorption edges for Cd adsorption on four soils at two initial Cd
355 concentrations. (a) Downer loamy sand; (b) Birdsboro silt loam; (c) Boonton Bergen
356 County loam; and (d) Boonton Union County loam soils. Solid lines are WHAM VI
357 predictions. The SOC and initial Cd concentrations are indicated in the figure.

358 Figure 4. Adsorption isotherms for Cd adsorption on four soils at three pHs: (a) Downer
359 loamy sand; (b) Birdsboro silt loam; (c) Boonton Bergen County loam; and (d) Boonton
360 Union County loam soils. Solid lines are WHAM VI predictions. The SOC
361 concentrations and pH values are indicated in the figure. The C_p and C_w represent Cd
362 concentrations in soils and solutions, respectively.

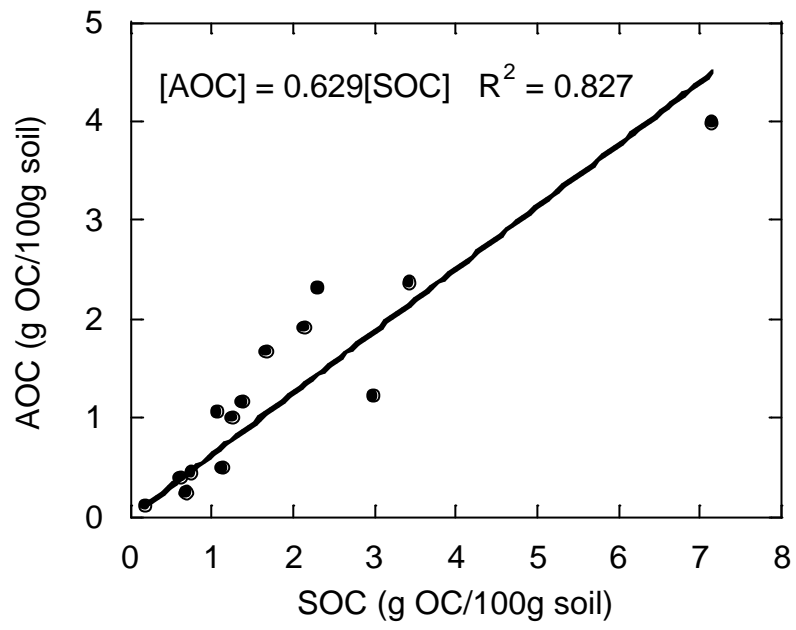
363 Figure 5. Comparison of K_p values predicted by WHAM VI with values from adsorption
364 edge experiments at different pH ranges. Solid line is the 1:1 line and dashed lines
365 indicate \pm one order of magnitude.

366 Figure 6. Comparison of K_p values predicted by WHAM VI with values from adsorption
367 isotherm experiments at three pHs. Solid line is the 1:1 line and dashed lines indicate \pm
368 one order of magnitude. The pH values are indicated in the figure.



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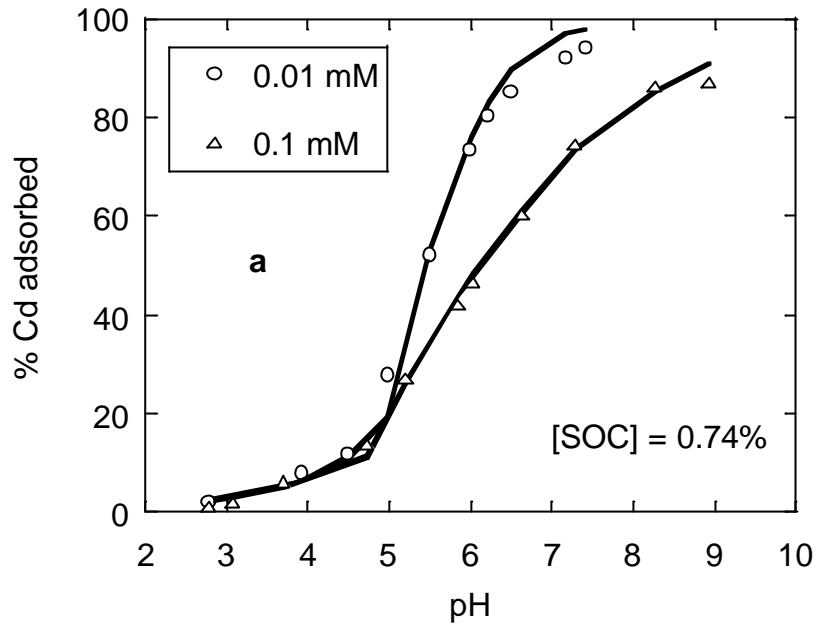
370 Figure 1.



371

372 Figure 2.

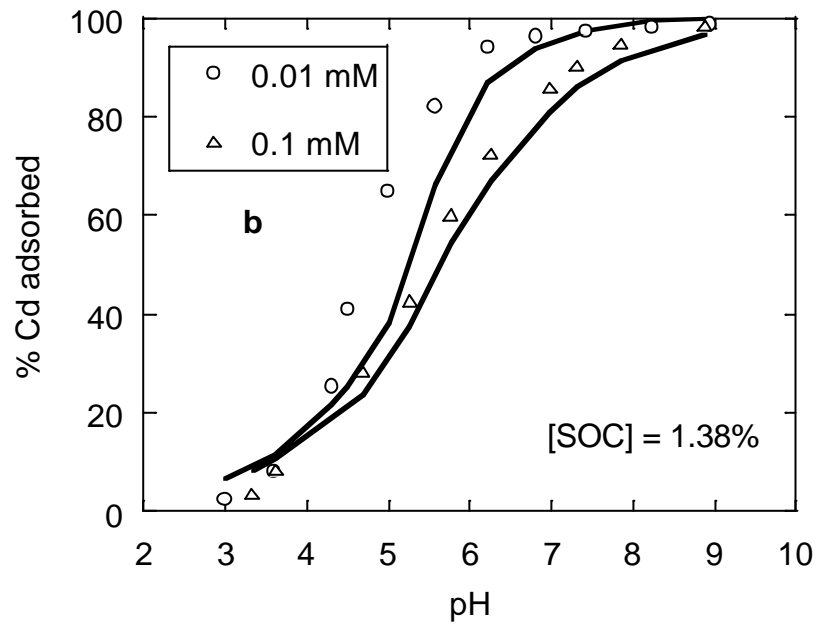
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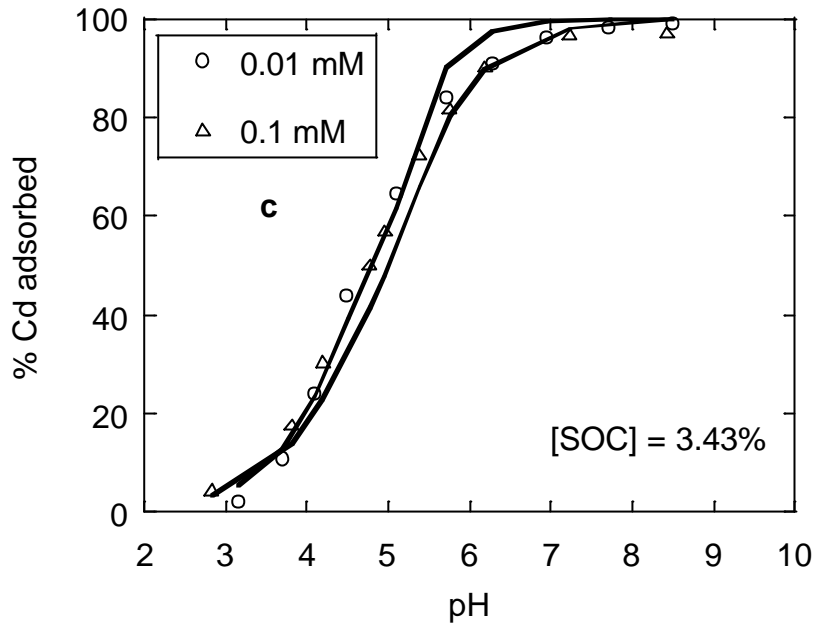
(a)



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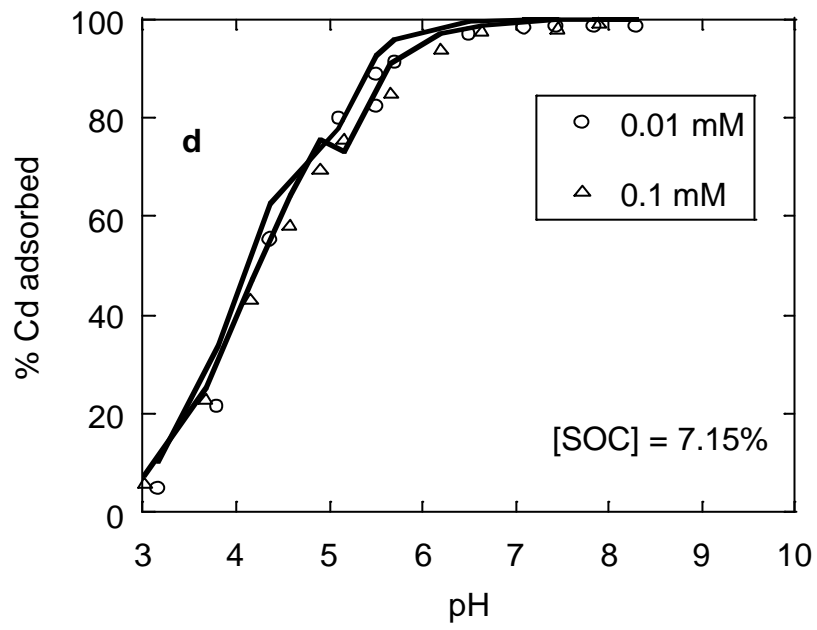
(b)



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(c)



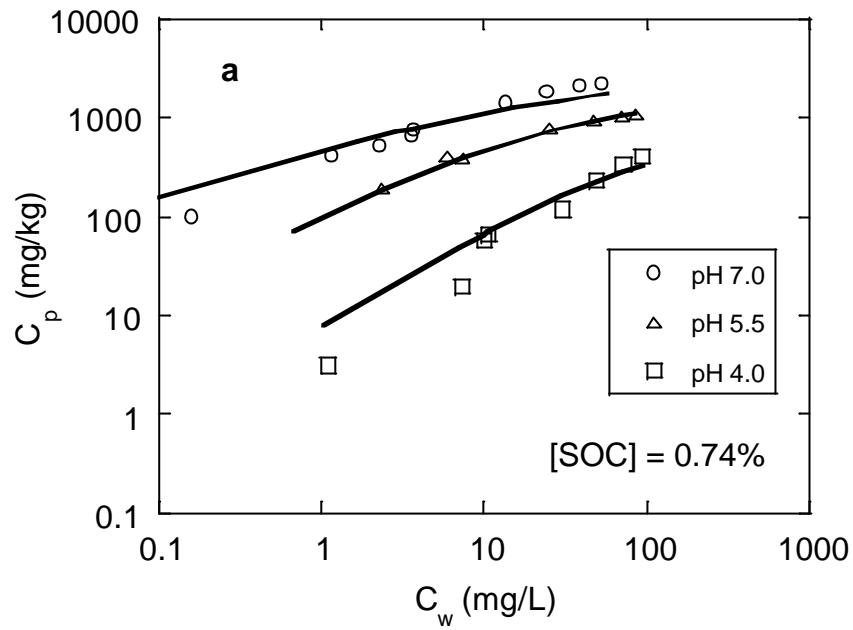
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(d)

382 Figure 3.

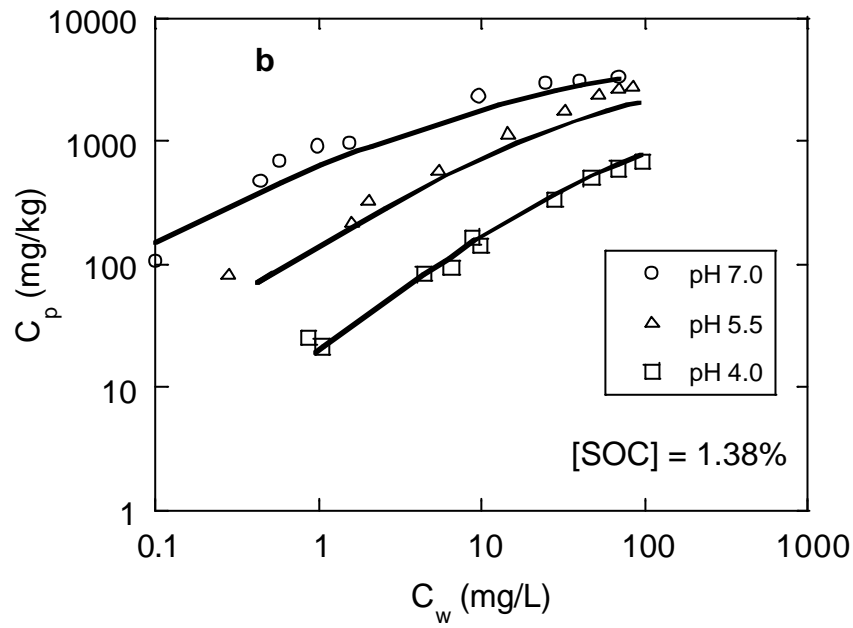
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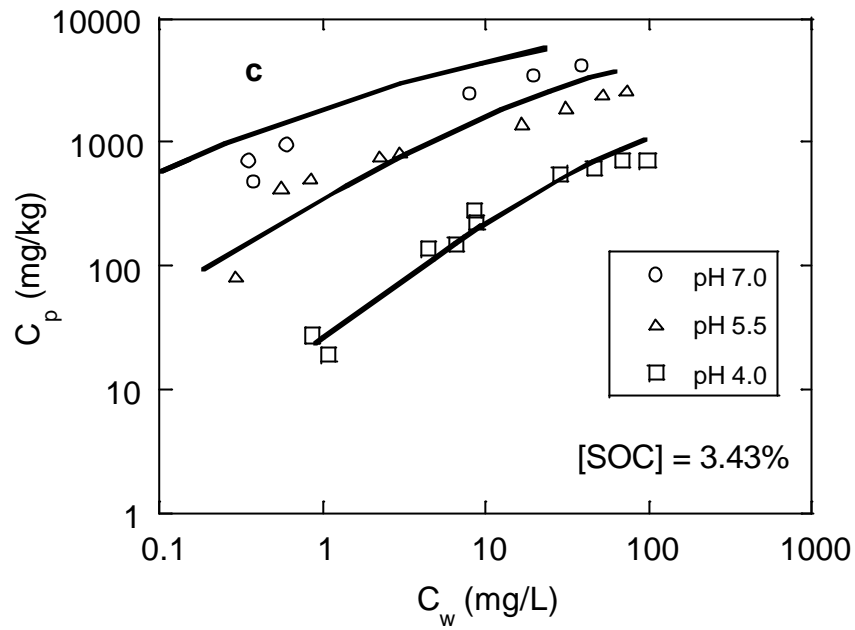
(a)



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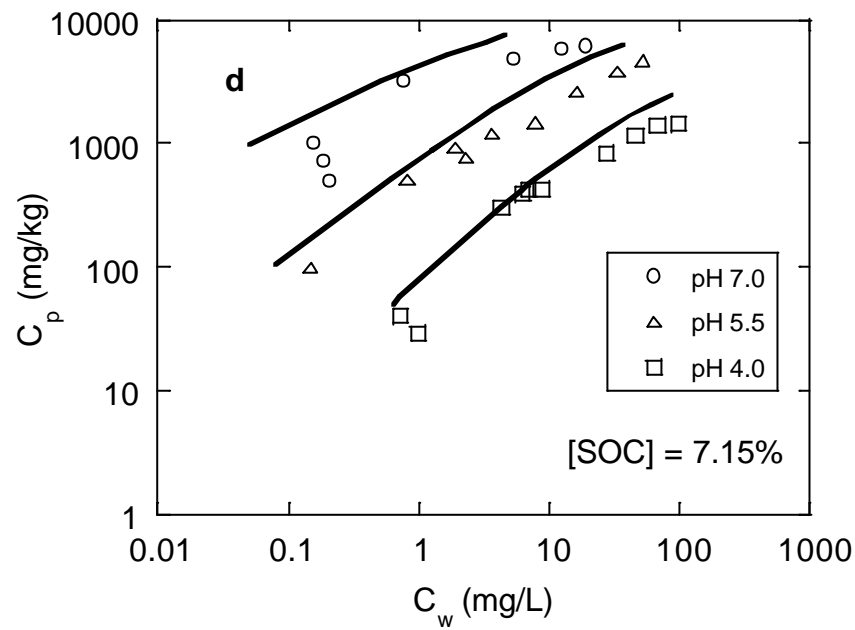
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(b)



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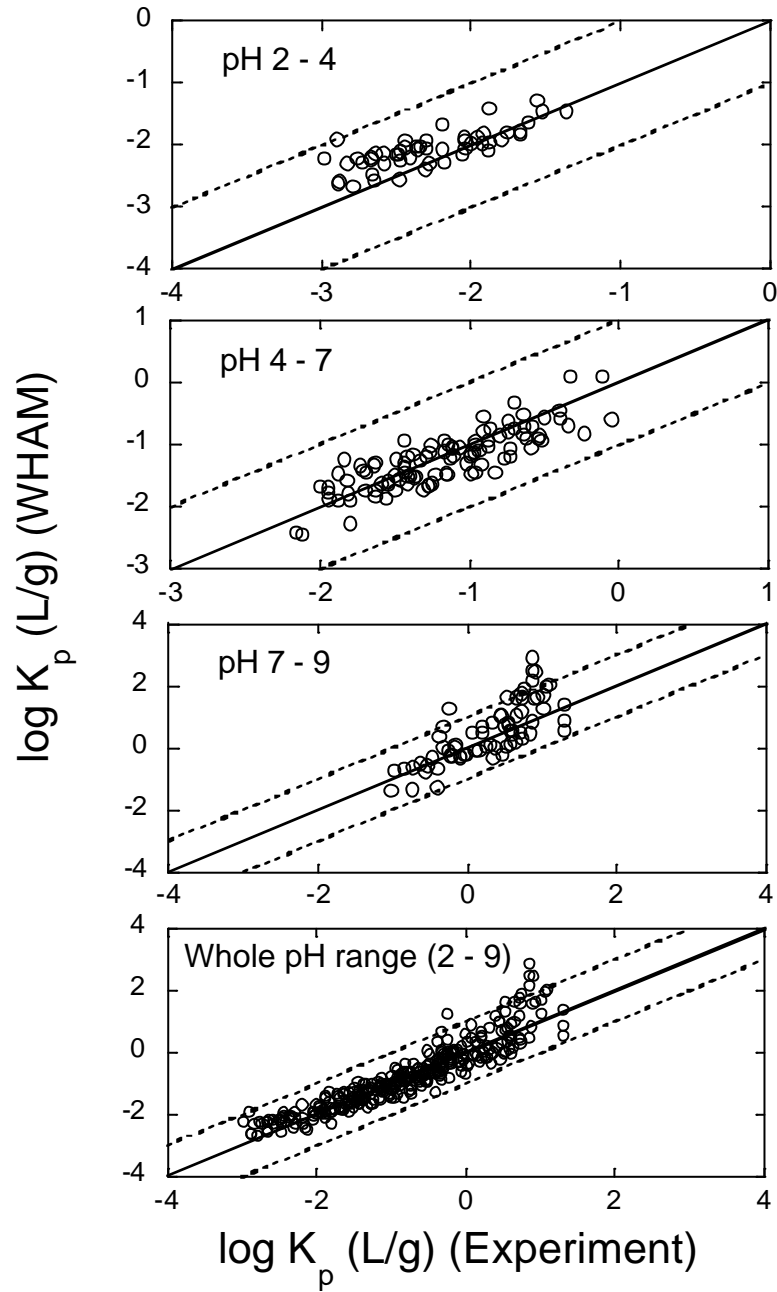
(c)



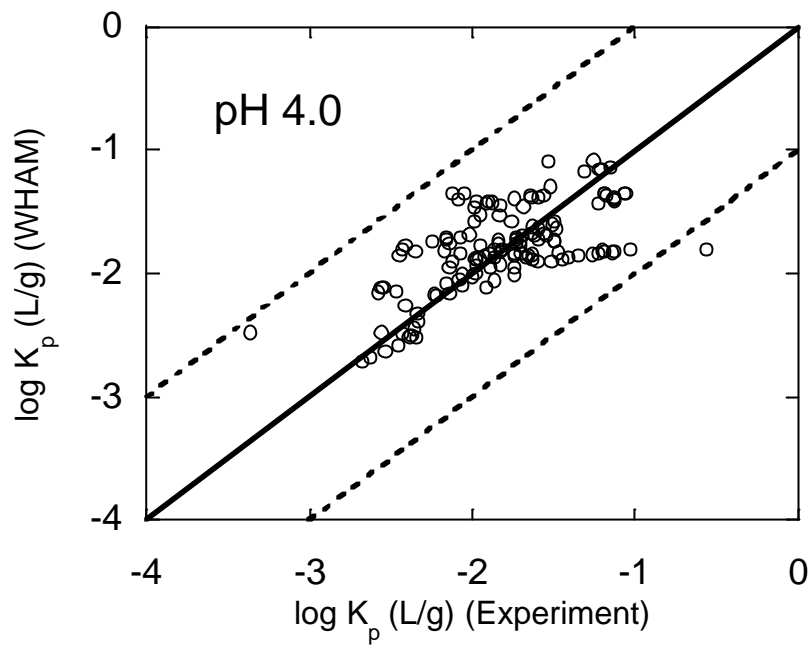
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(d)

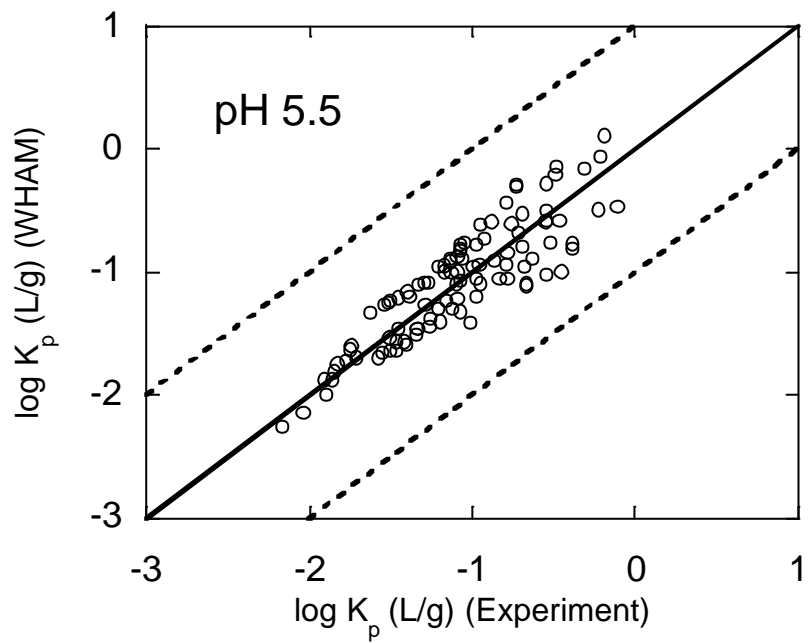
392 Figure 4.



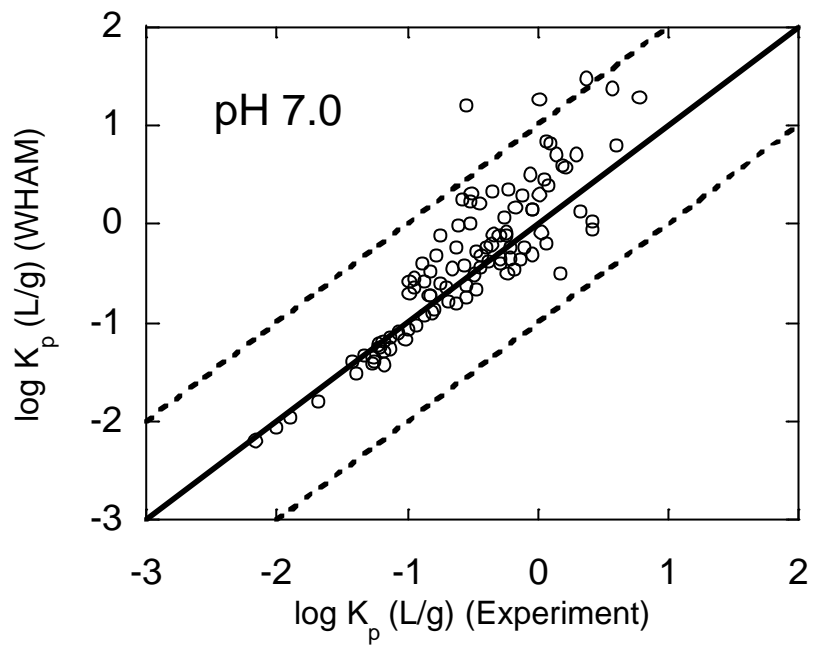
394 Figure 5



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398 Figure 6.

399 Table 1 Selected soil properties*

Soil Name	Particle Size Distribution			pH	SOC	[Ca] (BaCl ₂)	ECEC
	Sand	Silt	Clay				
	%			in H ₂ O	%	mg/kg	meq/100g
Birdsboro silt loam	50	32	18	5.7	1.38	769	5.3
Boonton loam (Bergen County)	60	27	13	5.1	3.43	405	4.2
Boonton loam (Union County)	49	35	16	5.1	7.15	394	4.2
Downer loamy sand	87	5	8	4.7	0.74	5	2.3
Dunellen sandy loam	56	30	14	5.6	1.25	573	4.2
Freehold sandy loam (A horizon)	92	2	6	5.2	0.18	66	0.8
Freehold sandy loam (B horizon)	37	42	21	6.4	1.06	671	4.3
Hazen gravelly loam	39	38	23	6.0	2.31	1590	9.3
Lakewood sand	91	3	6	4.2	0.69	1	0.9
Penn silt loam	25	48	27	4.7	1.13	268	3.8
Rockaway stony loam	54	30	16	4.7	2.99	143	2.7
Sassafras sandy loam	45	37	18	5.8	0.62	384	3.1
Washington loam	20	49	31	6.03	2.14	1461	8.9
Whippany silty clay loam	49	16	37	6.17	1.67	1508	9.5

400 * Metal oxides concentration can be found in Lee et al. (1996).

401 Table 2 WHAM VI calculation parameters

Fraction of active organic carbon (f) and active Al ([Al] _a) at low pH obtained from model fittings							
Soil	Freehold (A)	Sassafras	Lakewood	Downer	Freehold (B)	Penn	Dunellen
SOC (%)	0.18	0.62	0.69	0.74	1.06	1.13	1.25
f	0.600	0.634	0.349	0.598	1.000	0.430	0.806
[Al] _a (M)	6.41 × 10 ⁻⁵	9.16 × 10 ⁻⁵	4.00 × 10 ⁻⁵	1.00 × 10 ⁻⁴	1.10 × 10 ⁻⁴	9.75 × 10 ⁻⁵	1.18 × 10 ⁻⁴
Soil	Birdsboro	Whippany	Washington	Hazen	Rockaway	Boonton Bergen	Boonton Union
SOC (%)	1.38	1.67	2.14	2.31	2.99	3.43	7.15
f	0.835	1.000	0.894	1.000	0.408	0.688	0.557
[Al] _a (M)	1.27 × 10 ⁻⁴	1.00 × 10 ⁻⁴	2.90 × 10 ⁻⁴	2.82 × 10 ⁻⁴	2.11 × 10 ⁻⁴	2.90 × 10 ⁻⁴	4.47 × 10 ⁻⁴
WHAM VI input parameters for solution phases							
[Na ⁺]	[NO ₃ ⁻]	pCO ₂	log* K ₀ (Al)	log* K ₃₀ (Fe(III))	Particle concentration		
M		atm			g/L		
0.01	0.01	3.16E-04	8.5	3	10		

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