Predicting cadmium adsorption on soils using WHAM VI

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Abstract

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

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

Introduction

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

Compared with traditional statistical regression models, more recently mechanistic models have been used to describe metal partitioning between soils and solutions (Weng et al., 2001; Gustafsson et al., 2003; Tipping et al., 2003; Lumsdon, 2004; Ponizovsky et al., 2006), including the Windermere humic aqueous model (WHAM) (Tipping, 1994). SOM has been reported to be the major component among soil components accounting for metal binding. Furthermore, it has been reported that only a fraction of SOM, which is called active organic matter (AOM), is responsible for metal binding (Tipping et al., 2003; Gustafsson et al., 2003; Lumsdon, 2004). The AOM may be due to the difference between the SOM and the generic humic substance to which the equilibrium models are calibrated. SOM consists of non-humic substances such as amino acids, carbohydrates, and lipids, as well as humic substance, a series of high-molecular-weight, brown to black substances formed by secondary synthesis reactions (Stevenson, 1994). SOM may also coat on mineral phase and thus some inner part of SOM may be not accessible due to coating (Nachtegaal and Sparks, 2003). However, there are no well-established methods to determine AOM.

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

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

Materials and Methods

The 14 New Jersey soils those were used to conduct adsorption experiments are described in Table 1. The sample of Delaware River fill material that was included in the original study (Lee et al., 1996) has not been included in the present analysis as it is not a soil. All soils are non-calcareous soils with pH less than 7. These soils cover a variety of soil properties. The soil organic carbon (SOC) concentration ranging from 0.18% to 7.15%, which was measured with a Variomax CN analyzer. The ammonium oxalate extractable soil metal (hydro)oxides were presented in Lee et al. (1996). The exchangeable Ca and Mg were extracted with the 0.1 M $BaCl_2$ for 24 h (Carter, 1993). The Al was extracted with the 0.43 M HNO_3 for 24 h (Dijkstra et al., 2004).

1. Adsorption edge experiment

Batch equilibration studies were conducted with soil concentration = 1.00 ± 0.01 g per 100 mL solution and ionic strength = 0.01M with $NaNO_3$. Cd nitrate concentrations = 1×10^{-5} and 1×10^{-4} M with pH = 3 to 9 and temperature = 25 ± 2 °C. Samples were shaken at 150 rpm for 24 hours and filtered through 25 mm diameter, 0.45 µm membrane filters.

2. Adsorption isotherm experiment

The soil samples, 1.0 gram of each, were immersed in 100 mL of 0.01 M $NaNO_3$. The pH was adjusted in order to approach the desired pHs, 4.0, 5.5, and 7.0 and temperature = 25 ± 2 °C. The initial Cd concentrations ranged from 1.0×10^{-6} to 5×10^{-3} M, and the equilibration time was 24 hours. After 24 hours, the pH was readjusted to the initial value and the samples were filtered through 0.45 µm membrane filters.

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

Modeling Method

WHAM VI was used to calculate Cd adsorption equilibrium at different conditions. WHAM is capable of calculating the equilibrium chemical speciation in surface and ground waters, sediments, and soils, especially when the chemical speciation is dominated by organic matter (Tipping, 1994; Tipping et al., 2003). WHAM uses Model VI, a computer model, to describe the reactions of ions with humic substances, mainly through complexation which is modified by electrostatic reactions. Previous modeling results have demonstrated that, for most non-calcareous soils except for soils with very low SOM concentrations, the SOM is the major adsorbent for trace metals (Tipping et al., 2003; Ponizovsky et al., 2006). Preliminary WHAM calculations showed that metal oxides have little effect on Cd adsorption for most of our soils, so only SOM and clay fraction were used in WHAM calculations. The WHAM input parameters include particulate humic acid (HA) and fulvic acid (FA) concentrations ([HA] and [FA]), the clay concentration, pH, the CO_2 pressure (pCO_2), and solution cations and anions concentrations or activities including $[Na^+]$, $[Ca^{2+}]$, $\{Al^{3+}\}$ or $[Al^{3+}]$, $\{Fe^{3+}\}$ and $[NO_3^-]$. The pCO_2 was set at $10^{-3.5}$ atm. Ponizovsky et al. (2006) have demonstrated that the variation of pCO_2 from 10^{-4} to 10^{-2} atm had little effect in their model calculations. The Mg concentrations were low which had little effect on Cd adsorption. For the solution species, the concentrations were input as measured in the experiments. For the SOM, only the active fraction, AOM, was used in WHAM VI calculations and the active fraction was assumed to consist of 84% HA and 16% FA (Tipping et al., 2003).

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

$$\log\{\mathrm{Al}^{3+}\} = \log {}^{*}K_{s0} - 3\mathrm{pH} \tag{1}$$

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

$$\log\{\mathrm{Al}^{3+}\} = -1.59\,\mathrm{pH} + 2.22 \tag{2}$$

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

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

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

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

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

Results and Discussion

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

Overall, the amount of AOC for all 14 soils increases with the increase of SOC and the quantity of AOC is linearly related to SOC, with $R^2 = 0.827$ (Figure 2). The linear regression equation has a slope of 0.629 which results in about 63% AOC for all soils. Gustafsson et al. (2003) tried to optimize the fraction of AOM for different soils to model trace metals adsorption using their Stockholm humic model, but they did not find any clear relationship between the optimized values and SOM. Tipping et al. (2003) did not find a clear relationship between active humic substance and SOM in their study. In our study, we focused on the mineral soils, which have much lower SOM than most of the organic soils used by Tipping et al. (2003). The Cd concentrations used in this study are also higher.

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

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

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

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

The importance of mineral phases such as metal (hydro)oxides on Cd binding has been reported by many studies (Tessier et al. 1985; Zachara, et al., 1992; Trivedi and Axe, 2000). In natural soils, with the competition of SOM for Cd binding, other sorbents besides SOM may be less important with the increase of SOM concentration. Furthermore, the dominant importance of SOM observed in this study is based on laboratory adsorption experiments, which may be different from highly contaminated field soils. The field contaminated soils may experience various contamination processes and thus the metal speciation could differ significantly (Manceau et al., 1996; Roberts et al., 2002).

Conclusions

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

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Figure captions

Figure 1. Adsorption of Cd on three soils at the initial Cd concentration of 0.1 mM. The SOC concentrations are indicated in the figure. Solid lines are WHAM VI fit. The dash line indicates the model fit with Tipping's regression equation for the highest SOC soil at pH <= 5.0.

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

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

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

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

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

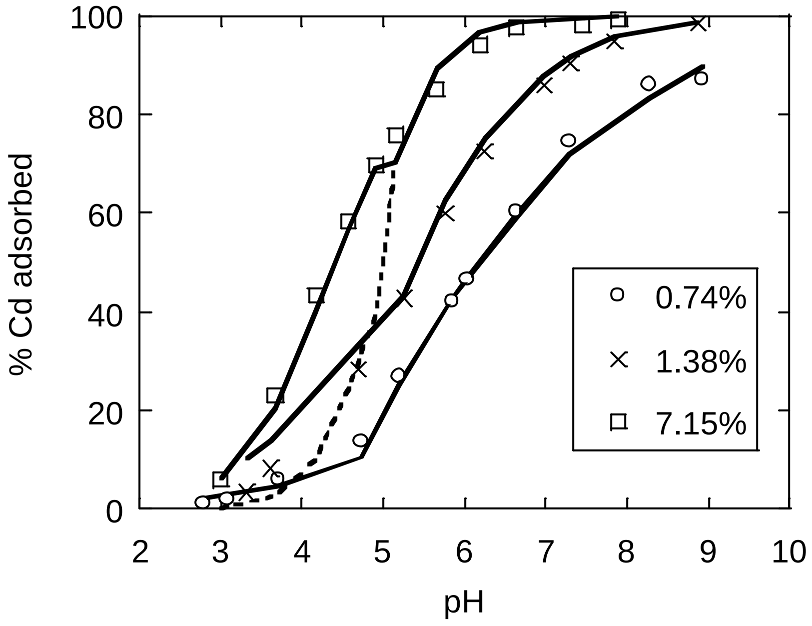


Figure 1.

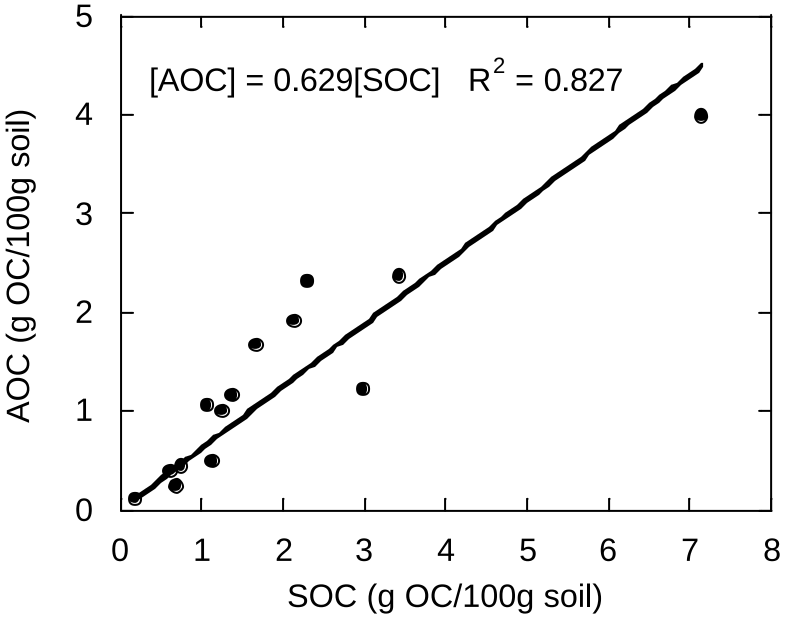
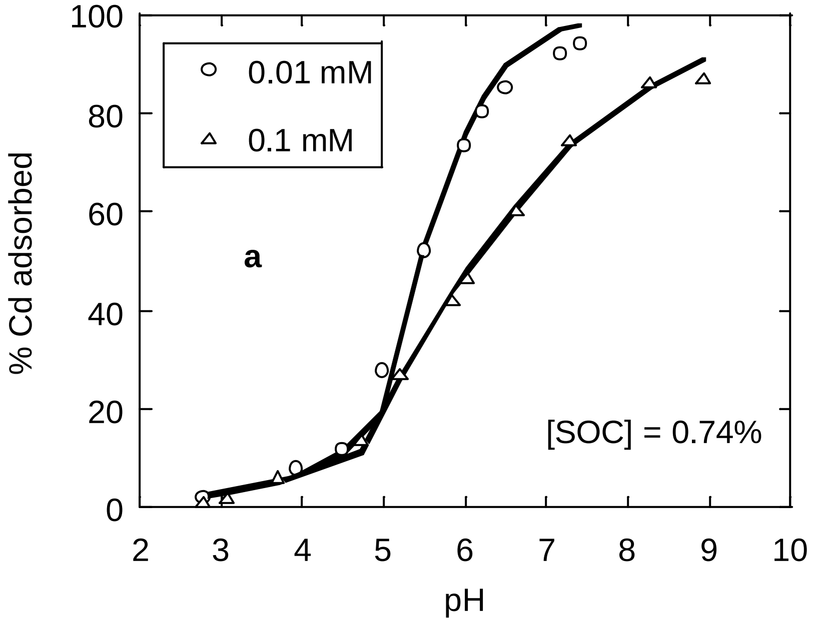
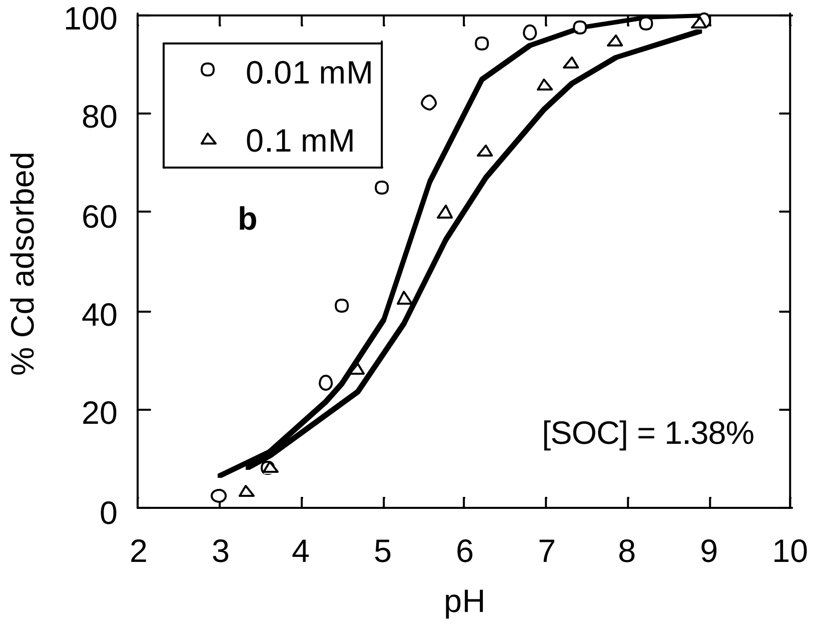

[AOC] = 0.629[SOC] R^2 = 0.827
AOC (g OC/100g soil)
SOC (g OC/100g soil)
0
1
2
3
4
5
0
1
2
3
4
5
6
7
8

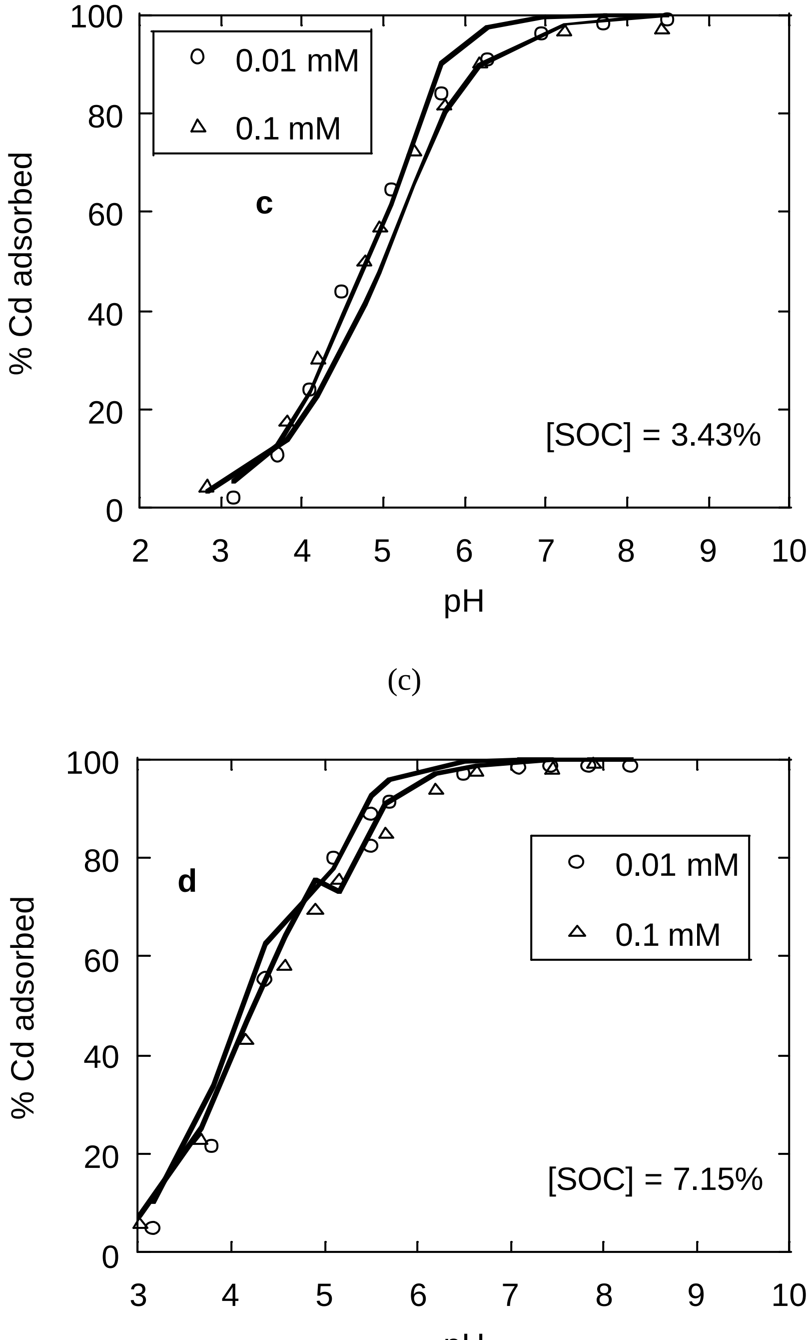
Figure 2.


100
80
60
40
20
0
% Cd adsorbed
0.01 mM
0.1 mM
a
[SOC] = 0.74%
2
3
4
5
6
7
8
9
10
pH

(a)


100
80
60
40
20
0
% Cd adsorbed
0.01 mM
0.1 mM
b
[SOC] = 1.38%
2
3
4
5
6
7
8
9
10
pH

(b)

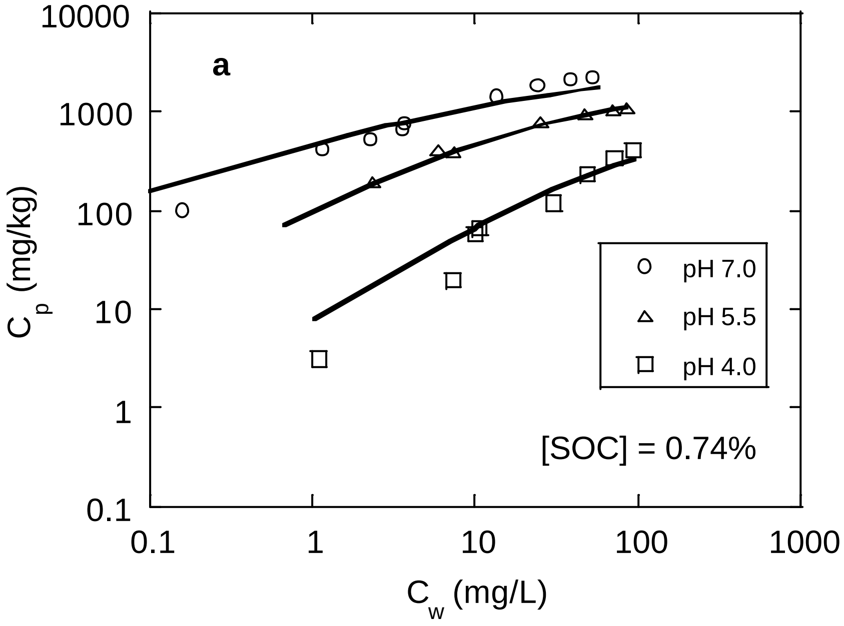


100
80
60
40
20
0
% Cd adsorbed
0.01 mM
0.1 mM
c
[SOC] = 3.43%
2
3
4
5
6
7
8
9
10
pH
100
80
60
40
20
0
% Cd adsorbed
d
0.01 mM
0.1 mM
[SOC] = 7.15%
3
4
5
6
7
8
9
10
pH

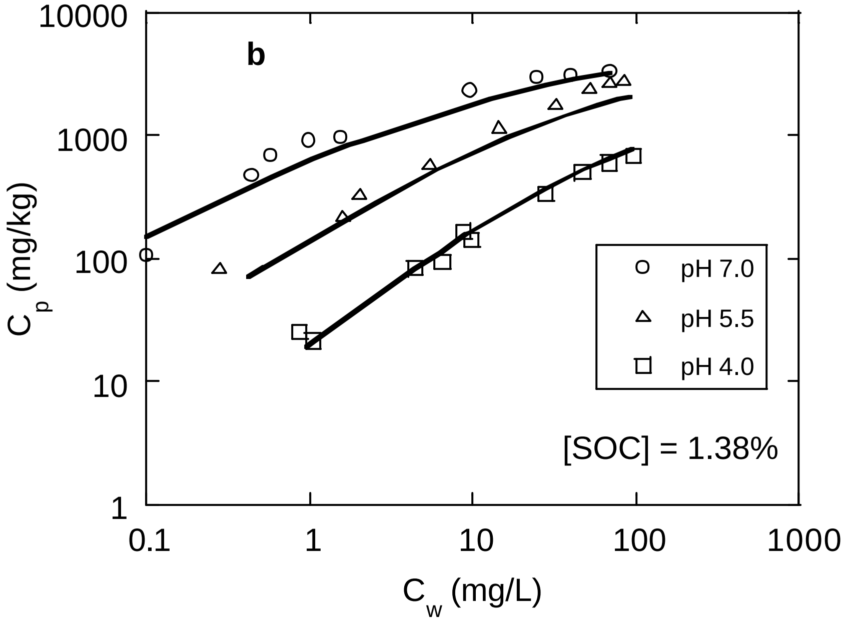
(c)

(d)

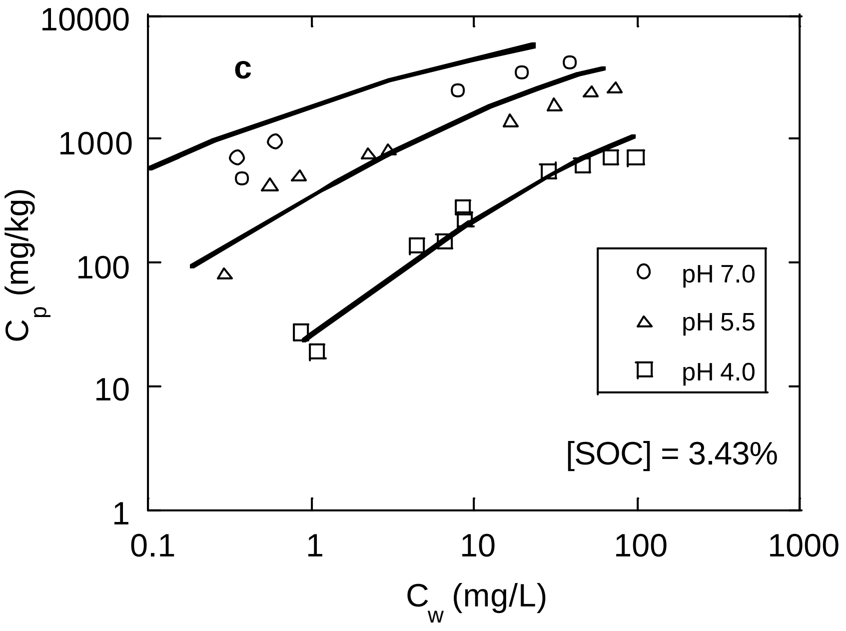
Figure 3.


a
10000
1000
100
10
1
0.1
C_p (mg/kg)
0.1
1
10
100
1000
C_w (mg/L)
pH 7.0
pH 5.5
pH 4.0
[SOC] = 0.74%

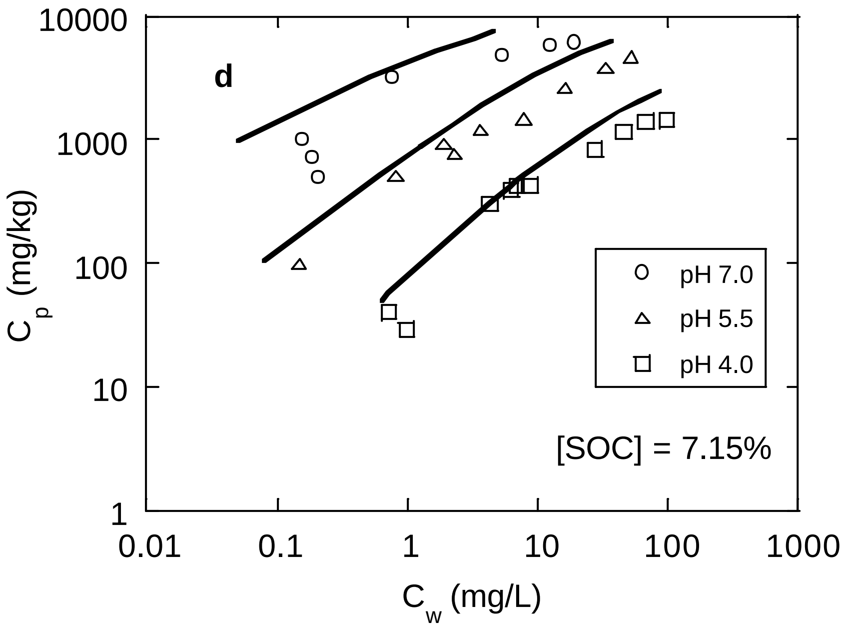
(a)


b
10000
1000
100
10
1
C_p (mg/kg)
0.1
1
10
100
1000
C_w (mg/L)
pH 7.0
pH 5.5
pH 4.0
[SOC] = 1.38%

(b)


c
10000
1000
100
10
1
C_p (mg/kg)
0.1
1
10
100
1000
C_w (mg/L)
pH 7.0
pH 5.5
pH 4.0
[SOC] = 3.43%

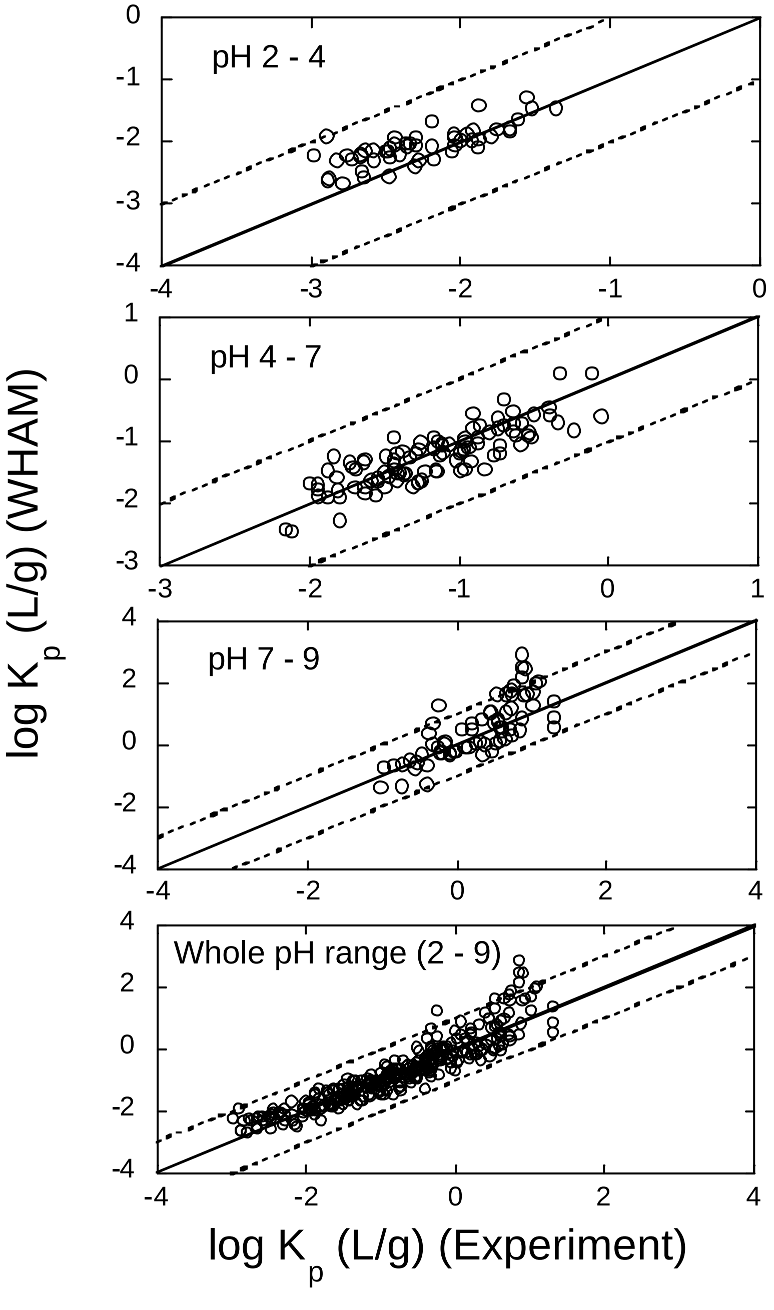
(c)


d
10000
1000
100
10
1
C_p (mg/kg)
0.01
0.1
1
10
100
1000
C_w (mg/L)
pH 7.0
pH 5.5
pH 4.0
[SOC] = 7.15%

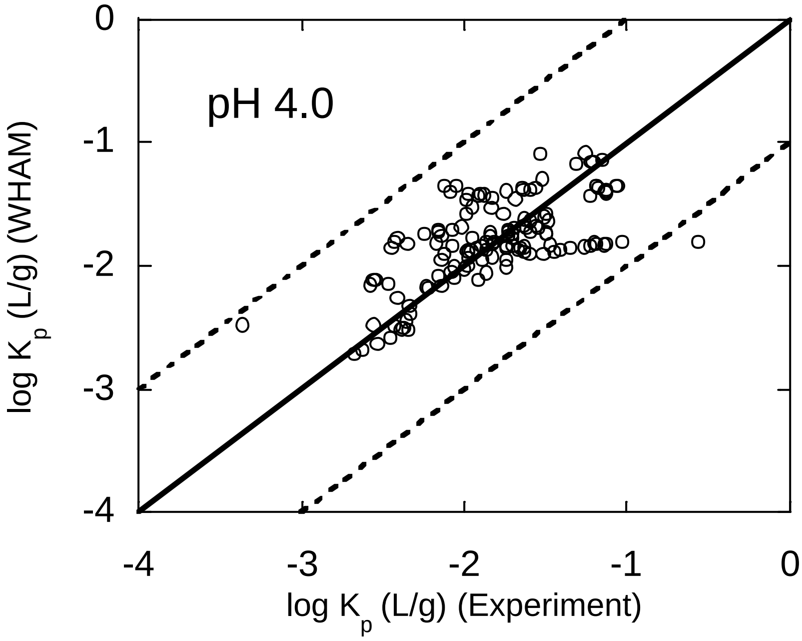
(d)

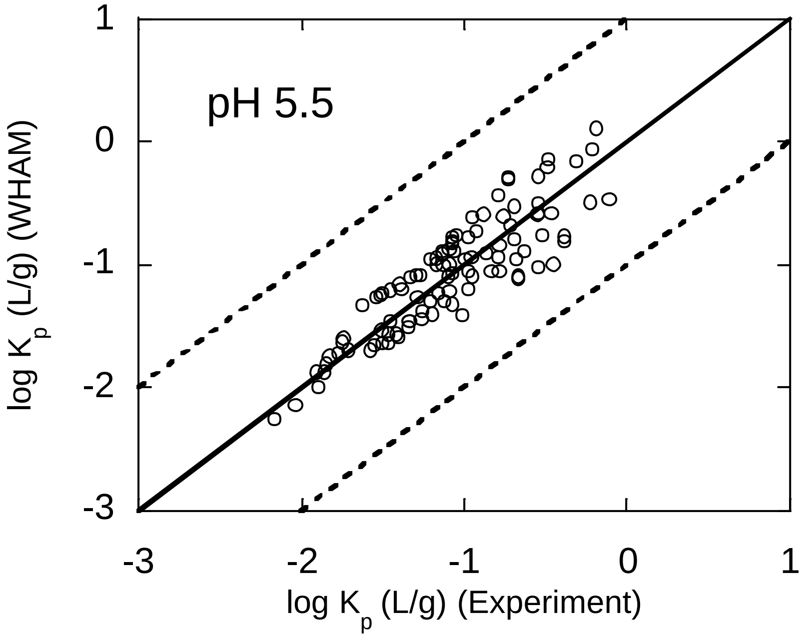
Figure 4.

393



394 Figure 5


pH 4.0
log K$_p$ (L/g) (WHAM)
log K$_p$ (L/g) (Experiment)
0
-1
-2
-3
-4
-4
-3
-2
-1
0


pH 5.5
log K$_p$ (L/g) (WHAM)
log K$_p$ (L/g) (Experiment)
1
0
-1
-2
-3
-3
-2
-1
0
1

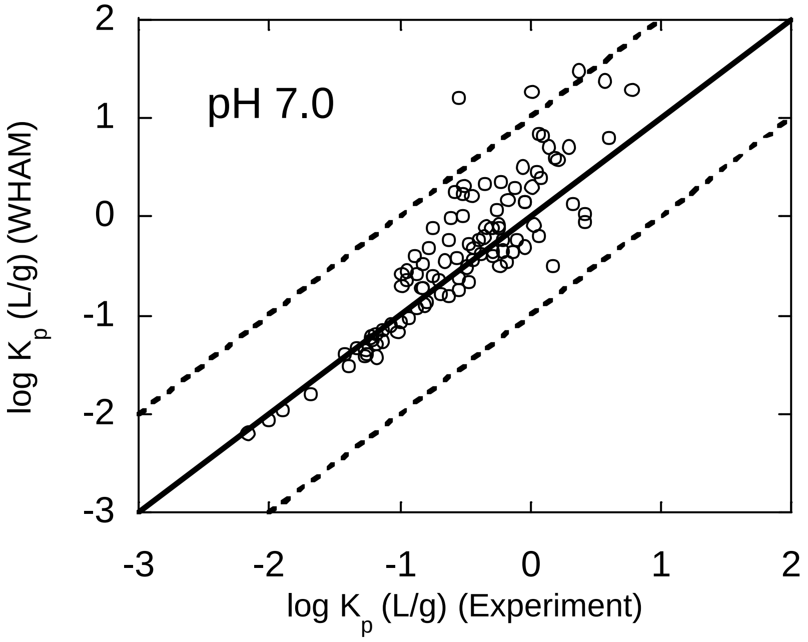


Figure 6.

Table 1 Selected soil properties*

Soil Name	Particle Size Distribution			pH	SOC	[Ca]	ECEC
	Sand	Silt	Clay			($BaCl_2$)	
		%		in H_2O	%	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

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

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	$\log {}^*K_{s0}$ (Al)	$\log {}^*K_{s0}$ (Fe(III))	Particle concentration
M		atm			g/L
0.01	0.01	3.16E-04	8.5	3	10