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Predicting Soil−Water Partition Coefficients for Cadmium

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Equilibrium batch measurements were made of the adsorption of Cd(II) on 15 New Jersey soils. The soils were characterized in terms of surface properties and chemical composition, particularly organic matter and metal oxides. The adsorption of Cd(II) followed the Langmuir relation and increased with increasing pH between pH 3 and pH 10. At constant pH and metal concentration, greater adsorption was observed for soils with higher organic matter content. To better understand the mechanism of adsorption, the experimental results for the adsorption of Cd by the 15 soils were tested using a partition coefficient model that related the adsorption of the Cd(II) to the soil components: organic matter, iron oxides, aluminum oxides, and manganese oxides. This model was not successful when applied to measurements at the natural soil pH because of the competition of protons with Cd(II) for available sites. However, at constant pH, partition coefficients obtained from experimental data were highly correlated with those calculated for a partition coefficient between Cd(II) and organic matter alone. Normalization of the partition coefficients, K_d, for the organic matter content of the soils, K_{om}, greatly improved the relationship between the partition coefficient and pH (R^2 increased from 0.799 to 0.927). This suggests that the surficial adsorption sites are principally composed of organic matter. For the 24-h equilibration period employed, diffusion of Cd(II) through this superficial organic matter coating to underlying sorptive materials, including metal oxides, is unimportant in the partitioning of Cd(II).

Introduction

The mobility and fate of metals in the soil environment are directly related to their partitioning between soil and soil solution (*1*). The presence of trace metals in the solid phase is a result of precipitation and adsorption to components of the soil, processes that are highly pH dependent. For trace metals, adsorption is normally of greater importance than is precipitation. Varying contents of organic matter and metal oxides may result in varying capacity for metal sorption onto soils.

The interaction of metal ions with natural soil particles is complex, involving multiple mechanisms. Much of the work relating to trace metal sorption by surfaces in natural systems has involved the use of well-defined "model" surfaces such as clay, aluminum oxides, iron oxides, and manganese oxides. These substances are present in soils, and including them is necessary to develop an understanding of mechanisms for the adsorption of metals.

Boekhold et al. (*2*), Boekhold and Van der Zee (*3*), and Van der Zee and Van Reimsdijk (*4*) have used equations in which the Cd(II) sorption by soil is proportional to the hydrogen ion concentration raised to the −0.5 power. Anderson and Christensen (*5*) studied 38 soils with samples being taken at several depths. For their 117 sorption measurements made at very low Cd(II) concentrations, from 0.7 to 12.6 μg/L, regression of log of the Cd(II) sorption K_d on the pH gave a slope of 0.64. The regression had an R^2 value of 0.776, indicating that the proton concentration is the principal factor affecting the partitioning process. More recently, Boekhold et al. (*6*) have found an exponent for the hydrogen ion concentration of −0.69 for sodium electrolytes and −0.77 for calcium electrolytes, values considerably more negative than −0.5. Apparently, the value is a function of the type of soil considered. A different approach has been taken by Schulte and Beese (*7*), who showed that, over specified pH intervals, the sorption of Cd(II) onto different soils could be related to their specific surface areas. Both Luoma and Davis (*8*) and Jenne et al. (*9*) have considered the modeling of metal sorption by incorporating the contributions of different types of binding phases, such as metal oxides and organic matter.

In this study, we investigated the sorption of Cd(II) on 15 soils collected in New Jersey. We conducted both adsorption isotherm and adsorption edge measurements on the soils. We developed a relationship to describe the sorption of Cd(II) by the different soils that predicts sorption by other soils. We considered the influence of solution pH, of the concentrations of iron, manganese, and aluminum oxides, and of organic matter in the soil on Cd sorption.

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TABLE 1

Physicochemical Properties of Soils

soil type	pH[a] in water	clay (%)	metal oxides (%)[b] Al	Fe	Mn	organic matter (%)
Birdsboro silt loam	5.69	18	0.714	1.035	0.025	2.2
Boonton Bergen County	4.12	13	1.321	1.563	0.013	5.3
Boonton Union County	5.14	16	1.447	0.773	0.065	8.6
Downer loamy sand	4.74	8	0.120	0.076	0.0003	0.8
Dunellen sandy loam	5.57	14	0.355	0.435	0.011	1.9
Delaware River fill material	4.77	10	0.105	0.578	0.012	1.2
Freehold sandy loam (A horizon)	6.44	6	0.442	0.519	0.009	0.2
Freehold sandy loam (B horizon)	5.22	21	0.052	0.178	0.001	2.4
Hazen gravelly loam	6.02	23	0.574	1.117	0.034	3.1
Lakewood sand	4.18	6	0.096	0.344	0.0002	0.5
Penn silt loam	4.67	27	0.593	0.743	0.022	1.3
Rockaway stony loam	4.69	16	1.181	0.832	0.028	4.9
Sassafras sandy loam	5.78	18	0.461	0.699	0.005	0.6
Washington loam	6.03	31	0.684	0.900	0.038	2.9
Whippany silty clay loam	6.17	37	0.388	0.736	0.004	2.3

[a] Soil pH was determined after 30 min stirring and then 1 h standing. [b] Expressed as Al_2O_3, Fe_2O_3, and Mn_2O_3.

Materials and Methods

The 15 New Jersey soil samples are listed in Table 1. They are representative of the major soil types present in New Jersey.

The soils were air dried, and agglomerates were broken by hand and by using a wooden mallet. Particles larger than 2 mm were removed by sieving. All further tests were performed on the less than 2-mm size fraction of the soils. For the soil analyses presented in Table 1, organic matter was measured by the Walkey–Black wet combustion method; soil pH was determined in water; and soil particle size distribution was determined by a sedimentation (hydrometer) method (*10*). Soil metal oxides were determined by the ammonium oxalate extraction method of Iyengar et al. (*11*), using a Perkin Elmer Model 5000 atomic absorption spectrophotometer to analyze the solubilized metal. The natural Cd concentrations of the soils were negligible.

Samples for the determination of adsorption isotherms were prepared by adding 1.0 g of soil to 100 mL of 0.01 M $NaNO_3$. The pH was adjusted by the addition of small volumes of HNO_3 or NaOH, as necessary, to attain the desired pHs of 4.0, 5.5, and 7.0. The initial Cd(II) concentrations ranged from 1.0×10^{-6} to 5×10^{-3} M, and the equilibration time was 24 h at room temperature (25 ± 2 °C). Preliminary testing of Sassafras sandy loam and Washington loam at pH 4 and pH 7 established the adequacy of a 6–12-h equilibration time for these soils. After 24 h, the pH was readjusted to the initial value, and the samples were filtered through 0.45-μm membrane filters. The changes in pH after 24 h were small (all pH values were within ±0.3 pH). The amount of adsorbed Cd was calculated as the difference between the amount added initially and that remaining in solution.

Adsorption edge measurements were conducted for Cd(II) for each of the 15 soils. The soil suspensions were 1.00 ± 0.01 g/100 mL. Ionic strength was maintained at 0.01 M with $NaNO_3$. We added $Cd(NO_3)_2$ at a concentration of 1×10^{-4} M. Fifteen pH values covering the range from 3 to 10 were employed. The pH values of the samples were adjusted by adding NaOH or HNO_3 as required. Samples were shaken at 150 strokes/min on a reciprocating shaker (Lab-Line Instruments, Melrose Park, IL) for 24 h at room temperature (25 ± 2 °C). The pH values were determined again after the 24 h of shaking. The samples were then filtered through 25 mm diameter, 0.45-μm membrane filters (Gelman Sciences, Ann Arbor, MI). The Cd(II) concentration in the filtered solution was determined by atomic absorption spectrophotometry.

Results and Discussion

Soil Characteristics. A summary of soil characteristics is presented in Table 1. The soils ranged from sand to silty clay loam; the range in clay content is 6 to 37%. Soil pH ranged from 4.18 to 6.44. Organic matter ranged from 0.2 to 8.6%. The Boonton Union County soil had the highest concentration of aluminum and manganese oxides, whereas the Washington loam had the highest iron oxide content among the soils.

Adsorption Isotherms. The adsorption data obtained from isotherm experiments were fitted by nonlinear regression (*12*) to Langmuir adsorption isotherms:

$$[\mathrm{Cd}]_s = \frac{\Gamma_m K[\mathrm{Cd}]_w \times 1000}{1 + K[\mathrm{Cd}]_w \times 1000} \qquad (1)$$

where $[\mathrm{Cd}]_s$ is the cadmium concentration in soil (μg/g); $[\mathrm{Cd}]_w$ is the cadmium concentration in water (μg/L); Γ_m = maximum sorbed cadmium concentration (μg/g); K is the constant (L/mg).

Table 2 presents the values of the Langmuir Γ_m and K parameters from the nonlinear regression of $[\mathrm{Cd}]_w$ vs $[\mathrm{Cd}]_s$. At a given pH, for example pH 7.0, the maximum adsorption concentrations, Γ_m, for the New Jersey soils varied widely, from 714 to 6469 μg/g, but correlated with the soil organic matter content ($R^2 = 0.812$). At pH 7, the Boonton Union County soil had the greatest Γ_m, 6469 μg/g, and the highest concentration of organic matter, 8.6%, while the Freehold sandy loam (A horizon) had the smallest Γ_m, 714 μg/g, and the smallest concentration of organic matter, 0.2%. There was a much weaker relationship between Γ_m and soil iron, aluminum, or manganese oxides (R^2 = 0.229, 0.599, and 0.564, respectively at pH 7). Results for the other pH values were similar in that sorption correlated to organic matter much better than it did to the metal oxides.

TABLE 2

Parameters for Nonlinear Regression of C_s vs C_w of Langmuir Equation for Adsorption of Cadmium on 15 New Jersey Soils at Three pH Values

	pH 4.0			pH 5.5			pH 7.0		
soil type	Γ_m (μg/g)	K (L/mg)	R^2	Γ_m (μg/g)	K (L/mg)	R^2	Γ_m (μg/g)	K (L/mg)	R^2
Birdsboro silt loam	1123	0.016	0.999	4113	0.027	0.998	3300	0.310	0.996
Boonton Bergen County	930	0.043	0.995	2718	0.121	0.983	3977	0.357	0.956
Boonton Union County	1864	0.037	0.996	6285	0.049	0.994	6469	0.847	0.989
Downer loamy sand	2644	0.002	0.996	1208	0.075	0.996	2580	0.120	0.997
Dunellen sandy loam	1123	0.017	0.998	3021	0.040	0.995	2897	0.245	0.998
Delaware River fill material	886	0.014	0.997	1987	0.054	0.997	2161	0.210	0.999
Freehold sandy loam (A horizon)	293	0.019	0.999	740	0.030	0.997	714	0.171	0.995
Freehold sandy loam (B horizon)	942	0.004	0.996	2286	0.115	0.991	3170	0.277	0.981
Hazen gravelly loam	1973	0.014	0.995	5110	0.050	0.997	4333	0.602	0.980
Lakewood sand	161	0.034	0.985	323	0.215	0.999	826	0.378	0.998
Penn silt loam	154	0.175	0.994	1174	0.095	0.996	1524	0.549	0.998
Rockaway stony loam	1180	0.012	0.997	3370	0.048	0.995	3939	0.210	0.970
Sassafras sandy loam	116	0.289	0.983	984	0.081	0.997	1124	0.297	0.998
Washington loam	826	0.119	0.997	3038	0.075	0.998	2050	1.550	0.985
Whippany silty clay loam	1273	0.075	0.997	1418	0.358	0.998	1968	0.821	0.996

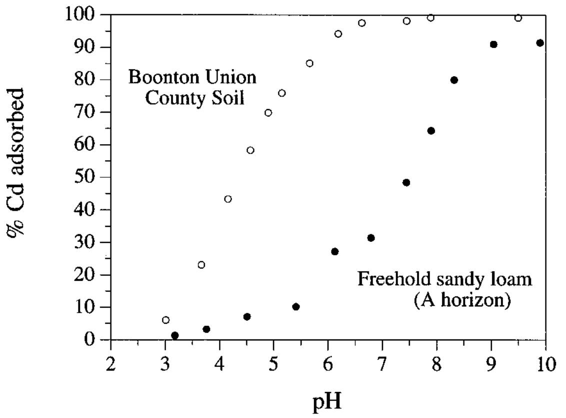

FIGURE 1. Adsorption of 1×10^{-4} M cadmium onto Freehold sandy loam (A horizon) and Boonton Union County soil; the soils with the least and greatest adsorption. Soil/water = 1 g/100 mL; $I = 0.01$ M $NaNO_3$; $T = 25$ °C.

Adsorption Edge. The most important factor controlling the partitioning of a metal to soil is the solution pH (*13*). In general, the percentage of a cationic metal adsorbed increases as pH increases with a transition range of 2−3 pH units in which the percentage of the metal that is adsorbed increases from nearly 0 to almost 100%. This transition range does not occur at the same value of pH for different soils. In this study, the extremes were represented by Boonton Union County soil and Freehold sandy loam (A horizon), which reach nearly 100% Cd(II) adsorption at pH 6 and p 9, respectively (Figure 1). The high dependence of Cd(II) adsorption on pH is explained by the fact that hydrogen ions affect the surface charge of the adsorbent and the degree of ionization and the speciation of the adsorbate (*14*).

Partition Coefficients. The ratio of the Cd concentration in the soil, $[\mathrm{Cd}]_s$, to the concentration of Cd(II) in the solution phase, $[\mathrm{Cd}]_w$, may be described by a partition coefficient (K_d, mL/g), which is a function of pH, metal concentration, and other properties of the solution and the solid matrix:

$$K_d = \frac{[\mathrm{Cd}]_s}{[\mathrm{Cd}]_w} \tag{2}$$

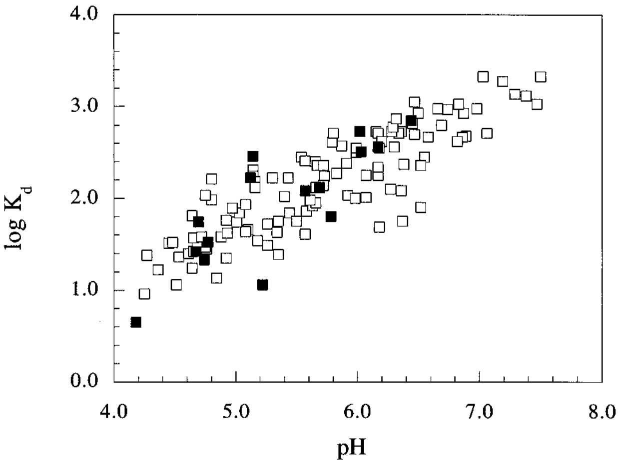

FIGURE 2. Log K_d for Cd as a function of pH from Anderson and Christensen (*5*) for Danish agricultural soils (open symbols) and that from our laboratory for 15 New Jersey soils at their natural pH (closed symbols).

We transformed the partition data from the adsorption edges for the 15 soils into K_d values using the added and equilibrium concentrations of Cd(II). The Cd in the soil was assumed be due solely to the adsorption of cadmium from the solution. The K_d values varied greatly from soil to soil. Figure 2 shows the large K_d data set of Anderson and Christensen (*5*) for Danish agricultural soils and that from our laboratory for 15 New Jersey soils at their natural pH. Although our solution concentrations (97.8−11 124 μg/L) are much higher than those from Anderson and Christensen (0.7−12.6 μg/L), our log K_d values are still within the envelope of those of Anderson and Christensen. The slope of the regression for our soils (0.804) is about one-third higher than the value of 0.603 reported by Anderson and Christensen. Figure 3 shows all the adsorption edge data, transformed into K_d values, plotted versus pH for all 15 of our soils. Although it is clear from Figures 2 and 3 that pH is the major factor controlling partitioning, the variation in K_d is still substantial. This indicates that although pH is the most important parameter, it is not the sole one.

A portion of the removal of cadmium may have been a result of precipitation of $CdCO_3$, but we believe that this is not likely as the media was $NaNO_3$, and these soils contained little inorganic carbon. We evaluated whether

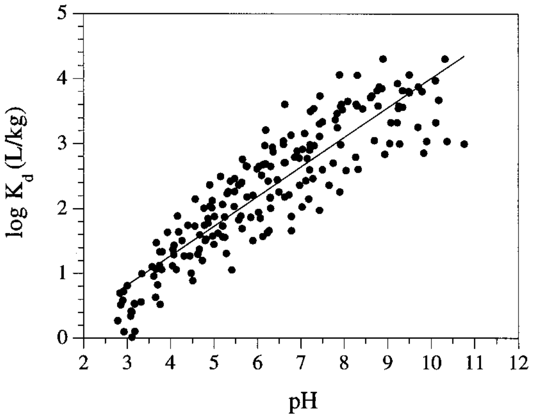

FIGURE 3. Log K_d as a function of pH for adsorption of cadmium onto 15 New Jersey soils. Soil/water = 1 g/100 mL; I = 0.01 M $NaNO_3$; T = 25 ± 2 °C. Regression equation: log $K_d = -0.552 + 0.455$ pH; $R^2 = 0.799$.

the high concentrations of cadmium used in the experiment invalidated the use of the linear partitioning relationship of eq 2 to describe the distribution between soluble and sorbed cadmium. We compared the partition coefficient obtained for the linear portion of the Langmuir isotherm using the constants at pH 5.5 in Table 2 to the experimental values of soluble and sorbed cadmium using eq 2. The mean deviation between these values for the 15 soils was 51%, and the maximum deviation was a factor of 3. This difference is a small contribution to the scatter of our data in Figure 2 or Figure 3.

In an attempt to better predict the partitioning of Cd to soil, a general partitioning model for the sorption of Cd(II) by soil surfaces at fixed pH was developed. The model uses fixed ionic strength and fixed initial metal concentration. A preliminary statistical analysis of the variation of Cd(II) adsorption with measured soil properties was made. Clay content and surface area showed low correlation to adsorption. Based on this analysis, the major adsorbing sites for binding Cd(II) are considered to be organic matter, and to a lesser degree, oxides of Fe, Al, and Mn.

The reaction between Cd(II) and a single sorption phase, in which the ionic charge has been omitted, can be expressed as follows:

$$\equiv\mathrm{S} + \mathrm{Cd} \rightleftharpoons \equiv\mathrm{S{-}Cd} \tag{3}$$

$$K_{\equiv\mathrm{S-Cd}} = \frac{[\equiv\mathrm{S{-}Cd}]}{[\equiv\mathrm{S}][\mathrm{Cd}]} \tag{4}$$

where $K_{\equiv\mathrm{S-Cd}}$ is the conditional stability constant for the reaction; $\equiv$S is a binding site on iron, aluminum, or manganese oxide or on organic matter; $\equiv$S$-$Cd is the quantity of Cd(II) sorbed by the binding site; [Cd] is the equilibrium Cd(II) concentration.

The total quantity of the Cd sorbed by the soil, $[\equiv\mathrm{S{-}Cd}]_{\mathrm{tot}}$, is the sum of the quantities of the Cd sorbed by the individual sorption phases:

$$[\equiv\mathrm{S{-}Cd}]_{\mathrm{tot}} = [\mathrm{FeO}_x\mathrm{{-}Cd}] + [\mathrm{AlO}_x\mathrm{{-}Cd}] + [\mathrm{MnO}_x\mathrm{{-}Cd}] + [\mathrm{OM{-}Cd}] \tag{5}$$

TABLE 3

Conditional Stability Constants for Binding of Cd(II) by One, Two, and Three Soil Components at pH 5.0

soil component considered	conditional stability constants $K_{\mathrm{OM-Cd}}$	$K_{\mathrm{AlO}_x-\mathrm{Cd}}$	$K_{\mathrm{MnO}_x-\mathrm{Cd}}$	R^2
OM[a]	29.98			0.941
OM and Al	25.07	24.04		0.955
OM, Al, and Mn	21.96	16.87	689.29	0.969

[a] OM organic matter content. Sample calculation of predicted K_d by considering three components:

$$K_d = 21.96[\mathrm{OM}] + 16.87[\mathrm{AlO}_x] + 689.29[\mathrm{MnO}_x]$$

The equilibrium Cd(II) concentration present in solution then can be obtained by consideration of the binding of Cd(II) by all binding sites:

$$[\mathrm{Cd}] = [\equiv\mathrm{S{-}Cd}]_{\mathrm{tot}}/\{K_{\mathrm{FeO}_x-\mathrm{Cd}}[\mathrm{FeO}_x] + K_{\mathrm{AlO}_x-\mathrm{Cd}}[\mathrm{AlO}_x] + K_{\mathrm{MnO}_x-\mathrm{Cd}}[\mathrm{MnO}_x] + K_{\mathrm{OM-Cd}}[\mathrm{OM}]\} = \frac{[\equiv\mathrm{S{-}Cd}]_{\mathrm{tot}}}{\sum_{\mathrm{sites}} K_{\equiv\mathrm{S}_i-\mathrm{Cd}}[\equiv\mathrm{S}_i]} \tag{6}$$

where $[\equiv\mathrm{S}_i]$ is the concentration of the ith class of sorption sites; $K_{\equiv\mathrm{S}_i-\mathrm{Cd}}$ is the conditional stability constant for the reaction of Cd with the ith class of sorption sites. Rearranging eq 6:

$$\frac{[\mathrm{Cd}]}{[\equiv\mathrm{S{-}Cd}]_{\mathrm{tot}}} = \frac{1}{\sum_{\mathrm{sites}} K_{\equiv\mathrm{S}_i-\mathrm{Cd}}[\equiv\mathrm{S}_i]} = \frac{1}{K_{\mathrm{d}}} \tag{7}$$

Therefore, the partition coefficient is

$$K_{\mathrm{d}} = \sum_{\mathrm{sites}} K_{\equiv\mathrm{S}_i-\mathrm{Cd}}[\equiv\mathrm{S}_i] \tag{8}$$

Equation 8 was applied to the Cd(II) adsorption data for the New Jersey soils. For each of the 15 soils, the adsorbed Cd is divided by the soluble Cd(II) to obtain experimental partition coefficients at the soil natural pH and at fixed pH values of 4.0, 5.0, and 6.0. Data for the fixed pH values were obtained by interpolation of the adsorption edge curves. These partition coefficients were regressed stepwise against site concentrations for the organic matter, and iron, aluminum, and manganese oxides using eq 8 to obtain conditional stability constants for each phase. The concentrations of organic matter and of the metal oxides were considered to be proportional to their site concentrations. Separate regressions omitted one or more sorption phases. These stability constants were then used to calculate predicted partition coefficients. The example equation shown in Table 3 utilizes stability constants for the binding of Cd(II) by organic matter, aluminum oxide, and manganese oxide to predict K_d. Boonton Union County soil, for example, contains 8.6% organic matter, 1.5% aluminum oxide, and 0.065% manganese oxide. The predicted K_d value (258.1 mL/g) at pH 5.0 is virtually identical to that observed (239.5 mL/g). We evaluate the success of including different components in the model by regression of experimental partition coefficients against partition coefficients calculated from the conditional stability constants. At soil natural pH, we found very low R^2 values (0.040−0.172, Table 4) for the relation of the partition coefficient to the concentration of single or multiple potential binding sites. The inability

TABLE 4

Comparison of R^2 for Regression of Experimental Partition Coefficients against Predicted Values Obtained from Conditional Stability Constants

soil component considered	R^2 natural pH	pH 4.0	pH 5.0	pH 6.0
OM[b]	0.104	0.928	0.958	0.966
Fe	0.087	0.275	0.357	0.263
Al	0.040	0.722	0.789	0.720
Mn	0.105	0.705	0.684	0.593
OM and Al	0.149	0.931	0.968	0.973
OM, Al, and Mn	0.172	0.958	0.973	0.975

[a] The regressions were performed at three different pH values and at the natural pH of each of the soils by considering one, two, and three soil components in the model (eq 8). [b] OM, organic matter content.

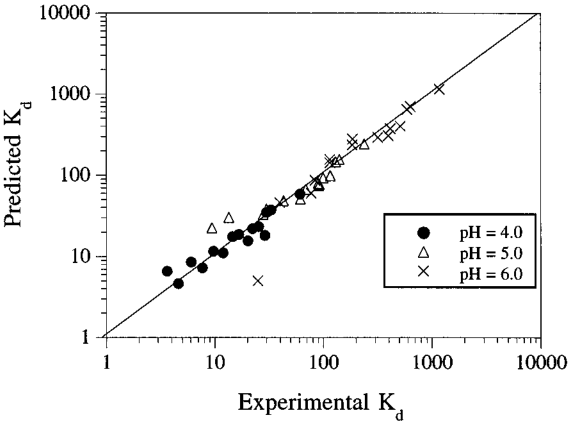

FIGURE 4. Correlation between experimental and predicted partition coefficient by considering organic matter only at three pH values. Line of equality is shown. $R^2 = 0.982$.; 1×10^{-4} M cadmium; soil/water = 1 g/100 mL; $I = 0.01$ M $NaNO_3$; $T = 25 \pm 2$ °C.

to relate the sorption of metal to the concentration of binding sites can be attributed to the fact that the effect of pH is not considered in this analysis.

Table 4 also shows the comparisons of the results predicted by the model with the experimental data for three different pH values (4.0, 5.0, and 6.0) for the 15 soils. The single component that gives the best correlation is organic matter. A small improvement is obtained by including aluminum, but only a slight additional improvement is obtained when three components (organic matter, aluminum oxide, and manganese oxide) are considered. At each of the fixed pH values, this model fits the experimental data very well by considering organic matter as the only sorption phase ($R^2 > 0.92$). Of the four components considered, iron oxide was the least important to the binding of Cd(II) by the soils. Adding a second phase to the model gains only a marginal improvement at great cost in the form of required additional information that is difficult to experimentally obtain. Figure 4 shows the importance of organic matter to the binding of Cd(II).

The differences in the regression model used in this study and that used by Anderson and Christensen (*5*) and many others should be noted. Their partitioning has been measured at natural soil pH, and soil pH has been included as one of the variables in the regression. This implies independence of pH from the other regression parameters. However, the extent of sorption of Cd(II) and other metals by metal oxides and organic matter is dependent on the pH. Consequently, pH must be fixed or the dependency of the sorption of metal by the sorbing phases must be explicitly included in the model. Since the later is difficult, we chose to fix the pH. Furthermore, consistent with eq 8, we have forced our regressions through the origin. This implies that in the absence of the sorption phases considered, there will be no sorption of Cd(II).

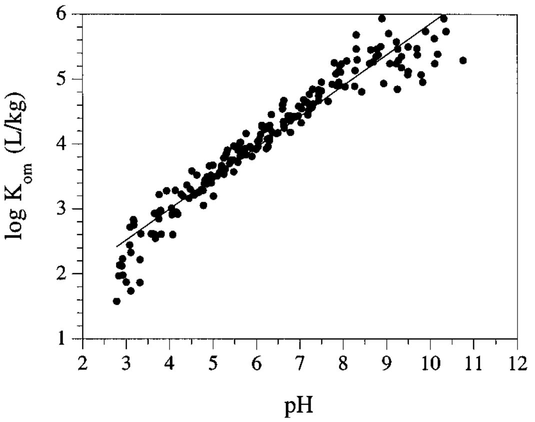

FIGURE 5. Log K_{om} as a function of pH for adsorption of cadmium onto 15 New Jersey soils. Soil/water = 1 g/100 mL; $I = 0.01$ M $NaNO_3$; $T = 25 \pm 2$ °C. Regression equation: $\log K_{om} = 1.084 + 0.477$ pH; $R^2 = 0.927$.

TABLE 5

Regression Coefficients for Log K_d vs pH (Figure 3) and Log K_{om} vs pH (Figure 5)

regression	n[a]	slope	intercept	R^2
log K_d vs pH	194[b]	0.455	−0.552	0.799
log K_{om} vs pH	194[b]	0.477	1.084	0.927
log K_d vs pH	136[c]	0.478	−0.582	0.858
log K_{om} vs pH	136[c]	0.491	0.996	0.928
log K_d vs pH	146[d]	0.488	−0.666	0.698
log K_{om} vs pH	146[d]	0.522	0.892	0.951

[a] Number of samples. [b] All data sets. [c] Samples with organic matter content less than 0.5% have not been included. [d] Samples with pH less than 3.5 and greater than 8.5 have not been included.

To reduce the variance in the pH-dependent K_d's that are shown in Figure 3, the K_d values were normalized to the organic matter content of the soils. Normalization of K_d to the amount of organic carbon is commonly done for hydrophobic organic compounds (*15, 16*). The organic matter normalized partition coefficients, K_{om}, for the 15 soils are plotted versus pH for the 15 soils in Figure 5. The data collapse to form a single curve in which the data scatter is far less than was present in Figure 3. The regression parameters for Figures 3 and 5 are given in Table 5. When K_{om} rather than K_d is considered, the R^2 value increases from 0.799 to 0.927. Table 5 also shows the effect of truncating the data set. If soils have low concentrations of organic matter, the contribution of other binding sites, such as metal oxides and ion exchange sites on clay minerals, might be expected to become more important in the partitioning of Cd(II). When only samples with an organic matter content greater than 0.5% were included in the regressions, the R^2 value for the K_d vs pH regression increased from 0.799 to 0.858. The R^2 values for the regressions of K_{om} on pH were almost the same. The regression in Figure 5 deviates at both low and high pH. We have recently demonstrated that significant concentrations of organic matter dissolve from these soils at high pH (*17*). These organics would be expected to form soluble com-

TABLE 6

Predicted Partition Coefficients for 13 Soils from The Netherlands (Data from Ref 19)

soil	organic matter (%)	pH	K_d	log K_{om}		measured − predicted
				measured[a]	predicted[b]	
A	7.0	6.0	810	4.063	3.946	-0.117
B	73.3	4.7	583	2.901	3.326	0.425
C	8.8	7.8	619	3.847	4.804	0.957
D	39.1	6.0	2864	3.865	3.946	0.081
E	2.6	4.0	9.0	2.539	2.992	0.453
F	0.5	5.1	18.0	3.556	3.517	−0.039
G	4.4	6.5	719	4.213	4.184	−0.029
I	2.7	4.2	5.0	2.268	3.087	0.819
J	4.6	7.8	872	4.278	4.804	0.526
K	5.4	6.7	1211	4.351	4.280	−0.071
L	7.6	4.5	83	3.038	3.231	0.193
M	3.9	5.5	70	3.254	3.707	0.453
N	4.4	6.0	1294	4.468	3.946	−0.522

[a] Measured log K_{om} = log (K_d × 100/% organic matter). [b] Predicted using the regression in Figure 5.

plexes with Cd that would decrease the measured partition coefficient. Furthermore, in the K_{om} values we have not applied any correction for the solubilization of organic matter at higher pH.

Application to Field Soils. In our 24-h adsorption experiments, it was found that primarily the organic matter and not the metal oxides were involved in the sorption of the added Cd(II). This conclusion regarding the partitioning of Cd(II) in our work is in contradiction to that obtained from sequential fractionation data which show a distribution of Cd among various sorption phases (see, for example, ref 18 and references cited therein). The fractionations are of soils that are field contaminated and therefore aged. We believe that the results of our experiments demonstrate that organic matter is the surficial coating of the soil and, in the 24-h period that we used to equilibrate the samples, diffusion of the Cd to underlying metal oxide and other sorption phases was not important in controlling the partitioning of the Cd(II) between the soil and the solution phases. In a like manner, the desorption will be controlled by the equilibrium of Cd between the soil organic matter and soil water. The underlying oxide materials serve as a reservoir of Cd but do not affect the soil water concentration of cadmium. The uptake and release of Cd by these underlying metal oxide and other sorptive phases appears to be a diffusion controlled process.

We have applied the model for Cd(II) partitioning that is shown in Figure 5 to data for 13 soils that were collected in The Netherlands (see Table 6) (*19*). The reported K_d values were computed from Cd released from the soil by nitric acid digestion and from measurements of Cd(II) in pore water. We predicted the log K_{om} using the equation presented in Figure 5. All predicted K_{om} values were within one order of magnitude of the measured K_{om} values. The mean deviation of log K_{om} was 0.241.

Summary and Conclusions

The results of both adsorption edge and adsorption isotherm studies showed that Cd(II) adsorption is highly pH dependent. The different soils have very different adsorption abilities. Among all soil properties, the organic matter plays the most important role in controlling Cd(II) sorption by soils.

The adsorption coefficient (K_d) increases with increasing pH values. We have developed a model for the sorption of metal by soil surface substances at fixed pH. The results show that the conditional partition coefficients were highly correlated to the organic matter content at a fixed pH. The R^2 of the regression line was improved from 0.799 to 0.927 when log K_{om} vs pH rather than log K_d vs pH was considered for the 194 measurements for the 15 soils that we investigated. We tested the model using data for soils from The Netherlands and were able to predict the partition coefficient within 1 order of magnitude for soils to which Cd(II) had not been added in the laboratory.

For the 24-h equilibration period employed, diffusion of Cd through the superficial organic matter coating to underlying sorptive materials, including metal oxides, appears to be unimportant in the partitioning of Cd(II).

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