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Soil Partition Coefficients for Cd by Column Desorption and Comparison to Batch Adsorption Measurements

HERBERT E. ALLEN,* YU-TUNG CHEN,†
YIMIN LI,‡ AND C. P. HUANG
Department of Civil and Environmental Engineering,
University of Delaware, Newark, Delaware 19716

PAUL F. SANDERS

New Jersey Department of Environmental Protection and
Energy, Division of Science and Research,
Trenton, New Jersey 08625

Desorption of metals from contaminated soils is the initial step in a transport pathway that may ultimately result in contamination of groundwater. Because partition coefficients can be obtained easily from batch adsorption measurements, it is desirable to utilize them if they provide a good estimate of the concentration of metal that can desorb from the soil. Batch adsorption experiments were conducted as a function of pH and metal concentration for a series of eastern United States acidic soils. For comparison purposes, column desorption studies were also carried out as a function of flow rate and metal loading. Eluant samples were collected at several elution volumes for each of several column flow rates. These column eluant data were treated by a double extrapolation technique to evaluate the partition coefficient obtained under desorption conditions. The apparent partition coefficient increased with increasing column velocity and duration of flow. For each flow rate, the results were extrapolated to that for zero time. These zero-time partition coefficients were then extrapolated to zero flow. The zero-time, zero-flow desorption results from the column data were compared to those for the batch adsorption equilibrium. The partition coefficient obtained for batch adsorption provided a good estimate of the value obtained for desorption of the cadmium contaminant in the dynamic system. The slope of the regression of column K_d versus batch K_d values was greater than 0.90.

Introduction

Partitioning of contaminants onto soil is usually studied in batch experiments conducted in shake flasks that provide characteristic coefficients of adsorption. However, the conditions in these experiments are very different from those found in the field where the soil is stationary and the question frequently is the prediction of desorption behavior.

Environmental conditions such as the soil moisture, temperature history, contaminant concentration, duration of contaminant exposure, time since contamination, and water flow rate change the rate and the extent of chemical reaction on soils.

Comparisons between batch and column measurements for assessing adsorption–desorption of organic chemicals have been published (1, 2). These conclude (a) that because the batch method is simpler and more reproducible, it will probably remain the most-used method for measuring equilibrium adsorption–desorption, whereas (b) the column method is more realistic in simulating field conditions. Johnson and Farmer (3) have also shown that batch and flow column methods give similar results for the retention and release of some organic contaminants in soils. For the flow method, the column was packed uniformly with soil, and then chemicals were continuously introduced at a fixed rate until equilibrium was achieved. The partition coefficients were determined by linear and nonlinear Freundlich sorption isotherm measurements.

Adsorption–desorption of inorganic contaminants on soils and soil components has frequently been reported not to be completely reversible. The extent of irreversibility or hysteresis of cadmium and other metals increases with time of aging (4). Bruemmer et al. (5) described the adsorption of cadmium and other metals by goethite to be diffusion-dependent with fixation of the metals inside the goethite structure, which helps explain the observed desorption hysteresis. Di Toro et al. (6) modeled metal adsorption–desorption by considering there to be reversible and resistant components to the sorption.

In this study, we investigated a means to relate the batch adsorption and column desorption behavior of cadmium on soils. Desorption was studied as a function of cadmium loading onto five soils and on the flow rate of water through the soil column. The partition coefficients determined from the column desorption experiments were corrected for the effects of water velocity and extent of metal desorption and compared to the partition coefficient determined from the batch adsorption experiments. Because the equilibration period was short and the desorption immediately followed the adsorption step, these results should be considered to relate principally to the reversible component.

Materials and Methods

Field soil samples from the A or B horizons were collected from five sites in New Jersey. Upon collection, agglomerates were broken by hand and wooden mallet. These soils were passed through a 2-mm screen and were then air-dried before use. Soil characteristics are given in Table 1.

For the batch equilibration studies, 1.00 ± 0.01 g samples of each soil were immersed in 100 mL of 0.01 N NaNO$_3$ containing cadmium nitrate at initial concentrations of 5 $\times$ 10^{-5}, 1 $\times$ 10^{-4}, or 5 $\times$ 10^{-4} M. Ten samples of each soil were prepared for each initial cadmium concentration. The pH of these samples were adjusted to cover the range from

TABLE 1
Soil Characteristics

soil name	particle size distribution			organic matter (%)	pH	
	sand (%)	silt (%)	clay (%)		in water	in 0.01 M CaCl₂
Boonton loam (Union County)	60	27	13	8.6	5.12	4.31
fill material dredged from Delaware River	85	5	10	1.2	4.77	4.09
Downer loamy sand	87	5	8	0.8	4.74	3.74
Freehold sandy loam (A horizon)	92	2	6	0.2	5.22	4.87
Rockaway stony loam	54	30	16	4.9	4.69	4.23

3 to 9 by adding NaOH or HNO_3 after an initial shaking for 0.5 h. Samples were shaken at 150 strokes/min on a reciprocating shaker (Lab-Line Instruments, Melrose Park, IL) for 24 h at a room temperature of 25 ± 2 °C. The pH values were determined and, if necessary, adjusted at 1, 2, 4, 8, 16, and 22 h. After 24 h of shaking, the final pH value of each sample was measured and used as the batch adsorption reaction value. The samples were then filtered through 0.45-μm polypropylene fiber membrane filters (Gelman Sciences, Ann Arbor, MI). The cadmium concentrations of the filtrate were analyzed using atomic absorption spectrophotometry (Perkin-Elmer Zeeman Model 5000). The difference between the amount of metal remaining in the solution and the amount initially present in the solution was taken as the amount of metal adsorbed by soil.

Samples for the column desorption experiments were prepared by adding 500 g of soil/50 L of 0.01 N $NaNO_3$ in a 80-L container. Cadmium nitrate was added at a concentration of 5×10^{-5}, 1×10^{-4}, or 5×10^{-4} M. The suspension, at natural soil pH, was stirred at 150 rpm for 24 h at room temperature (25 ± 2 °C). After 24 h, we measured the pH of the suspension. A 10-mL aliquot was filtered through a 0.45-μm polypropylene fiber membrane filter (Gelman Sciences, Ann Arbor, MI), and the cadmium concentration of the filtrate was analyzed by atomic absorption spectrophotometry.

The suspension was allowed to settle for 4 h to separate liquid and solid phases. To reduce the loss of fine-grain solids from the supernatant, we passed the supernatant through a 65-μm filter twice prior to discarding, and then the solids retained on the filter were added to the slurry remaining in the container. After the second passage of the supernatant through the filter, no turbidity was visible. Six plexiglass columns 5 cm in diameter by 15 cm in length were packed identically with the soil slurry that had been equilibrated with cadmium. The soil slurry was packed into each of the plexiglass columns by adding small increments while gently tapping the sides of the column. The increments were added until the soil height was 3 cm.

A multichannel peristaltic pump was used to apply a 0.01 N $NaNO_3$ solution to elute the columns. Six flow rates ranging from 0.5−13 mL/min (unsaturation or saturation) were employed.

For the column experiments, the natural soil pH was used, and aliquots of the column effluent were collected. After complete mixing of the column effluents, the pH was determined on one portion of the solution, and a separate 10-mL portion was acidified by adding 0.1 N HNO_3. The effluent pH values varied ±0.15 for any column. The acidified samples were analyzed by atomic absorption spectrophotometry to determine the concentration of cadmium.
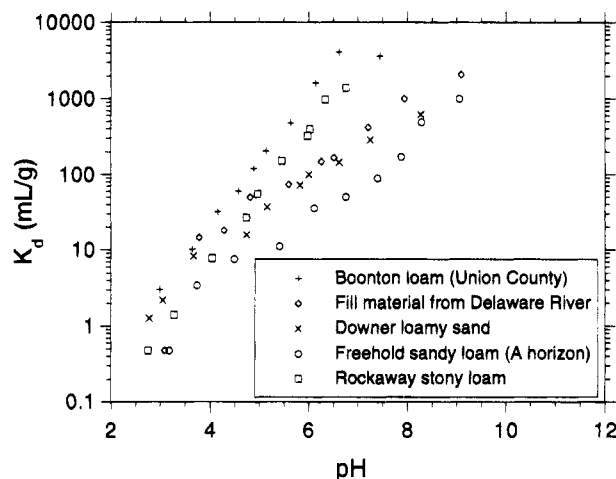

FIGURE 1. Partition coefficient (K_d) for the adsorption of 1×10^{-4} M initial cadmium concentration onto Boonton loam (Union Country), fill material dredged from the Delaware River, Downer loamy sand, Freehold sandy loam (A horizon), and Rockaway stony loam. Soil: water = 1 g/100 mL; I = 0.01 N $NaNO_3$; T = 25 °C.

Results and Discussion

Batch Equilibration. We determined the concentration of the added cadmium that remained in solution after the 24-h equilibration for each soil at each of the 10 pH values and at each of the three initial concentrations of cadmium. We assumed that the difference between the cadmium added and that remaining in solution at the end of the 24 h was sorbed to the soil. We converted these partitioning data to partition coefficients (K_d):

$$K_d = C_s / C_w \tag{1}$$

where C_s is the cadmium concentration in the soil (μg/g), and C_w is the concentration of cadmium in the solution (mg/L). The K_d values for 1×10^{-4} M initial cadmium concentration are shown in Figure 1. We used these sets of data to estimate the K_d values that would have been obtained for batch equilibration of samples at the same pH as in the column measurements. For these batch equilibration studies, we used low concentrations of suspended soil to minimize particle collisions so that the batch adsorption partition coefficients could be appropriately compared to those for the column measurements (6).

We compared our batch K_d values to the results for the large study of Anderson and Christensen (7), who obtained their partition coefficients at the pH of the soils and with low (0.7−12.6 μg/L) equilibrium solution concentrations of cadmium. The K_d values for our soils are comparable (Figure 2), even though our soluble cadmium concentrations are much greater. The strong dependency of partition coefficient on pH is shown in this figure.
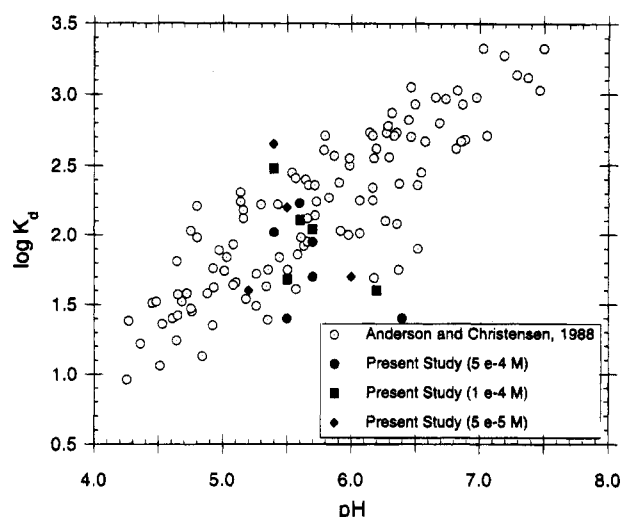
FIGURE 2. Cadmium partition coefficients on soil. Results for the present study are for batch equilibration at natural pH.

Column Desorption. Column desorption studies were carried out as a function of flow rate and initial cadmium concentration for the five New Jersey soils. An example of the two-phase curve that was found for desorbed concentration vs cumulative leaching volume is shown in Figure 3. The first phase is the portion with a steep decline in effluent concentration of cadmium (C_w) due to the flushing of the residual cadmium solution from pore water; the second phase has a slower decline in C_w due to desorption from the solids.

The rate of release of cadmium from the soil is dependent on transport and chemical processes. Sparks (8) stated that the effects of transport phenomena and chemical reactions are often experimentally inseparable. Apparent rate laws, including both chemical kinetics and transport-controlled processes, have usually been employed to treat these desorption data in dynamic systems. Skopp and Warrick (9) stated that the apparent rate depends on water flux or other physical processes and also usually that either first- or zero-order kinetics are operational. Zero-order (linear) and first-order (exponential) kinetics were used as two boundary conditions to treat the desorption part of our data:

linear

$$C_w = C_w^0 - (kV) \qquad (2)$$

exponential

$$C_w = C_w^0 \exp(-kV) \qquad (3)$$

where C_w is the concentration of desorbed cadmium (mg/L) at volume V (L), C_w^0 is the apparent concentration of desorbed cadmium (mg/L) at zero-volume (L), k is the rate coefficient (mg/L^2 for zero-order or 1/L for-first order), and V is the cumulative volume (L) that is proportional to time.

Results for the second phase are shown in Figure 4 for the Downer loamy sand that had been equilibrated with 5 × 10⁻⁴ M cadmium. For each flow rate, the data were extrapolated to zero cumulative volume (zero-time) using eq 2 or 3 as appropriate to obtain the zero-volume desorption concentration of cadmium (C_w^0) for the initial volume of water passed through the column. The value of
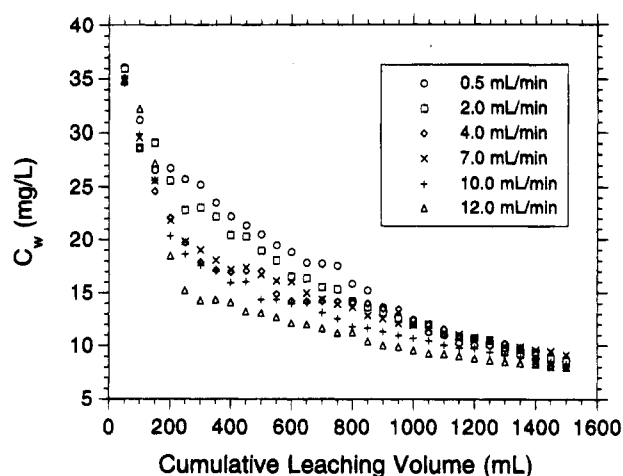

FIGURE 3. Concentration of cadmium in column effluent at six flows from Downer loamy sand equilibrated with 5 × 10⁻⁴ M initial cadmium concentration. Soil pH = 5.5; I = 0.01 N NaNO₃; T = 25 °C.

C_w^0 is a function of flow rate; as the flow rate increased, the concentration of desorbed cadmium decreased.

Because the first phase of flushing of the residual cadmium solution cannot be clearly distinguished from the second part of curve (Figure 3), we investigated the effect of the choice of the volume range of the second phase for the data analysis. Several initial volumes ranging from 300 to 600 mL were used as the starting point of the second part of the curve. The choice had only a slight effect on the value of C_w^0.

The zero-volume desorption concentrations of cadmium (C_w^0) were converted into apparent zero-volume partition coefficients (K_d^0) that are also a function of flow rate. The value of K_d^0 is determined by

$$K_d^0 = C_s / C_w^0 \qquad (4)$$

where C_s is the cadmium concentration in the soil (μg/g) as determined from the batch equilibrium, and C_w^0 is the zero-volume desorption concentration of cadmium (mg/L). K_d^0 (mL/g) represents the partitioning for the initial desorption of cadmium from the soil at a solution cadmium concentration that can be compared to that given by the adsorption equilibrium.

At the natural soil pH, less cadmium was desorbed from the lower initial concentration of cadmium than was desorbed from the higher initial concentration of cadmium. The lowest initial cadmium concentration had the highest adsorption capacity. Therefore, desorption should be more difficult for the lower initial cadmium concentration than the higher initial cadmium concentration. This behavior is attributed to variations in site-cadmium binding energies.

The apparent zero-volume partition coefficients were determined for the six different flows. The apparent zero-volume partition coefficients (K_d^0) increased with increasing flow velocity. The higher the K_d^0 value, the higher the amount of cadmium still bound by soil, because the higher flow velocity provided less contact time between the leaching solution and the soil, resulting in a lower desorption of cadmium for a given volume of eluent.

In the second step of extrapolation, the zero-volume apparent partition coefficients were then extrapolated to zero-flow rate to give a zero-volume, zero-flow rate partition coefficient (K_d^{0*}). This procedure is shown in Figure 5. This zero-flow condition matches the static conditions of batch studies.
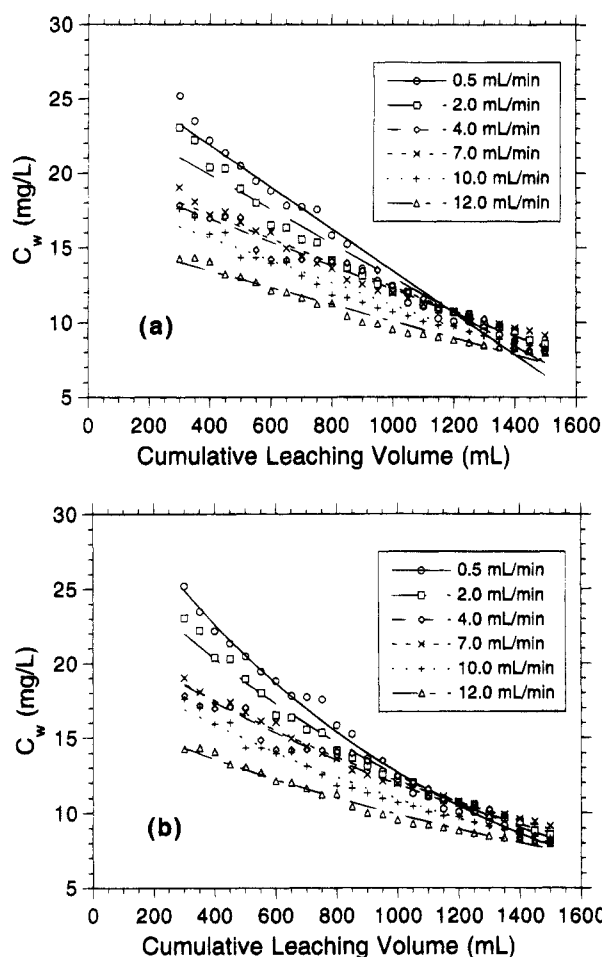
FIGURE 4. Extrapolation to zero cumulative leaching volume of the second part of the curves shown in Figure 3 for desorption of cadmium at six flows from Downer loamy sand that had been equilibrated with 5 × 10⁻⁴ M initial cadmium concentration using (a) linear extrapolation (zero-order kinetics) or (b) exponential extrapolation (first-order kinetics). Results are shown using 300-mL cumulative leaching volume as the starting point of the second part curve.
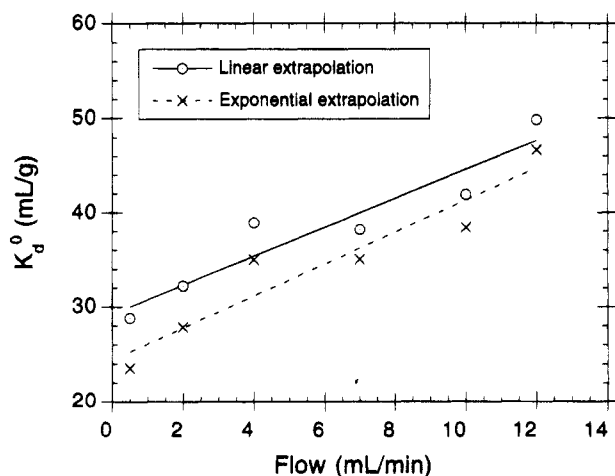

FIGURE 5. Dependence of zero-flow, apparent partition coefficients on flow. Results are for Downer loamy sand that had been equilibrated with 5 × 10⁻⁴ M initial cadmium concentration. Results are shown for both linear and exponential extrapolation from 300-mL cumulative leaching volume as the starting point of the second part curve.

The zero-volume, zero-flow rate desorption results (K_d^{0*}) were compared to those for the batch adsorption equilibrium at the same pH. A plot of the column
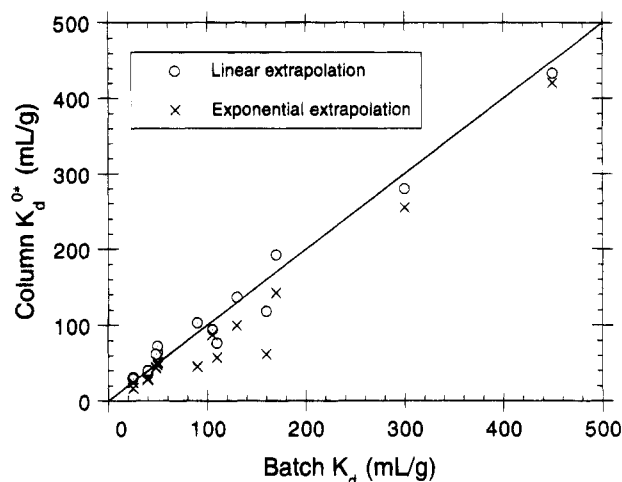

FIGURE 6. Relationship between the value of the batch partition coefficient and the zero-volume, zero-flow column partition coefficient for five soils equilibrated with three different cadmium concentrations. Line of equality is shown.

desorption versus batch partition coefficients is shown in Figure 6. The K_d^{0*} value for the linear extrapolation is always greater than that for the K_d^{0*} value from the exponential extrapolation. The slope for the linear relationship between the column desorption and batch equilibrium partition coefficients for linear (slope = 0.93) and exponential (slope = 0.90) extrapolations are both near unity. Therefore, the equilibrium obtained for batch adsorption provides a good estimate of the value obtained for desorption of the cadmium contaminant in the dynamic systems.

Summary and Conclusions

We have developed a procedure to determine partition coefficients of a contaminant on soil based on desorption under dynamic flow conditions. Contaminant desorption from a series of columns is determined as a function of the flow of water through the column. For each flow, the concentration is extrapolated, using either a linear or exponential extrapolation, to that for zero-flow to give a zero-flow concentration. This concentration is used to compute an apparent zero-volume partition coefficient. The apparent zero-volume partition coefficients are then plotted versus the water flow, and these data are extrapolated to zero-flow to give a zero-flow rate desorption partition coefficient. We determined the zero-volume, zero-flow rate desorption partition coefficients for five soils that had each been equilibrated with three different concentrations of cadmium. There is a linear relationship between the desorption partition coefficients and the corresponding adsorption coefficients. The slopes of the regression of column desorption on batch equilibrium partition coefficients are near unity for linear and exponential data extrapolation methods. We conclude that batch equilibrium partition coefficients provide good estimates of the values that could be obtained for desorption in dynamic systems.

Presently, column studies are periodically conducted to evaluate the potential for contaminant movement to groundwater, for example, in the registration of pesticides. These studies are very difficult and time-consuming. On the basis of the results of the present investigation, many such studies are conducted under inappropriate conditions and are interpreted erroneously due to the manner that

water flow is considered. If the much easier batch studies, done under the appropriate conditions, can provide results similar to those obtained from column studies done under the appropriate conditions and interpreted correctly, then the potential for significant time savings exists when conducting required environmental studies for chemical product development. The column studies are not necessary.

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