Empirical Models of Pb and Cd Partitioning Using Data from 13 Soils, Sediments, and Aquifer Materials

by

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FOREWORD

The Ecosystems Assessment Branch of the Ecosystems Research Division, National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency conducts research that is designed to meet the agency's needs in areas related to assessing the ecological health of diverse biological communities. As part of this mission, a significant amount of research is devoted to improving tools to assess low level, ecological exposures to toxicants of national concern.

Lead (Pb) and cadmium (Cd) are two of the most commonly found contaminants of concern at Superfund National Priorities List (NPL) sites. Because these contaminants are elements, they do not degrade and hence when present at elevated concentrations in soils, sediments and aquifer materials, may pose a risk to the biological community over geological time periods. The risk posed by an environmental toxicant is dependent upon its fate in the environment. Among the properties governing the environmental fate of a metal toxicant, the solid/water partition coefficient (K_d) is perhaps the most significant. Unfortunately, in common with many other toxicants existing as ions in aqueous solution, theoretical models for predicting K_ds for Pb and Cd that are applicable to all environmental systems do not exist. This document develops improved, default, empirical partitioning models for Pb and Cd that assist in achieving this objective.

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ABSTRACT

Lead (Pb) and cadmium (Cd) are two of the most common toxicants found in contaminated environments. Because solubilization of these metallic elements from the solid phase can influence their fate, transport and bioavailability, the partitioning coefficient (K_d) for these metals between environmental solids and natural waters is a key parameter needed for assessing the risks posed by these two elements when present in environmental solids at elevated concentrations.

In common with other ionizable contaminants, theoretical models applicable to all environments for assessing the partitioning behavior of Pb and Cd do not exist. Consequently, empirical partitioning models have been developed by the international technical research community. Using large datasets of Pb and Cd partitioning obtained from 13 aquifer materials, soils and sediments, two improved, commonly applicable, empirical models of extended accuracy and applicability were developed in this work:

$$\log_{10}K_{d,Pb} = -1.66596 + 0.54782*pH_{soln} - 0.0125584*sand + 0.585286*\log_{10}OC$$

$$(\text{adj. } r^2 = 0.757; SEE = 0.484; n = 432; P < 0.01)$$

$$\log_{10}K_{d,Cd} = -2.87671 + 0.495043*pH_{soln} - 0.00500349*sand + 0.55245*\log_{10}OC$$

$$(\text{adj. } r^2 = 0.780; SEE = 0.534; n = 676; P < 0.01)$$

where OC is the sediment organic carbon content in mg/Kg, sand is the % sand content of the sediment, adj. r^2 designates the r^2 value of the model adjusted for the degrees of freedom, and SEE represents the standard error of the estimate of the model.

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CHAPTER 1

INTRODUCTION

Lead (Pb) and cadmium (Cd) have been identified as contaminants of concern at 1,026 and 582 active Superfund sites, respectively, in the United States of America (U.S. EPA, 2004). Neither element is considered to be essential and when present at soil/sediment/aquifer solids concentrations in excess of guideline values, both elements are considered to pose an unacceptable risk to human health and the environment.

Current risk assessment methodologies consider numerous potential exposure pathways when evaluating the risks posed by environmental contaminants. Among these, direct aqueous exposure to aquatic biota and human exposures occurring through ingestion of contaminated drinking water are two significant pathways of concern (Salhotra et al., 1990; U.S. EPA, 1992; Hill et al., 1993). Hence, the environmental solids/water partitioning behavior of lead and cadmium is a key consideration in conducting exposure assessments at contaminated sites.

Porewater concentrations of dissolved Pb and Cd in soil/water systems can be limited by a variety of natural biogeochemical processes. For example, in porewaters with elevated sulfide ion concentration, aqueous Pb and Cd concentrations can be limited by the formation of galena (PbS) and greenockite (CdS) minerals. In porewaters without significant, reactive sulfide ion concentrations, aqueous Pb concentrations can be controlled by the precipitation of $Pb_5(PO_4)_3OH$ (pyromorphite), $Pb_4O(PO_4)_2$, $Pb_3(PO_4)_2$, $PbSO_4$ (anglesite), and $PbCO_3$ (cerrusite) phases (Nriagu, 1974; Santillan et al., 1975; Lindsay, 1979). Similarly, Cd porewater concentrations can be limited by the formation of $CdCO_3$ (otavite), $Cd_3(PO_4)_2$, and mixed hydroxy carbonate minerals (Santillan et al., 1975; Lindsay, 1979; Bank et al., 1989). At the lower porewater Pb and Cd concentrations more commonly encountered by the environmental research community, the solubilities of these two metals can be limited by both solid solution formation with background phases including oxide, phosphate and carbonate minerals, and by adsorptive phenomena with reactive, ionizable sites present on particulate organic carbon, aluminosilicates, and the oxide minerals of iron, manganese, aluminum and silicon.

Although there have been successful applications of both adsorptive and solid solution mechanistic models for describing the low-porewater-concentration pH-dependent partitioning behavior of metal contaminants with natural soils and sediments (e.g., Rai and Zachara, 1986; Loux et al., 1989; Smith et al., 1993), the lack of general, rigorous mechanistic models applicable to all environmental solids has prompted the development of numerous empirical models (Hassett, 1974; Gerritse and Van Driel, 1984; Christensen et al., 1989; Rai et al., 1986; Loux et al., 1990; Basta and Tabatai, 1992; Boekhold and Van Der Zee, 1992; U.S. EPA, 1999; Sauve et al., 2000; Tipping et al., 2003). Table 1 illustrates a number of the empirical models described in the technical literature. Generally speaking, empirical models have related the dependent variable metal K_d (partition coefficient) to the independent variables aqueous pH, sediment organic carbon content (LOI or loss on ignition is a surrogate for sediment organic carbon content) and sediment total metals content. Other work (U.S. EPA, 1996 and references cited within) also has demonstrated that metals tend to have a greater affinity for the smaller grained particulate matter contained within the sediments. Some of the r^2 values for the models listed in Table 1 appear to be quite impressive (i.e., $r^2 > 0.9$); however, it should be noted that these high r^2 value models appear to either be based on very limited datasets or result from a partial interpretation of the data with geochemical speciation models.

Table 1.   Literature-reported sediment/water partitioning models for Pb and Cd with diverse soils and sediments.

Relationship	Reference.
$\log_{10}(K_{d,Pb}) = 0.055*pH + 0.24$	($r^2 = 0.02$; n = 33 temperate soils) Gerritse and Van Driel (1984).
$\log_{10}(K_{d,Pb}) = 0.0768*pH + 1.55$	($r^2 = 0.17$; n = 146; 6 aquifer material samples) Loux et al. (1990).
$K_{d,Pb} = 1,639 - 902.4*pH + 150.4*pH^2$	($r^2 = 0.94$; n = 5 ?) Rhoades et al. (1992).
$\log_{10}(K_{d,Pb}) = 0.29287*pH + 0.37806$	(n = 5; 5 sandy sediments). Hassan et al. (1996).
$\log_{10}(K_{d,Pb}) = 0.60*\log_{10}(LOI) + 1.13*pH - 4.36$	($r^2 = 0.94$; n = 98 English soils). Tipping et al. (2003).
$\log_{10}(K_{d,Cd}) = 0.39*pH - 2.5$	($r^2 = 0.6$; n = 33 temperate soils). Gerritse and Van Driel (1984)
$\log_{10}(K_{d,Cd}) = 0.529*pH - 0.738$	($r^2 = 0.72$; n = 78 ; 21 Danish soils at three depths). Christiansen, (1989).
$\log_{10}(K_{d,Cd}) = 0.397*pH - 0.943$	($r^2 = 0.55$; n = 146; six aquifer materials). Loux et al. (1990).
$\log_{10}(K_{d,Cd}) = 0.29287*pH - 0.20276$	(n = 5; 5 sandy sediments). Hassan et al. (1996).
$\log_{10}(K_{d,Cd}) = 0.45*pH - 0.55$	($r^2 = 0.56$; n = 174). U.S EPA (1999)
$\log_{10}(K_{d,Cd}) = -0.23*\log_{10}(tot\ Cd) + 0.54*pH - 0.23$	($r^2 = 0.76$; n = 64 contaminated soils). Sauve et al. (2000).
$\log_{10}(K_{d,Cd}) = 0.71*\log_{10}(LOI^1) + 0.43*pH - 2.93$	($r^2 = 0.73$; n = 98 English soils) Tipping et al. (2003).

1-   LOI designates loss on ignition.

The empirical models listed in Table 1, while not necessarily accounting for all of the variables responsible for partitioning, nevertheless provide the most robust relationships currently available to the technical exposure assessment community. The present work was designed to expand the applicability of these empirical models through increasing the operational ranges of the more commonly encountered variables associated with metals partitioning .

CHAPTER 2

METHODS

2.1   Inductively Coupled Plasma Atomic Emission Analyses

Unless otherwise noted, all metals analyses in this work were performed using a Perkin Elmer Plasma II Inductively Coupled Plasma (ICP) Atomic Emission Spectrometer. Analyses were generally conducted as per the manufacturer's instructions. All ICP analyses were reported after averaging three emission intensity readings. In addition, QA/QC standards were placed after every fifth sample in the sample train, and analytical results of the preceding samples were discarded if the concentration of the subsequent QA standard deviated by more than 5% from the true value. Pb analyses were conducted using either the 220.353 nm or 216.999 nm emission lines. Cd analyses were conducted using the 214.435 emission line. The nebulizer was typically set at a flow rate of 1 mL/min and all Pb and Cd analyses were conducted using the Myers-Tracy scandium internal standard methodology (Myers and Tracy, 1983).

2.2   Aqueous pH Measurements

Because soluble phase pH has been identified as a master variable associated with metals partitioning on natural soils and sediments, great care was taken in making the pH measurements in this study. Generally speaking, pH meters (and electrodes) were calibrated with commercially available pH buffers before and after pH determinations were made on each set of samples.   All pH measurements were performed using commercially available pH meters and an Orion Ross[R] high flow pH electrode. Previous experience indicated that the Ross pH electrode displays superior stability in low ionic strength media.   The accuracy of pH measurements using our procedure is generally considered to be within the range of 0.05 to 0.10 pH units (APHA, AWWA, and WEF, 1995).

2.3   Sediment/Aquifer Material Samples

The seven aquifer material samples used in this study were obtained from Florida, New Jersey, Oregon, Texas, Utah, Wisconsin and Georgia. Paired aquifer material/groundwater samples were collected and stored at 4°C until used in this work. The EPA soil/sediment samples 1, 7, 9, 13, 17 and 18 used in this study were described by Means et al. (1978). These samples were air-dried, sieved through a 2 mm mesh and stored in closed containers at room temperature until use. A summary of the properties of the aquifer material/sediment/soil samples is given in Table 2.

Table 2.   Physical/chemical properties of aquifer material/soil/sediment samples used in the study.

Site	OC[1] mg/kg	pHsed[2]	extCa[3] mg/kg	extMg[3] mg/kg	extFe[4] mg/kg	extMn[4] mg/kg	extAl[4] mg/kg
TX	200	6.16	31000	152	64	19.8	66.9
UT	1340	7.58	15300	1847	688	63.8	339
FL	8350	5.94	12.4	9.14	70.9	0.52	106
NJ	11100	6.01	73.4	0.01	1690	48.2	317
OR	1620	7.81	8330	1610	6070	657	662
WI	810	7.54	492	213	130	15.2	14.5
EPA1	2200	7.30	2410	193	665	37	98
EPA7	20900	8.34	5200	1477	3010	582	827
EPA9	1100	8.55	14500	2405	589	151	342
EPA13	30400	6.74	1100	295	334	331	779
EPA17	8900	7.21	1270	180	4010	1000	1530
EPA18	6600	7.79	2710	676	4810	842	1460
GA	700	5.8	57.4	46.8	645	278	610

Table 2.　　　　(continued).

Site	ext P[5] mg/kg	CEC[6] cM/kg	Sand[7] %	Silt[7] %	Clay[7] %	AVS[8] mg/kg
TX	5.3	2.6	79.6	13.8	6.6	0.012
UT	4.5	10.5	21.2	33.8	45	3.58
FL	15.2	11.7	90.3	1.6	8.1	0.002
NJ	9	9.8	34.6	14.4	51	0.013
OR	5.5	88.9	40.6	28.9	30.5	0.007
WI	6.4	7.10	99.3	0.6	0.1	0.004
EPA1	13.5	1.07	93.9	6.1	0	
EPA7	225	19.6	12.8	29.1	58	
EPA9	21.7	12.4	7.1	17.4	75.6	
EPA13	5.8	11.9	20.3	52.6	27.1	
EPA17	477	10.6	18.1	35.7	46.2	
EPA18	36.5	15.4	34.6	39.5	25.8	
GA	3.6	2.3	70	22	8	

1- OC analyses for aquifer materials performed courtesy of Dr. Everett Jenne, Battelle Laboratories, Pacific Northwest; OC analyses for EPA sediments reported in Means et al. (1978).

2- Sediment pH = groundwater pH for aquifer materials; sediment pH (1:2) for EPA sediments given by Means et al. (1978).

3- Extractable Ca and Mg represents the extractable Ca and Mg at pH = 4.5; analyses performed by the authors.

4- Extractable Fe, Mn and Al determined using the method of Jenne and Crecelius (1988) (1 hr extraction at 50 $^{\circ}$C with a 0.25 $\underline{M}$ NH_2OH/HCl solution).

5- Extractable P determined using the method of Burke et al. (1989) (0.001 $\underline{M}$ H_2SO_4).

6,7- Cation Exchange Capacity and size distribution determinations on aquifer material samples performed by Dr. Kim Tan, University of Georgia (ammonium acetate CEC method); EPA sediment CEC and size distribution values reported by Means et al. (1978). cM/kg designates centimoles per kilogram.

8- Acid Volatile Sulfides determined by the distillation method of U.S. EPA (1969).

The study aquifer material, soil and sediment samples were generally from uncontaminated sites. Nitric/perchloric acid extractions of all our study solid samples (except for the Georgia aquifer material sample) yielded undetectable quantities of both extractable Pb (ICP method limit of detection = 7.8 mg/kg) and Cd (ICP method limit of detection = 0.93 mg/kg). Hence "background" concentrations of Pb and Cd were ignored in calculating the subsequent experimentally determined K_d values.

2.4   Equipment and Stock Solutions for Lead Partitioning Studies

Lead partitioning was conducted using 50-mL teflon centrifuge tubes cleaned by soaking for 24 hours in 5% nitric acid solution and rinsed several times with deionized water prior to use. Stock Pb solutions (1000 mg/L) were prepared by dissolving 1.6 g of analytical reagent grade $Pb(NO_3)_2$ in 1 L of deionized water; 2 drops of 5% nitric acid solution were added to stabilize each stock solution. Lead concentrations in the stock solution were verified by comparison with commercial standards for atomic absorption/inductively coupled plasma spectroscopy. A 1:10 dilution of the 1000 mg/L stock solution with distilled-deionized water produced the 100 mg/L Pb solutions used in some portions of the study.

2.5   Lead Partitioning Procedures with air-dried EPA Sediments

Three grams each of the air-dried EPA sediment/soil samples were hydrated with 15 mL of distilled-deionized water for 48 hours in 50-mL-capacity teflon centrifuge tubes held at 4 °C (samples were stored in darkness and were "vortexed" initially and after 24 hours of storage). Subsequently, fifteen mL of distilled-deionized water acidified with measured quantities of Ultrex[R] grade nitric acid were added to each sample. Lastly, sequential volumes of 100 or 1000 mg/L Pb^{2+} were added to each sample to produce the desired initial Pb concentration. Samples were "vortexed", equilibrated for 24 hours at 20-25 °C in darkness and again "vortexed" and equilibrated for an additional 24 hours. After equilibration, samples were centrifuged at 10000 relative centrifugal force for 46 minutes; this procedure is designed to remove from solution all particles with a radius greater than 50 nm and a density equal to or greater than 2.5 g/cm^3. Approximately three 10-mL aliquots were decanted from each sample-- one was analyzed for pH, one was acidified and analyzed via inductively coupled plasma spectroscopy, and the last aliquot was saved in the event dilutions were necessary.

2.6   Lead Partitioning Procedures with Aquifer Material Samples

Five grams each of groundwater-saturated aquifer material were placed in the 50 mL teflon centrifuge tubes. 30 mL of the groundwater collected at the same time and location as the aquifer material samples was acidified with measured sequential volumes of Ultrex[R] grade nitric acid and added to each sample. Subsequently, measured sequential volumes of 100 or 1000 mg/L stock Pb solution were added to each sample to reach the desired initial Pb concentration. Samples were equilibrated for 48 hours and analyzed via the methods described previously.

2.7   Equipment and Stock Solutions for Cadmium Partitioning Studies

The Cd partitioning work was performed using 50-mL teflon centrifuge tubes that were cleaned by soaking for 24 hours in a 5% nitric acid solution and rinsed four times with deionized water prior to use. Stock solutions of Cd (1000 mg/L) were prepared by dissolving analytical reagent grade $Cd(NO_3)_2$ in deionized water; 0.1mL of a 0.5% nitric acid solution was added to stabilize the solutions. Commercially prepared Cd standard solutions were used to verify stock solution concentrations.

2.8   Cadmium Partitioning with air-dried EPA Sediments

Three grams of air-dried EPA sediments were hydrated with 15 mL of distilled-deionized water for 48 hours. As with the lead studies, samples were refrigerated at 4°C in darkness and vortexed at 0 and 24 hours. After hydration, an additional 15 mL of distilled-deionized water acidified by the addition of metals grade nitric acid was added to each sample to obtain the desired pH. Measured, sequential volumes of the 1000 mg/L Cd^{2+} stock solution were then added to each sample to produce the desired initial Cd concentration. Centrifuge tube caps were loosened to permit exchange of atmospheric gases. Samples were "vortexed", placed in darkness for 24 hours at room temperature (20-25 °C), "vortexed" again and equilibrated for an additional 24 hours. Samples were centrifuged at 10000 relative centrifugal force for 46 minutes and three aliquots were obtained from each sample and analyzed as described previously.

2.9   Cadmium Partitioning with Aquifer Material Samples

Five grams of groundwater-saturated aquifer material were placed in the precleaned teflon centrifuge tubes. Due to limited quantities of groundwater, the Florida, Wisconsin, Texas and Utah groundwater samples were mixed 50:50 with distilled-deionized water and allowed to equilibrate for at least one week prior to being added to the aquifer material. Subsequently, 25 mL of the groundwater solution acidified with measured, sequential volumes of metals grade nitric acid were added to the centrifuge tubes. Measured sequential volumes of the 1000 mg/L stock Cd solution were then added to each sample to reach the desired initial Cd concentration. Samples were equilibrated for 48 hours at room temperature, centrifuged, and analyzed using the methods described in the previous section.

2.10   Regression Analysis of Data

All regression analyses were performed using Statgraphics Plus Version 5.1[R] (Manugistics, 2001). Models were developed by first generating simple least squares analyses between $\log_{10}K_d$ values for Pb and Cd with sediment/system properties. Sediment/system properties yielding adjusted r^2 values in excess of 5% were then used to create multiple regression expressions. Because some of the sediment/system properties were collinear, variables were deleted from the more complex equations if the variable probability was not significant at the 90th percentile in a previous run. Lastly, simpler expressions also were generated for both the purpose of comparing our results with earlier models and to provide exposure assessors the ability to estimate metal K_d values using commonly available sediment properties.

As will be demonstrated in the results section, the high initial solution phase Pb concentration partitioning results with the Utah aquifer material samples could plausibly be interpreted within the context of a possible precipitation of solid phase $PbSO_4$. Because the second pK for bisulfate is well below the typical pH conditions examined in this work, the precipitation of $PbSO_4$ is unlikely to be pH-dependent (at least within the conditions of this study) and consequently the high initial Pb concentration data obtained with the Utah aquifer material was not included in the regression analyses. Finally, unlike the procedure utilized by Loux et al. (1990), K_ds were calculated from data only when the final equilibrated porewater dissolved metal concentrations were above the ICP method detection limit.

CHAPTER 3

RESULTS

3.1   Lead Partitioning

Figures 1a through 1l display the raw Pb partitioning data (i.e., percent Pb remaining in solution as a function of pH) obtained with six aquifer materials and six EPA sediments. Inset numbers designate initial soluble lead concentrations. The individual points in these figures represent experimental data and the lines are "eyeball" and/or cubic spline fits to the data; the lines were added to assist the reader. Although error bars are not depicted in these figures, the pH values should be considered to be within $\pm$ 0.1 pH units and the percent remaining in solution values should be considered to be the depicted value $\pm$ 5 percent. Three major points can be easily discerned from figures 1a-1l: 1) pH has a major influence on lead partitioning to natural soils/sediments, 2) the nature of the solid phase has a major impact on lead-sediment/soil pH-dependent partitioning, and 3) with the exception of the Utah aquifer material sample, virtually all of the other solid phases displayed an increased affinity for Pb as initial Pb solution concentration decreased. This third observation supports the contention that binding sites of variable energies exist in natural soils and sediments, and that the highest energy sites are the first to sequester lead.

Table 3 depicts the results from geochemical speciation model simulations (MINTEQA2; Allison et al., 1990) of the high initial lead solution concentration data obtained with the Utah groundwater/aquifer material. Using either the Davies or extended Debye-Huckel activity coefficient algorithms, these simulated results suggest that $PbSO_4$ was supersaturated under the high initial Pb solution concentration conditions (i.e., the simulated Ion Activity Product [IAP] was greater than the literature-reported solubility product). Hence, the inconsistent excess removal of Pb from solution with the high initial lead solution concentration samples is believed to have resulted from $PbSO_4$ precipitation. The relative pH independency of the low-pH, high initial lead solution concentration data also indirectly supports this hypothesis. Because of this presumptive $PbSO_4$ precipitation, these data were excluded from the subsequent regression analyses.

3.2   Cadmium Partitioning

Figures 2a through 2l display the raw Cd partitioning results (as with the Pb data, these results are presented as percent Cd remaining in solution as a function of pH). Because there were insufficient quantities of the paired Utah aquifer material/groundwater samples to conduct Cd partitioning work, paired aquifer material/groundwater samples obtained in Georgia were used instead. As with the Pb results displayed in figures 1a - 1l, the nature of the soil/sediment had a major impact on partitioning results. Also as with the Pb results, the lowest initial Cd solution concentrations generally displayed the greatest affinity for the solids. Compared with the Pb partitioning results, Cd does appear to have a lesser affinity for these test aquifer materials, soils and sediments.

3.3   Empirical Partitioning Models

Table 4 illustrates the adjusted r^2 values obtained between $\log_{10}K_{d,Pb}$ and the various sediment system properties given in Table 2. Generally speaking, the following adjusted r^2 values between $\log_{10}K_{d,Pb}$ and system properties exceeded 5 percent: percent sand, pH_{soln}, $\log_{10}Al$, $\log_{10}P$, $\log_{10}Fe$, $\log_{10}Mn$, and $\log_{10}OC$. Because percent sand, percent silt and percent clay sum to 100 percent, these variables are collinear and for this reason, only one is used in the subsequent statistical analyses.
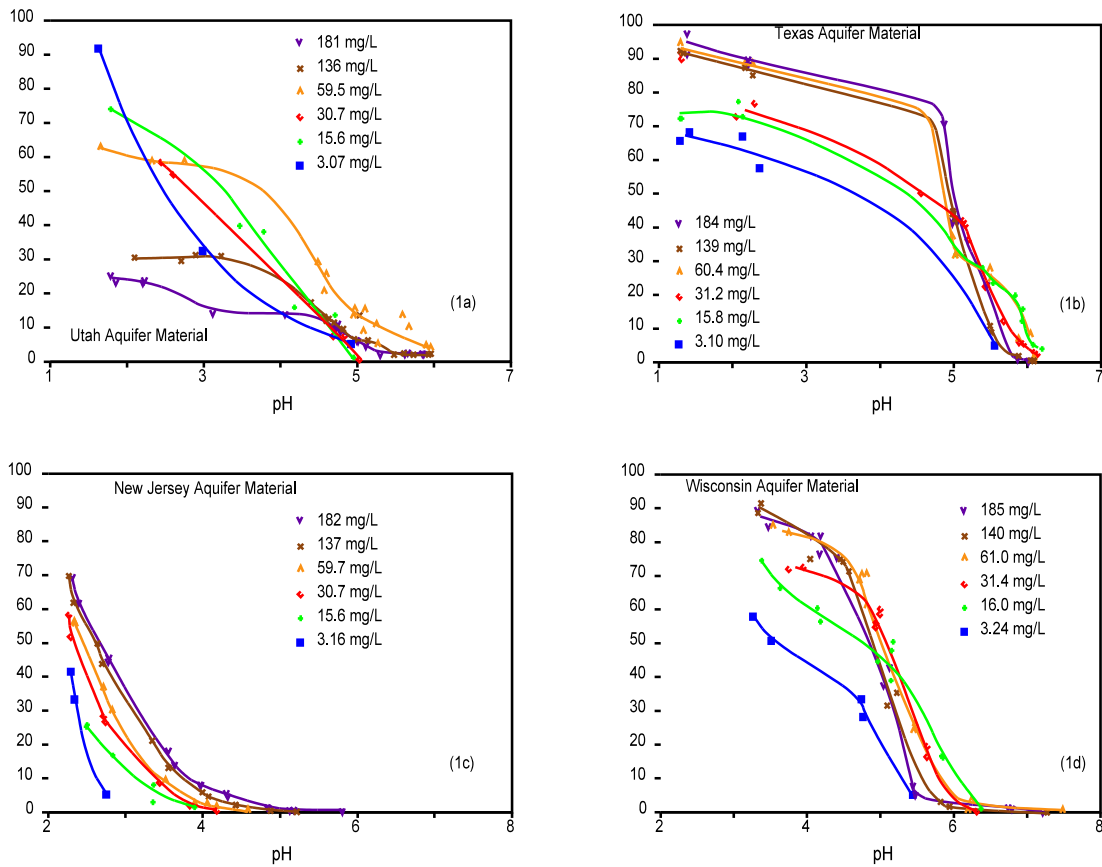
Figures 1a-1d. Percent lead remaining in solution as a function of pH obtained with aquifer materials from Utah (a), Texas (b), New Jersey (c) and Wisconsin (d). Inset numbers depict initial Pb concentrations. Note that although error bars are not given in these figures, the error bars for the pH measurement technique is approximately ± 0.1 pH units and error bars for Pb concentrations represent ± 5% of the measured values.
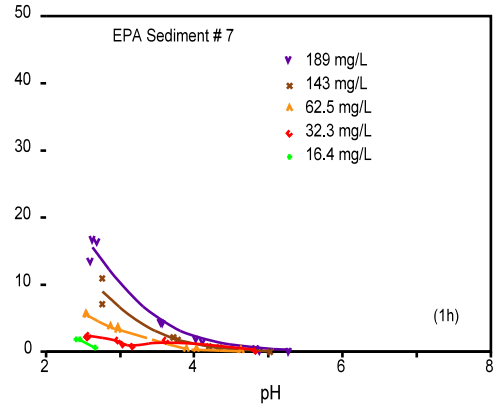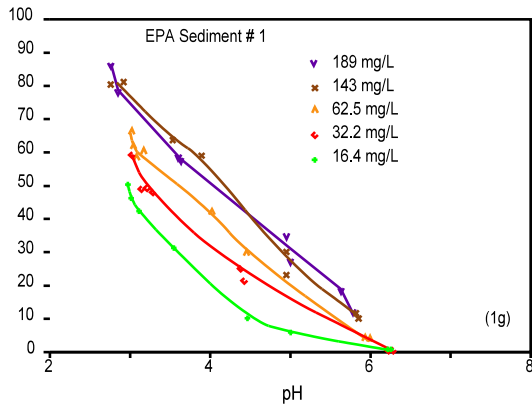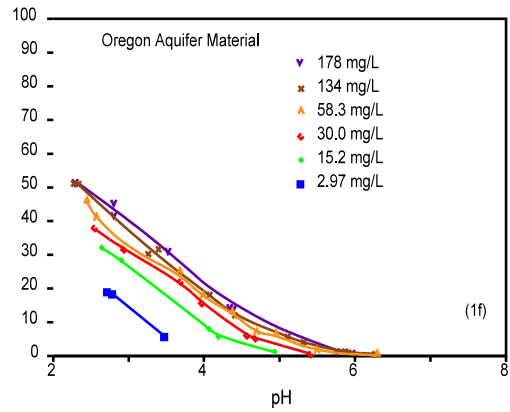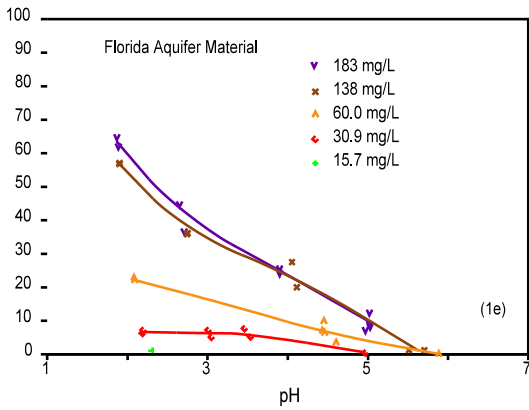
Figures 1e-1h.   Percent lead remaining in solution as a function of pH obtained with aquifer materials from Florida (e) and Oregon (f) and with EPA sediments 1 (g) and 7 (h). Inset numbers depict initial lead concentrations. pH measurements are within ± 0.1 pH units and lead concentrations are within ± 5% of the measured values.
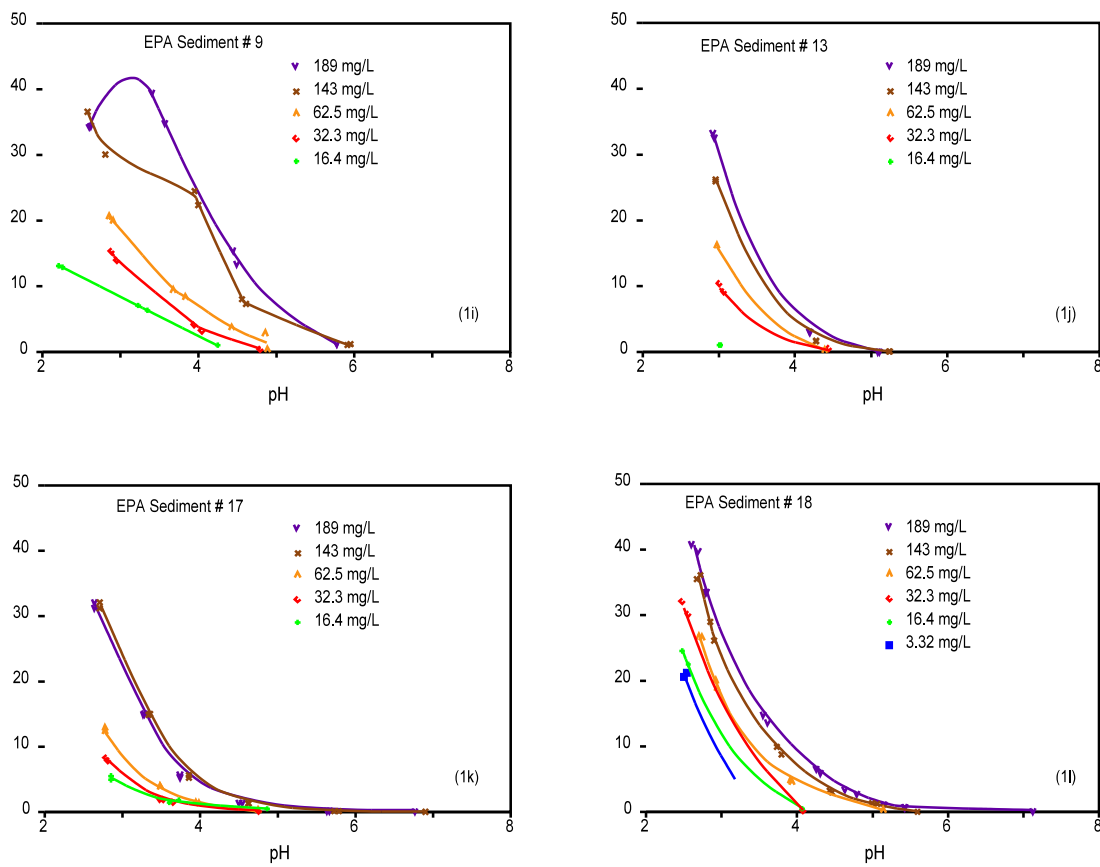
Figures 1i-1l. Percent lead remaining in solution as a function of pH obtained with EPA sediments 9 (i), 13 (j), 17 (k) and 18 (l). Inset numbers depict initial lead concentrations. pH measurements are within ± 0.1 pH units and lead concentrations are within ± 5% of the measured value.
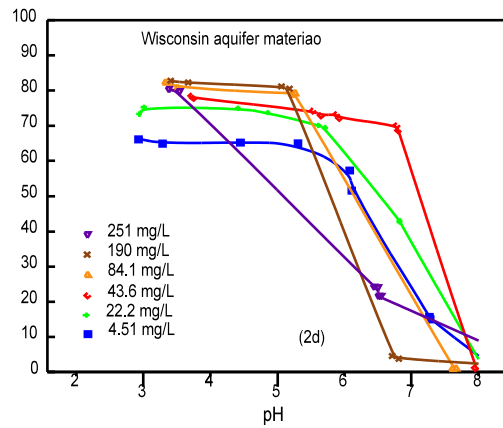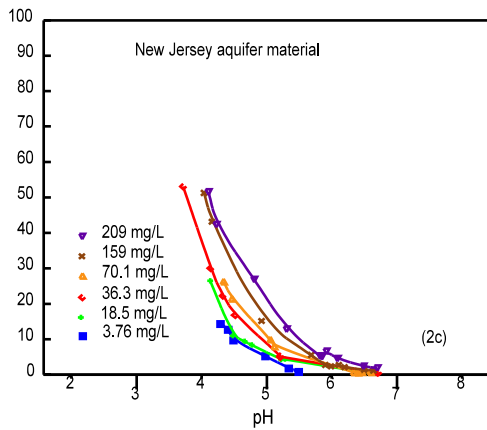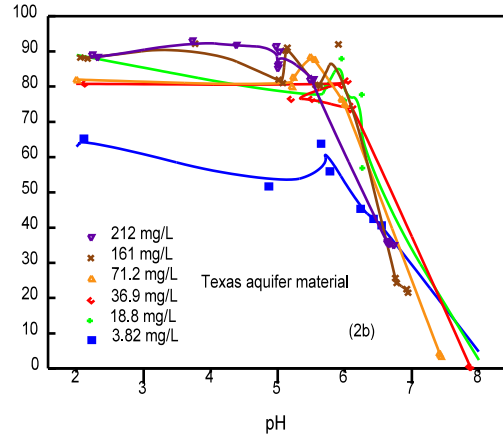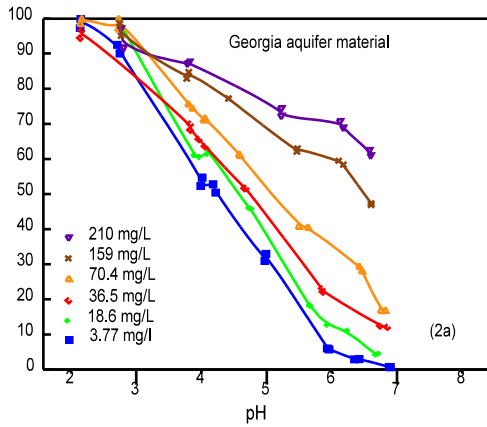
Figures 2a-2d.   Percent cadmium remaining in solution as a function of pH obtained with aquifer materials from Georgia (a), Texas (b), New Jersey (c) and Wisconsin (d). Inset numbers depict initial cadmium concentrations. pH measurements are within ± 0.1 pH units and dissolved cadmium concentrations are within ± 5% of the measured value.
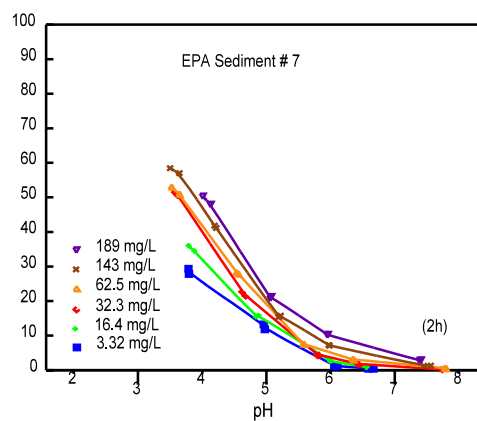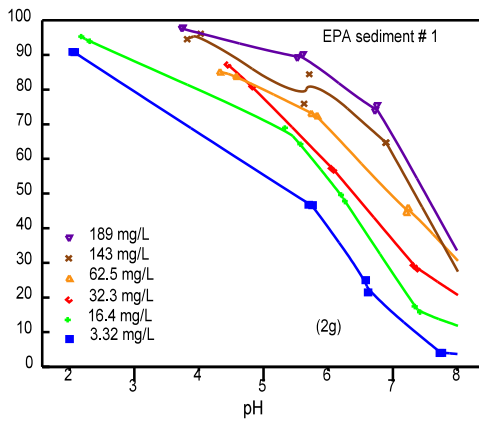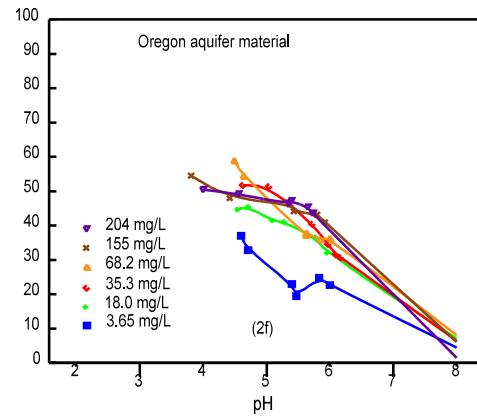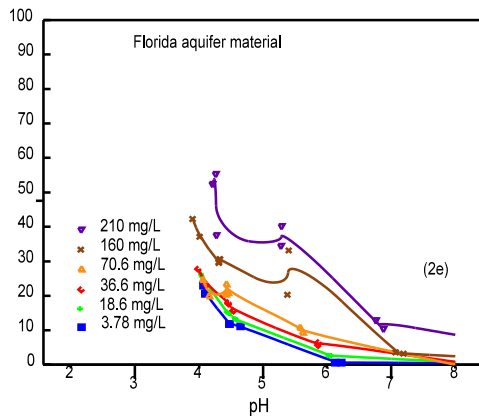
Figures 2e-2h.   Percent cadmium remaining in solution as a function of pH obtained with aquifer materials from Florida (e) and Oregon (f) and with EPA sediments 1 (g) and 7 (h). Inset numbers depict initial cadmium concentrations. pH measurements are within $\pm$ 0.1 pH units and dissolved cadmium concentrations are within $\pm$ 5% of the measured value.
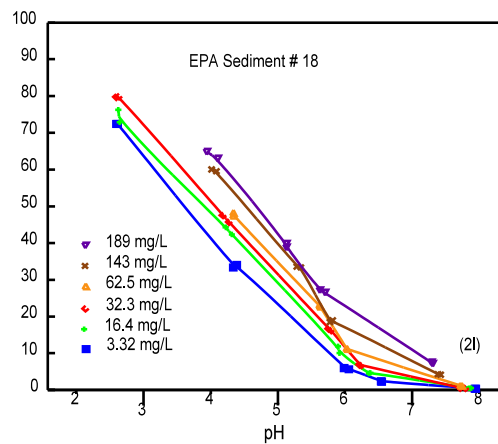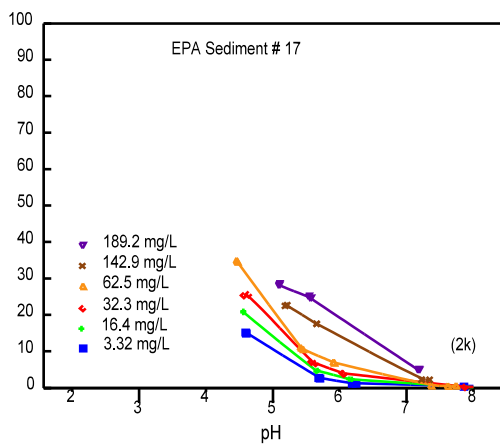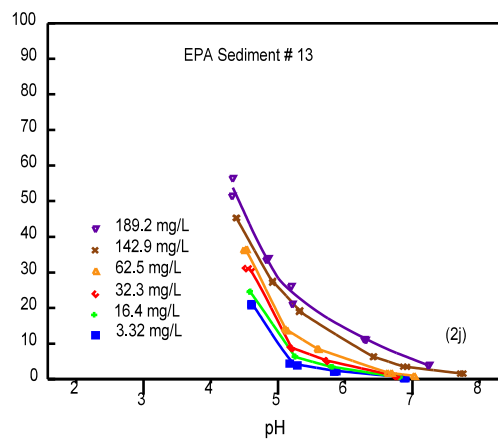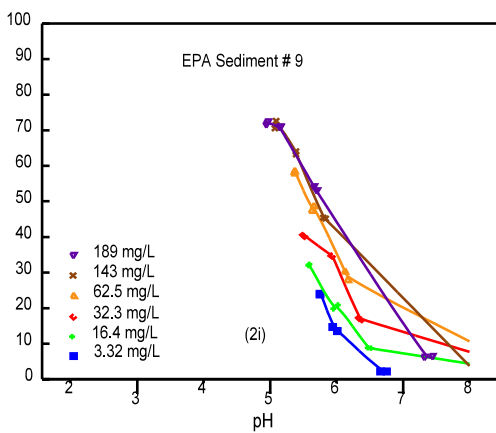
Figures 2i-2l. Percent cadmium remaining in solution as a function of pH obtained with EPA sediments 9 (i), 13 (j), 17 (k) and 18 (l). Inset numbers depict initial cadmium concentrations. pH measurements are within ± 0.1 pH units and dissolved cadmium concentrations are within ± 5% of the measured value.

Table 3.   Geochemical interpretation of high initial Pb concentration
partitioning data for the Utah aquifer material/groundwater
samples (unless otherwise designated, all concentrations
in units of molarity).

Given:

pH = 3.0 (fixed activity) $[Pb]_{total} = 6.564 \times 10^{-4}$
Temp. = 25 °C $[Pb]_{dissolved} = 2.037 \times 10^{-4}$

$[Na]_{total} = 1.756 \times 10^{-1}$ $[Cl]_{total} = 1.461 \times 10^{-1}$
$[Ca]_{total} = 1.180 \times 10^{-3}$ $[Mg]_{total} = 1.560 \times 10^{-3}$
$[K]_{total} = 4.420 \times 10^{-3}$ $[SO_4]_{total} = 1.856 \times 10^{-2}$

$pCO_2 = 3.5E-4$ atm.

$$a_X = [X] * \gamma_X$$

$$-\log_{10}(IAP) = -\log_{10}(a_{Pb(2+)} * a_{SO4(2-)})$$

MINTEQA2 (Allison et al., 1990) simulated results:

Computed Ionic Strength = 0.196 $\underline{M}$

Computed difference in charge balance = 1.5 %

$\gamma_{Pb2+} = \gamma_{SO42-} = 0.2948$ (Davies extension)
$\gamma_{Pb2+} = 0.2946$ (Extended Debye-Huckel)
$\gamma_{SO42-} = 0.2633$ (Extended Debye-Huckel)

Therefore:

$$-\log_{10}(IAP_{PbSO4}) = 7.18 \text{ to } 7.20$$

$$pK_{sp,PbSO4,literature} = 7.79 \text{ (MINTEQA2, Smith and Martell, 1976)}$$

Table 4. Adjusted r^2 values (in percentages) for 1 parameter least squares analyses between $\log_{10}K_{d,Pb}$ and sediment/system properties (n = 432).

Property	Adj. r^2	Property	Adj. r^2
ext Al	18.9	$\log_{10}Al$	27.4
ext Ca	6.06	$\log_{10}Ca$	0.33
ext Fe	14.2	$\log_{10}Fe$	21.1
ext Mg	4.08	$\log_{10}Mg$	0.00
ext Mn	15.1	$\log_{10}Mn$	17.3
ext P	12.0	$\log_{10}P$	17.5
OC	18.5	$\log_{10}OC$	23.2
Pb_{tot}[1]	0.64	$\log_{10}Pb_{tot.}$[1]	1.45
CEC	1.61		
clay	19.0		
sand	24.7		
silt	16.6		
pH_{sed}	4.61		
pH_{soln}	25.9		

1- Total metals concentrations were normalized to mg/kg.

Two other observations are apparent in Table 4: a) neither Pb_{total} nor $log_{10}Pb_{total}$ yield adjusted r^2 values in excess of 5 percent, and b) log_{10} transformation of the extractable Al, P, Fe, and Mn variables improved the adjusted r^2 values for the relationships between system properties and $log_{10}K_{d,Pb}$.

Table 5 presents the various empirical models developed during the study to account for the 432 Pb partitioning data points displayed in Figures 1a-1l. Equation (1), relating $log_{10}K_{d,Pb}$ to pH_{soln}, $log_{10}Al$, $log_{10}P$, $log_{10}Fe$, $log_{10}Mn$, $log_{10}OC$ and percent sand, yielded an adjusted r^2 value of 79.4 percent. This is the "best" empirical model developed for Pb in the study. However, as noted in Appendix A, the P value for the $log_{10}P$ variable exceeds 10 percent. Hence this variable was removed to generate equation (2) in Table 5. Note that both the adjusted r^2 values and standard errors of the estimate (SEE) for both models (1) and (2) are identical. Note also that both models (1) and (2) are significant at the 99th percentile. Equations (3-5) were developed for use by exposure assessors with limited available datasets. Decreasing the number of "independent" variables in these models results in a degradation of both the model adjusted r^2 values and the standard errors of the estimate (although not severely).

Tables 6 and 7 illustrate a similar analysis performed on the Cd data depicted in Figures 2a-2l. From Table 6, in contrast to the Pb data, the adjusted r^2 for simple models between $log_{10}K_{d,Cd}$ and sediment system properties exceeded 5 percent only for the variables pH_{soln}, $log_{10}OC$, $log_{10}Fe$, $log_{10}P$, percent clay and percent sand content. Again, because percent sand and percent clay are collinear, only one of these two variable was exclusively used to develop Equations (1) and (2) in Table 7. However, the P values for the $log_{10}P$ and $log_{10}Fe$ variables used in Equations (1) and (2) exceeded 10 percent (see detailed statistics in Appendix B), hence these two variables were removed to develop Equations (3) and (4). Note the minimal impact of removing these variables on model adjusted r^2 and SEE values. Lastly, to enable a comparison between the present findings and those reported in the literature, a simple $log_{10}K_{d,Cd}$ vs. pH relationship was developed as Equation (5) in Table 7.

CHAPTER 4

DISCUSSION

The relatively high adjusted r^2 values associated with our "best" models depicted in Tables 5 and 7 are somewhat surprising in light of the fact that the partitioning results were obtained using a variety of soils/sediments/aquifer materials subjected to different collection, preservation and equilibration procedures. This observation suggests that these empirical models do have a considerable degree of robustness.

Our findings both agree and disagree with the technical literature. For example, the y-axes intercepts for the simple pH models document that Pb has a significantly greater affinity for soils and sediments than does cadmium. Secondly, solution pH and sediment organic carbon content both appear to impact Pb and Cd partitioning behavior. However, adding a pH^2 term to the regression equations did not greatly improve Pb partitioning model adjusted r^2 values (Table 5). Similarly, neither total metal nor log_{10}(total metal) variables greatly improved the empirical partitioning models.

The technical literature suggests that labile phosphorus may play a role in Pb partitioning (Nriagu, 1974; Hassett, 1974; Lindsay, 1979)). At first glance, our findings suggest that $log_{10}P$ can be a significant variable in the regression equations. However, subsequent analyses led to

Table 5. Regression equations relating $\log_{10}K_{d,Pb}$ to various sediment/system properties.

_____

1- $\log_{10}K_{d,Pb}$ = -0.670728 + 0.776537*$\log_{10}$Al - 0.455826*$\log_{10}$Fe + 0.117675*$\log_{10}$Mn + 0.607061*$\log_{10}$OC + 0.0000416702*$\log_{10}$P - 0.00518428*sand + 0.561895*pH_{soln}

(adj. r^2 = 0.794; SEE^1 = 0.446, P < 0.01)

2- $\log_{10}K_{d,Pb}$ = -0.670967 + 0.776562*$\log_{10}$Al - 0.455873*$\log_{10}$Fe + 0.117702*$\log_{10}$Mn + 0.607089*$\log_{10}$OC - 0.00518412*sand + 0.561896*pH_{soln}

(adj. r^2 = 0.794; SEE = 0.446, P < 0.01)

3- $\log_{10}K_{d,Pb}$ = -1.66596 + 0.54782*pH_{soln} - 0.0125584*sand + 0.585286*$\log_{10}$OC

(adj. r^2 = 0.757; SEE = 0.484, P < 0.01)

4- $\log_{10}K_{d,Pb}$ = 0.821913 - 0.0194336*sand + 0.50909*pH_{soln}

(adj. r^2 = 0.646; SEE = 0.585, P < 0.01)

5- $\log_{10}K_{d,Pb}$ = -3.27603 + 0.909033*$\log_{10}$OC + 0.520959*pH_{soln}

(adj. r^2 = 0.645; SEE = 0.586, P < 0.01)

6- $\log_{10}K_{d,Pb}$ = -0.903834 + 1.09284*pH_{soln} - 0.0887548*pH_{soln}^2

(adj. r^2 = 0.277; SEE = 0.836, P < 0.01)

7- $\log_{10}K_{d,Pb}$ = 0.302684 + 0.401918*pH_{soln}
(adj. r^2 = 0.259; SEE = 0.847, P < 0.01)

_____

1- SEE designates standard error of the estimate.

Table 6. Adjusted r^2 values (in percentages) for 1 parameter least squares analyses between $\log_{10}K_{d,Cd}$ and sediment/system properties (n = 676)

Property	Adjusted R-Squared	Property	Adjusted R-Squared
ext Al	3.07	$\log_{10}Al$	2.59
ext Ca	4.88	$\log_{10}Ca$	0.43
ext Fe	6.81	$\log_{10}Fe$	5.13
ext Mg	1.58	$\log_{10}Mg$	0.15
ext Mn	2.02	$\log_{10}Mn$	0.06
ext P	4.05	$\log_{10}P$	7.57
OC	9.31	$\log_{10}OC$	18.3
Cd_{tot}	0.62	$\log_{10}Cd_{tot}$	0.98
CEC	3.54		
% clay	7.80		
% sand	7.10		
% silt	1.93		
pH_{sed}	2.08		
pH_{soln}	60.7		

Table 7.   Regression equations relating $\log_{10}K_{d,Cd}$ to various sediment/system properties.

_____

1) $\log_{10}K_{d,Cd}$ = -2.72079 + 0.57592*$\log_{10}$OC - 0.00594147*sand +
     0.495213*pH_{soln} - 0.0383169*$\log_{10}$P - 0.0495951*$\log_{10}$Fe

(adj. r^2 = 0.780; SEE = 0.534, P < 0.01)

2) $\log_{10}K_{d,Cd}$ = -3.45769 + 0.491611*pH_{soln} + 0.00697647*clay +
     0.589151*$\log_{10}$OC + 0.0375007*$\log_{10}$Fe - 0.0678679*$\log_{10}$P

(adj. r^2 = 0.781; SEE = 0.532, P < 0.01)

3) $\log_{10}K_{d,Cd}$ = -2.87671 + 0.495043*pH_{soln} - 0.00500349*sand +
     0.55245*$\log_{10}$OC

(adj. r^2 = 0.780; SEE = 0.534, P < 0.01)

4) $\log_{10}K_{d,Cd}$ = -3.38864 + 0.489278*pH_{soln} + 0.00665484*clay +
     0.583745*$\log_{10}$OC

(adj. r^2 = 0.781; SEE = 0.534, P < 0.01)

5) $\log_{10}K_{d,Cd}$ = -1.24069 + 0.497497*pH_{soln}

(adj. r^2 = 0.608; SEE = 0.714, P < 0.01)

_____

this variable being removed from the equations. This finding suggests that the $\log_{10}P$ variable was probably collinear with one or more of the other significant variables. Given that both $\log_{10}P$ and $\log_{10}Al$ were significantly related to Pb partitioning and only $\log_{10}P$ was significantly related to Cd partitioning, this could be interpreted within the context of possible plumbogummite mineral $(PbAl_3(PO_4)_2(OH)_5-H_2O)$ formation with the Pb partitioning data.

As indicated previously, the high initial soluble Pb concentration partitioning data with the Utah aquifer material/groundwater samples was consistent with a $PbSO_4$ precipitation mechanism (the Utah groundwater was apparently in contact with the Great Salt Lake and had a relatively high sulfate content) . Conversely, sediment organic carbon content appeared to be more heavily involved in the loss of Cd from solution than in Pb partitioning. The role of organic carbon in cadmium partitioning has been discussed elsewhere in the technical literature (Christensen, 1989; Holm et al., 2003). Lastly, a negative correlation term with the sediment per cent sand content suggests that soil/sediment/aquifer material sand content is a particularly good variable to account for the composite metal affinities displayed by the combined silt and clay sediment particulate fractions.

Figure 3 compares the simple pH-dependent partitioning models for Pb developed in this work with models in Table 1 generated by Gerritse and Van Driel, (1984), Loux et al. (1990), Rhoades et al. (1992), and Hassan et al. (1996). Generally speaking, the models from the present work and those developed by Loux et al. (1990) and Hassan et al. (1996) tended to cluster together. The model from Hassan et al. (1996) was derived from partitioning data obtained using 5 sandy solid phases and was selected to be conservative in nature (i.e., to err on the side of underestimating the K_d). The curve developed by Loux et al. (1990) was generated under competitive conditions (with other cations). In addition, the equilibrium porewater Pb concentrations were below the method detection limit for many of the higher pH data points used by Loux et al. (1990) (~0.165 mg/L Pb); hence, K_d values for these data points were estimated by assuming that the porewater Pb concentration equaled the method detection limit. This curve likely underestimates Pb partitioning at high pH conditions and overestimates Pb partitioning at low pH values. The shape of the polynomial curve obtained in this work does not compare favorably with that obtained by Rhoades et al. (1992). Lastly, none of the curves compare favorably with the results obtained by Gerritse and Van Driel (1984).

Figure 4 illustrates various simple pH-dependent Cd K_d relationships published in the technical literature (in Table 1) and the findings from this work. The curves derived by Christiansen (1989), Loux et al. (1990), Hassan et al. (1996), USEPA (1999) and the present work also tend to cluster together. The slopes of the curves from the present work and the model developed by Christiansen (1989) also tend to be comparable. As with the Pb data, differences between the present findings and the expression developed by Loux et al. (1990) can be attributed to the fact that the data used by Loux et al. (1990) were developed under competitive cationic partitioning conditions and that a number of data points at higher pH conditions had porewater Cd concentrations below the method detection limit (~.013 mg/L); K_d values for these data points were calculated assuming that the porewater Cd concentration equaled the method detection limit. Hence, the slope of the Cd expression generated by Loux et al. (1990) is likely to be less than the true value.

There are several limitations associated with the empirical models developed in this work. Numerous authors have described a solids concentration effect (SCE) on measured
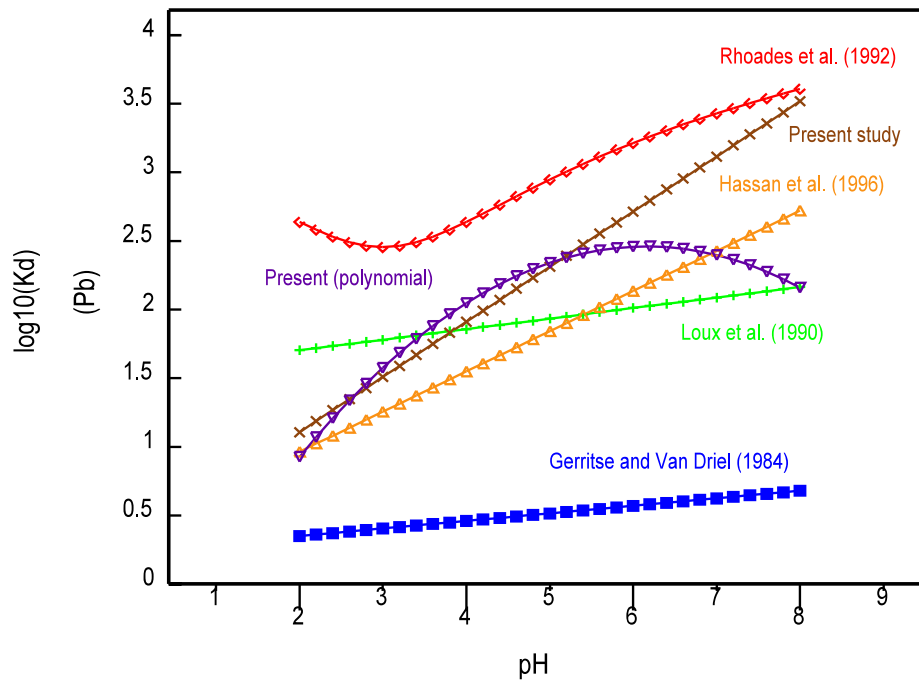
Figure 3.   Comparison of simple pH-dependent K_d relationships for lead in the literature with those obtained in the present study. A second order polynomial did not greatly improve the adjusted r-squared value with our data.
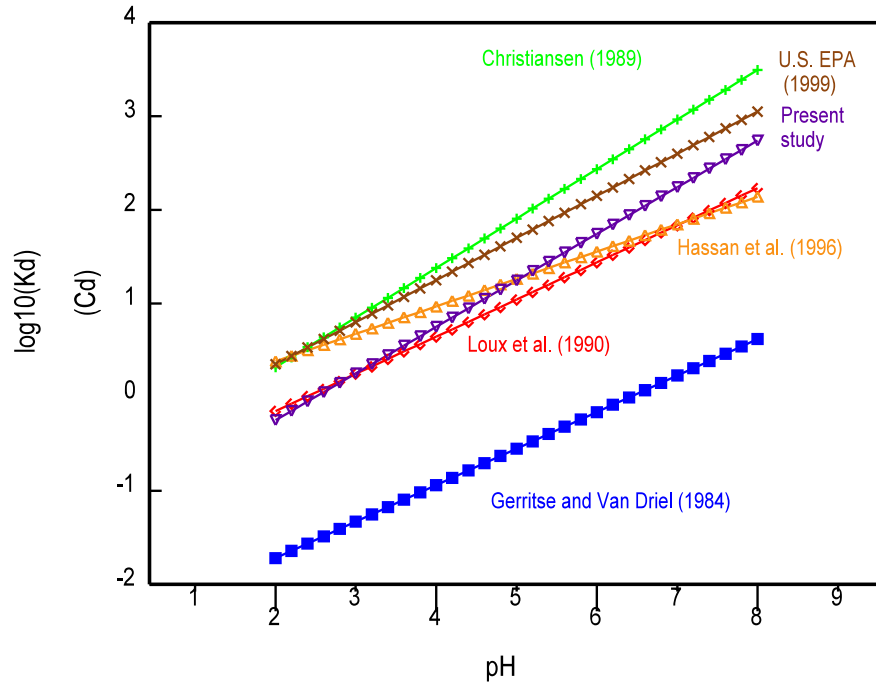
Figure 4.   Comparison of simple pH-dependent K_d relationships for cadmium reported in the literature with those obtained in the present study.

experimental K_ds for both metals and organic toxicants (e.g., see Benoit, 1995 and references cited therein). Generally speaking, the inverse relationships between metal K_ds and solids concentrations are either considered to be "real" or are attributed to experimental artifact. Even if one accepts the hypothesis that the SCE is the result of including colloid-associated metals in the "dissolved" metal concentration measurement (e.g., Benoit, 1995), the ramifications are such that these colloid-associated metals also may be mobile and hence, the SCE may well be "real" to the exposure assessment technical community regardless of whether or not the SCE is an experimental artifact (e.g., Puls et al., 1990). The experimental conditions utilized in this work produced sediment concentrations ranging from 0.08 to 0.13 kg/L. The findings from Gerritse and Van Driel (1984) were obtained using a solids concentration of ~0.2 kg/L; this difference in solids concentration might explain some of the disparities between the findings from the two works.

Our procedure of ignoring extractable concentrations of background Pb and Cd is supportable from a quantitative perspective. For example, the weak nitric acid extract method limit of detection for extractable Pb was determined to be 7.8 mg/kg. Given that the typical solids concentration used in the study was ~0.1 kg/L, then the maximum extractable background Pb concentration in the centrifuge tubes can be estimated to be 0.78 mg/L. Only for the initial added concentrations of ~3 mg/L would this quantity be a significant contribution (26%). At an initial added Pb concentration of ~15 mg/L, the maximum possible background extractable Pb would be approximately 5.2% of the added spike. Similarly, the background extractable Cd method limit of detection was estimated to be ~0.93 mg/kg. At a solids concentration of ~0.1 kg/L the maximum background Cd contribution would be ~0.1 mg/L. Hence even at initial added Cd concentrations of ~3 mg/L, a background Cd contribution of circa 3.3% is well with the limits of precision for atomic emission inductively coupled plasma spectrometry.

As noted in Table 2, the Utah aquifer material sample contained a significant quantity of acid volatile sulfides. Hence, it is possible that PbS precipitation also may have occurred during experimentation involving the Utah samples. Given a solids concentration of 0.1 kg/L, possible PbS production could have precipitated as much as ~2 mg/L of Pb with the Utah samples. Even if PbS precipitation occurred, it would have been most significant only for the two lowest initial Pb concentration sets of runs. Given that the second pK_a for H_2S is approximately 7, PbS precipitation would likely display a pH dependency within the conditions of the study (unlike the probable $PbSO_4$ precipitation).

One source of error in this work is the result of mineral phase dissolution under the conditions of our study. Adjusting the system pH may lead to the significant dissolution of calcareous minerals (at pH values less than 5) and aluminosilicate minerals (at pH values less than 4). For those low pH datapoints where more solid has dissolved than precipitated (on a weight basis), our methodology may lead to an underestimation of the true K_d value. This error, if it occurred, would be conservative in the sense that it underestimates metals partitioning and hence also overestimates potential metals solubilization, transport and bioavailability. Alternatively, from Table 2, the maximum pH 4.5 extractable sedimentary Ca content is given as 31,000 ppm (or 3.1 % of the sediment). Assuming that this Ca was present as $CaCO_3$, then the maximum estimated $CaCO_3$ content of the sediment is 7.74 %. Consequently, the maximum estimated error in estimated K_d values as the result carbonate mineral dissolution at pH conditions less than 5 is 7.74 %.

A question also has arisen as to the significance of mineral phase dissolution and/or precipitation under the conditions of our study. An objective for conducting this study was to study phenomena as they occur in the environment. Given that mineral phase dissolution and/or precipitation probably occurred in our work, these processes also occur in the environment. The significance of these processes has been previously addressed.

Another limitation in this work is that while the EPA sediment samples were composited and relatively homogeneous, the aquifer material samples were not. A visual inspection of the aquifer material solids illustrated "patchiness" in these samples. Hence, background variation in aquifer material properties presumably contributed to the unexplained variation in the results from the derived empirical models.

There is evidence in the technical literature suggesting that carbonate mineral formation may be involved in both environmental Pb and Cd partitioning (Rai et al., 1986; Bank et al., 1989; Rhoades et al., 1992). Although there was no effort in this work to identify the actual mechanisms leading to Pb or Cd partitioning, carbonate mineral formation may have been significant. If so, then this effect must be taken into account when the results from this work are applied to groundwater systems because the partial pressure of carbon dioxide in aquifers is generally much greater than the atmospheric value (e.g., Loux et al., 1991 and references cited therein).

The empirical models for Pb and Cd presented in Tables 5 and 7 represent the most robust empirical models available to the technical community. Expressions developed herein yield estimated K_d values less than corresponding values actually measured by some other researchers; however, this likely results from the lesser organic carbon content sediments and higher initial porewater Pb and Cd concentrations used in our study to develop our models. Therefore, our models may have more general applicability for assessments related to contaminated sites with low organic carbon content surficial soils. Lastly, our expressions yield more conservative results in risk assessments containing a significant drinking water exposure pathway of concern.

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Appendix A

Summary of statistics used to generate regression equations for Pb listed in Table 5.

Regression equation (1).

Equation

$$\log_{10}K_{d,Pb} = -0.670728 + 0.776537*\log_{10}Al - 0.455826*\log_{10}Fe + 0.117675*\log_{10}Mn$$
$$+ 0.607061*\log_{10}OC + 0.0000416702*\log_{10}P - 0.00518428*sand +$$
$$0.561895*pH_{soln}$$

Multiple Regression Analysis

Dependent variable: $\log_{10}K_{d,Pb}$

Parameter	Estimate	Standard Error	T Statistic	P-Value
CONSTANT	-0.670728	0.471192	-1.42347	0.1553
$\log_{10}Al$	0.776537	0.0982006	7.90767	0.0000
$\log_{10}Fe$	-0.455826	0.10453	-4.36071	0.0000
$\log_{10}Mn$	0.117675	0.0603468	1.94997	0.0518
$\log_{10}OC$	0.607061	0.0631243	9.61692	0.0000
$\log_{10}P$	0.0000416702	0.0597063	0.000697919	0.9994
sand	-0.00518428	0.00155686	-3.32996	0.0009
pH_{soln}	0.561895	0.0179919	31.2305	0.0000

Analysis of Variance

Source	Sum of Squares	Df[1]	Mean Square	F-Ratio	P-Value
Model	332.305	7	47.4721	238.29	0.0000
Residual	84.4677	424	0.199216		

| Total (Corr.) | 416.772 | 431 | | | |

R-squared = 79.7329 percent
R-squared (adjusted for d.f.) = 79.3983 percent
Standard Error of Est. = 0.446337
Mean absolute error = 0.355951
Durbin-Watson statistic = 1.69009 (P=0.0006)
Lag 1 residual autocorrelation = 0.147307

1-   Df designates degrees of freedom

Regression equation (2).

Equation

$$\log_{10}K_{d,Pb} = -0.670967 + 0.776562*\log_{10}Al - 0.455873*\log_{10}Fe + 0.117702*\log_{10}Mn$$
$$+\ 0.607089*\log_{10}OC - 0.00518412*sand + 0.561896*pH_{soln}$$

Multiple Regression Analysis

Dependent variable: $\log_{10}K_{d,Pb}$

Parameter	Estimate	Standard Error	T Statistic	P-Value
CONSTANT	-0.670967	0.323513	-2.074	0.0387
$\log_{10}Al$	0.776562	0.0915385	8.48345	0.0000
$\log_{10}Fe$	-0.455873	0.0804758	-5.66472	0.0000
$\log_{10}Mn$	0.117702	0.045402	2.59245	0.0099
$\log_{10}OC$	0.607089	0.0481764	12.6014	0.0000
sand	-0.00518412	0.00153934	-3.36775	0.0008
pH_{soln}	0.561896	0.017966	31.2755	0.0000

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	332.305	6	55.3841	278.67	0.0000
Residual	84.4677	425	0.198748		

| Total (Corr.) | 416.772 | 431 | | | |

R-squared = 79.7329 percent
R-squared (adjusted for d.f.) = 79.4468 percent
Standard Error of Est. = 0.445811
Mean absolute error = 0.355951
Durbin-Watson statistic = 1.69009 (P=0.0006)
Lag 1 residual autocorrelation = 0.147303

Regression equation (3).

Equation

$$\log_{10}K_{d,Pb} = -1.66596 + 0.54782*pH_{soln} - 0.0125584*sand + 0.585286*\log_{10}OC$$

Multiple Regression Analysis

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------------------------------------------------------------------------------------
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Dependent variable: $\log_{10}K_{d,Pb}$
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```

Parameter	Estimate	Standard Error	T Statistic	P-Value
CONSTANT	-1.66596	0.193836	-8.59467	0.0000
pH_{soln}	0.54782	0.0193298	28.3406	0.0000
sand	-0.0125584	0.0008877	-14.1471	0.0000
$\log_{10}OC$	0.585286	0.0415855	14.0743	0.0000

Analysis of Variance

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```

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	316.329	3	105.443	449.30	0.0000
Residual	100.444	428	0.234682		

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Total (Corr.)	416.772	431

R-squared = 75.8996 percent
R-squared (adjusted for d.f.) = 75.7307 percent
Standard Error of Est. = 0.48444
Mean absolute error = 0.388245
Durbin-Watson statistic = 1.5065 (P=0.0000)
Lag 1 residual autocorrelation = 0.239135

Regression equation (4).

Equation

$$\log_{10}K_{d,Pb} = 0.821913 - 0.0194336*sand + 0.50909*pH_{soln}$$

Multiple Regression Analysis

Dependent variable: $\log_{10}K_{d,Pb}$

Parameter	Estimate	Standard Error	T Statistic	P-Value
CONSTANT	0.821913	0.0960819	8.55429	0.0000
sand	-0.0194336	0.000895416	-21.7035	0.0000
pH_{soln}	0.50909	0.0231137	22.0255	0.0000

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	269.842	2	134.921	393.93	0.0000
Residual	146.931	429	0.342496		

| Total (Corr.) | 416.772 | 431 | | | |

R-squared = 64.7456 percent
R-squared (adjusted for d.f.) = 64.5812 percent
Standard Error of Est. = 0.585231
Mean absolute error = 0.463089
Durbin-Watson statistic = 1.73709 (P=0.0031)
Lag 1 residual autocorrelation = 0.129666

Regression equation (5).

Equation:

$$\log_{10}K_{d,Pb} = -3.27603 + 0.909033*\log_{10}OC + 0.520959*pH_{soln}$$

Multiple Regression Analysis

Dependent variable: $\log_{10}K_{d,Pb}$

Parameter	Estimate	Standard Error	T Statistic	P-Value
CONSTANT	-3.27603	0.189863	-17.2547	0.0000
$\log_{10}OC$	0.909033	0.0420158	21.6355	0.0000
pH_{soln}	0.520959	0.0232767	22.3811	0.0000

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	269.359	2	134.68	391.94	0.0000
Residual	147.413	429	0.34362		

| Total (Corr.) | 416.772 | 431 | | | |

R-squared = 64.6299 percent
R-squared (adjusted for d.f.) = 64.465 percent
Standard Error of Est. = 0.586191
Mean absolute error = 0.467002
Durbin-Watson statistic = 1.66961 (P=0.0003)
Lag 1 residual autocorrelation = 0.159717

Regression equation (6).

Equation

$$\log_{10}K_{d,Pb} = -0.903834 + 1.09284 * pH_{soln} - 0.0887548 * pH_{soln}^{2}$$

Polynomial Regression Analysis

Dependent variable: $\log_{10}K_{d,Pb}$

Parameter	Estimate	Standard Error	T Statistic	P-Value
CONSTANT	-0.903834	0.374977	-2.41037	0.0164
pH_{soln}	1.09284	0.203356	5.37402	0.0000
pH_{soln}^2	-0.0887548	0.025792	-3.44118	0.0006

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	116.793	2	58.3964	83.51	0.0000
Residual	299.979	429	0.699253		

| Total (Corr.) | 416.772 | 431 | | | |

R-squared = 28.0232 percent
R-squared (adjusted for d.f.) = 27.6876 percent
Standard Error of Est. = 0.836213
Mean absolute error = 0.657179
Durbin-Watson statistic = 1.66392 (P=0.0002)
Lag 1 residual autocorrelation = 0.165565

Regression equation (7).

Equation:

$$\log_{10}K_{d,Pb} = 0.302684 + 0.401918*pH_{soln}$$

Regression Analysis - Linear model: $Y = a + b*X$

Dependent variable: log10Kd
Independent variable: solnpH

Parameter	Estimate	Standard Error	T Statistic	P-Value
Intercept	0.302684	0.134629	2.24827	0.0251
Slope	0.401918	0.032668	12.3031	0.0000

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	108.512	1	108.512	151.37	0.0000
Residual	308.26	430	0.716883		

| Total (Corr.) | 416.772 | 431 | | | |

Correlation Coefficient = 0.510259
R-squared = 26.0364 percent
R-squared (adjusted for d.f.) = 25.8644 percent
Standard Error of Est. = 0.84669
Mean absolute error = 0.68069
Durbin-Watson statistic = 1.61928 (P=0.0000)
Lag 1 residual autocorrelation = 0.189019

Appendix B

Summary of statistics used to generate regression equations for Cd listed in Table 7.

Regression equation (1).

Equation:

$$\log_{10}K_{d,Cd} = -2.72079 + 0.57592*\log_{10}OC - 0.00594147*Sand + 0.495213*pH_{soln} - 0.0383169*\log_{10}P - 0.0495951*\log_{10}Fe$$

Statistics:

Dependent variable: $\log_{10}K_{d,Cd}$

Parameter	Estimate	Standard Error	T Statistic	P-Value
CONSTANT	-2.72079	0.216514	-12.5664	0.0000
$\log_{10}OC$	0.57592	0.0411699	13.9889	0.0000
sand	-0.00594147	0.00106336	-5.58745	0.0000
pH_{soln}	0.495213	0.0116394	42.5463	0.0000
$\log_{10}P$	-0.0383169	0.0418937	-0.914622	0.3604
$\log_{10}Fe$	-0.0495951	0.0483949	-1.0248	0.3055

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	685.427	5	137.085	480.11	0.0000
Residual	191.306	670	0.285532		

| Total (Corr.) | 876.734 | 675 | | | |

R-squared = 78.1796 percent
R-squared (adjusted for d.f.) = 78.0168 percent
Standard Error of Est. = 0.534352
Mean absolute error = 0.405888
Durbin-Watson statistic = 0.730478 (P=0.0000)
Lag 1 residual autocorrelation = 0.629705

Regression equation (2).

Equation:

$$\log_{10}K_{d,Cd} = -3.45769 + 0.491611*pH_{soln} + 0.00697647*Clay + 0.589151*\log_{10}OC + 0.0375007*\log_{10}Fe - 0.0678679*\log_{10}P$$

Statistics

Dependent variable: $\log_{10}K_{d,Cd}$

Parameter	Estimate	Standard Error	T Statistic	P-Value
CONSTANT	-3.45769	0.138702	-24.9288	0.0000
pH_{soln}	0.491611	0.0115897	42.4178	0.0000
clay	0.00697647	0.00118019	5.9113	0.0000
$\log_{10}OC$	0.589151	0.0409778	14.3773	0.0000
$\log_{10}Fe$	0.0375007	0.0395088	0.949173	0.3425
$\log_{10}P$	-0.0678679	0.0433684	-1.56492	0.1176

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	686.438	5	137.288	483.37	0.0000
Residual	190.296	670	0.284024		
Total (Corr.)	876.734	675			

R-squared = 78.2949 percent
R-squared (adjusted for d.f.) = 78.1329 percent
Standard Error of Est. = 0.532939
Mean absolute error = 0.402332
Durbin-Watson statistic = 0.734254 (P=0.0000)
Lag 1 residual autocorrelation = 0.627921

Regression equation (3).

Equation:

$$\log_{10}K_{d,Cd} = -2.7463 + 0.494383*pH_{soln} - 0.00562497*Sand + 0.562986*\log_{10}OC - 0.044992*\log_{10}Fe$$

Statistics

Dependent variable: $\log_{10}K_{d,Cd}$

Parameter	Estimate	Standard Error	T Statistic	P-Value
CONSTANT	-2.7463	0.214683	-12.7923	0.0000
pH_{soln}	0.494383	0.0116026	42.6098	0.0000
sand	-0.00562497	0.00100536	-5.595	0.0000
$\log_{10}OC$	0.562986	0.0386603	14.5624	0.0000
$\log_{10}Fe$	-0.044992	0.0481267	-0.934867	0.3499

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	685.188	4	171.297	600.07	0.0000
Residual	191.545	671	0.285463		

| Total (Corr.) | 876.734 | 675 | | | |

R-squared = 78.1524 percent
R-squared (adjusted for d.f.) = 78.0222 percent
Standard Error of Est. = 0.534287
Mean absolute error = 0.406058
Durbin-Watson statistic = 0.729923 (P=0.0000)
Lag 1 residual autocorrelation = 0.63002

Regression equation (4).

Equation:

$$\log_{10}K_{d,Cd} = -2.87671 + 0.495043*pH_{soln} - 0.00500349*Sand + 0.55245*\log_{10}OC$$

Statistics

Dependent variable: $\log_{10}K_{d,Cd}$

Parameter	Estimate	Standard Error	T Statistic	P-Value
CONSTANT	-2.87671	0.163175	-17.6295	0.0000
pH_{soln}	0.495043	0.01158	42.7498	0.0000
sand	-0.00500349	0.000754123	-6.63484	0.0000
$\log_{10}OC$	0.55245	0.0369777	14.9401	0.0000

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	684.939	3	228.313	799.95	0.0000
Residual	191.795	672	0.285409		

| Total (Corr.) | 876.734 | 675 | | | |

R-squared = 78.1239 percent
R-squared (adjusted for d.f.) = 78.0263 percent
Standard Error of Est. = 0.534237
Mean absolute error = 0.406539
Durbin-Watson statistic = 0.729352 (P=0.0000)
Lag 1 residual autocorrelation = 0.630415

Regression equation (5).

Equation:

$$\log_{10}K_{d,Cd} = -3.38864 + 0.489278*solnpH + 0.00665484*Clay + 0.583745*\log_{10}OC$$

Statistics
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Dependent variable: $\log_{10}K_{d,Cd}$
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Parameter	Estimate	Standard Error	T Statistic	P-Value
CONSTANT	-3.38864	0.128545	-26.3615	0.0000
pH_{soln}	0.489278	0.011511	42.5052	0.0000
clay	0.00665484	0.000981515	6.78017	0.0000
$\log_{10}OC$	0.583745	0.0344532	16.9431	0.0000

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Analysis of Variance
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Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	685.46	3	228.487	802.74	0.0000
Residual	191.274	672	0.284634		

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Total (Corr.)	876.734	675

R-squared = 78.1833 percent
R-squared (adjusted for d.f.) = 78.0859 percent
Standard Error of Est. = 0.533511
Mean absolute error = 0.402237
Durbin-Watson statistic = 0.731466 (P=0.0000)
Lag 1 residual autocorrelation = 0.629254

Regression equation (6).

Equation:

$$\log_{10}K_{d,Cd} = -1.24069 + 0.497497*pH_{soln}$$

Statistics

Dependent variable: $\log_{10}K_{d,Cd}$
Independent variable: pH_{soln}

Parameter	Estimate	Standard Error	T Statistic	P-Value
Intercept	-1.24069	0.0932551	-13.3042	0.0000
Slope	0.497497	0.0153971	32.3112	0.0000

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	532.779	1	532.779	1044.01	0.0000
Residual	343.955	674	0.510318		

| Total (Corr.) | 876.734 | 675 |

Correlation Coefficient = 0.779542
R-squared = 60.7686 percent
R-squared (adjusted for d.f.) = 60.7104 percent
Standard Error of Est. = 0.714366
Mean absolute error = 0.582519
Durbin-Watson statistic = 0.412912 (P=0.0000)
Lag 1 residual autocorrelation = 0.792533