COMPLETE CHARACTERIZATION OF PARAMETERS USED IN RISK ASSESSMENT MODELS FOR HEAVY METAL TRANSPORT ASSOCIATED WITH FERTILIZER APPLICATIONS IN OREGON

Final Report

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William Fish and Gwynn R. Johnson
Portland State University

Contacts:

W. Fish fishw@cecs.pdx.edu (503) 725 – 4278
G.R. Johnson gjohnson@pdx.edu (503) 725 - 8710
Executive Summary

This report summarizes research activities performed at Portland State University under contract with the Oregon Department of Agriculture (ODA) related to understanding the behavior of fertilizer derived metals in Oregon agricultural soils. The goal of the PSU project was to create a model of metal solubility, transport, and accumulation in agricultural soils that requires a minimal number of measured physical and chemical parameters, yet represents a diversity of Oregon soil types and agricultural practices.

The project completed the following tasks that were outlined in the original proposal for this work submitted to ODA:

Task 1. Collect bulk and intact-core soil samples from four trial site locations in Oregon
Task 2. Obtain fertilizer samples and other necessary reagents and supplies
Task 3. Process soil samples in laboratory for particles size distribution, pH, and metal content
Task 4. Laboratory-based soil characterizations
Task 5. Perform dissolution and metal release experiments on fertilizer samples
Task 6. Adsorption isotherms for Cd on field site soils
Task 7. Set up flow-through columns – homogenized and undisturbed soil columns
Task 8. Selected unsaturated soil columns
Task 9. Diagnostic Model Formulation

All of these tasks have been completed and the results of the work presented herein in three major sections. Several appendices are also present that contain supplemental work relevant to the project but not included in the original scope of work.

The major findings of the project are summarized as follows:

• The project has yielded a useful diagnostic model of the equilibrium chemistry of Cd in Oregon agricultural soils. Equilibrium data and model results are valuable for describing many aspects of the soil system and also as a reference point. For example, they are useful for comparison to the results of the equilibrium DGT and other bioavailability work performed by OSU researchers. Also our equilibrium results are applicable to standard regulatory approaches. Our experiments have dramatically
reduced the uncertainty about Cd partitioning on Oregon agricultural soils to within one order of magnitude.

• In both the equilibrium and kinetic column experiments we see that Cd mostly in soil with very slow release. Plant uptake can still be important to human exposure for a metal as toxic as Cd, but soil is the main reservoir of Cd mass in an agricultural system. This is consistent in our studies and those of other researchers that show any elevated Cd is generally confined to the upper (tilled) portion of the soil profile. We therefore expect Cd to slowly accumulate in soil over long run.

• We elucidate the rates at which Cd is released from P fertilizer in unsaturated soil conditions. The rate of release is briefly rapid, but then slows dramatically, most likely due to interactions of Cd with P itself in the fertilizer/soil-water system. Our soil column experiments show that uptake by Oregon soil are faster than release from fertilizer, so release rate is an important limit on Cd transport. It is likely that plant uptake is also faster than fertilizer release and so the slow release kinetics also limit bioavailability to crops, and hence potential human exposure.

• Transfer of Cd to sampled agricultural soil was essentially complete in our column experiments, consistent with equilibrium batch results. However, when soils were loaded with Cd and then eluted, the very slow leaching of Cd (over hundreds of elution pore volumes) was most accurately modeled by a nonequilibrium transport model that included a so-called dynamic retardation factor (R) which accounts for the possibility of sorption/desorption onto both slow and fast sites or for small scale diffusive transport in or out of micropores.
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**Overall Goal and Specific Objectives**

Our overall goal was to create a model of metal solubility, transport, and accumulation in agricultural soils that requires a minimal number of measured physical and chemical parameters, yet represents a diversity of Oregon soil types and agricultural practices. The model and its supporting data were used to assess the leachability and availability of soluble metals; characterize the potential for long-term buildup of metals in soils; and identify whether accumulated metals tend to either leach from the soil or remain sequestered. The specific objectives of this research project were to:

1. Collect intact “undisturbed” core samples along with corresponding conventional grab samples of soils from trial sites located in Oregon, coordinating with K. Anderson (OSU) and representatives from ODA.

2. Characterize the physical properties of undisturbed soils using advanced column techniques that reveal the role of natural heterogeneity in soil structure and chemistry.

3. Analyze soil grab samples for conventional physical/chemical characteristics such as pH, grain–size distribution, and extractable metal content.

4. Identify the metal sorption/desorption properties of the various soil samples over a wide range of metal concentrations, pH, and for relevant toxic metals (Cd and Pb).

5. Characterize the importance of rate-limited mass-transfer processes of Cd release from fertilizer as it affects the sorption and desorption of cadmium.

6. Create a practical model of metal-soil interactions based on parameters obtainable from conventional soil characterization methods.

7. Verify the diagnostic utility of the model with column studies of undisturbed cores that bridge the gap between conventional lab studies and actual behavior of metals in the field.
Project Background:

Three major research areas were identified as critical to this project. Brief background information is provided on each of them in this section to highlight the rationales for the goals and the experiments we performed. An important element of all research was that we bridge previous laboratory investigations with an approach that emphasized application to Oregon agricultural conditions and practices.

Sorption and Desorption of Metals on Soil Phases

Toxic metals bind to surfaces by several mechanisms. Metals exhibit typical cation-exchange behavior on clay minerals; ions such as Cd\(^{2+}\) and Pb\(^{2+}\) are attracted to layer silicates by electrostatic forces. However, these metals must compete with more abundant major cations for the available exchange sites, so a large degree of metal partitioning onto exchange sites is not expected. Sorption of metals on metal oxides (such as hydrous ferric oxide) is generally far more important and can be expressed as a surface-complexation reaction of the type:

\[
\text{Fe--OH}^- + \text{Cd}^{2+} = \text{Fe}--\text{O}--\text{Cd}^+ + \text{H}^+
\]

Anions such as arsenate/ite adsorb via corresponding ligand-exchange reactions. At higher concentrations of metals, surface complexation transitions into surface precipitation of (hydr)oxide phases. In practice it is very difficult to differentiate between precipitation and sorptive processes in soils. In most cases one can only speculate as to what process is controlling the solution-phase concentration of metals and an empirical Freundlich-type isotherm is often used to model surface binding over a wide range of concentrations. Finally, metals can coordinate rather strongly to natural organic matter (NOM or humic substances) in soils. Binding to heterogeneous NOM can be successfully modeled by multi-ligand complexation models or by binding-affinity distribution models (Fish et al., 1986). Humic materials also can be soluble and thereby enhance the transport of metals they bind to, metals that otherwise would be rather immobile (e.g. Sauvé et al., 2000).

To be relevant to agricultural practice, adsorption studies need to be performed at relatively low levels of toxic metals. Previous studies of metals in soils have typically emphasized conditions more applicable to soils polluted by sewage sludge or industrial wastes.
In our adsorption studies, Cd and Pb were employed at levels as close as possible to those anticipated for fertilizer-derived metals. We therefore used ICP-MS analyses for many of our studies and reserved the less sensitive atomic absorption spectrometry (AAS) for background characterization of soil adsorption.

Modeling adsorption has typically been done assuming equilibrium conditions between metal ions in solution and the solid phase. Slow metal uptake may change the distribution between solid and porewater over time because of rate-limited metal sorption/desorption (Smith and Comans, 1996; Strawn et al., 1998). Failing to account for slow release or uptake may result in either overpredictions of contaminant availability in the environment or an underprediction of the contaminants that can potentially accumulate on soils. To understand the effect of fertilizer-derived cadmium of soils it is also important to consider the rate at which Cd is released from fertilizer

**Rate of Release of Metals from Fertilizers**

The release of metals from a fertilizer is the input of contamination to the system. Therefore, the rate of delivery of these metals may be an important factor controlling soil-water concentrations. Fertilizers are designed or expected to dissolve and release their major nutrients at certain rates until they are depleted. However, the release of metal contaminants to the soil may not, in general, parallel the release of the major nutrients. For example, Cd has been shown to be a major contaminant of some phosphate (PO$_4$) fertilizers.

Some PO$_4$ forms (such as superphosphate) dissolve relatively quickly. However, Cd was expected to be bound up in relatively insoluble Cd-phosphate or Cd-substituted hydroxyapatite mineral phases. These phases would not be expected to release significant soluble Cd until PO$_4$ levels have declined below the relevant solubility limits. In such a case, Cd release significantly lags the PO$_4$ release.

Few studies have looked specifically at fertilizers as a source of metals so there is a dearth of information about the rates at which metals are released from commercial fertilizers. The kinetics of Cd release from fertilizer therefore were examined in this project to enhance the applicability of our results to agricultural conditions.
Soils are heterogeneous and contain many mineral phases and organic materials. Thus, the interaction of trace elements with soils is a naturally heterogeneous process. Several sorption mechanisms have been proposed to reflect this inherent heterogeneity and variability: diffusion into micropores and solids followed by subsequent sorption onto interior surfaces; sorption to sites of variable reactivity, including sites which involve different bonding mechanisms, i.e., inner-sphere vs. outer-sphere and monodentate vs. bidentate; and surface precipitation (Strawn et al., 1998; Strawn and Sparks, 1999). Measured sorption/desorption rate coefficients often reflect a combination of all of these mechanisms. However, it is possible that one mechanism may dominate at a particular time in the sorption reaction and the measured rate is primarily an expression of that reaction rate. The significance of this is that, while sorption and desorption reactions may appear to have reached equilibrium, in fact the reaction may be continuous and the rate-limited mechanism will not be measured if the experiment covers too short a reaction time. In such cases, these rate-limited processes may be completely overlooked and predictions of metal concentrations and resulting risk assessments may be inaccurate.

Researchers often have overlooked two important aspects of soil kinetics: (1) the amount of time soils are exposed to a contaminant in the laboratory is relatively short compared with the much longer residence times that exist in field-contaminated soils; and (2) the kinetics of metal adsorption and desorption may be either fast or slow relative to the scales of porous medium transport in a heterogeneous agricultural soil. Neglect of these factors can lead to improper calculation of contaminant behavior in soils, resulting in inappropriate regulations (Strawn and Sparks, 1999). But, conventional laboratory kinetic experiments on isolated soil samples cannot capture the aggregate effects that occur in a real soil system in the field.

We concluded that the most efficient and accurate approach to the problem of adsorption kinetics in heterogeneous agricultural soils was to directly measure the rates at which Cd and other ions move through intact-core samples of the Oregon test soils. The cumulative effects of sorption and desorption kinetics can thus be inferred from the results, without performing time-consuming and hard-to-interpret batch-kinetic studies. This innovative intact-core approach is discussed further in the methodology section below.
Overall Experimental Design

Research Approach

This project has approached its scientific objectives through laboratory experiments that have allowed a well controlled microcosm of processes occurring in the field. Although laboratory based, the overall research plan was designed to ensure that results are directly transferable to actual conditions in Oregon agricultural practice. Experiments were conducted using samples of agricultural soils from trial sites located in Oregon identified as Willamette Valley (Hyssop Station), Columbia Basin Agricultural Research Center, Hermiston Experiment Station, and Klamath Experiment Station. Our samples followed the gridding, sample identification, and methodology used in the OSU studies to allow for the comparison of results as desired.

The initial studies involved homogenized soil samples to achieve reproducibility. As we discuss below, we performed experiments to measure fertilizer release of Cd, the adsorption of Cd and Pb, and in-situ adsorption/desorption with continuous-flow and pulsed-flow soil column experiments. The column experiments and batch isotherm determinations provide complementary data on both rapid, quasi-equilibrium binding reactions and more kinetically limited adsorption and desorption.

After we gained insight into the sorption processes of the experimental soils from homogenized samples, we also performed experiments on undisturbed soil cores that retain the natural physical and chemical heterogeneity of the parent soils. Our experience in the difficult technique of undisturbed (intact) core handling and experimentation (Johnson et al., 2003a) allowed us to add a critical dimension of reality to our models of the soil-water system. Undisturbed column data allowed us to construct a more complete understanding of fertilizer-derived metals in field soils.

Methodology for Meeting Objectives

Our experimental plan was constructed to assure that each project objectives was addressed by procedures and experiments that yield the desired outcomes. In the sections below, the originally
proposed tasks are defined and the methodology is mapped to a specific objective. Only a brief summary of methodology is provided here to show how the tasks were achieved. More detailed methodologies are provided in the subsequent report section on each experimental phase.

**Task 1. Collect bulk and intact-core soil samples from trial site locations in Oregon**

Oregon agricultural soils were collected from targeted regions of Oregon, i.e., Willamette Valley (Hyslop Station), Columbia Basin Agricultural Research Center, Hermiston Experiment Station, and Klamath Experiment Station. Conventional grab (e.g. disturbed/homogenized) samples were collected from each plot at each trial site. A total of 16 surface-soil and 8 deep-soil grab samples were collected from each trial site. These grab samples included both baseline/background soils and soils treated with experimental fertilization. Undisturbed soil samples (e.g., intact cores) were collected from three of the four trial site. (Hermiston collection proved impossible due to the sandy texture of the soil).

**Task 2. Obtain fertilizer samples and other necessary reagents and supplies**

Commercially available fertilizer, selected by ODA, was sampled and characterized accordingly in the laboratory. Quantification of target heavy metals (Cd and Pb) were comparable to those obtained independently by ODA.

**Task 3. Process soil samples in laboratory**

This task included sieving, weighing, sub-sampling, cataloging, and storage.

**Task 4. Laboratory-based soil characterizations.**

We performed basic soil characterizations on samples from each trial site according to standard soil methods: grain size analysis, pH, and extractable metals via the double-acid method (0.05N HCl in 0.25N H$_2$SO$_4$; Perkins, 1970). Measurements of density, surface area, cation exchange capacity and organic carbon content were to be performed in the laboratory of K. Anderson of OSU.

**Task 5. Perform dissolution and metal release experiments on fertilizer samples**

Aliquots of fertilizer were mixed with clean silica sand that was ashed in a Muffle furnace and acid washed. Concentrations/application rates were designed to approximate field-application
rates. Sand-fertilizer mixes were then packed into columns of actual soil (described in Task 7 below). Initial tests used a continuous flow of eluent water at a slow flow rate to simulate infiltration in soils. Sequential eluent samples were collected and analyzed for Cd and relevant major ions. The data will yield profiles of Cd release; the elution profiles were used to define fertilizer release. These continuous flow experiments were followed by pulse flow tests that more accurately simulated intermittent field infiltration. Also, we identified chemical amendments to the eluent that helped elucidate the mechanisms controlling Cd release from the fertilizer.

**Task 6. Collect metal isotherm data on soils for each metal**

Batch experiments were conducted on selected homogenized samples from each trial site to determine Freundlich isotherm coefficients for all metals. Most isotherms were collected at the pH of the native soil, but selected isotherms were collected at approximately one pH unit above and below soil pH to assess the proton stoichiometry and pH dependence of the sorption reactions. In the batch experiments, specific amounts of air-dried uncontaminated (e.g. baseline/background) soil and solutions with incremental metal concentrations were added to a series of acid-washed HDPE screw-cap vials. To investigate nonlinear partitioning behavior, at least five initial metal concentrations were used for each experiment set. Samples will be continuously shaken using a bench-top shaker-table and equilibrated for approximately 24 hours to ensure equilibrium of the solution with the “fast” exchangeable soil binding sites. Selected samples will be equilibrated for a period of weeks to estimate “slow” uptake kinetics for comparison with slow-kinetics data from column experiments (see below). Blanks containing no soil will be used to determine mass loss, and all experiments conducted in triplicate. Vials were centrifuged and aliquots of supernatant will be removed using metal-clean technique, filtered through a 0.1 µm Whatman GFC filter, and analyzed for pH (by electrode) and metals (by AAS or ICP-MS). The sorbed concentration of heavy metal will be determined by mass balance. Additionally, sequential soil extractions will be conducted on selected samples to directly estimate the solid-phase concentration.

**Task 7. Set up flow-through columns – homogenized and undisturbed soil columns**

Column experiments were conducted for undisturbed and homogenized samples for select plots at each trial site to address reproducibility and complete characterization of heavy metal
transport and sorption/desorption processes. To obtain undisturbed soil columns, the experimental columns were inserted along the vertical axis of the intact core thereby maintaining the same direction of flow in relation to structure orientation as that existing in the field. Homogenized columns were packed with selected soils (either baseline/background soils or heavy metal loaded soils) in incremental steps to establish uniform bulk density. Experiments were conducted using methods we have successfully used previously for characterizing contaminant transport in saturated porous media (Johnson et al., 2003a & b). Specifically, once the column is prepared, either a pulse of metal solution or metal-free water were introduced into the column at a selected flow rate until the metals have been completely eluted from the column. Hydrodynamic properties for the homogenized soils were determined by conducting conventional tracer studies and compared to those measured for the corresponding undisturbed soil systems. The data were analyzed using the method of moments to determine mass recoveries and travel times. Analyses were done both with and without extension of the low-concentration tail to evaluate the impact of below-detection concentrations on travel times. Furthermore, the resulting kinetic sorption/desorption data were compared to those measured in Task 6 from batch experiments.

For soils from selected trial sites, following complete elution of target metals from the loaded soil, a pulse of metal solution followed by metal-free water were introduced to the undisturbed soil column. The resulting data (e.g. heavy metal transport as well as sorption/desorption properties) were compared to that measured for the long-term loaded soil.

Task 8. Selected unsaturated soil columns

Unsaturated column experiments were conducted using undisturbed soil samples collected from selected trial sites. The metal-free water or metal solution (for cores collected from treatment plots and pre-treatment plots, respectively) were applied to the top of the column at a flux-rate smaller than the saturated hydraulic conductivity of the soil, maintaining unsaturated conditions in the soil cores. The resulting data (e.g. heavy metal transport as well as sorption/desorption properties) were compared to that measured for the saturated column experiments.
Task 9. Diagnostic Model Formulation

The experiments were interpreted within a framework of a dynamic model of metal behavior with the soil. The overall model structure is a dynamic mass balance in which metals are released from fertilizer into soil pore water. As discussed in an earlier section, the released porewater metals can move in three major pathways: uptake by soil constituents (clay minerals, metal oxides, microbes and organic matter); uptake by plant roots; and advective loss to ground or surface waters (leaching). In our model, each of these pathways were represented by a flux of metals with characteristic rate coefficient for each process for a given soil and system. The resultant system of differential equations can be solved readily using commercially available software such as the Stella dynamic modeling program.

The proposed model is diagnostic rather than prognostic. That is, the goal is not to be able to make exact prediction of metal behavior under a particular field condition, but rather to have a quantitative framework for understanding the relative importance of each transport process. A critical value of diagnostic modeling is that it was used iteratively to design experiments, test the results, and then further refine our conceptual understanding. For example, we can pose hypotheses about how the soil system will respond to a particular treatment, use the diagnostic model to predict the response in, say, a soil column experiment, and then design an experiment to look for those specific effects. The experiments will reveal the extent to which we have correctly conceptualized the actual process, and may suggest further refinements in both the model and in future experiments. As a consequence of this process of iteration, the basic model were developed early in the project, but then expanded and improved as we progress with the experimental work.
Part 1. Surface Charge Characterization and Adsorption of Cd and Pb on the Four Oregon Agricultural Soils

Summary

Cd and Pb adsorption isotherms and alkalimetric titrations were performed on four Oregon agricultural soils collected from different soil and climatic regions of the state. Soil surface stability constants, points of zero salt effect and adsorption coefficients were calculated and used to explain the difference in the susceptibility of the soils to heavy metals derived from phosphate fertilizer application. Cd is the metal of greatest concern in agricultural practice and its adsorption behavior was described best by Langmuir adsorption isotherms. The adsorption K values calculated were 0.40, 0.81, 0.65 and 0.78 for Hermiston, Hyslop, Klamath, and Pendleton respectively with the latter having the greatest adsorption maximum. The alkalimetric titrations showed the Hyslop site had the greatest buffering capacity and the largest number of different surface functional groups. The surface charge densities were 102, 65, 50 and 38 for Hyslop, Pendleton, Klamath Falls and Hermiston respectively. Overall, the soils from the Hermiston site are expected to be the most susceptible to leaching of cadmium while the Pendleton site soils had the greatest probability of long-term Cd or Pb accumulation.

Introduction

Heavy metal pollution from phosphate fertilizer application continues to be an area of concern in many parts in the USA (White, 2002). Cadmium, the heavy metal of greatest concern, is known to be mutagenic, carcinogenic, attack bones and teeth and accumulate in the kidneys and liver (Jarup, 1998). Differences still abound about the health risk associated with this non-source point of pollution. Of all the trace metals of environmental concern, cadmium is the most weakly bound and thus most easily leached by cations (Harter and Naidu, 2001) Cd does not degrade into end products but instead accumulates in the surface soil layers where it is bio-available and can end up in the food chain (Palagyi and Rigas, 2004). Cd and Pb frequently occur simultaneously and are usually the metals of greatest environmental concern (Rodriguez-Maroto et al, 2002).
The rate of movement of heavy metals such as Cd and Pb through the soil profile is determined by interactions with the soil surface. Particle-particle interactions, ion sorption and mineral dissolution are the chemical and physical processes occurring at the mineral-water interface. Soil charge is a result of protonation and deprotonation of the surface sites and is a function of pH and ionic strength of the soil solution (Gaboriaud and Ehrhardt, 2003). The surface sites are a mixture of the edges of lattice clay minerals, the surfaces of sesquioxides and amorphous materials including imogolite and organic matter (McBride, 1994). The soil intrinsic charge can be determined using alkalimetric titrations, crystallography, tritium exchange and measuring maximum adsorption densities (Lutzenkirchen et al, 2002; Dzombak and Morel, 1990; Stumm, 1992). The first method was used due to its versatility and ease of experimental set-up. The disadvantage of using this technique is lack of distinct points of inflexion and overlap of pKa values (Andjelkovic et al, 2006).

The surface chemistry of a soil determines how it will react with a species. Adsorption, desorption, precipitation and formation of inner or outer complexes are all determined by the functional groups at the soil surface. These groups are all affected by the soil pH with protonation and de-protonation changing the charge on them. Soil pH is one of the major factors controlling metal sorption (Christensen, 1984; Sposito, 1984) thus determining the pH dependent soil surface charge and point of zero charge, the adsorptive nature of a soil can be predicted and compared.

Using alkalimetric titrations, the various points of zero charge (pzc) can be determined and this parameter, according to Sparks (2003) is one of the most useful and significant chemical parameters that can be determined for a soil. The points of zero charge are pH values associated with specific conditions on the soil surface and they give information on adsorption characteristics and colloidal stability (Zelazny, 1996). The conventional PZC is the pH value when the total net particle charge vanishes. This point is also called the isoelectric point when measured by an electrokinetic experiment.

Another important pH value is the point of zero net proton charge (PZNPC) which occurs when the net proton charge density is equal to zero and it can be determined by alkalimetric titration. The point of zero salt effect (PZSE) can also be determined through this titration and it
is the located at the point of common intersection of plots of net proton surface charge versus pH measured at different ionic strengths of a background electrolyte. The point of zero net charge (PZNC) is the point where the difference in the cation exchange capacity (CEC) and anion exchange capacity (AEC) equals zero (Sposito, 1984).

A soil with a native pH greater than its PZC it will have a net negative charge whilst a lower pH will give the soil a net positive charge (Appel et al, 2003). These researchers showed that the PZSE and the PZNPC of an oxisol and ultisol were very similar but Zelazny et al, 1996 there may be some error to this estimation in some soils and other solid phase mixtures. Table 1 shows the pzc values of common soil constituents.

The acid base chemistry of whole soils is due to the complex mixture of hydrous metal oxides and humic acids present (Sposito, 1984). These structures have surface functional groups that bind metals through several different mechanisms. One such mechanism is cationic exchange. Exchange at hydrous metal oxide surfaces, through outer sphere metal complexation reactions, affects the soil solution pH. The reactions generally involve electrostatic bonding processes and thus are not as stable as inner sphere complexes. Ferrous hydrous oxide is one such surface:

\[ \text{Fe-OH} + \text{Cd}^{2+} = \text{Fe-O-Cd}^{2+} + \text{H}^+ \]

Similarly humic acids, a mixture of weakly acidic carboxylic acids and phenolic functional groups also play a major role in determining the soil solution pH (Fu et al, 1992, Takamatsu and Yoshida, 1978). The major disadvantage of direct alkalimetric titrations is the lack of distinct inflexion points and the overlap of pKa values of acidic groups (Andjelkovic et al, 2006).

Adsorption is believed to be one of the most important physicochemical processes involved in the binding organic and inorganic species in soils. It is affected by pH, ionic strength, presence of competing and complexing ions and nature of the substrate or adsorbing ion. (Srivastava et al, 2005). By determining the adsorption isotherms for the different soil the
kinetics of sorption reactions as well as near equilibrium conditions can be analyzed. Previous research work has shown soil has a higher affinity for lead than cadmium (Forbes et al, 1976; Chaturvedi et al, 2006).

The two major adsorption isotherms used to describe the binding of metals onto soil surfaces are the Langmuir and Freundlich isotherm. These non-linear isotherms have been found to more accurately explain heavy metals sorption which is often non-linear due to the many interactions and reactions occurring at the soil surfaces. For the Langmuir isotherm adsorption is said to only occur at independent sites with constant sorption energy independent of surface cover and it is limited by the formation of a monolayer (Weber and DiGiano, 1996). It is linear at low surface coverages but non linear at the higher surface adsorbent coverages. The Langmuir isotherm is represented by this equation:

\[
m = \frac{S_m K C_{eq}}{1 + K C_{eq}} \tag{1}
\]

where \( S \) is the mass of solute sorbed per dry unit weight of solid (mmol/kg), \( S_m \) is the maximum sorption capacity (mmol/kg), \( K \) is the sorption constant (L/mg), related to the binding energy of the metals and \( C_{eq} \) is the concentration of solution in equilibrium with the mass of solute sorbed onto the solid (mM). The linearized form is

\[
\frac{C_{eq}}{S} = \frac{C_{eq}}{S_m} + \frac{1}{K S_m} \tag{2}
\]

A plot of \( C_{eq}/S \) vs. \( C_{eq} \) yields a straight line with a slope of \( 1/S_m \) and an intercept of \( 1/ K S_m \).

The Freundlich isotherm shows the relationship between the sorbate and sorbent to be an exponential function of the solution.

\[
S = K_f C^{n_f} \tag{3}
\]

Where \( S \) is the mass of solute sorbed per dry unit weight of solid (mmol/kg), \( K_f \) is the Freundlich coefficient (L^n mg^{n-1}/kg), \( C \) is the concentration of solution in equilibrium with the mass of solute sorbed onto the solid (mM), and \( n_f \) the Freundlich exponent. The Langmuir isotherm is often preferred to the Freundlich form as it allows for calculation of a sorption maximum that can be correlated to intrinsic soil properties.
Materials and Methods

Reagents and Cleaning Techniques

Ultrapure water (resistivity = 8 MΩ; Nanopure system) was used in the preparation of all samples. All the glassware used was cleaned in detergent, rinsed thoroughly, soaked in a 5% HNO₃ acid bath for at least 24 h and then triple rinsed with ultrapure water prior to use. All chemicals were ACS reagent grade or better. Acids for dilution of standards (HNO₃ or HCl) were Baker Ultra Pure grade and all standards were spectrometry grade and NIST-traceable.

Sample Collection

Cleaned trowels were used to collect multiple surfaces samples (0 – 20 cm below ground surface, or bgs); so called deep intact core soil samples (100 – 120 cm bgs) were collected by drilling prewashed polyvinyl chloride tubing into the ground at the four different research sites representing agricultural areas of Oregon: Upper Klamath Basin Experiment Station (KB), Columbia Basin Experiment Station (Pendleton) (CB), Hyslop Experiment Station (Willamette Valley) (WB), Hermiston Experiment Station (HB). Three soils samples were taken from each site in Subplots 1203, 3303 and 4403

<table>
<thead>
<tr>
<th>Site</th>
<th>Soil Classification</th>
<th>Soil Name/Texture</th>
<th>pH</th>
<th>Bulk Density</th>
<th>Khₛ (µmsec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyslop</td>
<td>Fine – silty, mixed, superactive, mesic aquultic agrierolls</td>
<td>Woodburn silt loam</td>
<td>5.1-6.5</td>
<td>1.25-1.45</td>
<td>4.0 – 14</td>
</tr>
<tr>
<td>Columbia Basin</td>
<td>Fine silty, mixed, mesic Pachic Ultic Haploxerolls</td>
<td>Palouse silt loam</td>
<td>5.6-7.3</td>
<td>1.10 - 1.30</td>
<td>4.0 – 14</td>
</tr>
<tr>
<td>Klamath Falls</td>
<td>Sandy, mixed, mesic torripsammentic Haploxerolls</td>
<td>Fordney Loamy fine sand</td>
<td>6.6-8.4</td>
<td>1.30-1.40</td>
<td>14-42</td>
</tr>
<tr>
<td>Hermiston</td>
<td>Coarse – loamy, mixed mesic Xerollic Camborthids</td>
<td>Adkins fine sandy loam</td>
<td>6.6-9.0</td>
<td>1.55 -1.70</td>
<td>14-42</td>
</tr>
</tbody>
</table>

Table 1. Soil characteristics.
To obtain composite samples, 2-3 kg of the samples were randomly collected from the same horizon at a site and combined prior to being doubled bagged. The samples were air dried, crushed and sieved through a 2mm sieve (U.S. Standard Sieve Series No. 10) using a Tyler Combustion Engg. Inc. Portable Sieve Shaker Model RX24, prior to characterization.

**General Soil Analysis**

Detailed soil analyses were performed by researchers at Oregon State University. We conducted basic analyses of soil pH, particle-size distribution, and soil Pb and Cd to verify the characteristics of the actual samples used in our studies. Soil pH was measured (pH meter Orion Expandable ionAnalyzer EA920) in a background electrolyte of 0.01 M LiClO$_4$ (1:2 solid to solution). An ionic strength of 0.01 M is a good simulation of field soil solution conditions (Harter and Naidu, 2001). The concentrations of available Pb and Cd were determined using the Mehlich double acid extraction method (Methods of Soil Analysis Part 2 Ch. 19 Pg. 334). Particle size analysis was determined using the hydrometer method (Table 1).

**Alkalimetric Titrations**

A 1.0-g sample of soil was mixed with 100ml of 0.01N LiClO$_4$ background electrolyte and the solution allowed to equilibrate. The soil solution was acidified with standardized 0.1 N HCL to a pH of 4.5. The soil solution was gently stirred continuously and equilibrated overnight in a CO$_2$ free environment under purified N$_2$ gas. Fig. 1 shows the apparatus schematic. From the pH of 4.5, the system was titrated in eight to ten steps using CO$_2$ free, standardized 0.50 M LiOH to pH of 8.5. After each addition the system was allowed to equilibrate and the pH monitored until the pH drift was less than 0.01mV/min, typically after 30 min. The titration vessel was maintained at a slight over pressure of nitrogen throughout the titration to exclude atmospheric CO$_2$. To determine the effect of Cd on the soil acid–base chemistry, the soil solutions were spiked with 0.1 mM cadmium and a similar procedure as above was followed. The point of zero salt effect was determined by changing the background electrolyte concentration of 0.001 M LiClO$_4$ to 0.01 M LiClO$_4$ and 0.1 M LiClO$_4$. 

[20]
**Isotherm Experiments**

Batch equilibrations were performed by placing 1-g soil samples in 50 ml acid-washed polypropylene screw cap vials and equilibrating with 30 ml of 0.01N LiClO₄ containing 5.6 ppm (0.05 mM), 28 ppm (0.25 mM) and 56 ppm (0.5 mM) Cd and 10.3 ppm (0.05 mM), 51.8 ppm (0.25 mM) and 103.6 ppm (0.5 mM) Pb (The analysis concentrations were made from 1000 ppm Assurance certified standards). All isotherms were done in duplicate; controls with no soil and no Cd were also performed. The soil suspensions were equilibrated for 36 hrs at 25 ± 2 °C using a table top shaker (IKA Vibrax VXR) at 150 rpm. The pH of the soil solutions was adjusted to the native soil pH prior and after shaking. Adjustment was done using required amounts of 0.1N HNO₃ and 0.1N NaOH. The pH of the sorption isotherms was not controlled to better approach field soil conditions. Following equilibration the samples were centrifuged for 30 mins at 3600 rpm (International Clinical Centrifuge Model CL) and the supernatants were filtered using 0.45 μm membrane pore filters. With the replicates on each of the three subplots, and analyzing both Cd and Pb, a total of 48 isotherms were collected.

The filtrates were analyzed for Cd and Pb by either Inductively Coupled Plasma Mass Spectrometer (ICP-MS; Perkin Elmer HP-4500) or flame atomic adsorption spectrophotometer (Perkin Elmer AAnalyst-300 Atomic Absorption Spectrophotometer (AAS)). The samples were stored at 4 °C prior to analysis. The differences between the initial (C₀) and the equilibrium solution concentrations (Cₑ) were calculated to determine the sorbed (S) per unit mass of soil. The data was fit to linearized Freundlich and Langmuir isotherms to determine the best fit and determine a distribution coefficient.

**Results and Discussion**

**Alkalimetric Titrations**

The alkalimetric curves for the four soils studied are seen in Fig. 2 and show a decreasing buffering capacity in the soils; Hyslop > Pendleton > Klamath Falls > Hermiston. Buffering capacity is the ability for a soil to resist a change in pH and is usually dependent on the clay and humic content of the soil. Soils with a high buffering capacity tend to have a high cation exchange capacity (CEC) (Brady and Weil, 1996). The titration curves have no clear
points of inflection which is consistent with soil titrations. A plot of the dpH/dv as a function of pH (Fig 3) showed the number of different soil surface functional groups in the soils with the maxima denoting the neutralization of the functional groups and the minima corresponding to the pKa values of the functional groups present in the soil.

The Hyslop site has the most complex chemistry and the behavior of the soils in the alkalimetric titrations was consistent with the particle size analysis which showed the Hyslop soil having 8 times the clay content of Hermiston soils, by percent. The alkalimetric titrations also allowed for calculation A-, the number of free functional groups at the soil surface sites. At pH zero, the Hyslop soil has about 103ueq functional groups /g of soil and the least reactive soil, the Hermiston soil has about 2.5 times less available functional groups (Fig.4.)

An important characteristic of soils used to describe variable surface-charge is the common intersection point or point of zero salt effect (PZSE) (Fig. 5) which is the point where the net adsorption of potential-determining ions are independent of the electrolyte concentration (Appel et al, 2003) For the Klamath Falls site, this occurs at a pH of 6.7, equal to that of α-Fe2O3 (Stumm and Morgan, 1981). As the native soil pH is 5.7, the soil has a negative surface charge. At lower pH there is very little variability in the titration curves and this could be due to a predominant consumption of protons by mineral dissolution reactions instead of generating surface charge (Lindsay, 1979) Table 2 shows the PZSE values of the soils. Figs 6-8 show the sequential transformation of alkalimetric data to the Henderson-Hasselbach plot which gives the single “effective” pKa for the soil surface acid base sites.
Titration of Oregon soils in 0.01M LiClO₄ background electrolyte

Figure 2. Alkalimetric titration curves for four Oregon soils
Neutralization of Acidic groups

Figure 3. Plot showing neutralization of soil-surface acidic groups; the inflections reveal the differences among soil surface functional groups.
Alkalimetric Soil Titrations for Oregon soils

Figure 4. Plot to determine soil surface charge density

Figure 5. Potentiometric (alkalimetric) titration curve for Klamath Falls soil
Figure 6. Transformation of alkalimetric (potentiometric) titration data to show accumulation of negative soil surface charge (A-) as a function of pH. Willamette (Hyslop) and Hermiston Soils
Figure 7. Transformation of alkalimetric (potentiometric) titration data to show the apparent surface acid-ionization constant (effective pKa = -log Ka) as a function of pH. Willamette (Hyslop) and Hermiston Soils.
Figure 8. Transformation of alkalimetric (potentiometric) titration data to Henderson-Hasselbach plots which show the most effective single pKa for a multiprotic system. In this case 7.2 for Willamette (Hyslop) and 7.5 for Hermiston Soils.
Willamette Cadmium Adsorption Isotherm

Cadmium Adsorption Isotherm for Hermiston

Figure 9. Cd isotherms for Willamette (Hyslop) soil.

Figure 10. Cd isotherms for Hermiston soil.
Figure 11. Cd isotherms for Columbia Basin soil.

Figure 12. Pb isotherms for Willamette (Hyslop) soil.
Figure 13. Comparative Cd and Pb adsorption isotherms (I = 0.01 M LiClO$_4$)
Figure 14. Model fitting of the Oregon soil isotherm data using the Langmuir and the Freundlich models
Table 2. Point of zero charge (PZC) values of some common soil constituents.

<table>
<thead>
<tr>
<th>Soil Component</th>
<th>pzc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>9.1</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>6.5</td>
</tr>
<tr>
<td>FeOOH</td>
<td>7.8</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2.0</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Table 3. Point of zero salt effect (PZSE) which measures the effective pH of neutralization of charged soil binding sites (PZC)

<table>
<thead>
<tr>
<th>Soil Site</th>
<th>PZSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hermiston</td>
<td>5.9</td>
</tr>
<tr>
<td>Hyslop</td>
<td>6.2</td>
</tr>
<tr>
<td>Klamath Falls</td>
<td>6.7</td>
</tr>
<tr>
<td>Pendleton</td>
<td>6.6</td>
</tr>
</tbody>
</table>
Table 4. Soil Characteristics: pH and particle size distribution

<table>
<thead>
<tr>
<th>Soil</th>
<th>pHa</th>
<th>Sand –Silt -Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hermiston</td>
<td>4.9</td>
<td>88-10-2</td>
</tr>
<tr>
<td>Hyslop</td>
<td>5.5</td>
<td>38-46-16</td>
</tr>
<tr>
<td>Klamath Falls</td>
<td>5.7</td>
<td>89-7-4</td>
</tr>
<tr>
<td>Pendleton</td>
<td>5.9</td>
<td>62-27-11</td>
</tr>
</tbody>
</table>

*a 1:2 soil/water ratio,

Table 5. Summary of Oregon Soils Cd Equilibrium Modeling parameters

<table>
<thead>
<tr>
<th>Model</th>
<th>Pendleton</th>
<th>Hermiston</th>
<th>Hyslop</th>
<th>Klamath Falls</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cmax</td>
<td>15.51</td>
<td>9.67</td>
<td>10.06</td>
<td>12.10</td>
</tr>
<tr>
<td>K</td>
<td>0.78</td>
<td>0.40</td>
<td>0.81</td>
<td>0.65</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kf</td>
<td>497</td>
<td>285</td>
<td>392</td>
<td>305</td>
</tr>
<tr>
<td>nf</td>
<td>0.503</td>
<td>0.416</td>
<td>0.38</td>
<td>0.403</td>
</tr>
</tbody>
</table>

[34]
Adsorption Isotherms

All the sites showed non-linear adsorption isotherms for cadmium and lead (Figs. 9-13). The Pendleton (CB) soil had the greatest adsorption of both metals and while the soil affinity for Pb was greater than for Cd at all the sites. Similar sorption behavior was seen by Appel and Ma, 1994, Hooda and Alloway, 1998 and Phillips, 1999. At an initial concentration of 0.05mM all the sites had similar adsorption but there is a very marked difference in behavior as the concentration increased. The smaller hydrated radius of Pb, 0.401nm compared to 0.426nm for Cd (Evans, 1989) and higher affinity for most functional groups in organic matter make it more likely to undergo inner sphere complexation (Appel and Ma, 1994) Lead forms monodentate inner- sphere complexes compared to bidentate complexes for cadmium (Srivastava, 2005) The lead adsorption isotherms for Pendleton and Hyslop are linear but the remainder of the isotherms show considerable deviation from linearity for the range of concentration studied. The cadmium adsorption isotherms for this range of concentration tended towards an adsorption maximum.

Metal sorption followed the general trend of Pendleton > Hyslop > Klamath falls > Hermiston. This followed the pH trend but was contrary to the clay content (Table 3), a deviation that was also observed by Appel and Ma, 1994. The correlation of pH and adsorption suggested the soil variable charge was the major determinant for adsorption in these soils. The Cd (II) speciation diagram shows that in the soil solution pH ranges Cd $^{2+}$ and Cd(OH)$^{+}$ are the main species and they compete with the H$_3$O$^+$ ions for soil adsorption sites. As the pH decreases H$_3$O$^+$ ions increase and electrostatic repulsion from the soil surface increases reducing the adsorption of the Cd ions (Agrawal and Sahu, 2006)

The data from the adsorption isotherm experiments were modeled using the Langmuir and Freundlich models and model parameters determined (Table 4). For all the sites the Langmuir isotherm model gave a better fit (Appel and Ma, 1994) (Fig. 14). For the range of concentration studied all the Cd isotherms had sorption maxima ($S_{\text{max}}$) but only the Hermiston Pb isotherm had a clear maximum, due to the very high affinity of the other soils for Pb. The Pendleton soil exhibited the greatest affinity for both metals although it had a very similar sorption constant as that of the Hyslop soil.
Effects of Major Cations in Soil Water and Soil Particle Size

The choice of background electrolyte affects the adsorption of Cd onto soil. In order to obtain consistent and reproducible results that can be compared easily with other researchers, we used LiClO4 in most experiments. However, it is known that divalent cations such as Ca can diminish the amount of sorption by competing with Cd for binding sites on the soil. We verified this for the Klamath Basin soil (Fig. 15). Substituting Ca for Li induces up to about a 30% decrease in the amount of Cd sorption, but the effect is only significant at relatively high levels of Cd. At levels typical of agricultural soils, the isotherm parameters indicate that effect of Ca is minimal.

Grain size variation is also a potential source of Cd parameter variability, since smaller grains have a higher specific surface area and thus tend to show more adsorption pr unit mass of soil. It is desirable to factor out the grain size effect since it is due to the dimension of particle surface and not an intrinsic chemical characteristic of the surface binding sites.

To examine this effect we took sieved fractions of Klamath Basin soil: Large (> 125 um), Medium (>63 um - <125 um) and small (<63 um). Some variation was detected as shown in Figs. 16-19. The large soil size fraction showed the least strong adsorption (effective K_d = 43.9 to 174 L kg^-1) while the capacity for adsorption was greatest in Small soil size fraction (effective K_d = 152 to 460 Lkg^-1). However, the amount of fines in this relatively sandy soil was modest so the small size fraction had little influence of the adsorption of the total soil. The composite mixture was represented best by the medium soil size fraction (Fig. 20), although the large fraction only slightly underestimated the adsorption.
Figure 15. Effect of Ca vs. Li background ions on Cd adsorption on Klamath soil.

Figure 16. Effect of grain size fraction of Cd adsorption on Klamath soil. Large size (Replicates I and II) and the Composite mixture
Figure 18. Effect of grain size fraction of Cd adsorption on Klamath soil.
Medium size fraction (Replicate I and II) and the Composite mixture

Figure 19. Effect of grain size fraction of Cd adsorption on Klamath soil.
Small size fraction (Replicate I and II) and the Composite mixture
Figure 20. Modeling the composite Klamath soil mixture: Bulk soil behavior dominated by medium-to-large grains
Comparison of Model Prediction to Field Observations

Core samples from the upper approximately 40 cm of soil at the Oregon field sites showed that levels of Cd in the tillage zone, although low, were somewhat elevated compared to deeper soils that presumable reflect a more background concentration. A typical plot is shown in Fig. 21 for Klamath Basin soils, but the data are quite similar for all other sites. This field evidence of gradual accumulation in the upper zones is consistent with the results we found for strong adsorption of Cd at low Cd levels and relatively low mobility.

Figure 21. Depth of elevated levels of Cd in soil at the Klamath Basin site compared to deep soil “background level”. The depth of Cd is taken as the inflection point of the Cd vs. depth plot.
Summary and Conclusions: Part 1

The alkalimetric titrations showed the Hyslop soils had the greatest buffering capacity and the Hermiston soils had the least. Cd$^{2+}$ is mobile under $< pH 5$ conditions so the low buffering capacity of the Hyslop soils make them susceptible to leaching of cadmium. The low adsorption maximum, low clay content and low surface charge density determined in this paper are consistent with this conclusion. The order for potential of accumulation of cadmium in the surface soil of the sites from fertilizer is Pendleton > Hyslop > Klamath Falls > Hermiston. The behavior of Pb over the concentration range studied suggests there is negligible concern of its movement in the vadose zone of the soils as it strongly adsorbed onto the soils. The greatest mobility of Pb would be expected in the Hermiston soils although this is also expected to be slow.

Background electrolyte has some effect of adsorption of Cd, as Ca tends to depress it. However, the relative strength of Cd binding compared to Ca binding means that the effect is only pronounced at high total Cd levels and is not significant at the levels of Cd found in typical agricultural soils in Oregon. Particle size distribution can influence the variability in apparent adsorption strength for a given soil. A large fraction of fines can enhance adsorption. However as long as the percent of fines does not vary great at a site (often true for tilled agricultural soils) then this effect will be minimal. It can be accounted for by examining the variation in the percent of soil in the fraction $<63$ um.

Finally, core samples from all the field show evidence of gradual accumulation in the upper part of the soil profile. This accumulation is consistent with the results we found for strong adsorption of Cd at low Cd levels and relatively low mobility.
Part 2: Kinetics of Fertilizer-Derived Cd in Agricultural Soils and the Factors that Affect its Rate of Release.

Background

Fertilizer dissolution has been an area of considerable interest (Liang et al, 2007, He et al 2005, Shavit et al, 1997) with a view to determining nutrient release and environmental problems arising herein. Slow release fertilizers are a result of this research and although they address the former issue, they do not address the latter issue of environmental fate. There is a dearth of information with regards to the fate and transport of the trace metals such as Cd that leach into soils as a result of fertilization. Cd, a trace metal and impurity of phosphate fertilizer is known to be present in substantial amounts depending on the parent rock. Accumulation of Cd in soil can occur due to the long term use of phosphate fertilizers although this does not always lead to a bio-accumulation of Cd in plants. Williams and David, (1976) both showed that about 80% of the Cd added as phosphate fertilizer over a 20 year period accumulated in the top 7.5 cm of soil except when the soils were podozols. There is also very little information on the short term release kinetics (0-24 h) of phosphate fertilizers which can be of issue in waterlogged, poorly irrigated and areas with frequent heavy rains.

The dissolution of one of the major minerals in phosphate fertilizer, mono-calcium phosphate monohydrate has been extensively studied (Lehr et al, 1959; Lindsay and Stephenson, 1959) and it involves dissolution to brushite and monetite accompanied by a drop in pH according to the following reaction

\[ \text{Ca}(\text{H}_2\text{PO}_4)\cdot\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{CaHPO}_4\cdot2\text{H}_2\text{O} + \text{H}_3\text{PO}_4 \]

The drop in pH mobilizes heavy metals such as Cd which is very mobile under acidic conditions however the drop in pH is quickly corrected by the buffering capacity of the soil and precipitation of phosphate salts.
In soils, Cd and phosphorus soil levels have been shown to be well correlated. Substantial experimental evidence has also shown that phosphate rock, the chief constituent of phosphate fertilizers, is capable of immobilizing heavy metals in contaminated soils. (Ruby et al, 1994; Ma et al, 1995; Mustafa et al, 2004) Co-adsorbents such as oxalate, sulfate and phosphate are known to affect the adsorption of Cd onto soils (Collins et al, 1999; Lee and Doolittle, 2002) with phosphate being known to enhance Cd adsorption on goethite (Wang and Xing, 2002). Krishnamurti et al (1999) showed the opposite was true due to the formation of phosphate complexes in solution. The Lee and Doolittle paper further suggested the source of phosphate, mono-potassium phosphate versus di-potassium phosphate, also affected adsorption with the former decreasing adsorption whilst the latter enhanced adsorption. In a study of potassium phosphate fertilizer, the release profile of potassium has been found to very similar to that of phosphate. (Notario del Pino et al, 1995). These researchers also found the P release follows first order kinetics with an initial slow step.

This part of the project addressed the hypothesis that the release of Cd is controlled by the dissolution and precipitation reactions of phosphorus and the release of Cd is partially diffusion controlled due to the fertilizer coating which aids in the slow release of the macronutrients. Also the release of the Cd and P follows first order kinetics with pH, organic content of the soil and ionic strength of the rain water affecting the rate of release of both ions.

By understanding the release kinetics the environmental fate and transport of both P and Cd can be ascertained. This part of the project focused on whether there is a re-release of Cd after extraction of P from the soil by plants and if so, how quickly the Cd move through the soil profile?

Materials and Methods

A series of column experiments were conducted to determine the dissolution of fertilizer in Monterey sand. Several different solvents were used to leach out the Cd, each with the intention of answering some questions as to the chemistry behind the release of Cd. By determining the release of the phosphorus and the Cd, the chemistry occurring could elucidated. See table below.
<table>
<thead>
<tr>
<th>Question</th>
<th>Experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>What is the profile for Cd release, conductivity, pH, phosphorus release.</td>
<td>Column eluted with 18m_ Nanopure water</td>
</tr>
<tr>
<td>What effect do chelating agents have on the Cd release?</td>
<td>Column eluted with 10-4M EDTA (EDTA proxy for soil humic matter)</td>
</tr>
<tr>
<td>Can pH make a difference to the Cd release?</td>
<td>Column eluted with acetate buffer solution of pH 5.5</td>
</tr>
<tr>
<td>Does grain size of fertilizer affect the Cd release profile?</td>
<td>Ground fertilizer pellets were used</td>
</tr>
<tr>
<td>What effect does ionic strength have on the Cd release?</td>
<td>The column will be eluted with 0.001N, 0.01N and 0.1NLiClO4</td>
</tr>
</tbody>
</table>

Acid-washed Monterey sand (Uniformity coefficient =1.5, Effective size = 0.45 - 0.55cm) was repeatedly washed with ultrapure water and then allowed to air dry for 2 days prior to use. The sand (200g) was placed in a polyethylene column (internal diameter, 15cm; length,10cm). The column was flushed with ultrapure water to moisten it and determine the background eluent conditions. The Cd and phosphate concentrations obtained were negligible. Fertilizer (1g, 30grains) was then overlain on the sand and solutions of differing composition (see table below) were flushed through. Ground fertilizer was also used to determine how much of an effect the fertilizer granules have on Cd release. The eluents were introduced as a wash at 50ml/hr and the eluates collected with pH and conductivity being measured. The eluates were also analyzed for orthophosphate content (using the Hach ammonium paramolybdate test) and then Cd content (using flame atomic adsorption spectroscopy, FAAS and inductively coupled plasma mass spectroscopy ICP-MS).
# Differing Experimental Conditions

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Column eluted with 18m_ ultrapure water</td>
</tr>
<tr>
<td>2.</td>
<td>Column eluted with $10^{-4}$M EDTA</td>
</tr>
<tr>
<td>3.</td>
<td>Column eluted with 0.01 M acetate buffer solution of pH 5.5</td>
</tr>
<tr>
<td>4.</td>
<td>The column will be eluted with 0.01N LiClO$_4$</td>
</tr>
<tr>
<td>5.</td>
<td>Phosphate fertilizer of different Cd content will be used</td>
</tr>
</tbody>
</table>

---

**Schematic of apparatus**

Fertilizer overlain

Sand

Mesh

Solute wash

Leachate collected and analyzed for pH, orthophosphate, conductivity and Cd.
Results and Discussion

**Elution with Ultrapure Water.** Elution of the fertilizer by ultrapure water only resulted in a striking and reproducible pattern in which Cd concentrations spike relatively quickly but then drop to low levels (Fig. 22). The Cd release is mirrored in the elution by a very similar time course for electrical conductivity (EC), which is an index of total salts released from the fertilizer. The pH dips only very slightly (<0.2 units) during the spike of Cd and EC and not to the extent that might be expect from the dissolution reaction noted above. It is likely that, at the microscale of the zone immediately surrounding a fertilizer pellet that the pH drop is greater, but our results show that even in a poorly buffered (pure water) eluent, the pH at a porous-medium scale of just a few centimeters is relatively constant and is probably buffered by the combination of phosphate salts eluting from the fertilizer.

Phosphorus release rises rapidly, as expected, and unlike the Cd, remains high throughout the elution. Because the Cd release rose and dropped so quickly compared to P release, we next examined the fate of Cd and P in the system to identify the total amount of each that was released from the original fertilizer levels. Cd and P were measured in the water phase, the amount clinging to the sand after a brief rinse, and in the remaining identifiable pieces of fertilizer granules. As shown in Fig 23, only about 10% of the Cd in the fertilizer was released in the first 24 hr of elution, whereas over 95% of the total P was released in the same period. This important finding shows that Cd release cannot be assumed to mimic the release of the parent P minerals in the fertilizer and that some chemical process inhibits the solubility of Cd in the fertilizer-water system. The mostly probable explanation seemed to be the existence or formation of a low-solubility Cd-phosphate solid phase. This was tested by the addition of a chelator to the eluent.

**Elution with EDTA Chelator**

If a C-P solid phase inhibits the release of Cd, then the addition of a chelating agent that binds up soluble Cd and thereby reduces the activity of Cd\(^{2+}\) in solution should enhance the release of Cd. We used a dilute (1 x 10\(^{-4}\)M) Na\(_2\)EDTA solution. The reaction for an unspecified “Cd-P” solid is:
“Cd-P” + EDTA  = Cd-EDTA + P

Where the soluble Cd-EDTA complex appears in solution as released Cd.

When the column was eluted with $10^{-4}$M EDTA, there was indeed a marked increase in the amount of Cd released in the initial spike. The peak concentration was about 80% higher and the total Cd released in the first 7 h was 3.5 times greater (Fig 24). The EDTA had negligible effect on the P release. The initial EC spike was enhanced by the EDTA, in approximate proportion to the enhancement of Cd release, suggesting that EC is a fairly consistent marker of the release of Cd from the fertilizer. EDTA thus appears to promote the dissolution of the phase that otherwise limits the release of Cd. However, the pH of the solution can also affect release rates.

The pH varies more in the EDTA experiments than in the water-only elution (Fig. 25). The initial pH with EDTA is 6.8 (compared to 6.1 for water only) because of the mildly basic effect of the sodium EDTA salt, but the pH quickly drops to about 5.5 as Cd ions displace protons from the EDTA. The pH then gradually rises back to 6.1 after 6 h of elution, presumably because of the buffering effect of the dissolved phosphates. The drop in pH potentially complicates the interpretation of the EDTA experiment because a lower pH could also enhance solubility of a Cd-P solid phase.

Note also that in soils, natural humic substances can chelate Cd. Although EDTA is a more powerful Cd chelator that humic or fulvic acids, our results suggest that naturally occurring organic matter, especially in very organic-rich soils, could accelerate the release of Cd from fertilizer.

**Elution with a Buffered Solution to Fix pH.** To test the effect of pH only, we created an eluent solution with a dilute acetate buffer to fix the pH at the lowest pH (approximately 5.5) observed in the EDTA elution. This elution thus mimics the lowest pH created by EDTA but with no chelating agent (acetate is only an extremely weak ligand for Cd). As shown in Fig. 26, eluting
the column at pH 5.5 resulted in an initial peak of Cd that was similar to that of the water-only elution and which was about 50% less than the peak Cd observed in the EDTA elution. The “tail” of the Cd elution (after 4 h) was greater with buffer than with water only, but the total release of Cd after 7 h was less than two times as much as the water-only, compared to 3.5 times greater with the EDTA. The results suggest that a consistently lower pH (near 5.5) does enhance Cd release but that the effect of EDTA is substantially greater than the effect of pH alone, especially given that the pH in the EDTA experiments was higher than 5.5 for most of the elution. We conclude that the Cd-chelating effect of the EDTA explains most of the enhanced dissolution that the EDTA induced. Note that both the EDTA and the acetate buffer results are consistent with the release of Cd being regulated by a relative insoluble phase after the initial flush of rapid dissolution.

**Effect of Pellet Size: Grinding Fertilizer.** We were interested in seeing whether the size of the fertilizer pellet significantly affect the release of Cd. For these experiments we ground the pellets in a mortar and pestle to a coarse powder and then replicated the water elution experiment using the same mass of fertilizer. The peak Cd in the initial spike was virtually identical in the crushed fertilizer compared to the original uncrushed result (Fig 28) and the EC and pH patterns were likewise almost identical for crushed and uncrushed (Fig. 29). However, there cumulative release of Cd over time was actually less for the crushed pellets for the uncrushed (Fig. 30). The reduction if release from smaller pellet sizes is counterintuitive until one examines the cumulative release of P which is expectedly larger for the crushed pellets (Fig. 31). We interpret this result to indicate that Cd solubility after the initial peak flush is indeed controlled by a relatively insoluble Cd-phosphate phase because the higher P in the crushed pellet experiment would drive down the solubility of a Cd-P solid phase, thereby suppressing the total release of Cd. A comparison of the relative effects of EDTA and crushing on Cd and P release is shown in Figs. 32 and 33.

**Elution of Fertilizer in Oregon Agricultural Soils.** The elution experiments were repeated using columns packed with homogenized soil samples from the four Oregon sampling sites
(Hyslop, Columbia Basin, Klamath, and Hermiston). The soils were eluted under the same condition as the sand experiments using ultrapure water with a dilute neutral electrolyte (0.01 M LiClO4) to simulate rainfall or irrigation. In all cases, no Cd was ever observed to elute from the columns, even after over 100 pore volumes were passed through the columns. The detection limit for Cd with the ICP-MS was less than 1 ppb. These results are completely consistent with our adsorption isotherm data (previous section) that showed that Cd was strongly bound to all soils at the low total Cd concentrations produced by the elution of fertilizer.

Figure 22. Cd, P and EC as a function of time during elution with ultrapure water.
Figure 23. Distribution Cd and P after 24 h: Amounts found in water, sand or remaining fertilizer.
Figure 24. Cd and P release from fertilizer during elution with a 1 x 10^{-4} M EDTA solution.
Figure 25. Cd and P release from fertilizer during elution with a 1 x 10^{-4} M EDTA solution.

Figure 26. Cd and P release from fertilizer during elution with a 0.01 M acetate buffer solution (pH 5.5-5.6, see Fig 6).
Figure 27. pH and EC during fertilizer elution with a 0.01 M acetate buffer solution. Control experiment with buffer but no fertilizer demonstrates that EC due to acetate was low and did not swamp out the EC signal of the fertilizer.

Figure 28. Cd and P release from fertilizer ground to a coarse powder to test effect of fertilizer grain size on release.
Comparison of Conductivity and pH change

![Graph showing conductivity and pH change over time](image)

Figure 29. pH and EC in elution of fertilizer ground to a coarse powder to test effect of fertilizer grain size on release.

Comparison of Cumulative Cadmium Release

![Graph comparing cumulative cadmium release](image)

Figure 30. Comparison of the effects of EDTA and pellet crushing on the cumulative elution of Cd
Figure 31. Comparison of the effects of EDTA and pellet crushing on the cumulative elution of P.

Figure 32. Comparison of eluent Cd concentrations showing relative effects of EDTA chelation and pellet crushing.
Figure 33. Comparison of eluent P concentrations showing relative effects of EDTA chelation and pellet crushing.
**Energy Dispersive X-ray Analysis and SEM Imaging.** Energy Dispersive X-ray (EXD) was used to determine the chemical composition of the surface. The results show the main cation is Ca while Cd is only about 1% by weigh (Fig 34).

![Quantitative results](image)

*Figure 34. Energy Dispersive X-ray (EXD) of fertilizer, showing preponderance of Ca and phosphate at the pellet surface with only a small signal for Cd.*

SEM images of the fertilizer surfaces were taken to determine there were any evident irregularities in the fertilizer surfaces that might contribute or inhibit the release of Cd and P. Prior to elution (Fig 35a), surfaces generally were more amorphous and less microporous than the surfaces after 4- h of elution (Fig 35b) where exposed crystals were more evident on the fertilizer surface and there was possibly greater microporous structure as a result of the dissolution of readily soluble amorphous phases. We believe the relative disappearance of
amorphous material in the early stages of particle dissolution is consistent with the initial spike in both Cd and EC. The residual, more crystalline, phases can be expected to have lower solubility.

Figure 35. SEM images of the 2005-06 fertilizer (10,000X) a) before elution (left), and b) after 4 h of water elution (right).
Summary and Conclusions: Part 2

These experiments showed the importance of dissolution kinetics in understanding the release of Cd in unsaturated porous media such as soils. Under typical conditions we expect that only about 10-20% of Cd will be released quickly in soluble form and that most of the Cd will remain associated with very slowly dissolving solids. The experiments with EDTA, acetate buffer, and particle grinding are all consistent with a Cd-phosphate phase regulating the slow release of Cd. The finding of limited rapid release followed by slow release of most Cd is very significant because it means that the rate of uptake of Cd by soil surfaces will be more rapid than the release of most Cd. That is, Cd released by the fertilizer will be sorbed by the soil faster than it can leach away.

This finding is confirmed by the experiments in which Oregon agricultural soils were used instead of the washed sand. With real soil, the uptake of Cd by the soil surfaces ensures that no detectable Cd eluted from the columns, even after 100 pore volumes or more. The results thus show the predictive value of the isotherm data presented in the prior section. An equilibrium model is appropriate for these Oregon agricultural soils because the release of Cd fertilizer is slow enough to allow sorption equilibrium to be broadly applicable to field-scale behavior. These data furthermore reinforce our prior conclusion that Cd is most likely to accumulate in rather than leach from Oregon agricultural soils. Any losses of Cd from the soil column are expected to be at extremely low (part per billion) levels and are expected to occur over long spans of time (time scale of years).
Part 3: Miscible Displacement of Cd in Undisturbed (Intact) Cores

Background

As discussed in the report introduction, one goal of the research was to examine the transport of Cd and other solutes in laboratory columns that retain as much as possible of the heterogeneity found in the field. This section describes column experiments for undisturbed and homogenized samples for select plots at each trial site to address reproducibility and complete characterization of heavy metal transport and sorption/desorption processes. The pros and cons of the batch methods discussed in Part 1 of this report and column methods are summarized:

**Batch Method**

- Mix soil with a solution containing the contaminant for a specific amount of time.
- Amount sorbed is the difference between the initial and final contaminant concentration.
- Adsorption and desorption are assumed reversible.

**Advantages:**

- Can be completed quickly and relatively easily.

**Disadvantage:** Does not reproduce the rates at which chemical reactions take place in the real environment.

**Miscible-Displacement Method**

- Pass a liquid spiked with contaminant of interest through a soil column.
- Amount sorbed can be evaluated by “breakthrough curves” (BTC).
- Adsorption need not be fully reversible

**Advantages:**

- Combines the chemical effects of sorption and the hydrologic effects of groundwater flow to provide a direct estimate of R.
- Influence of partial saturation can be studied.

**Disadvantage:** High equipment cost, time consuming, experimental complexity.
Methodology

To obtain undisturbed soil columns, the experimental columns were inserted along the vertical axis of the intact core thereby maintaining the same direction of flow in relation to structure orientation as that existing in the field. Homogenized columns (Fig. 36) were packed with selected soils (either baseline/background soils or heavy metal loaded soils) in incremental steps to establish uniform bulk density. Experiments were conducted using methods we have successfully used previously for characterizing contaminant transport in saturated porous media (Johnson et al., 2003a & b). Specifically, once the column is prepared, either a pulse of metal solution or metal-free water was introduced into the column at a selected flow rate until the metals have been completely eluted from the column. Background electrolytes used were $0.01 \text{ N LiClO}_4$ and $0.01 \text{ N CaCl}_2\cdot2\text{H}_2\text{O}$. For selected samples, an unsaturated flow system was used (e 38).

Hydrodynamic properties for the homogenized soils were determined by conducting conventional tracer studies and compared to those measured for the corresponding undisturbed soil systems. The data were analyzed using the method of moments to determine mass recoveries and travel times. Analyses were done both with and without extension of the low-concentration tail to evaluate the impact of below-detection concentrations on travel times. Furthermore, the resulting kinetic sorption/desorption data were compared to those measured from batch experiments.

Two models were employed to understand the data: a local equilibrium (LEA) model which assumes transported Cd is in equilibrium locally with soil particles, and a Two-domain Nonequilibrium model which allows for slow sorption or micropore transport within the soil structure.

For soils from selected trial sites, following complete elution of target metals from the loaded soil, a pulse of metal solution followed by metal-free water were introduced to the undisturbed soil column (Fig 37). The resulting data (e.g. heavy metal transport as well as sorption/desorption properties) were compared to that measured for the pulse loaded soil.
Figure 36. Acrylic Flow Cell for homogenized column - 5 cm long, 2.6 cm wide
Figure 37. Acrylic flow cell for Intact Column – 10 cm long, 7.58 cm wide

Figure 38. Schematic diagram of the experimental setup for unsaturated flow
Results and Discussion

Experiments to test the extent of Cd absorbed onto Klamath soil in a homogenized column (Table 6) show that, while pushing a “slug” of Cd through the column, the final eluent has been largely stripped of Cd, although the exact amount depends on the background electrolyte. With LiClO₄ (a more “neutral” electrolyte) only 17% of the Cd breaks through, but with the addition of the divalent Ca ion, the substitution of Ca for Cd on some surface binding sites allows 33% of the Cd to break through.

In Table 7 the amounts of Cd desorbed from homogenized soil materials in sequential extractions using the two eluants shows that desorption even of soil saturated with Cd in the column is slow and is enhanced by the presence of Ca ion, which may occur in some soils or irrigation waters.
As shown in Figure 40, the elution of the bromide (Br) nonreactive tracer breaks through somewhat more rapidly and more sharply in the unsaturated soil experiment compared to the saturated soil experiment. This is explained by the fewer porous paths in the unsaturated soil. The saturated soil shows more evident microporosity and thus nonideal transport behavior. This effect can then be incorporated into modeling of the reactive Cd transport.

Figure 41 Depicts the leaching out of Bromide (unreactive tracer) in Klamath Basin Soil. As in the previous figure, much nonideal transport (long elution tail) in the saturated system. In comparison to the NRT (Br), Figure 42 shows the elution of Cd from Klamath soil after initial saturation with Cd. Note the necessity of hundred of pore volumes to elute most of the Cd fully from the column, consistent with column experiments described in the previous section.

The relative elution of negatively charged Br (nonreactive tracer) from Klamath soil column is affected by soil charge as shown by the influence of different background cations (Fig. 40). The tracer elutes faster in the Ca eluent due to less interaction of Br- with soil surfaces, possibly due to suppression of some of the microporosity. An ideal LEA model (no nonideality such as microporosity) works well to predict the breakthrough of Br- in the Ca eluent, whereas the noticeably more nonideal breakthrough behavior of the Br- in a Li eluent require a nonequilibrium model. The ability to model both ideal and nonideal breakthrough is well illustrated by the plots in Fig. 43.

In Fig. 41 the elution pattern of Cd from intact Klamath soil shows that the dynamic nonequilibrium model we proposed yields superior fit for the transport of Cd in an actual heterogenous soil. These data also show the importance of performing experimentation on intact (undisturbed) cores because the elution pattern is significantly different (more “tailing”) than the behavior predicted by an equilibrium model based solely on batch experiments. The model is equally good at representing the Cd breakthrough in either CaCl₂ eluent (Fig. 44) of LiClO₄ eluent (Fig. 45).

Although the nonequilibrium model is important in predicting the correct elution over long time scales and many hundreds of pore volumes, the equilibrium approach discussed in earlier sections is quite satisfactory for explaining seasonal to annual time scales of Cd behavior under Oregon agricultural conditions.
Table 6. Total Cd adsorbed onto the column material, homogenized column. Note that Ca tends to depress Cd adsorption.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>% of cadmium adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01N LiClO₄</td>
<td>83</td>
</tr>
<tr>
<td>0.01N CaCl₂·2H₂O</td>
<td>67</td>
</tr>
</tbody>
</table>

Table 7. Amounts of Cd desorbed from homogenized soil materials in sequential extractions using the two eluants.

<table>
<thead>
<tr>
<th>Sequential Extraction Number</th>
<th>% desorbed using 0.01N LiClO₄</th>
<th>% desorbed using 0.01N CaCl₂·2H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.2</td>
<td>39.9</td>
</tr>
<tr>
<td>2</td>
<td>15.4</td>
<td>41.7</td>
</tr>
<tr>
<td>3</td>
<td>14.5</td>
<td>50.0</td>
</tr>
<tr>
<td>4</td>
<td>13.5</td>
<td>64.3</td>
</tr>
<tr>
<td>5</td>
<td>15.8</td>
<td>&gt;100</td>
</tr>
</tbody>
</table>
Figure 42. Nonreactive (Br) tracer in Klamath soil. Saturated media shows the effects of preferential flow paths with fast arrival of solute, more nonideal transport conditions compared to unsaturated.
Figure 43. Leaching out of Bromide (unreactive tracer) in Klamath Basin Soil
Figure 44. Elution of Cd from Klamath soil after initial saturation with Cd. Note the necessity of hundred of pore volumes to elute most of the Cd.
Figure 45. Relative elution of Br (nonreactive tracer) from Klamath soil column. The LEA model is calibrated using these data. Note the tracer elutes faster in the Ca eluent due to less interaction of NRT with soil surfaces.
Figure 46. Elution of Cd from intact Klamath soil showing that the dynamic nonequilibrium model we proposed yields superior fit to actual heterogenous soil. CaCl$_2$ eluent.
Figure 47. Elution of Cd from intact Klamath soil showing that the dynamic nonequilibrium model we proposed yields superior fit to actual heterogeneous soil. LiClO4 eluent.
Summary and Conclusions: Part 3

The data shown above display a great deal of complex information but we are able to distill the results down to some central and very practical conclusions:

- Batch studies tend to underestimate retardation factors.
- Batch studies provide a good approximation for R only in the absence of competing ions.
- The two-domain nonequilibrium transport model described well the breakthrough curve of cadmium in saturated, homogenized columns using measured R from observed dynamic (column) data.
- Transport studies in Undisturbed Soil Core shows little preferential flow in the region 0-20 cm bgs.

Even though we focused here on inherently dynamic transport, these conclusions mesh well with the conclusions we drew from the equilibrium isotherm experiments described in Part 1.
Overall Project Conclusions

From the many observations, data analyses, and modeling results we are able to draw a series of important conclusions about modeling Cd transport in Oregon agricultural soil.

1. We have created a comprehensive model of equilibrium chemistry of Cd in soils. Equilibrium experiments described in Part 1 are very valuable as “endpoint” or reference point. For example, they are good for comparing the results of the equilibrium DGT work performed by OSU researchers. In general the equilibrium results applicable to standard regulatory approaches. For example, in Appendix 1 of this report, we provide a statistical analysis of the data base promulgated by the USEPA for assessing Cd mobility in soils and we find that our Oregon soils are well within the probable values of Kd and retardation expected. Our experiments have dramatically reduced the uncertainty about Oregon agricultural soils to within one order of magnitude. These results should complement the overall OSU availability work, which assumes equilibrium.

2. Overall, in both the equilibrium and kinetic column experiments we see that Cd mostly in soil with very slow release. Plant uptake can still be important to human exposure for a metal as toxic as Cd, but soil is the main reservoir of Cd mass in an agricultural system. This is consistent in our studies and those of other researchers that show any elevated Cd is generally confined to the upper (tilled) portion of the soil profile. We therefore expect Cd to slowly accumulate in soil over long run.

3. We created a robust and quantitative model of Cd release from P fertilizer. The rate of release is briefly rapid, but then slows dramatically, most likely due to interactions of Cd with P itself in the fertilizer/soil-water system. Our column experiments show that uptake by soil are generally faster than release from fertilizer, so release rate is an important limit on Cd transport. It is likely that plant uptake is also faster than fertilizer release and so the slow release kinetics also limit bioavailability to crops, and hence potential human exposure.
4. Transfer of Cd to sampled agricultural soil was essentially complete in our column experiments, consistent with equilibrium batch results. However, when soils were loaded with Cd and then eluted, the very slow elution (over hundreds of elution pore volumes) was most accurately modeled by a nonequilibrium transport model that included a so-called dynamic retardation factor (R) which accounts for the possibility of sorption/desorption onto both slow and fast sites or for small scale diffusive transport in or out of micropores.
References


[76]


APPENDIX 1: Statistical Analysis of Probability Distributions of Kd Values for Cd based on USEPA Data for Reference Kd’s

Introduction

Cadmium (Cd) is one of the most important heavy metals present in agricultural soils and ground water. Several activities such as irrigation (using treated water), application of pesticides and fertilizers can cause an increasing concentration of cadmium as well as other heavy metals (Williams & David 1986; US EPA, 1977; Logan & Chaney, 1983; Robinson & Maris, 1985). As a consequence of these activities, the toxicity of cadmium can cause damage in the food chain by forming in the tissue of the plant which then consumed by humans and animals (Todd, 1972). As a result, many concerns about soil and water quality have directed us to obtain better understanding about the processes of solute reactions and the mobility in soil.

Distribution Coefficient (Kd)

One of the factors in our analysis is the distribution coefficient (Kd) (partition coefficient) which is defined as the ratio of the metal concentration in the solid phase to that in solution at equilibrium. Using the distribution coefficient under the requirement of low concentrations for metals allow us to characterize the mobility of these metals in the aquatic environment and describe their distribution through the soil (P.R. Anderson & T.H.Christensen 1988).

According to Hendrickson and Corey (1981), reviewing distribution coefficient data for several trace metal-soil systems, the coefficient increased dramatically as metal concentrations decreased relative to the concentration of other competing cations. There for, distribution coefficient model plays an important part to complete any methodology for modeling contaminant and radionuclide transport and risk analysis.

Soil Properties

The complex mixtures of sand, clays, organic matter, and metal oxides are the general phase of solid in aquatic environment. Beside cation competition and ionic strength effects, these components can affect the distribution of the metal in the soil (Anderson & Christensen 1988).
Logarithmic Isotherms

Logarithms are often used to determine the relationship between two kinds of isotherm. Langmuir isotherm is a graphical representation of the mass of contaminant adsorbed per unit dry mass of soil or organic matter (depending on whether Koc or Kd is being used) (s) versus the concentration (c) of the contaminant.

The disadvantage about this kind of isotherm that it is presented as a curved graph. That makes it impossible to obtain the slope and the intercept as shown in Figure 1.

Freundlich isotherm is a developed isotherm processed by taking the logarithm of both (s) and (c) for the Langmuir isotherm. The advantage about this isotherm is the linear relationship between (s) and (c). That makes it easier to obtain the slope and the intercept of the line as shown in Figure 2.
Although partitioning and descriptive factors like distribution coefficient (Kd) are important to describe metal behavior in soil, they do not give a visual sense to obtain better understanding of the movement of the metal through the soil.

Partition coefficient can be used to calculate a retardation factor, commonly used in transport models to describe the chemical interaction between the contaminant and geological materials, which can be a more practical measure of metal behavior.

**Retardation factor (Rf)**

The retardation factor which is defined as the rate of contaminant transport relative to that of ground water, in term of velocity, describes the movement of contaminant and water in the subsurface environment which is affected by the properties of the soil. In this case, partition coefficient (Kd) can be used to estimate the retardation factor (Rf) (Bouwer, H. 1991. Ground Water, 29:41-46) by the following equation:

\[ R_f = 1 + K_d \left( \frac{\Delta_b}{n} \right) \]  \hspace{1cm} Eq. 1

Where:

- \( R_f \): Retardation factor
- \( K_d \): Distribution coefficient (ml/g)
- \( \Delta_b \): Bulk density of soil (mass / cubic length)
- \( n \): porosity of soil

Since the unit density and the porosity are approximately 1.8 kg/m^3 and 0.3 respectively for most soil

Then:

\[ R_f = 1 + 6.0 \; K_d \]  \hspace{1cm} Eq. 2

For………Kd >10 (approximately)

[81]
6.0 Kd\(\gg 1\)

Then:

\[ R_f \approx 6.0 \text{ Kd} \quad \text{Eq.3} \]

**Retarded travel time \(Tr.t\)**

Retarded travel-time is the time it takes the heavy metal (cadmium) to reach a particular point (ground water source) starting from the source point. That is with respect to the impacted volume of the soil, the velocity of the water through the soil, the porosity of the soil, and the retardation factor for the heavy metal (cadmium).

**Source of partitioning data**

The approached data were obtained from literature and tabulated through the EPA. Through the analytical processors of EPA, a statement was established to give general guide lines of using partition coefficient and other factors to describe the behavior of cadmium in the soil.

The primary intention of this report is to extract maximum predictive results from previously published Kd data and detailed statements to give better understanding about the behavior of cadmium in soil. Practical measures were applied to the data after they were broken down in to several groups based on the original references and variation of soil identification. The goal was to minimize the possible variability which exists within and among data sets and then determine the behavior of each group of data individually.

**Methodology**

The approached data were collected from some literature and tabulated through the EPA website (appendix c: partition coefficient for cadmium). They were from studies that reported partition coefficient (Kd) values for cadmium from a system of agricultural soil consisting of:
1- natural soils (as apposed to pure mineral phases)
2- low ionic strength solutions (< 0.1 M)
3- ph values between 4 and 10
4- solution cadmium concentration less than 10⁻⁵ M
5- low humic materials concentrations (< 5 mg / L )
6- no organic chelates (such as EDTA)

These studies included ancillary data on partition coefficient (Kd) for cadmium, clay concentration (wt %), ph, cation exchange capacity CEC (meq/100g), total organic carbon TOC (wt %), cadmium solution concentration cd (mg/l) and iron–oxide concentration (wt %).

As a way to minimize variability in the procedure of approaching the data (in contrast to the EPA approach), the data as a first step, was divided based on reference variation. As a result, seven references were obtained. References 1,2,3,5 and 6 were discredited for a quantity reason. Based on variation of soil identification, reference number seven was discredited. Reference number four was the only Reference that met the requirements of fair quantity and noticeable variation of soil identification. That is beside the availability of a complete data for most of the ancillary parameters.

The correlation coefficients from the linear regression analyses were conducted between the ancillary parameters and Kd values to indicate which ancillary parameter have the biggest influence on Kd values.

**Data modification**

Based on the variation of soil identifications, reference 4 was divided to 5 parts for individual approach.

Special attention was paid to the ph dependence of Kd by establishing log Kd values at constant ph’s (4, 5, 6 and 7).

**Probability distribution (Ö)**

To calculate confidence intervals for parameters, normal probability distribution of log (Kd) values for ph (4, 5,6 and 7) were created by evaluating the following equation: [83]
\[ \phi (\log K_d) = \frac{1}{\sqrt{2\pi}} \left[ (\log K_d - m)^2 / (2\sigma^2) \right] \]  
Eq. 4

\[ \phi (\log K_d) : \text{probability distribution of log Kd.} \]

\[ \sigma : \text{standard deviation of log Kd.} \]

\[ m : \text{mean of log Kd.} \]

**Retardation factor (Rf)**

The retardation factor equation was calculated to give a visual sense of the probable range of log (Kd) and retardations expected in each soil at pH (4, 5, 6 and 7) using equation 2. with respect to the impacted volume of the soil, the velocity of the water through the soil, the porosity of the soil, and the retardation factor for cadmium, retarded travel time measure was determined to give a visual sense about the mobility of cadmium to the mobility of water through the soil, retarded travel times were determined at pH (4, 5, 6 and 7) using the following equation.

\[ Tr.t(cd) = Tc.f \times Rf \]  
Eq. 5

\[ Trt (cd) : \text{retarded travel time (cd).} \]

\[ Tc.f : \text{conservative front travel} \]
\[
= \frac{p_v}{Q_{in}}
\]

\(P_v\): - porosity volume (cm\(^3\))

\[= n \times V_{total}\]

\(n\): - standard percentage of porosity in 1000cm\(^3\) unit volume (given =0.3).

\(V_{total}\): - volume of soil unit volume (given = 1000 cm\(^3\)).

\[P_v = 0.3 \times 1000 \text{ cm}^3 = 300 \text{ cm}^3\]

\(Q_{in}\): - fluent of water due to irrigation.

\[= r \times A\]
r: standard irrigation rate (given = 5 cm/d).

A: area of impact unit volume (given = 100 cm^3).

Qin = 5 cm/d * 100 cm^2 = 500 cm^3/d

Then............ Tc.f = 300 cm^3 / 500 cm^3/d = 0.6 d

As a following step, velocity of cadmium were conducted for each retardation factor at ph (4, 5, 6 and 7) using the velocity of water.

Vw = D / Tc.t

D: depth of unit volume (given = 10 cm).

Vw = 10 cm * 0.6 d = 16.7 cm/d

At no retardation (Rf = 1), the velocity of cadmium is equal to the velocity of water. The velocity of cadmium is determined through the following equation.

V (cd) = Vw /Rf                  Eq. 6

Confidence Interval

As a final procedure, confidence intervals were used to estimate the amount of uncertainty involved in the data. Confidence Interval can be used to determine that including the precision of the statistical estimates. The confidence interval is defined in terms of the mean and standard deviation of number of samples (log Rf in the approached data) and it is based on three elements:

(a) A value of statistic (the mean).
(b) The standard error(SE) of the measure
(c) The desired width of the confidence interval (the 95% confidence interval or the 90% confidence interval).

The region within which it is 90% (±1) or 95% (±2) confident the true value lies is calculated by the following steps:
1- Determine the highest probability value (Ø max) and its coordinated Rf (Rf_).
2- Calculate the 0.61 of (Ø max) and determine its coordinated Rf (Rf_).
3- The 90% confidence interval is:
   \[ (±1 \mu) = Rf_ - Rf_ \]  \hspace{1cm} \text{Eq. 7}
4- The 95% confidence interval is:
   \[ (±2 \mu) = 2 * Rf_ - Rf_ \]  \hspace{1cm} \text{Eq. 8}

Results and Discussion

Source data:

As it was mentioned in methodology, data modification, Reference number four was the only Reference that met the requirements of fair quantity and noticeable variation of soil identification beside the availability of a complete data for most of the ancillary parameters. Based on this selection, the total of 174 coefficient values was reduced to the 43 partition coefficient (Kd) values. Those values had associated ph data, clay content, total organic carbon and cadmium concentration data. Note that none of these data included information about CEC or aluminum / iron oxide data. The descriptive statistics of the soil characteristics is presented as non-transformed data in table 1. The range in concentrations for most of the components is a factor of 10.

<table>
<thead>
<tr>
<th></th>
<th>Cd Kd (ml/g)</th>
<th>clay Cont. (wt%)</th>
<th>pH</th>
<th>TOC (wt %)</th>
<th>[Cd] (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean</td>
<td>356.67</td>
<td>10.58</td>
<td>5.87</td>
<td>6.35</td>
<td>11.20</td>
</tr>
<tr>
<td>median</td>
<td>92.00</td>
<td>10.00</td>
<td>6.00</td>
<td>2.40</td>
<td>11.20</td>
</tr>
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<td>mode</td>
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<td>2.55</td>
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<td>6.00</td>
<td>3.00</td>
<td>0.40</td>
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Regression models and soil-parameter correlations with cadmium Kd values

The correlation coefficients from the linear regression analyses were conducted between the ancillary parameters and Kd values to indicate which ancillary parameter have the biggest influence on Kd values.

As a result, the largest correlation coefficient (0.819) was between ph and log (Kd) as presented in table 2.

<table>
<thead>
<tr>
<th></th>
<th>Cd Kd (ml/g)</th>
<th>log (Kd)</th>
<th>clay Cont. (wt%)</th>
<th>pH</th>
<th>TOC (wt %)</th>
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</thead>
<tbody>
<tr>
<td>Cd Kd (ml/g)</td>
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<td></td>
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<tr>
<td>log (Kd)</td>
<td>0.65</td>
<td>1.00</td>
<td></td>
<td></td>
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<tr>
<td>clay Cont. (wt%)</td>
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<tr>
<td>pH</td>
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<td>-0.28</td>
<td>1.00</td>
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<tr>
<td>TOC (wt %)</td>
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<td>0.11</td>
<td>0.78</td>
<td>-0.37</td>
<td>1.00</td>
</tr>
<tr>
<td>[Cd] (mg/l)</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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</tr>
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</table>

Table 2. Correlation coefficients were conducted between the ancillary parameters and Kd values.

Cadmium Kd values as a function of ph

As a result of the high correlation coefficient between log (Kd) and ph, log Kd for cadmium values were plotted as a function of ph including the regression equation for the line as [88]
presented in Figure 3.

When all experimental data are plotted together, a considerable variability in log Kd as a function of pH was detected as reflected by a relatively low value of R^2 (0.619).
Based on the variation of soil identifications, reference 4 was divided into 5 sets, each set is corresponding to a single pH. Log (Kd) values were plotted as a function of pH including the regression equation for the line as presented in Figure 4, 5, 6, 7 and 8. Notice that as a result of this division, R-square value has improved from 0.618 to a range of 0.96-0.996. This is to be expected since the original data were generated at these specific pH values. However, the analysis underscores the importance of not lumping disparate Kd data sets together as the US. EPA did in their study. The variability in log Kd values must be assessed in light of known or predictable parameters such as specific pH.

Figure 3. Log Cd as a function of pH

Figure 4. Log Cd-Kd (Downer Loamy Sand) as a function of pH.
Figure 5. Log Kd (Freehold Sandy Loam A Horizon) as a function of pH.

Figure 6. Log Kd (Boonton Loam) as a function of pH.
Figure 7. Log Kd (Rockaway Stony Loam) as a function of ph.

Figure 7. Log Kd (Fill Material Delaware River) as a function of ph.
Intercept (a) and slope (b) were determined for each soil from the regression equation. For each soil, log (Kd) was determined using the regression equation at constant pH (4, 5, 6 and 7) as presented in Table 3 including the mean log (Kd) and standard deviation. The classification of pH gave the opportunity to indicate the behavior of Kd based on the pH behavior. For each soil, constant increasing in log (Kd) values was determined as pH increased. This increasing is 0.401 for Downer Loamy Sand, 0.48 for Freehold Sandy Loam A Horizon, 0.83 for Boonton Loam, 0.85 for Rockaway Stony Loam and 0.404 for Fill Material Delaware River.

<table>
<thead>
<tr>
<th>Soil</th>
<th>intercept (A)</th>
<th>slope (B)</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-0.62</td>
<td>0.40</td>
<td>0.99</td>
<td>1.39</td>
<td>1.80</td>
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<tr>
<td>Freehold sandy loam A horizon</td>
<td>-1.52</td>
<td>0.48</td>
<td>0.40</td>
<td>0.88</td>
<td>1.36</td>
<td>1.84</td>
</tr>
<tr>
<td>Boonton Loam</td>
<td>-2.13</td>
<td>0.84</td>
<td>1.23</td>
<td>2.06</td>
<td>2.90</td>
<td>3.74</td>
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<tr>
<td>Rockaway Stony Loam</td>
<td>-2.67</td>
<td>0.85</td>
<td>0.74</td>
<td>1.60</td>
<td>2.45</td>
<td>3.31</td>
</tr>
<tr>
<td>Fill Material Delaware River</td>
<td>-0.41</td>
<td>0.40</td>
<td>1.21</td>
<td>1.61</td>
<td>2.02</td>
<td>2.42</td>
</tr>
<tr>
<td>Mean log Kd</td>
<td>0.91</td>
<td>1.51</td>
<td>2.11</td>
<td>2.70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 8. Log Kd (Fill Material Delaware River) as a function of pH

[93]
| Std Dev log Kd | 0.35 | 0.43 | 0.59 | 0.79 |

Table 3. Intercept (a) and slope (b) and log (Kd) using the regression equation at constant ph (4, 5, 6 and 7)

**Generation of log Kd probability distribution**

Probability distribution was plotted as a function of log Kd at ph (4, 5, 6 and 7). Since there are just five probability distribution points for each ph, a modification processes were conducted by adding extra (synthetic) data points to improve the visibility of the curves presented in Figure 9. The Figure shows an expected increase in the mean value of log Kd. However, Figure 9 also reveals that the range and variance of log Kd also increase with ph. The greater variance with increasing ph naturally tends to flatter the log Kd distribution as the ph rises.

![Figure 9. Probability distribution as a function of log Kd at ph (4, 5, 6 and 7).](image-url)
Probability distribution and Retardation factor (Rf)

As mentioned in methodology section, the retardation factors were calculated to give a visual sense of the probable range of log (Kd) and the retardations expected in each soil at ph 4, 5, 6 and 7. Using Eq.3, probability distribution of retardation factor at ph 4, 5, 6 and 7 was calculated from the distribution of log Kd. As shown in the Figure 10, 11, 12 and 13, big differences between ranges of retardation factor at each ph were detected (7.7-4.7E2 at ph 4, 9.8-3.8E3 at ph 5, 8.5-3.0E4 at ph 6 and 16.0-3.0E5 at ph 7). The very wide ranges obtained were the reason for presenting each Figure (ph) individually. Although these linear plots show the extensive “tails” of potentially Rf values, these high values occur with very low probabilities. It is more appropriate and practical to focus on the most probable Rf values, what it was termed as the effective range of Rf. For each Figure, the effective range was estimated to be between the start point at each curve and ending at the point 3.0E2 for ph 4, 1.0E3 for ph 5, 1.8E4 for ph 6, 1.5E5 for ph 7.

Although the linear distributions show the actual values of Rf directly, another way of displaying the retardation factor vs probability distribution is a logarithmic transformation of the retardation factor in the same chart. The log transform compresses the scale of curves at different ph and gives more visual sense about the behavior of cadmium over a rang of ph. Figure 14 reveals a tendency of increasing in the mean of log Rf (1.69 for ph 4, 2.27 for ph 5, 2.68 for ph 6 and 3.29 for ph 7) and its rang (0.88 – 2.6 for ph 4, 0.99 – 3.5 for ph 5, 0.93 – 4.4 for ph 6 and 1.2 – 5.4 for ph 7) as ph increase. The retardation factor that has the highest probability value was 42.8 for ph 4, 187.8 for ph 5, 756.3 for ph 6 and 3250.7 for ph 7 which represent a high influence of ph and direct relationship.
Figure 10. Probability distribution as a function of $R_f$ at pH 4

Figure 11. Probability distribution as a function of $R_f$ at pH 5

Figure 12. Probability distribution as a function of $R_f$ at pH 6
Figure 13. Probability distribution as a function of Rf at ph 7
Expressing retardation distribution as travel-time distribution

Retarded travel time, the product of retardation factor ($R_f$) and the conservative front travel ($T_{c.f}$), was determined taking into account how much a contaminant’s velocity is affected by sorption through irrigation in the soil. Travel time depends on assumption about the bulk density of the media, the porosity as well as on the assumed irrigation rate and the distribution coefficient ($K_d$). Through the following equation Eq. 5, described in detail in the methodology section, retarded travel time was determined at each pH and plotted as a function of probability distribution.

Figure 14. Probability distribution as a function of log $R_f$ at pH 4,5,6 and 7. The log transform compresses the scale of...
\[ Tr.t (cd) = Tc.f \ast Rf \]  
\text{Eq. 5}

\begin{align*}
Trt (cd) & \text{:- retarded travel time (cd).} \\
Tc.f & \text{:- conservative front travel (0.6 day).} \\
Rf & \text{:- retardation factor}
\end{align*}

Since the retarded travel time is a product of the retardation factor and the constant value of conservative front travel (0.6 day), the curves presented in Figure 15, 16, 17 and 18 are identical in shape to the curves presented for the retardation factor in Figure 10, 11, 12, and 13 however, the horizontal axis now expresses the practical and intuitive values of cadmium travel time in soil. As shown in the Figures, the tendency for effective retarded travel time at each ph located between the start point (ranging between 4.6 and 9.6 days) in each curve and the end point of 181d for ph 4, 1139d for ph 5, 9043.3 for ph 6 and 90428.5d for ph 7. As detected, factor of ten is the difference between these ending points which clarify the huge influence of ph on the mobility of cadmium in the soil. The retarded travel time value that has the highest probability was 25.7 days for ph 4, 112.6 days for ph 5, 453.8 days for ph 6 and 1950.4 days for ph 7 which represent a direct relationship with ph.

![retarded t.t vs pro. Distribution at (ph4)](image)

Figure 15. Probability distribution as a function of Tr.t at ph 4

[99]
Figure 16. Probability distribution as a function of Tr.t at ph 5
Figure 17. Probability distribution as a function of Tr.t at ph 6
The velocity of (cm/day) cadmium was determined as a measure of velocity of cadmium at no retardation which is equal to the velocity of water and the retardation factor using the following equation.

\[ V_{(cd)} = \frac{V_w}{R_f} \]  

Eq. 6

\( V_w \): velocity of water (given) = 16.7 cm/d

Then, the velocity of cadmium was plotted as a function of probability distribution at ph 4, 5, 6 and 7 as presented in Figure 19, 20, 21 and 22. These Figures reveal how a retardation factor hinders the movement of cadmium in the soil at different ph. The velocity value that has the highest probability was 0.38 cm/d for ph 4, 0.088 cm/d for ph 5, 0.022 cm/d for ph 6 and 0.005 cm/d for ph 7. That represents a high influence of ph on the velocity of cadmium and inverse relationship.
Figure 19. Probability distribution as a function of cd velocity at pH 4
Figure 20. Probability distribution as a function of cd velocity at ph 5

Figure 21. Probability distribution as a function of cd velocity at ph 6
Figure 22. Probability distribution as a function of cd velocity at ph 7

As with Rf plots (fig. 10, 11, 12 and 13), a logarithmic transformation was conducted to present the velocity of cadmium was at each ph(4,5,6 and 7) in the same chart to simplify the relationship between curves and give more visual sense about the behavior of cadmium under the influence of different ph. Figure 23 shows the tendency of log velocity to diminish with increasing ph (-0.46 for ph 4, -1.05 for ph 5, -1.46 for ph 6 and -2.06 for ph 7). As expected from previous probability plots, the velocity range variance (0.33 – -1.45 for ph 4, 0.22 – -2.35 for ph 5, 0.29 – -3.25 for ph 6 and 0.01 – -4.25 for ph 7) and reveals as a strong function of ph.

Figure 23. Probability distribution as a function of logarithmic nonlinear transformation of cd velocity at ph 4, 5, 6 and 7
**Confidence interval for Cd retardation**

To estimate the amount of uncertainty involved in the retardation data, the desired two widths of the Confidence interval (95 % and 90%) were obtained by calculating the 0.61 of the maximum probability and the mean of log Rf as presented in table 4. Due to obtaining negative value at each ph, low Rf value for the 95 % confidence interval (± 2 _) was ignored and replaced by 1.

<table>
<thead>
<tr>
<th>ph</th>
<th>± 1 _</th>
<th>± 1 _</th>
<th>± 2 _</th>
<th>± 2 _</th>
</tr>
</thead>
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<td>4</td>
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<td>1</td>
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</tr>
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<td>74.6448</td>
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<td>1</td>
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<td>1</td>
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<td>5988.926</td>
<td>1</td>
<td>8727.09</td>
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</tbody>
</table>

Table 4. The Confidence interval (95 % and 90%)

To estimate the amount of uncertainty involved in the retardation data.

The examination of any unknown soil and the extraction of the concentrations of its parameters usually request high expenses and relatively long time. At some points, it is very urgent to make a decision about a particular site. Table 4, can be useful in term of practical use to assess an unknown soil. Besides using table 4, examining the ph is the only Maguire procedure needed to give a roughly values for the retardation factor and its products (retarded travel time, velocity and partition coefficient).
Conclusion

The hazardous presence of cadmium in soil, a consequence of several applications such as pesticides, irrigation (using treated water) and fertilizers, raises a lot of concerns about the quality of agricultural soil. Moreover, studies were conducted to demonstrate the acute toxicity and the mobility of cadmium in the soil.

The present report approaches this problem by focusing on the mobility and the behavior of cadmium in the soil. Data were obtained from some literature and tabulated through the US. EPA website (appendix c: partition coefficient for cadmium). They were from studies that reported partition coefficient (Kd) values for cadmium from a system of agricultural soil. These studies included ancillary data on aluminum / iron –oxide concentration, calcium and magnesium solution concentration, ph, cation exchange capacity (CEC), clay concentrations and sulfide concentrations. The US. EPA did some analytical procedures on the data and established a general statement to give general guide lines of using the partition coefficient and other factors to describe the behavior of cadmium in the soil.

The objective of this report is to extract maximum predictive results from previously published Kd data and detailed statements to give better understanding about the behavior of cadmium in soil. Practical measures were applied to the data after they were broken down into several groups based on the original references and variation of soil identification. The reason for these divisions was to minimize the possible variability which exists within and among data sets and then determine the behavior of each group of data individually.

As a result of this division, one (reference 4) out of seven references met the requirements of fair quantity and noticeable variation of soil identification. That is beside the availability of a complete data for most of the ancillary parameters.

As a result of conducting the regression model between ancillary parameters and Kd values, ph was found to have the largest correlation coefficient (0.8) with log Kd). As a following step, log Kd values were plotted as a function of ph after dividing reference 4 data into 5 sets based on the variation of soil identification. That led to an improvement detected in R-square value from 0.618 (before the division procedure) to a range of 0.96-0.996. However, the analysis underscores the importance of not lumping disparate Kd data sets together as the US.
EPA did in their study.

For each soil in reference 4, log (Kd) was determined using the regression equation at constant ph (4, 5, 6 and 7). The classification of ph gave the opportunity to indicate the behavior of Kd based on the ph behavior. For each soil, log (Kd) values were positively correlated with ph increase.

Log Kd probability distributions were generated and plotted as a function of log Kd at ph (4, 5, 6 and 7). That showed an increase in the mean as expected, the range and the variance of log Kd value with ph. The greater variance with increasing ph naturally tends to flatter the log Kd distribution as the ph rises.

To characterize the movement of cadmium in the subsurface environment which is affected by the properties of the soil and give a visual sense of the probable range of log (Kd) and retardations expected in each soil, the retardation factor was generated at ph (4, 5, 6 and 7) and plotted as a function of probability distribution. Charts reveal an effective range of R/f at each ph which increases rapidly as alkalinity raises. The logarithmic transformation of the distributed retardation factor indicates a strong and positive tendency of the mean of log Rf and its range to increase with ph.

Expressing the retardation distribution as a travel-time distribution indicates an effective range at each ph. in addition, as shown in the related charts, the range of travel-time increases by a factor of ten for each ph increase of one. The retarded travel time value that has the highest probability was 25.7 days for ph 4, 112.6 days for ph 5, 453.8 days for ph 6 and 1950.4 days for ph 7 which represent a geometric relationship with ph.

The velocity distribution, a product of the retardation distribution, reveals how a retardation factor controls the mobility of cadmium at different ph. The velocity value that has the highest probability was 0.38 cm/d for ph 4, 0.088 cm/d for ph 5, 0.022 cm/d for ph 6 and 0.005 cm/d for ph 7. That represents a high influence of ph on the velocity of cadmium and inverse relationship. The logarithmic transformation of the velocity distribution shows the tendency of log velocity to diminish with increasing ph. As expected from previous probability plots, the velocity range variance reveals a strong function of ph.

As a last procedure, a confidence interval (95% and 90%) table was established to estimate the
amount of uncertainty involved in the retardation data and to be practically useful in approaching a not well known soil.
APPENDIX 2: Background Information and Literature Review on Cd and Soils

Introduction

In July of 1997 the Seattle Times ran a series of articles entitled “Fear in the Fields” that highlighted the use of recycled waste in fertilizer and brought to the fore the need for standards in fertilizer composition. By March 1998 the Fertilizer Regulation Act was passed into law making Washington the first state to impose standards for metals in fertilizers. The act set limits for the levels of nine heavy metals in fertilizers namely arsenic (As), cadmium (Cd), cobalt (Co), mercury (Hg), molybdenum (Mo), nickel (Ni), lead (Pb), selenium (Se), and zinc (Zn). Since then several other states have taken similar strides to impose restrictions of heavy metal levels in fertilizers. Oregon passed a law in 2001 (House Bill 3815) that ensured all fertilizer sold in the state had packaging showing the levels of certain metals of interest and the Oregon Department of Agriculture also began work to set numerical limits for certain metals by 2006 based on environmental assessments. (White, 2002)

Regulation of phosphate fertilizers has generated considerable interest due to cadmium, a trace metal and impurity of this fertilizer that is known to be present in substantial amounts depending on the parent rock. There is no doubt that an accumulation of cadmium in soil occurs due to the long term use of phosphate fertilizers although this does not always lead to a bio-accumulation of cadmium in plants. Williams and David, (1976) both showed that about 80% of the cadmium added as phosphate fertilizer over a 20 year period accumulated in the top 7.5cm of soil except when the soils were podozols. In 1980 Mulla et al showed that after a 36 year period, the accumulated cadmium was in the top 15cm of the soil and the phosphate was more mobile than the cadmium. A study done by Washington State University concluded that there is a potential of metals to increase in soil with time especially cadmium and they showed that while extractable cadmium correlated well with lettuce retained cadmium, it was only 3% of the cadmium put onto the soil; the remainder accumulated in the soil. (WSDA, 2001)
Studying the use of phosphate fertilizers in the USA gives ample reason for alarm.

![Graph showing US Phosphate fertilizer use over the last 45 years](www.ers.usda.gov/Data/FertilizerUse/Tables/Table5.xls)

**Fig1.** US Di-ammonium phosphate fertilizer use over the last 45 years

Approximately 120 million tons of fertilizer has been over the last 45 years and assuming the fertilizer used had an average of 50mg/kg Cd per kg of fertilizer (Davister, 1994 calculated the European average to 60mg/kg.) then the amount of cadmium introduced into the agricultural fields of the US from diammonium phosphate alone over this time period is 6000 tons.

Most human exposure to cadmium comes from ingestion and a model proposed by Van Assche (1998) came up with the following relative importance of cadmium sources:
Phosphate Fertilizers 41.3%

Fossil Fuel Combustion 22.0%

Iron & Steel Production 16.7%

Natural Sources 8.0%

Non-ferrous metals 6.3%

Cement Production 2.5%

This clearly shows the importance of knowing what is happening to the fertilizer derived cadmium and on realizing this, the European Union has adopted the following phased in EU-wide limit on cadmium concentrations in fertilizers:

60 mg Cd/kg P$_2$O$_5$ by 2006, 40 mg Cd/kg P$_2$O$_5$ by 2010 and 20 mg Cd/kg P$_2$O$_5$ by 2015.

As was highlighted in the paper for the ODA White paper (2002), the following areas are still dearth of information; metal speciation, plant uptake, bioaccumulation, leachability, the rate of cadmium release from the fertilizer as well as the long term fate of the cadmium. This research will strive to shed more light on the last 3 issues.

Most studies of the behaviour of metals in soils have been carried out under equilibrium conditions. Equilibrium data indicate which reactions are likely to occur under prescribed conditions, but do not indicate the time period involved. The kinetic aspect of oxidation/reduction, precipitation/dissolution and adsorption/desorption reactions involving metals in soil matrix suffers from lack of published data. Thus the kinetic component which in many cases is critical to predict the behaviour of metals in soils cannot be assessed easily. Without the kinetic component, the current accepted approach is to assume that local equilibrium occurs in the soil profile. ( McClean et al, 1992) While equilibrium measurements are useful in providing information on the final state of a system, no information is garnered on the rates of the reactions. Such kinetic information is extremely important in accurately predicting fate and
transport of plant nutrients, metals, radionuclides, pesticides and other organic chemicals in soil with time.

**Background**

**Phosphate Fertilizer Source Materials**

Phosphate rock (PR) is a general term that describes naturally occurring mineral assemblages containing a high concentration of phosphate minerals. About 80 percent of world PR production is derived from deposits of sedimentary marine origin, some 17 percent is derived from igneous rocks and their weathering derivatives and the remainder comes from residual sedimentary and guano-type deposits. The rock is of the apatite group and the most common variants are Fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{F},\text{OH})_2$ and Francolite $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{F},\text{OH})_{2+x}$. The more easily mined is the sedimentary rock formed in the ocean and believed to arise from decomposition of organic matter and has provided about 80 – 90 percent of world production in the last ten years. They occur in formations of widely varying geological ages, exhibit a range of chemical compositions and physical forms, often occur as interstratified thick beds, and may underlie shallow overburden.

The deposits that account for most of world PR production are in Morocco and several other African countries, the United States of America, the Near East and China. Most sedimentary deposits contain the carbonate-fluorapatite called francolite. Francolites with high carbonate for phosphate substitution are the most highly reactive and are the most suitable for direct application as fertilizers or soil amendments. Igneous deposits are exploited in the Russian Federation, Canada, South Africa, Brazil, Finland and Zimbabwe but also occur in Uganda, Malawi, Sri Lanka and several other locations. These deposits usually contain varieties of fluorapatite that are relatively unreactive and are the least suitable for direct application. The weathering products of igneous and sedimentary apatites (iron and aluminium phosphate minerals) are generally not useful for direct application in agriculture in their natural state. The higher the phosphate ($\text{P}_2\text{O}_5$) content as apatite, the greater the economic potential of the rock. Factors that are important in the chemical conversion of PRs to fertilizer (free carbonates, iron
(Fe), aluminium (Al), magnesium (Mg) and chloride) are often not important where the rock is to be used for direct application (Gremillion and McClellan, 1975; McClellan and Gremillion, 1980; Van Kauwenbergh and Hellums, 1995). The cadmium content varies quite considerably as can be seen in Table 1 below.

<table>
<thead>
<tr>
<th>PR Deposit</th>
<th>As (mg/kg)</th>
<th>Cd (mg/kg)</th>
<th>Cr (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>V (mg/kg)</th>
<th>Zn (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Russia (Kola)</td>
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<td>30</td>
<td>3</td>
<td>100</td>
<td>19</td>
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<td>11</td>
<td>109</td>
<td>23</td>
<td>12</td>
<td>82</td>
<td>204</td>
</tr>
<tr>
<td>South Africa</td>
<td>6</td>
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<td>1</td>
<td>130</td>
<td>35</td>
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<td>129</td>
<td>43</td>
<td>4</td>
<td>122</td>
<td>315</td>
</tr>
</tbody>
</table>

(Adapted from Mortved and Beaton, 1995)

Table 1: Heavy Metal Concentration of phosphate rock deposits from major world sources.

Phosphate rock from North Africa and the island sources tend to have higher cadmium levels than the mainland sources. At the OECD workshop held in Stockholm (1995) several papers were presented addressing the issue of reducing cadmium content in phosphate fertilizers. Several ideas were proposed including direct extraction of cadmium from the phosphate rock, co-crystallization of cadmium in CaSO4 from phosphoric acid and use of ion exchange resins selective for cadmium. Most of the methods were deemed financially unviable so better methods are still being sought. The naturally high impurity levels are of concern because according to II’in and Kiperman (2001) previous research has shown the fertilizer manufacturing process retains about 80% of the cadmium in the parent phospherite rock.
Cadmium

This is a non-essential, toxic, trace metal that mainly occurs associated with zinc ores. Natural soil background levels of cadmium have been determined to be in the range of 0.01mg/kg to 0.7mg/kg (Lindsay, 1979), much lower than the current Oregon clean up standard for residential sites of 100mg/kg and the DEQ water quality limit of 5ppm.

Cadmium is found in phosphate rock where it is an impurity due to its isomorphous substitution with calcium. The radius of the Cd$^{2+}$ ion is 0.97 Å whilst that for Ca$^{2+}$ is 0.99Å thus substitution can readily occur. It also has an identical electronegativity of 1.7 to zinc allowing for further substitution. Zinc and calcium are both essential metals with wide use in the human body.

“Itai –itai”disease in Japan brought this metal to prominence where it was discovered that cadmium can be ingested or inhaled by both animals and humans and it gradually accumulates in the liver and kidneys leading to renal tubular damage, formation of stones in the kidneys, disturbed calcium metabolism, hypercalciuria and bone deterioration. At acute levels, lung and prostate cancer can occur (Jarup et al,1998) and cadmium is known to replace zinc a common cofactor in some enzymes leading to high blood pressure and kidney damage. Testicular tissue and red blood cells are also destroyed by cadmium. The US public health limit is 0.01mg/L whilst the half-life of cadmium in humans is believed to be 10-35 years. (WHO, 2003)

According to Morel (1983) in an aqueous environment cadmium is present as the following species Cd$^{2+}$, CdCl$^+$, CdCl$_2$, CdCl$_3^-$, CdOH$^+$, CdS, CdHS$^+$, Cd(HS)$_2$, Cd(HS)$_3^-$, Cd(HS)$_4^{2-}$, Cd(s), CdCO$_3$(s) and Cd(OH)$_2$(s).The chemical speciation of cadmium determines its bioavailability and this in turn is affected by pH, carbonate, organic carbon, calcium, zinc and chloride levels. (Jackson and Alloway, 1992; McLaughlin et al, 1994a) High pH, high calcium and elevated carbonate levels inhibit cadmium uptake whilst high elevated chlorides, low zinc levels and high concentrations of some organic compounds enhance cadmium uptake by plants.

There has been much debate over available cadmium versus bio-available cadmium with regards to determination and interpretation. Most of the geo-analytical methods used for determining cadmium use strong acid extractants such as concentrated nitric acid and hydrofluoric acid however using much weaker acid mixtures and chelating agents gives a more accurate representation of bio-available cadmium. EDTA, DTPA, dilute hydrochloric acid,
double acid extraction (using 0.05N HCl and 0.25N H$_2$SO$_4$) and CaCl$_2$ solutions have been used to estimate bio-available cadmium. (Baker and Amacher, 1982)

**Soil Properties.**

Soils are heterogenous mixtures of air, water, inorganic and organic solids and microbes. (Sparks, 2003) Soil chemistry looks at the reactions between these phases. The soils used in this study were collected from 4 field sites namely Hyslop Farm, Corvallis Oregon; Columbia Agricultural Research Center, Pendleton; Klamath Experiment Station, Klamath Falls and Hermiston Agricultural Center, Hermiston. These sites were chosen to be representative of the main farming regions in Oregon, which are under very different climatic conditions and have different soil types.

In soil, metals are found in one or more of several “pools” of the soil, as described by Shuman (1991):

1) dissolved in the soil solution;
2) occupying exchange sites inorganic soil constituents;
3) specifically adsorbed on inorganic soil constituents;
4) associated with insoluble soil organic matter;
5) precipitated as pure or mixed solids;
6) present in the structure of secondary minerals; and / or
7) present in the structure of primary minerals.

Metals introduced from anthropogenic sources are associated with the first 5 pools.

“Pools” 2, 3 and 4 are all associated with adsorption. Adsorption is the accumulation of a substance or material (adsorbate) at the interface between the solid phase (adsorbent) and the surrounding solution. This process is one of the most important chemical processes occurring in soils as it controls the quantity and transport of metals, pesticides and other organic chemicals retained at the soil surfaces.

Surface functional groups or “chemically reactive molecular units” bound into the structure of the solid play a pivotal role in adsorption (Sposito, 1989).
The two major adsorption isotherms used to describe the binding of metals onto soil surfaces are the Langmuir and Freundlich isotherm. These non-linear isotherms have been found to more accurately explain heavy metals sorption which is often non-linear due to the many interactions and reactions occurring at the soil surfaces.

For the Langmuir isotherm adsorption is said to only occur at independent sites with constant sorption energy independent of surface cover and it is limited by the formation of a monolayer. (Weber and DiGiano, 1996). It is linear at low surface coverages but non linear at the higher surface adsorbent coverages. The Langmuir isotherm is represented by this equation:

\[
S = \frac{S_m K C_{eq}}{1 + K C_{eq}}
\]

where \(S\) is the mass of solute sorbed per dry unit weight of solid (mg/kg), \(S_m\) is the maximum sorption capacity (mg/kg), \(K\) is the sorption constant (L/mg) and \(C_{eq}\) is the concentration of solution in equilibrium with the mass of solute sorbed onto the solid (mg/L). The Freundlich isotherm shows the relationship between the sorbate and sorbent to be an exponential function of the solution.

\[
S = K_f C^{n_f}
\]

Where \(S\) is the mass of solute sorbed per dry unit weight of solid (mg/kg), \(K_f\) is the Freundlich coefficient (L\(^n\) mg\(^{n-1}\)/kg), \(C\) is the concentration of solution in equilibrium with the mass of solute sorbed onto the solid (mg/L), and \(n_f\) the Freundlich exponent.

The Langmuir isotherm is often preferred to the Freundlich form as it allows for calculation of a sorption maximum that can be correlated to intrinsic soil properties.

Adsorption studies are done in a background electrolyte that mimics natural groundwater. Most isotherms have been done with a background electrolyte such as CaCl\(_2\) or NaClO\(_4\) to control the ionic strength with the assumption being the background electrolyte only forms weak outer sphere complexes at the soil surface by electrostatic attraction depending on soil charge. Heavy metals are believed to form inner sphere complexes thus the background electrolytes do
not compete.

Adsorption is made possible due to surface charge which develops in 2 ways, isomorphic substitution among ions of differing valence or from reactions of the surface functional groups with ions in solution. The surface can have a positive, negative or neutral charge depending on pH. The pH at which the net total particle charge is zero is called the point of zero charge (PZC) and this parameter is commonly used to characterize a soil and potentiometric titrations have become the preferred procedure to ascertain this point. (Sposito, 1984)

Some important terms that are used in describing the surface charge are:

The permanent structural surface charge which is the moles of charge per kilogram of soil created by isomorphic substitutions, and the net proton charge of the soil and that is the difference between the moles of protons and moles of hydroxide ions complexed by surface functional groups. Also important are the inner sphere complex charge and the outer sphere complex charge. Both arise solely from the constituents of the soil solution that are adsorbed onto the soil surface.

Surface charge can be used to characterize a soil. There are several points, points of zero charge, which are pH values associated with specific conditions on the soil surface. The conventional PZC is the pH value when the total net particle charge vanishes. This point is also called the isoelectric point when measured by an electokinetic experiment.

Another important pH value is the point of zero net proton charge (PZNPC) which occurs when the net proton charge density is equal to zero and it can be determined by potentiometric titration. The point of zero salt effect (PZSE) can also be determined through this titration and it is the located at the common intersection point of several plots of net proton surface charge versus pH at different ionic strengths of a background electrolyte. The point of zero net charge (PZNC) is the point where the difference in the cation exchange capacity (CEC) and anion exchange capacity (AEC) equals zero. (Sposito, 1984)