

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

Progress Report

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by:

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Executive Summary

This report summarized 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 is 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.

In the prior reporting period (January to June 2005) we reported that we had initiated or completed the following tasks in the proposal timeline:

- Task 1. Collected bulk and intact-core soil samples from four trial site locations in Oregon
- Task 2. Obtain fertilizer samples and other necessary reagents and supplies (complete).
- Task 3. Processed soil samples in laboratory for particles size distribution, pH, and metal content
- Task 4. Initiated laboratory-based soil characterizations

In this reporting period (July 2004 through December 2004) we accomplished the following tasks, as identified for this period in our proposal:

- Task 1. Collected additional bulk and intact-core soil samples from the trial site locations
- Task 3. Completed laboratory analyses for soil particle-size distribution, pH, and metal content
- Task 4. Continued laboratory-based soil characterizations, in particular the acid-base characteristics of the soil.

The results of this work have allowed us to continue to fully document the parameters we need for our ultimate goal of a robust model of fertilizer-derived metal behavior. Among our findings were that

- Soil particle-size distributions were completed, yielding important physical grain-size characteristics necessary for the modeling of water and metal transport in soils
- Depth profiles of Cd at the four field sites were obtained revealing that most of the soil Cd is present in the upper 30-40 cm, probably corresponding to the tillage zone.
- The concentration and the depth of elevated Cd in the soils did not correlate with the treatment levels from the first-year experiment; no distinction was possible among the control or any of the three treatments.
- Alkalimetric (acid-base) titrations of soils from all sites were completed. The parameters obtained allow us to accurately model the effects of pH variation on metal behavior in soils.

Background

Fertilizers, agricultural minerals, agricultural amendments, and lime products may contain toxic metal contaminants that can adversely affect human health and the well-being of livestock and natural ecosystems. The levels of heavy metals in fertilizers and related materials are thus subject to regulation by the Oregon Department of Agriculture. Regulators need to balance the benefits of economical fertilizers with the risks posed by excessive levels of metals in these essential products. Balancing benefits and risks can be achieved with risk-based standards. Human health risk assessments are a key part of creating reasonable and prudent regulations for permissible levels of metals in fertilizers.

Although studies in recent years have greatly expanded the base of knowledge for such systems, much of the work has focused on metals derived from hazardous wastes or sewage sludge application. Also, there is very little available information pertinent to metal behavior in Oregon soils under a variety of agricultural practices and climate conditions. Thus it is difficult or impossible to transfer the results of those studies to the specific problem of metals leaching from fertilizers as they are used in Oregon agriculture. There is an urgent need for a detailed yet practical study of key heavy metals in the fertilizer-soil systems that are relevant to Oregon applications.

OVERALL GOAL AND SPECIFIC OBJECTIVES

Our overall goal is 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 will be used to: 1) assess the leachability and availability of soluble metals; 2) characterize the potential for long-term buildup of metals in soils; and 3) identify the rate at which accumulated metals either leach from the soil or are sequestered via an “aging” process. The specific objectives of this research project are 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 porosity, mineralogy, cation exchange capacity, organic carbon content and extractable metal oxides.
4. Identify the metal sorption/desorption properties of the various soil samples over a wide range of metal concentrations, pH, and for relevant (target) toxic metals.
5. Characterize the importance of rate-limited mass-transfer processes of sorption and desorption with a special emphasis on the aging associated with long-term heavy metal loaded soils that may potentially effect the eventual leaching of metals.
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.

Research Accomplishments in this Reporting Period

1. Completed grain –size distribution determinations for all soil samples. We now have the necessary size data such as the d10 and d90 values that are essential for quantifying soil particle size heterogeneity, hydraulic conductivity, and predicted solute dispersion coefficients. Typical grain size distribution data are shown below in Fig. 1

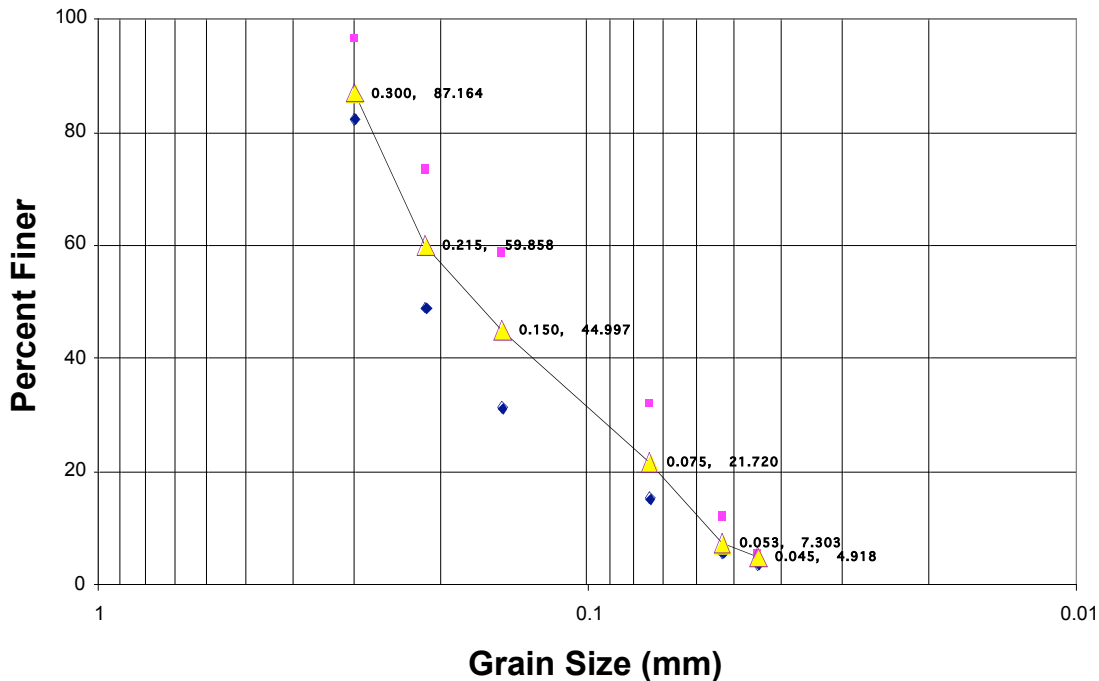


Fig. 1: Grain Size Distribution for Columbia Basin soils.

2. Completed collection of additional bulk and intact-core soil samples from the trial site locations, including cores for characterizing depth distribution of Cd. Sites that we were unable to sample last fall due to dry soil conditions were sampled and sets of bulk, intact, and depth cores collected. The Intact cores are archived for future experimentation. During this reporting period we analyzed the depth cores (1" diameter cores taken to a depth of 50 cm) for the distribution of soil-bound Cd with depth. Depth profiles of Cd from the four field sites revealed that most of the soil Cd is present in the upper 30-40 cm, probably corresponding to the tillage zone (Figs. 2 and 3).

Also, no significant variation in Cd levels could be detected among the control and three treatment levels, probably because of the low levels of Cd in the fertilizer used in the first year. Variations were on the order of 50% but they did not correlate with treatment levels and the control plots were not statistically significantly different from any of the treatment levels.

However, useful information can still be gleaned from the Cd profiles. The persistence and concentrations of Cd in the upper, tillage zone of the field plots, when coupled with the absence of a Cd signal from the treatments, suggests that the Cd profiles are the result of many prior years of ordinary fertilization in the course of station experimentation. This implies that there may be a slow but

measurable accumulation of relatively low levels of Cd in these soils. The accumulation in the tillage zone (down to 20-40 cm) is consistent with a fertilizer-derived source but could also possibly be explained by atmospheric deposition or other causes.

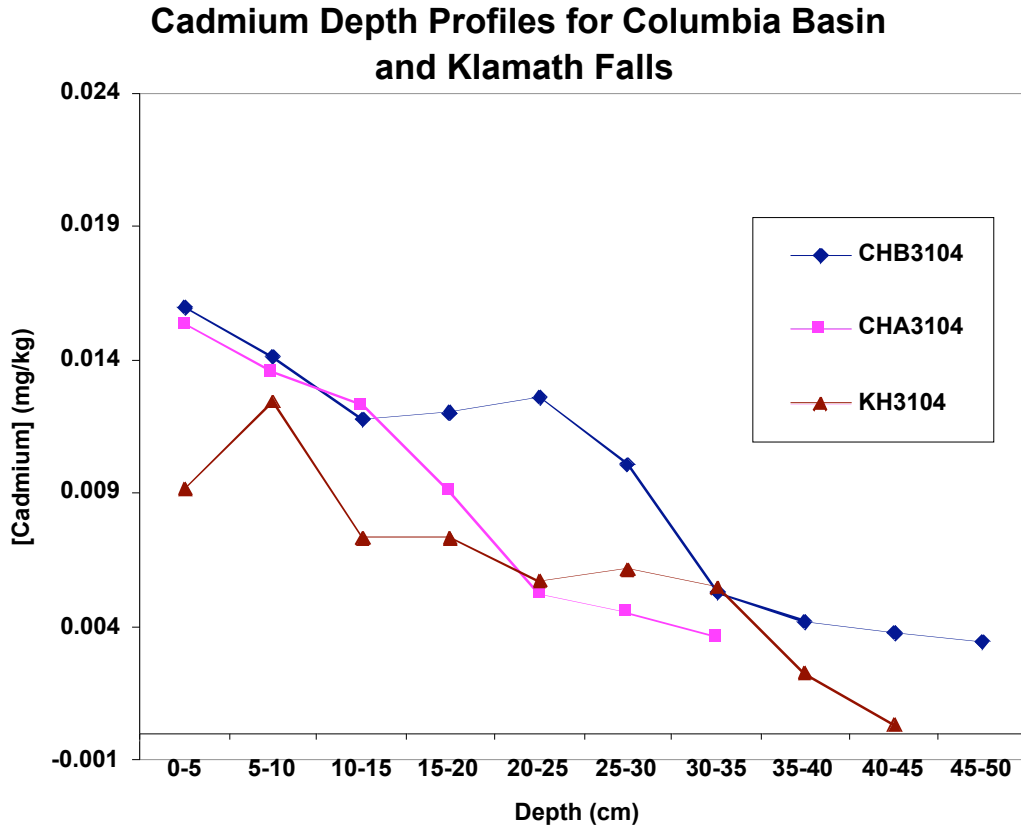


Fig. 2. Depth variation of Cd in the upper 50 cm of core samples from Klamath and Columbia Basin

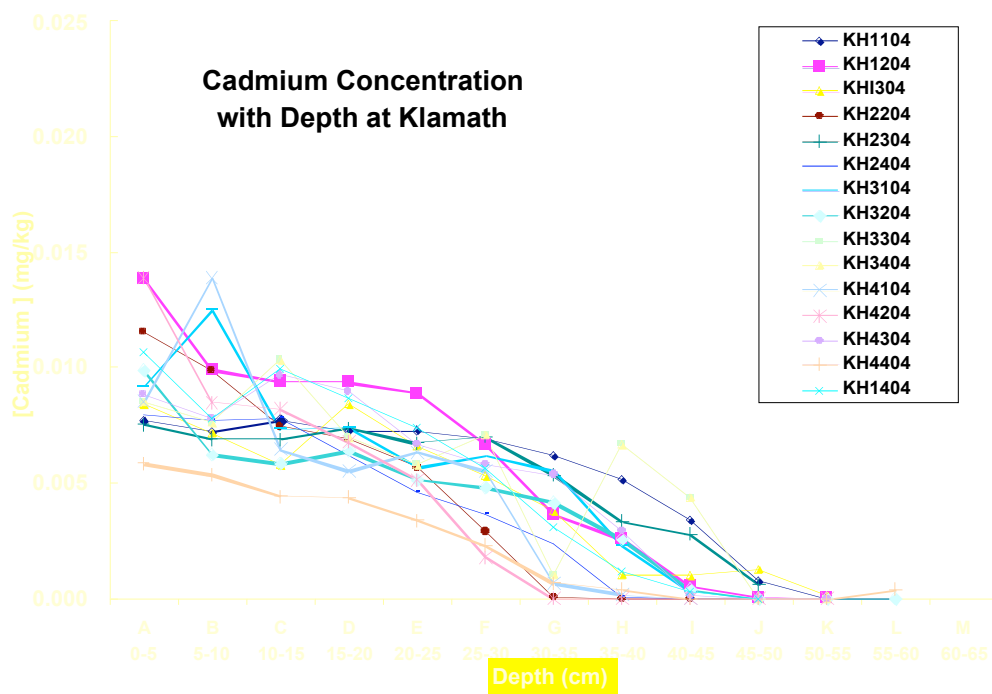
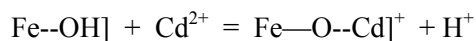


Fig. 3. Variation in Cd with depth in all samples plots at Klamath station, showing no significant difference among treatment levels.

3. Alkalimetric (acid-base) titrations of soils from all sites were completed. The parameters obtained allow us to accurately model the effects of pH variation on metal behavior in soils. 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:



Note the involvement of the hydrogen ion in the reaction, meaning that the reaction is pH dependent. In this stage of the research we focused on obtaining detailed information about the acid-base (proton) reactions of the soil samples.

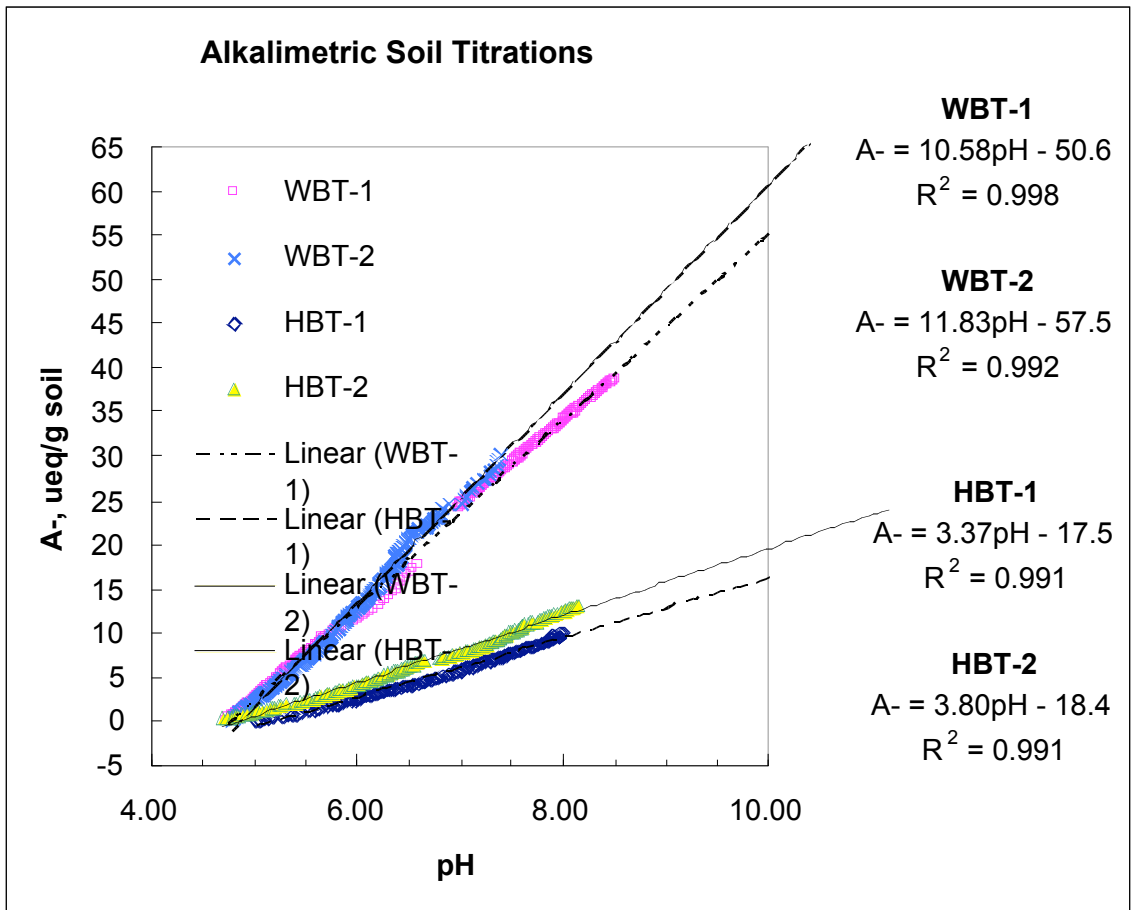


Fig 4. Alkalimetric (acid-base) titrations of Willamette and Hermiston soil samples. Note the consistency within replicates of a station site but the significant different between the stations.

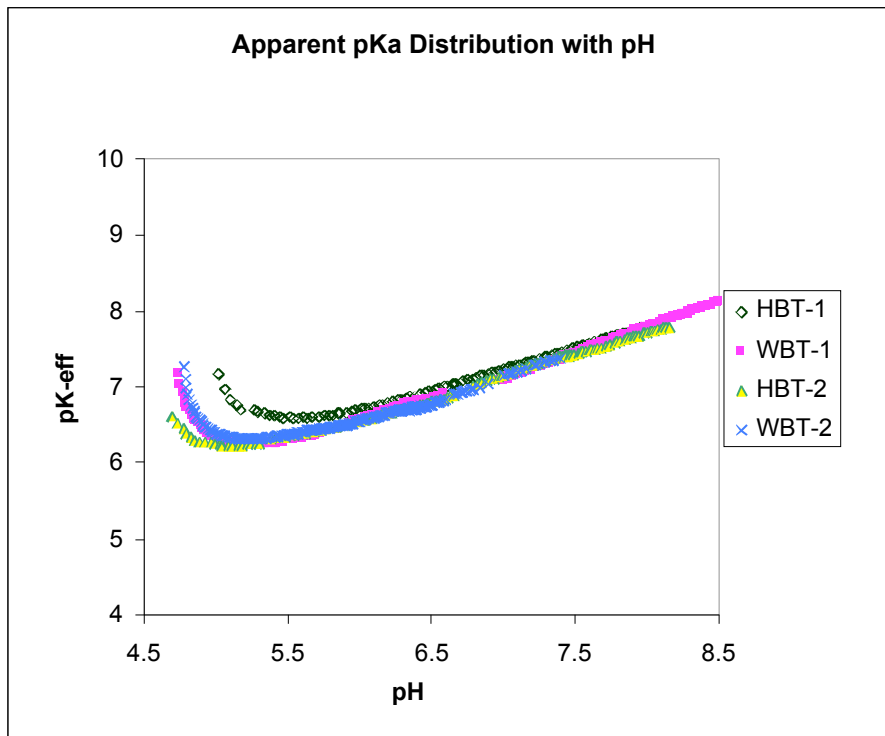


Fig.5 Apparent pKa distribution with pH for site soils.

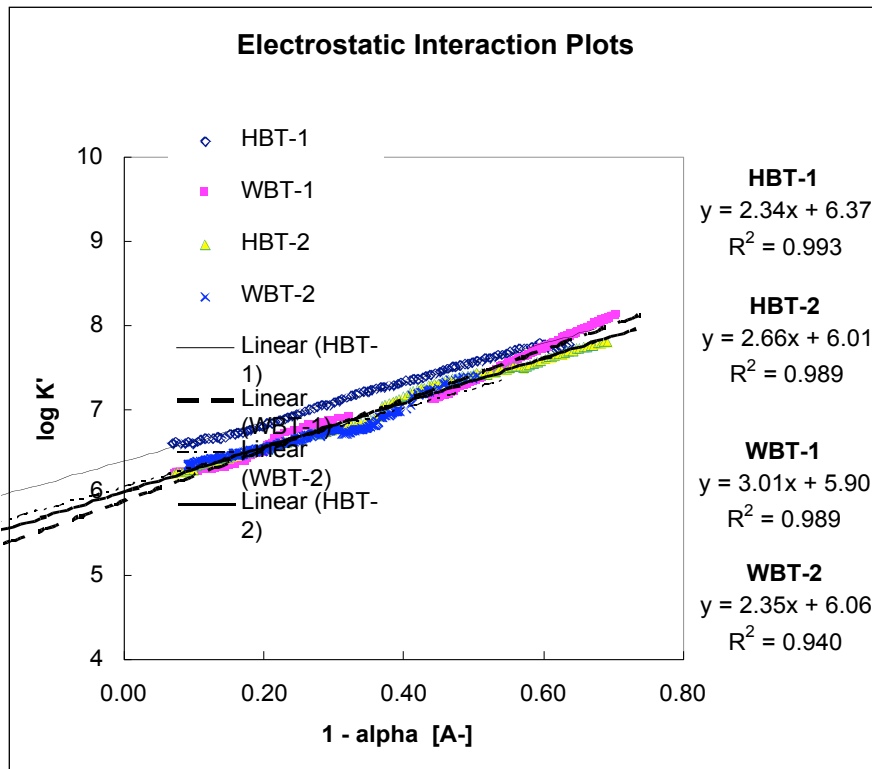


Fig.6 Electrostatic interaction plots for site soils.

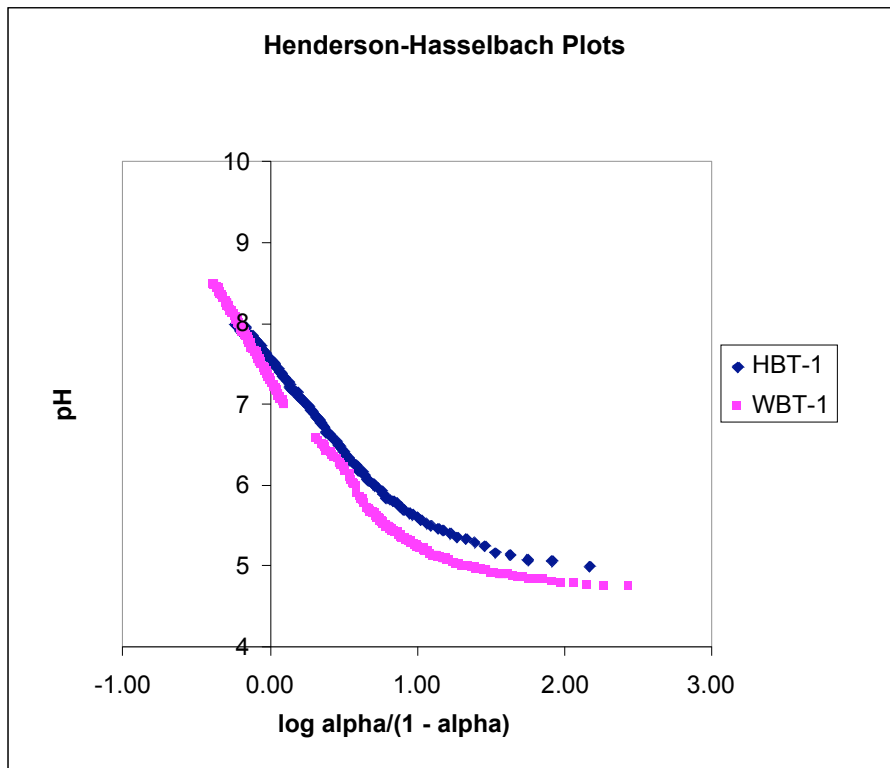


Fig. 7 Henderson-Hasselbach plots of the alkalimetric titrations for site soils.

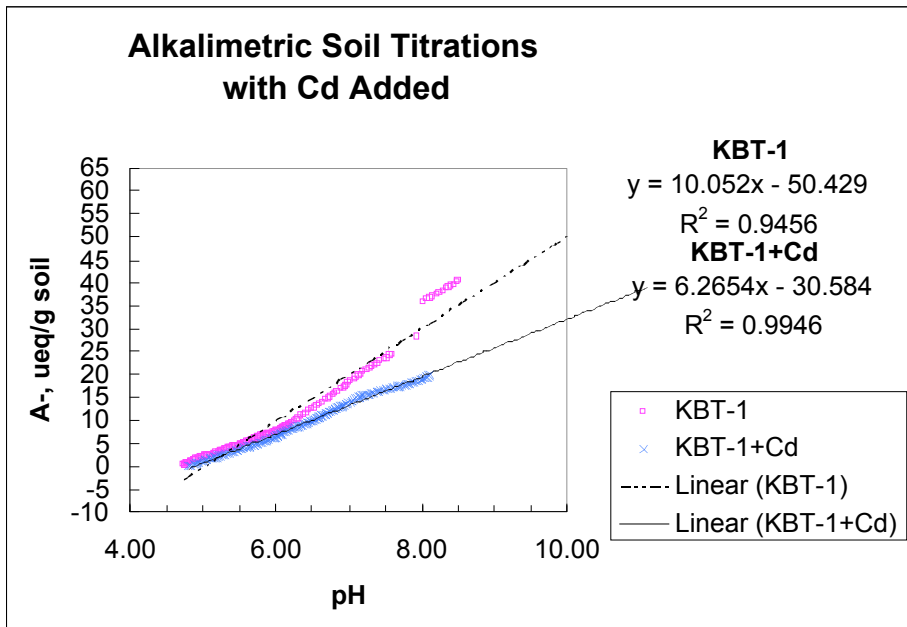


Fig 8. Effect of added Cd on the pH behavior of the soil, providing alternative information about proton-metal interactions.

Next Steps in the Research Plan.

- Measure Cd adsorption explicitly as a function of pH
- Work up model of surface-site/proton interaction (surface acid-base)
- Combine with adsorption isotherms previously described to create comprehensive model on metal binding for all soils
- Look at variation at and among sites

PRINCIPAL INVESTIGATORS

Biographical Sketches

Dr. William Fish

Dr. Fish is an Associate Professor at Portland State University with joint appointments in both the Department of Civil & Environmental Engineering and the Environmental Sciences & Resources program. Dr. Fish's expertise focuses on the interactions of chemical and physical processes in soils and aquatic environments, and the ways those interactions influence the behavior of pollutants. Dr. Fish uses both laboratory experimentation and computer simulations to better characterize how contaminants such as heavy metals move through the environment. He has published a number of articles on metal-humate interactions, surface-complexation modeling of metal adsorption of oxide surfaces and analytical methods for metals in soils and sediments. One recent project focuses on ways in which protective capping materials for contaminated sediments can be chemically modified to enhance their ability to trap and retain toxic metals. In related work, Dr. Fish has collaborated on a study of the redistribution of metals during episodic disruption of sediments in dynamic estuarine systems. Another project centered on modeling of fate and transport of PCBs and toxic metals in the Columbia Slough. The goal in all of these projects is to use scientific understanding to foster better decision-making in the realm of environmental management.

Dr. Gwynn R. Johnson

Dr. Johnson is an Assistant Professor at Portland State University with joint appointments in both the Department of Civil & Environmental Engineering and the Geology Department. Dr. Johnson's expertise focuses on contaminant transport and fate in porous materials. Specifically, Dr. Johnson has investigated and published on the effects of physical and chemical heterogeneities on contaminant transport through undisturbed vs. homogenized aquifer cores. Her interests encompass many fields of study, including environmental chemistry, soil and water sciences, groundwater hydrology, water resources, and environmental engineering. Much of her research has focused on the multiple physical and chemical mass transfer processes influencing the transport, fate, and remediation of contaminants in the subsurface. Additionally, her research has involved characterization/modeling of flow and transport through porous media, including homogeneous and naturally heterogeneous materials.