

**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 (June to December 2004) we reported that we had initiated or completed the following tasks in the proposal timeline:

- 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.

In this reporting period (January through June 2005) we accomplished the following tasks, as identified for this period in our proposal:

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

- April 2005: Obtained remaining intact cores from HAREC and CBARC (Hyslop and Klamath collected last fall)
- Complete sets of depth-profile also taken at HAREC and CBARC in April 2005.

Task 4. Continued laboratory-based soil characterizations, in particular the acid-base characteristics and metal adsorption of the soil.

- Completed the alkalimetric (acid-base) titrations
- Continued the adsorption isotherm experiments, including studies of the effects of competing major ions such as calcium.

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

- Simulating infiltration events and subsequent metal release associated with our fertilizer
- Apparent metal-release kinetics
- Continuous-flow experiments vs. pulse-applications
- Preliminary batch experiments largely complete

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

- Acid-base properties of the soil samples were consistent among most soils, varying mainly in the amount of total exchangeable protons.
- Preliminary isotherm experiments demonstrated that the capacity of soil for Cd at a given site were consistent, but that the strength of Cd binding was influenced by major divalent cations such as calcium.

- Preliminary batch experiments on the release of Cd from dissolving fertilizer pellets is unusual and indicated that the release of Cd rises quickly to a moderately low level and then drops back to unmeasurable levels of Cd release on the time scale of less than a day.
- Preliminary modeling of Cd release suggests that it does not mimic phosphate release and that, in fact, phosphate release may inhibit Cd release via the presence of insoluble Cd-phosphate solids.

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.

Highlights of Accomplishments if the Current Reporting Period



Fig. 1. W Fish collecting an intact soil core, Columbia Basin Experiment Station

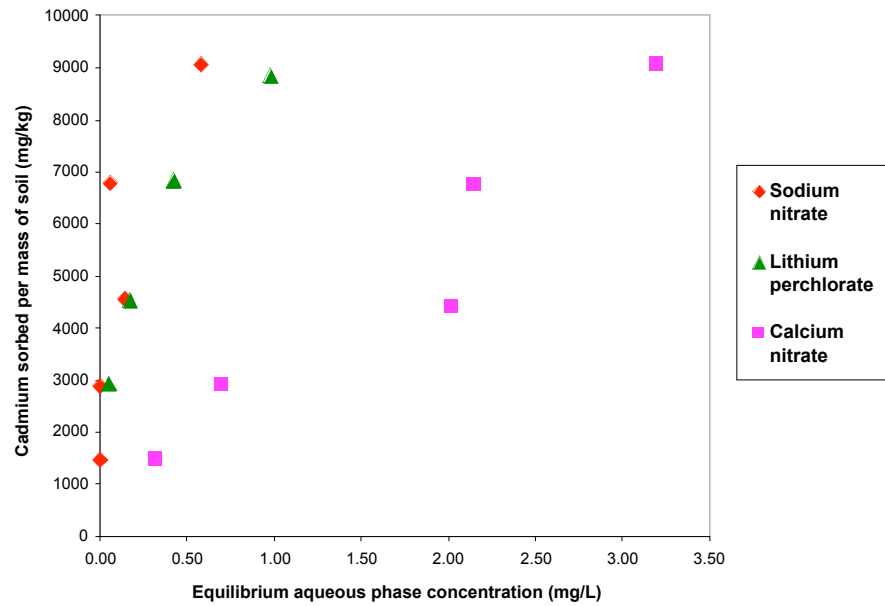


Fig. 2. Adsorption isotherms for Klamath soils, showing the effect of divalent cation Ca partially suppressing the sorption of Cd.



Fig. 3. Apparatus for studying dissolution of Cd from fertilizer particles.

**Fertilizer Dissolution:
Time vs Electrical Conductivity and Cadmium Concentration**

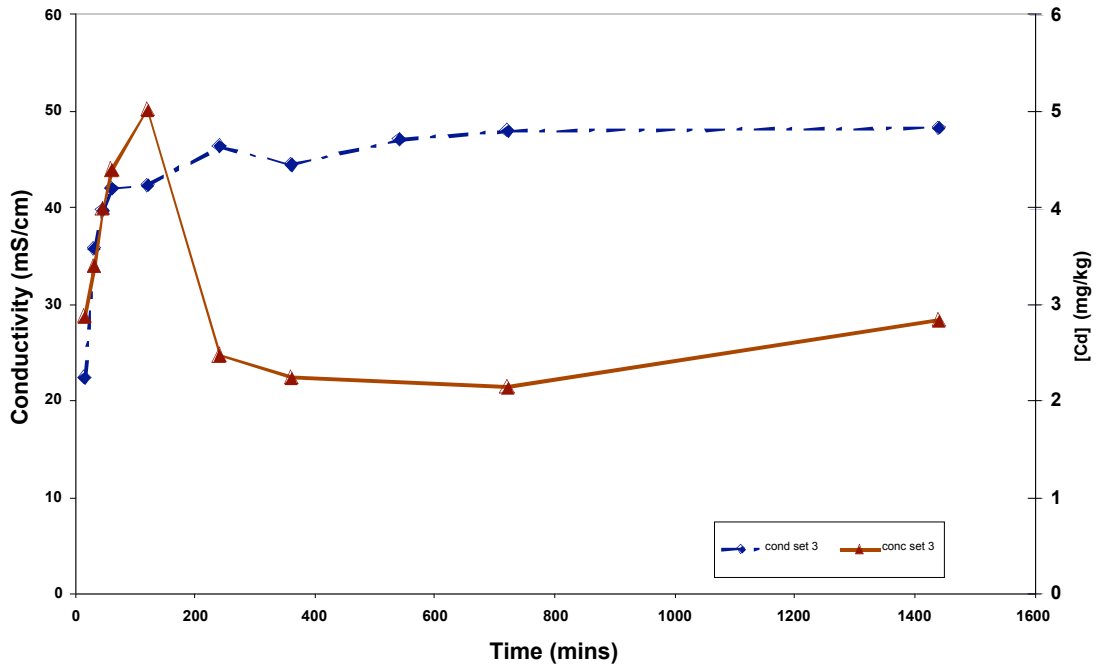
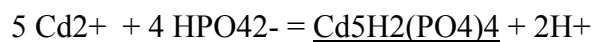


Fig. 4. Batch dissolution of fertilizer particles. Plots of electrical conductivity and soluble Cd as a function of time. Note the peak, then drop off in Cd release.

Possible Control of Cd Release by CdPO₄ Solid Phase



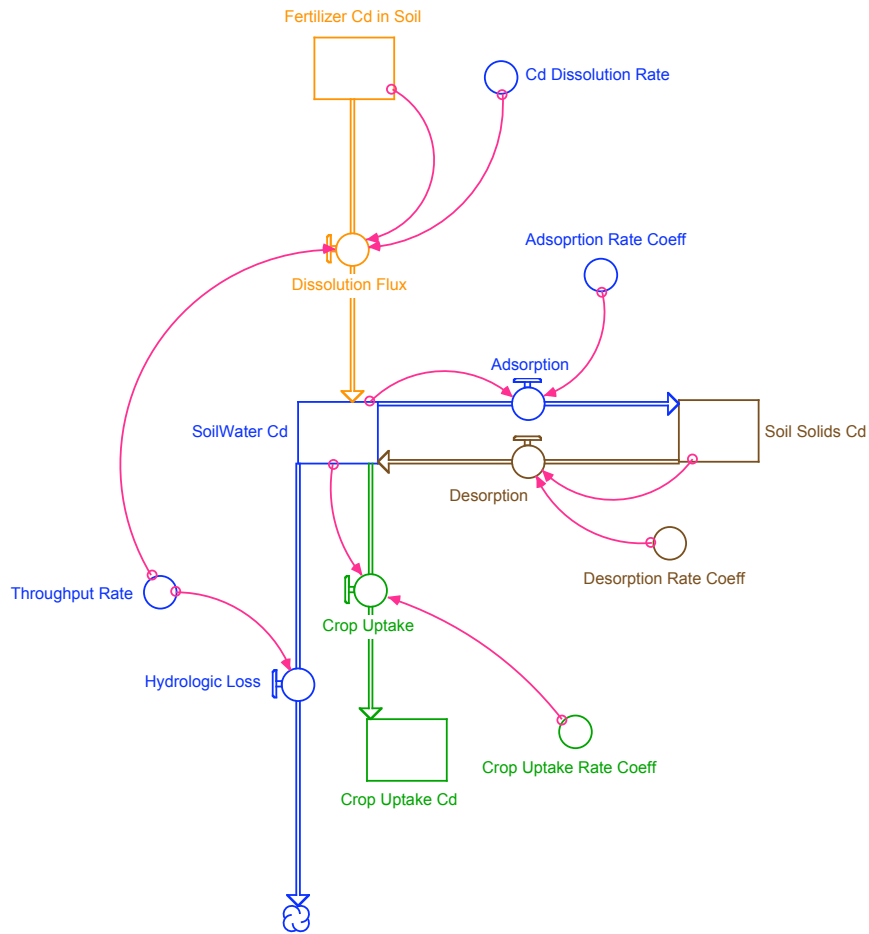
$$\log K_s = -25.4$$

Fertilizer Soln: P ~ 0.1 M

Max. Cd solubility: ~2 uM

These parameters and reactions are consistent with the data we see.

Dynamic Model of Cd Release from Fertilizer and Subsequent Transformations



Next Steps in Research Plan

Completion of the isotherm experiments.

Initiation of intact core transport experiments

More detailed studies of Cd release by fertilizer.