

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

**A Proposal Submitted to:
Oregon Department of Agriculture
Pesticides Division**

Submitted by:

**W. Fish and G.R. Johnson
Portland State University**

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Contacts:

W. Fish fishw@cecs.pdx.edu (503) 725 – 4278

G.R. Johnson gjohnson@pdx.edu (503) 725 - 8710

I. PROJECT RATIONALE

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.

Assessing the risks to humans from exposure to fertilizer-derived metals requires that we understand the pathways of exposure (e.g. via drinking water, food crops, or incidental soil ingestion/inhalation). Predicting these pathways, in turn, requires an accurate knowledge of the concentration of metals in soil porewater and in soil solids. It is not feasible to directly measure these concentrations in the nearly infinite variety of field conditions, so we must base our risk assessments on solute-transport models that accurately characterize the physical and chemical mechanisms affecting metal behavior in soil.

Risk assessments for fertilizer-derived metals have, of necessity, used a simplistic model of metal behavior in soil that assumes that metals reach an equilibrium state in which they partition between soil solid and soil porewater (e.g. Sheppard et al., 1997; Laniak et al., 1997; Buchter et al., 1989). This model relies on a single-value partition or distribution coefficient (K_d) for each metal, which is used to predict the concentration of metals in the porewater (which can be taken up by plants or leach into groundwater and surface water) and the metals associated with the soil solids (which potentially result in the long term accumulation of metals in the soil).

The equilibrium partition approach is used because it is easily integrated into various chemical models. Additionally, it is the only practical model for which sufficient data are available (e.g. see Sauvé et al. (2000) for a critical review of published K_d data). However, it is widely recognized that the equilibrium partition model is highly unreliable for predicting metal transport and fate for two main reasons: 1) the available K_d data for a given metal can vary by two to three orders of magnitude, resulting in hundredfold to thousandfold uncertainty in the human health risk estimates, and 2) the underlying premise of a static soil-water equilibrium is false because metal behavior in soils is a complex, variable, and highly dynamic set of processes. There is thus a critical need to improve our understanding of the transport and fate of fertilizer-derived metals in agricultural soils. 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.

II. 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.

III. BACKGROUND

As noted above, human-health risk assessments are the basis for Oregon's regulation of metals in fertilizers and such assessments depend critically on the results of physicochemical models of metal behavior in soils, particularly with respect to sorption of metals. Many studies have been conducted on metal sorption. Results of these studies have been used to guide government regulations and develop models of the fate of toxic metals in the environment. Many risk assessment models (e.g. RESRAD (DOE), MMSOILS (EPA), and MEPAS (DOE)) depend on simplistic equilibrium partition models that neglect the true dynamic nature of soil-metal interactions.

In recent years the research emphasis has moved away from equilibrium partitioning models in favor of models that explicitly include the kinetics of metal uptake and release from soil surfaces. Traditionally, research has focused on the interactions between porewater metals and soils in batch studies (e.g. Kookana and Naidu, 1998; Seuntjens et al., 2001; Seuntjens et al., 2002 among many others). The knowledge gained in such studies has been valuable, but the usefulness of these models for "real world" application in regulatory risk assessments is limited. While much research has been conducted to characterize solid-phase partitioning (sorption) of organic contaminants under dynamic conditions, i.e., using flow-through soil-column studies, this approach although recognized as more realistic of "real world" conditions is apparently rarely applied to the characterization of metal sorption.

Finally, researchers have concluded that not all reactions occurring between metals and soils are accounted for by traditionally applied adsorption isotherms (e.g. Freundlich), and as such have proposed empirical models to include the effects of pH, organic matter, complexation, and solution ionic strength (Temminghoff et al., 1995; Seuntjens et al., 2001; Seuntjens et al., 2002). These models then allow for estimation of metal-soil partitioning simply using basic soil information and may thus be applicable across a wide range of applications.

The overall behavior of metals in agricultural soils can be conceptualized as follows. Fertilizer applied to a soil dissolves and releases its nutrients over time, also releasing contaminant metals as a pulse distributed over the application duration. The released metals enter soil porewater from which they can move in three major pathways: 1) uptake by soil constituents (clay minerals, metal oxides, microbes and organic matter); 2) uptake by plant roots; and 3) advective loss to ground or surface waters (leaching). The importance of each of these pathways can be estimated from a characteristic rate coefficient for each process. For example, if the fertilizer release rate is rapid, the plant and soil uptake is slow, and the rate of advection is fast (e.g. during irrigation or rain), then most metals will be leached out of the soil. The main problem will be translocation to ground or surface waters. If however, the sorption rate is fast and the movement of porewater is slow, then most metals will adsorb to the soil and the main problem will be the accumulation of metals in the soil horizon. Other such scenarios may explain why metals are rapidly taken up by plants under some conditions, and not under others. Furthermore, more complete dynamic formulations can be elaborated to include the role of slow (long-term) uptake governed by diffusion into

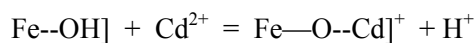
soil micro-porosity, and the possibility that, as contaminated soils age over time, the bound metals get sequestered into relatively irreversible phases.

It should be clear from this discussion that the critical determination of metal concentrations in porewater and soil needed for risk assessments cannot be made from a model (either equilibrium or kinetic, batch or flow-through soil-columns) unless that model accounts for *all* the major pathways as well as the composition of the soil solution. Although the interaction between dissolved and adsorbed metals is reasonably well understood, there are many areas of the larger problem that need to be better elucidated. These are identified in the following sections.

Rate of Release of Metals from Fertilizers: Since the release of metals from a fertilizer is the input of contamination to the system, the rate of delivery of these metals may be an important factor controlling soil-water concentrations. Fertilizers are designed (or at least understood) 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 (PO₄) fertilizers. Some PO₄ forms (such as superphosphate) dissolve relatively quickly. However, Cd will likely 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 PO₄ levels have declined below the relevant solubility limits. Cd release would then significantly lag the PO₄ release.

However, this pattern may not hold for other fertilizers. For example, Zn supplements may contain Cd contamination, but here the controlling phases of Cd could be quite different. Consequently, Cd (the chemistry of which is similar to Zn) might be released at faster rates, paralleling the Zn release. Few kinetic 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. This issue should be examined for various metals and for major classes of fertilizers.

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 Cd²⁺ and Pb²⁺ 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:



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).

As mentioned previously, modeling such processes has typically been done assuming equilibrium conditions between soil-solution and solid. Laboratory studies are seldom, if ever, at equilibrium. Slow sorption 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 kinetics results in either overpredictions of contaminant availability in the environment or an underprediction of the contaminants that can potentially accumulate on soils.

Soils are heterogeneous and contain many mineral phases and organic materials. Thus, the interaction of trace elements with soils is a 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 are typically slow. Neglect of these factors can lead to improper calculation of contaminant behavior in soils, resulting in inappropriate regulations (Strawn and Sparks, 1999). Furthermore, researchers have shown that more information is needed on the effects of long residence time (aging) (Seuntjens et al., 2001). For example, Christensen (1984) showed the 67 weeks of aging of Cd in a sandy loam soil did not significantly alter desorption rate kinetics of Cd (as discussed in Seuntjens et al., 2001). However, several researchers have shown an aging effect for Cd on soils depending on soil composition.

IV. PROCEDURES AND EXPERIMENTAL DESIGN

Research Approach: This project will achieve its scientific objectives through laboratory experiments that allow a precisely controlled microcosm of processes occurring in the field. Although laboratory based, the overall research plan is designed to ensure that results will be directly transferable to actual conditions in Oregon agricultural practice. Experiments will be conducted using samples of agricultural soils from trial sites located in Oregon identified as Willamette Valley (Hyslop Station), Columbia Basin Agricultural Research Center, Hermiston, and Klamath Experiment Station. Our objectives in collecting these samples will include both recently fertilized (field-applied) agricultural soils (herein referred to as *heavy metal loaded soils*) as well as “uncontaminated” soils (herein referred to as *baseline/background soils*) from each trial site location. We also propose to use samples of fertilizer selected in consultation and agreement with K. Anderson (OSU) and ODA as authentic sources of metals in our studies.

The initial studies will involve homogenized soil samples to achieve reproducibility, employing both heavy metal loaded and baseline/background soils. As discussed below, we will identify kinetic data for fertilizer release, sorption, and desorption with continuous-flow and pulsed-flow soil column experiments, since these yield the most realistic estimates of rate and sorption parameters. We will supplement column experiments with selected batch isotherm determinations to obtain correlating data on rapid, quasi-equilibrium binding reactions.

After we gain insight into the kinetic processes of the experimental soils from homogenized samples, we will perform experiments on undisturbed soil cores that retain the natural physical and chemical heterogeneity of the parent soils. Our extensive experience in the difficult technique of undisturbed core handling and experimentation (Johnson et al., 2003a) allows us to add a critical dimension of reality to our models of the soil-water system. Undisturbed column data will allow us to construct a more robust model of fertilizer-derived metals in field soils.

Our approach and time-line also allows for selected experiments to be conducted for relatively long periods so that slow kinetics and aging phenomena can be observed. This will allow us to address the crucial question of long-term accumulation of metals after repeated applications of fertilizer to ultimately be compared to the sorption/desorption characteristics observed for the heavy metal loaded soils. Finally,

we will use both saturated soil columns (in which hydraulic properties and residence times can be precisely defined) and selected unsaturated soil columns to validate the models for vadose zone soil conditions.

The Oregon Department of Agriculture has agreed to perform independent analysis of the selected fertilizer to be employed. Our primary experimental focus will be on target heavy metals naturally occurring in the selected fertilizer. However, selected experiments will be designed to compare the behavior of Cd to that of Pb, Hg, and Ni as well as the anionic As species.

Methodology for Meeting Objectives: Our experimental plan is carefully constructed to assure that each of our project objectives is addressed by procedures and experiments that will yield the desired outcomes. In the sections below, each of our methodologies is described in detail and is mapped to a specific objective.

Description of Project Tasks and Methods

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

Oregon agricultural soils will be collected from targeted regions of Oregon, i.e., Willamette Valley (Hyslop Station), Columbia Basin Agricultural Research Center, Hermiston, and Klamath Experiment Station. Conventional grab (e.g. disturbed/homogenized) samples will be collected from each plot at each trial site. A total of 16 surface-soil and 8 deep-soil grab samples will be collected from each trial site. These grab samples will include both baseline/background soils and heavy metal loaded soils. Furthermore, approximately 4 undisturbed soil samples (e.g. intact cores) will be collected from each trial site following the field application (as performed by K. Anderson at OSU) of ODA selected fertilizer.

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

Commercially available fertilizer, selected by ODA, will be sampled and characterized accordingly in the laboratory. Identification and quantification of major target heavy metals will be completed and these results will be compared to those obtained independently by ODA.

Task 3. Process soil samples in laboratory

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

Task 4. Laboratory-based soil characterizations.

Perform standard soil characterizations on select samples from each trial site according to standard soil methods, including grain size analysis, density, surface area, cation exchange capacity (in consultation and agreement with K. Anderson of OSU), organic carbon content, and extractable metals via the double-acid method (0.05N HCl in 0.25N H₂SO₄; Perkins, 1970).

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

Aliquots of fertilizer will be mixed with clean silica sand that has been ashed in a Muffle furnace and acid washed. Concentrations/application rates will match those field-application rates at the trial sites as determined in agreement with OSU extension recommendations and ODA input (again coordinating with K. Anderson at OSU). Sand-fertilizer mixes will then be packed into columns (described in Task 7 below). Initial tests will use a continuous flow of eluent water at a slow flow rate to simulate infiltration in soils. Sequential eluent samples will be collected and analyzed for metals and relevant major ions. The data will yield profiles of metal release; the elution profiles will be used to define fertilizer release kinetics for use in our soil model. These continuous flow experiments will be followed by pulse flow tests that more accurately simulate intermittent field infiltration. Effects of pulsing on apparent release kinetics will be identified.

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

Batch experiments will be conducted on selected homogenized samples from each trial site to determine Freundlich isotherm coefficients for all metals. Most isotherms will be collected at the pH of the native

soil, but selected isotherms will be 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 will be added to a series of acid-washed HDPE screw-cap vials. To investigate nonlinear partitioning behavior, at least five initial metal concentrations will be 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 will be 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 will be 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 column will be 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 will be packed with selected soils (either baseline/background soils or heavy metal loaded soils) in incremental steps to establish uniform bulk density. Experiments will be 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 will be 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 will be determined by conducting conventional tracer studies and compared to those measured for the corresponding undisturbed soil systems. The data will be analyzed using the method of moments to determine mass recoveries and travel times. Analysis will be 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 will be 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 will be introduced to the undisturbed soil column. The resulting data (e.g. heavy metal transport as well as sorption/desorption properties) will be compared to that measured for the long-term loaded soil.

Task 8. Selected unsaturated soil columns

Unsaturated column experiments will be 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) will be 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) will be compared to that measured for the saturated column experiments.

Task 9. Diagnostic Model Formulation

The experiments will be 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 will be 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.

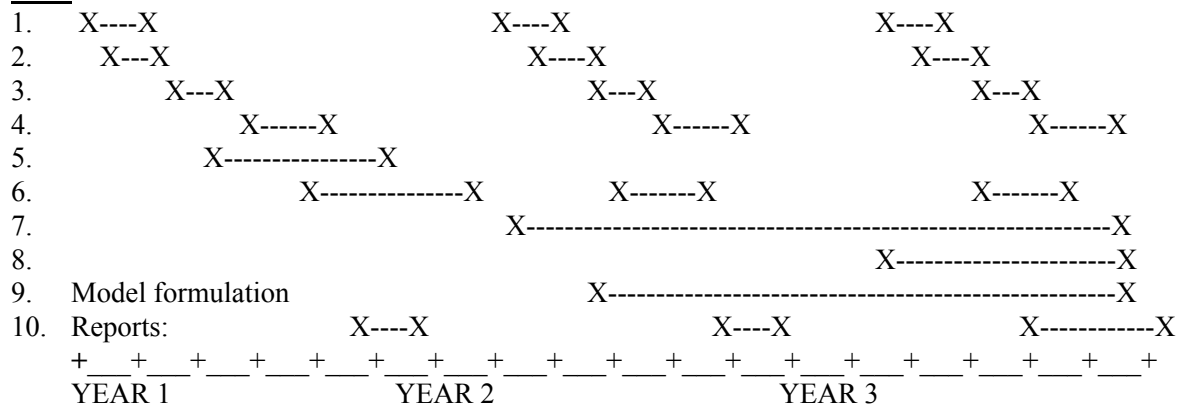
The proposed model is *diagnostic* rather than *prognostic*. That is, the goal is not to be able to make exact prediction of metal behavior under a particular field condition, but rather to have a quantitative framework for understanding the relative importance of each transport process. A critical value of diagnostic modeling is that it will be 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 will be developed early in the project, but then expanded and improved as we progress with the experimental work.

Task 10. Reports

A report of all project activities and findings will be prepared and submitted annually at the end of each 12 months of the project. Interim activity reports and updates will be prepared at shorter intervals at the request of ODA staff. A final report documenting all activities, experimental findings, and conclusions will be prepared at the end of the third year of the project. Because of the involvement of student researchers and because of the general scientific importance of this work, we anticipate submitting many of our findings to peer reviewed journals for general dissemination. We can provide advance copies of manuscripts to ODA staff for internal review prior to journal submission.

PROJECT TASK TIMELINE

Task



COLLABORATIVE ARRANGEMENTS

This project is designed as a collaboration between scientists from Portland State University. Dr. W. Fish will provide expertise on transport and fate of metals, metal complexation, redox chemistry, and metals analysis. Dr. G.R. Johnson will provide expertise on contaminant transport, sorption/desorption theory, tracer theory, and laboratory experimentation.

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QUALIFICATION OF 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.

CURRICULUM VITAE

William Fish

Associate Professor
Department of Civil Engineering
Environmental Sciences and Resources
Portland State University
P.O. Box 751, Portland, Oregon 97207-0751
Tel: (503) 725-4278 Fax: (503) 725-5950

Education

- 1979 University of Florida (B.S.E. in Environmental Engineering with High Honors)
1984 Massachusetts Institute of Technology (Ph.D. in Civil & Environmental Engineering)

Employment History

- 1998 - Present Portland State University, Department of Civil Engineering /Environmental Sciences and Resources. Associate Professor
1992 - 1998 Oregon Graduate Institute, Department of Environmental Science and Engineering. Associate Professor.
1987 - 1992 Oregon Graduate Institute, Department of Environmental Science and Engineering. Assistant Professor.
1986 - 1987 Oregon Graduate Institute, Department of Environmental Science and Engineering. Instructor/Research Scientist.
1984 - 1986 Oregon Graduate Institute, Department of Chemical, Biological, and Environmental Sciences. Postdoctoral Research Associate.
1979 - 1984 Massachusetts Institute of Technology, Graduate Research Assistant.

Research Interests and Expertise

The transport and behavior of organic contaminants and toxic metals in soil, groundwater, surface water, and sediment systems, with particular interest in the linkages among chemistry, biology, transport processes and effective cleanup strategies.

Courses Taught

Unit Operations in Water and Wastewater Treatment (CE 474/574)
Environmental Engineering (CE 371)
Transport and Fate of Toxics in the Environment (CE/ESR 465/565)
Environmental Cleanup and Restoration (CE/ESR 510)
Water Quality Problem Solving (CE/ESR 510)
Aquatic Speciation and Modeling (OGI)
Chemical Transport Dynamics (OGI)
Hydrogeochemistry (OGI)

Professional Affiliations

American Chemical Society, American Geophysical Union, Society for Environmental Toxicology and Chemistry, Sigma Xi, American Society of Limnology and Oceanography, Center for Coastal and Land Margin Research

Honors

Distinguished Teaching Award 1995, Oregon Graduate Institute

ACS Environmental Chemistry Division Paper-Presentation Award (194th National Meeting, September 1987)

Distinguished Teaching Award 1987, Oregon Graduate Institute

Arthur T. Ippen Graduate Student Award, 1982, Massachusetts Institute of Technology

Selected Publications

Fish, W., Nakae, Y. Fugacity modeling of polychlorinated biphenyl congeners in an urban watershed. (*In preparation*)

Fish, W., K. Mesuere. Ligand-promoted dissolution kinetics of iron oxides: Effects of oxalate and chromate co-adsorption. (*Submitted, Langmuir*).

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CURRICULUM VITA

GWYNN ROCHELLE JOHNSON

Assistant Professor

Department of Civil and Environmental Engineering

Portland State University

Phone: 503-725-8710; Fax: 503-725-5950

EDUCATION

Ph.D. Environmental Chemistry/Hydrology, 2001

The University of Arizona, Tucson, Arizona

Major: Contaminant Transport, Department of Soil, Water, and Environmental Science

Minor: Hydrology, Department of Hydrology and Water Resources

Advisor: Mark L. Brusseau

Dissertation: Mechanisms Contributing to Nonideal Transport Behavior of Contaminants in a Naturally Heterogeneous Aquifer Material

M.S.E. Environmental Engineering, 1996

University of Florida, Gainesville, Florida

Major: Contaminant Transport, Department of Environmental Engineering Sciences

Minor: Hydrology, Interdisciplinary Hydrologic Sciences Program

Advisors: Michael D. Annable and P. Suresh C. Rao

Thesis: Solvent Flushing of an LNAPL Contaminated Soil and the Effects of Weathered Contamination

B.S. with Honors, Environmental Engineering, 1993

University of Florida, Gainesville, Florida

EMPLOYMENT

Assistant Professor, Department of Civil and Environmental Engineering, Portland State University, Portland, Oregon, 2002 - present.

Post-Doctoral Research Associate, The University of Arizona, Tucson, Arizona. Supervisor: Mark L. Brusseau, 2001-2002.

Research Associate, The University of Arizona, Tucson, Arizona, Advisor: Mark L. Brusseau, 1996 - 2001.

Research Specialist, Contaminant Transport Research Laboratory, The University of Arizona, Tucson, Arizona, 1997 - 2001.

Partitioning Tracer Project Manager, The University of Arizona, Tucson, Arizona, 1997 - 2001.

Lab Safety and Operations Manager, The University of Arizona, Tucson, Arizona, 1997 - 1998.

Research Assistant, University of Florida, Gainesville, Florida, Advisors: Michael D. Annable and P. Suresh C. Rao, 1993 - 1995.

Undergraduate Assistant, University of Florida, Gainesville, Florida, 1992.

Assistant Engineer, Environmental Consulting & Technology, Gainesville, Florida, 1992 - 1994.

Engineering Intern, Larsen & Associates, Miami, Florida, 1991.

PUBLICATIONS

Peer-Reviewed Journal Articles

Johnson, G. R., Zhang, Z., and Brusseau, M. L. Characterizing and quantifying the impact of immiscible-liquid dissolution and non-linear, rate-limited sorption/desorption on low-concentration elution tailing. *Water Resources Research*, 39(5): art. no. 1120, 2003.

Johnson, G. R., Gupta, K., Hu, Q., and Brusseau, M. L. The effect of local-scale physical heterogeneity and non-linear, rate-limited sorption/desorption on contaminant transport in porous media. *Journal of Contaminant Hydrology*, 64(1-2), 35-58, 2003.

Johnson, G. R. and Brusseau, M. L. Influence of temporally variable dispersion on long-term contaminant elution tailing. (In review).

Blanford, W. J., Barackman, M. L., Boving, R. G., Klingel, E. J., Johnson, G. R., and Brusseau, M. L. Cyclodextrin-enhanced vertical flushing of a trichloroethene contaminated aquifer. *Ground Water Monitoring and Remediation*, 21(1), 58-66, 2001.

Brusseau, M. L., Nelson, N. T., Oostrom, M., Zhang, Z., Johnson G. R., and Wietsma, T. W. Influence of heterogeneity and sampling method on aqueous concentration associated with NAPL dissolution. *Environmental Science and Technology*, 34(17), 3657-3664, 2000.

Cain, R. G., Johnson G. R., McCray, J. E., Blanford, W. J., and Brusseau, M. L. Partitioning tracer tests for evaluating remediation performance. *Ground Water*, 38(5), 752-761, 2000.

Nelson, N. T., Brusseau, M. L., Carlson, T. D., Costanza, M. S., Young, M. H., Johnson, G. R., and Wierenga, P. J. A gas-phase partitioning tracer method for in situ measurement of soil-water content. *Water Resources Research*, 35(12), 3699-3707, 1999.

Peer-Reviewed Book Chapters

Brusseau, M. L., McCray, J. M., Johnson, G. R., Wang, X., Wood, A. L., Enfield, C. Field test of cyclodextrin for enhanced in-situ flushing of multiple-component immiscible organic liquid contamination: Project overview and initial results. Chapter 9 in: Innovative Subsurface Remediation: Field Testing of Physical, Chemical, and Characterization Technologies, Brusseau, M.L., Sabatini, D. A., Gierke, J. S., and Annable, M. D., eds., American Chemical Society, Washington DC, 1999.

McCray, J. M., Bryan, K. D., Cain, R. B., Johnson, G. R., Blanford, W., and Brusseau, M. L. Field test of cyclodextrin for enhanced in-situ flushing of multiple-component immiscible organic liquid contamination: Comparison to water flushing. Chapter 10 in: Innovative Subsurface Remediation: Field Testing of Physical, Chemical, and Characterization Technologies, Brusseau, M.L., Sabatini, D. A., Gierke, J. S., and Annable, M. D., eds., American Chemical Society, Washington DC, 1999.

Blanford, W. J., Klingel, E. J., Johnson, G. R., Cain, R. B., Enfield, C., and Brusseau, M. L. Performance assessment of in-well aeration for the remediation of an aquifer contaminated by a multi-component immiscible liquid. Chapter 12 in: Innovative Subsurface Remediation: Field Testing of Physical, Chemical, and Characterization Technologies, Brusseau, M. L., Sabatini, D. A., Gierke, J. S., and Annable, M. D., eds., American Chemical Society, Washington DC, 1999.

PROFESSIONAL CERTIFICATES Engineering Intern in Training No. 495ET159, April 1996
 OSHA 40-hour Training Certificate, April, 1996
 OSHA 8-hour Supervisory Certificate, May 1996

PROFESSIONAL AFFILIATIONS American Chemical Society
 American Geophysical Union
 Tau Beta Pi (National Engineering Honor Society)
 Officer, Vice-President 1992-1993
 Officer, Graduate Student Coordinator 1991-1992

RESEARCH GRANTS

Laboratory-Scale Testing of Gas-Phase Partitioning Tracers: An Innovative In-situ Method for the Detection and Quantification of Nonaqueous Phase Liquids in Unsaturated (Vadose-Zone) Media. Principal Investigator: M. L. Brusseau. Co-Investigator: G. R. Johnson. Sponsor: Department of the Army, New England District, Corps of Engineers; \$81,000 (12 months).

FACILITIES AND RESOURCES

The PSU Department of Civil and Environmental Engineering maintains approximately 2000 ft² of wet-chemistry laboratory space under the direction of the principal investigators. This laboratory is equipped for the handling and characterization of water and soil, including pH meters, balances, ovens, centrifuges, filtration apparatus, settling columns, and soils sieves. Advanced analytical equipment includes a Shimadzu GC-17A gas chromatograph equipped with gas-phase headspace and direct-inject aqueous autosamplers, a Gilson UV-VIS spectrophotometer, and a HIAC Royco Liquid Particle Analyzer. The project will also take advantage of the PSU Trace Element Analytical Laboratory (TEAL) which is fully equipped with advanced equipment for ultra-trace metal analysis, including a Hewlett Packard 4500 Series ICP-MS and a Perkin-Elmer graphite-furnace/flame atomic absorption spectrophotometer. The project also is supported by the investigators' computer laboratories equipped with multiple PCs.

QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

1. QA/QC in the Field

a. Sample Labeling

All samples will be labeled in the field using an ID system that coordinates with sample labeling used by K. Anderson and the OSU researchers. Sample logging and labeling will be documented in field log books.

b. Transportation and Preservation of Samples. Grab soil samples will be collected in either plastic zip-seal bags or clean Mason-type jars. Intact soil columns will be collected using clean aluminum tubes (3 to 4 inches in diameter) and sealed with plastic end caps. Refrigeration of soil samples for transport is not necessary as samples will typically be returned to the lab on the day of collection. However, during transit, samples will be kept in a cool environment, using plastic coolers as needed to maintain sample integrity. The samples will be placed in a freezer immediately upon arriving back at the laboratory, for later subsampling and cataloging.

c. Duplicate Samples

The number and type of samples to be collected are defined in the methodology section in the main text. Duplicate samples will be collected as described for field grab samples. Intact cores will be collected in replicate in selected plots, as discussed earlier.

d. Field Handling Procedures

All samples will be handled with clean technique, using deionized water to wash handling tools and other points of sample contact.

2. QA/QC in the Laboratory

a. General Handling Techniques

All containers, glassware or equipment in contact with samples or reagents will be subject to rigorous cleaning to eliminate any source of potential metal contamination. The cleaning protocols include washing in nonionic detergent, multiple rinsing in deionized water, acid washing (10% HNO₃), and final multiple rinses in ultraclean water. Sample blanks (discussed below) will verify the absence of contamination in handling.

b. Analytical Blanks and Spikes:

Analytical QA/QC will be accomplished by extensive use of standard analytical procedures as surrogate spikes, matrix spikes, duplicates, reagent blanks and calibration checks. All ICP/MS and AAS analyses for metals will be made using an autosampler to minimize sample handling variation. Each metal analysis will be performed in triplicate along with regular insertions of blanks and standards within each sample run.

c. Performance-Evaluation samples

Performance-evaluation (PE) samples evaluate the overall bias of the analytical laboratory and detect any error in the analytical method used. These samples will be prepared by a third party, using a quantity of analyte(s) which is known to the preparer but unknown to the laboratory. The third party will be an independent research staffer in the PSU trace element analytical facility.

The analyte(s) used to prepare the PE sample is the same as the analyte(s) of concern. Laboratory procedural error is evaluated by the percentage of analyte identified (percent recovery) in the PE sample. When analyzed, the minimum frequency of PE samples is one per analyte of interest.

d. Matrix-Spike samples

Matrix spike and matrix spike duplicate samples (MS/MSDs) are environmental samples that are spiked in the laboratory or in the field with a known concentration of a target analyte(s) to verify percent recoveries. Matrix spike and matrix spike duplicate samples are primarily used to check sample matrix interferences. They can also be used to monitor laboratory performance. The minimum frequency of MS/MSDs will be 10 percent of the total number of samples being analyzed for the target analyte(s). Matrix spike and matrix spike duplicate samples are also used to evaluate error due to laboratory bias and precision. One MS/MSD pair per target analyte will be analyzed and the average percent recovery should be calculated to assess bias. To assess precision, multiple matrix spike replicates from the same sample will be analyzed and the standard deviation and coefficient of variation determined.