

**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 first reporting period (September 2003 through June 2004) we accomplished the following tasks, as identified for this period in our proposal:

- 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

In addition, we initiated studies of the rate of release of cadmium from the trial fertilizer under conditions approximating field conditions.

The results of this work provide us with the background information about the soil characteristics that we need to proceed with subsequent experiments to obtain parameters for the model of metal behavior.

Among our findings were that

- All soils have low but detectable background levels of cadmium,
- the trial fertilizer was lower than expected in Cd content,
- distinct size distributions were obtained for the four regional soils, which will provide a good opportunity to calibrate the model to a range of soil types
- release of Cd from fertilizer appears to be relatively rapid in the first few hours of dissolution, but slows substantially after 24 h, leading to a long “tailing off” of release.

In addition, the field sampling has provided us with a cataloged library of soil samples from all experimental plots at all sites.

## **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.

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.

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.

## **Tasks Proposed for this Reporting Period**

### **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 H<sub>2</sub>SO<sub>4</sub>; 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. 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.

## **Results for this Reporting Period.**

**Sample Collection:** Soil samples were collected by from all 16 subplots at all four sampling sites (Hyslop/Willamette, Klamath, Columbia Basin/Pendleton, Hermiston) representing four major regions of Oregon agriculture. Samples were collected from surface hand augurs in randomized locations with each trail cell as well as from the bottom of ~1 m deep machine augured holes (in collaboration with OSU).

All samples have been handled with clean technique, cataloged with a standardized labeling system and stored in the lab in sealed plastic bags. The sample set represents a library of materials for our research activities on these soils.

**Soil Characterization:** Soil subsamples were dried overnight at 105 degrees C, and analyzed for particle size distribution, soil pH, and content of Cd and Pb.

**Soil Particle Size Distribution:** Particle size distributions were determined by standard sequential sieving of dried soil samples, following by weighing of the sieved fractions. Results are presented below in plots of the fraction of soil mass finer than the grain size depicted on the horizontal axis.

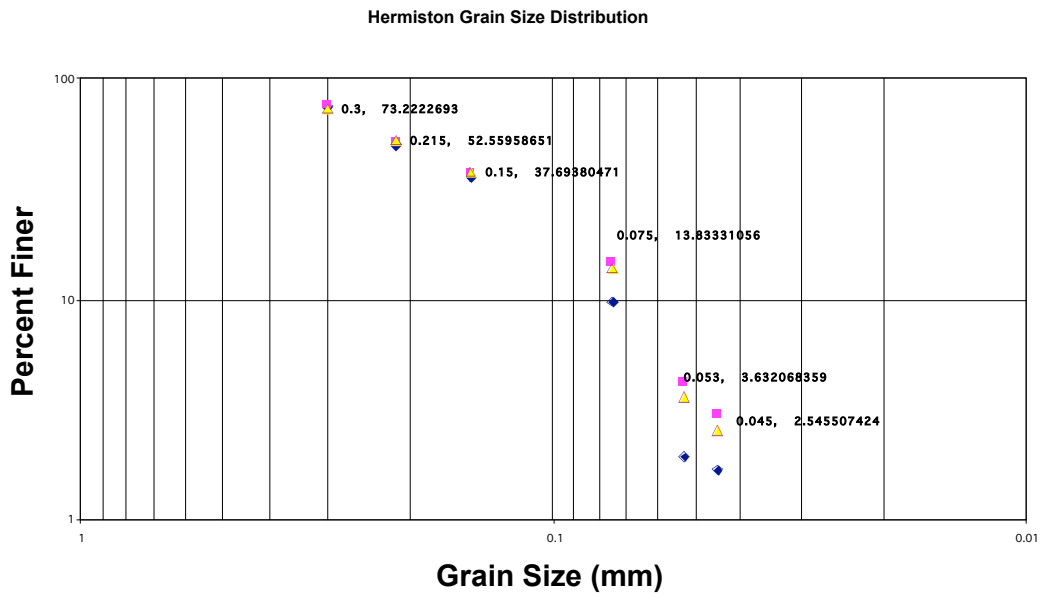


Figure 1: Hermiston soil size distribution.

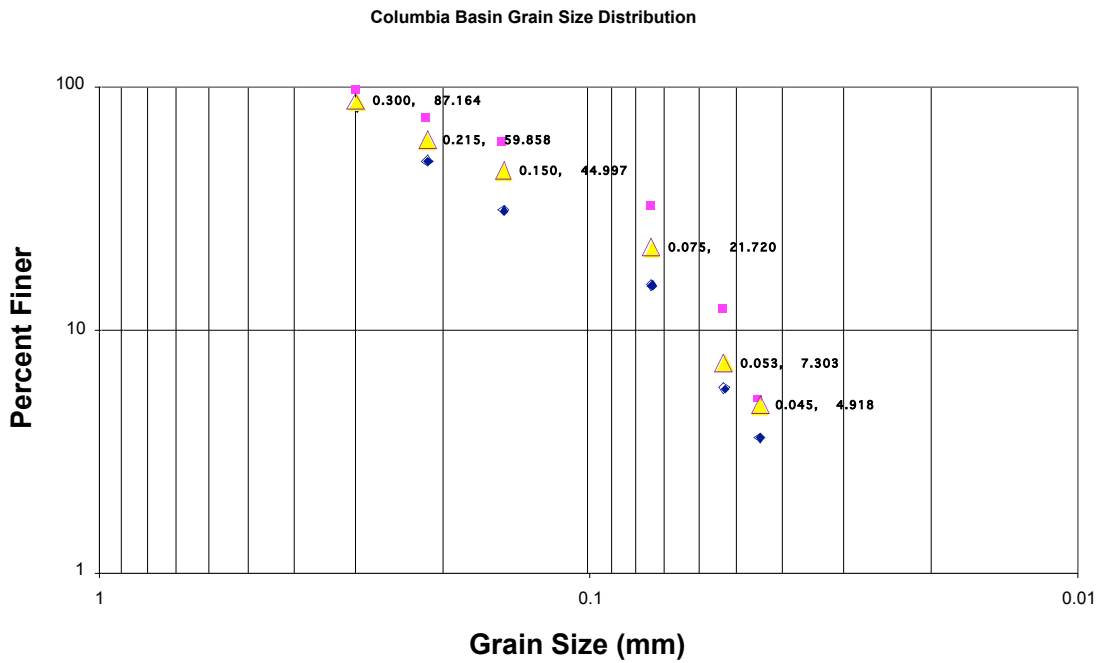
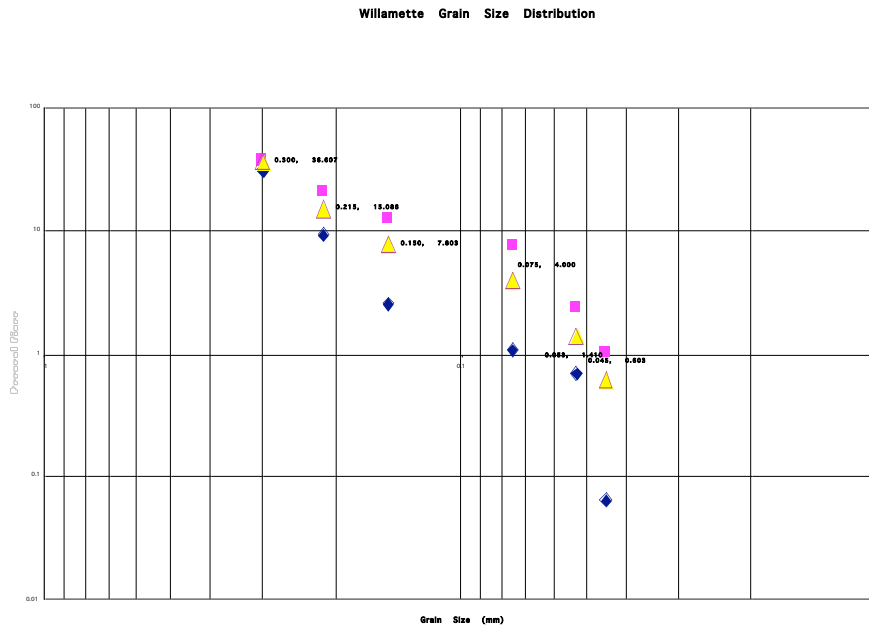


Figure 2: Columbia Basin soil size distribution.



### **Cd and Pb Content of Soils:**

Extractable metals on the soils were determined via via the double-acid method (0.05N HCl in 0.25N H<sub>2</sub>SO<sub>4</sub>). Extractions were analyzed via ICP-MS at PSU using appropriate quality control blanks, spikes, and standards. Metal-clean techniques was used in al stages of sample handling and analysis. Results are shown in Table 1 below.

- **Willamette:**
  - **Cd = 5.7 ug/kg**
  - **Pb = 18 ug/kg**
- **Columbia Basin**
  - **Cd = 13.2ug/kg**
  - **Pb = 12 ug/kg**
- **Pendleton**
  - **Cd = 11.5 ug/kg**
  - **Pb = 115 ug/kg**
- **Klamath**
  - **Cd = 12.9 ug/kg**
  - **Pb = n/a**

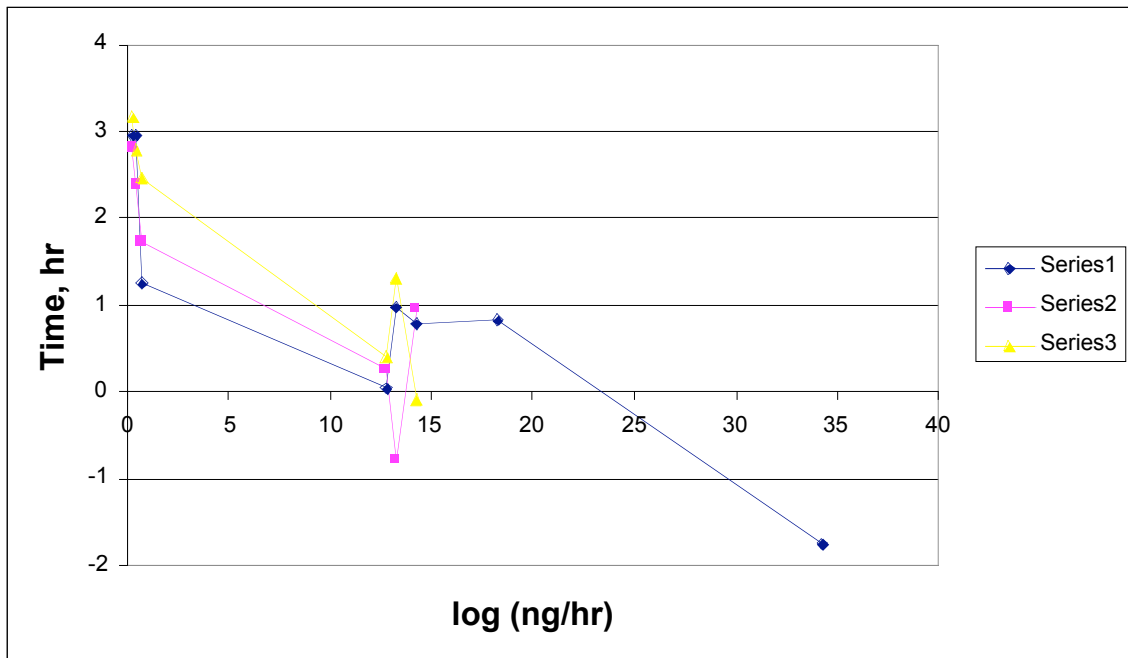
**Table 1:** Cd and Pb Content of Soils

**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 (PO<sub>4</sub>) fertilizers. Some PO<sub>4</sub> 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 PO<sub>4</sub> levels have declined below the relevant solubility limits. Cd release would then significantly lag the PO<sub>4</sub> 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 was examined in preliminary Cd release experiments shown below.



**Figure 5:** Experimental set-up for measuring the rate of Cd release from fertilizer in moist sand.



**Figure 6:** Rate of Cd release from fertilizer used in 2003 field trials.

## **Description of Next Project Tasks to Be Completed in Project Out-Years**

### **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  $\mu\text{m}$  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.

## 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**

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### **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*).

Kumar, A. and W. Fish. Competitive adsorption effects among Cu(II) and oxalate on heterogenous oxide surfaces. *Colloids and Surfaces A*. (*In press*).

Johnson, T.L., W. Fish, Y.A. Gorby, and P.G. Tratnyek. Degradation of carbon tetrachloride by iron metal: Complexation effects on the oxide surface. *J. Contam. Hydrol.* 29:377-396 (1999).

C. D. Palmer and W. Fish. Chemically enhanced removal of metals from the subsurface. In: *Subsurface Restoration* (Eds. C.H. Ward, J.A. Cherry, M.R. Scaif), Ann Arbor Press (1997)

W. Fish, W. Romanelli and C. Martin. Chemical Characteristics of a Seep at the St. Johns Landfill in Portland, OR. In: *International River Quality*, (Eds: D. Dunnette and A. Laenen), Lewis Publishers (1996).

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W. Fish. The afterlife of solid wastes: Managing a post-closure landfill. *Environ. Sci. Technol.* 27(10):10-13 (1993).

W. Fish. Sub-surface redox chemistry: A comparison of equilibrium and reaction-based approaches. In: *Metals in Groundwater* (H.E. Allen, E.M. Perdue, D.S. Brown, eds.) Lewis Publishers (1993).

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- Hutchins, D.A., J.G. Rueter, and W. Fish. Siderophore production and nitrogen fixation are mutually exclusive strategies in *Anabaena* 7120. *Limnol. Oceanogr.*, 36:1-12 (1991).
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- Johnson, R.L., C.D. Palmer, and W. Fish. Subsurface chemical processes. In: Transport and Fate of Contaminants in the Subsurface. U.S. Environmental Protection Agency Technology Transfer Seminar Publication, EPA/625/4-89/019, U.S. EPA, Washington, D.C. (1989).
- Palmer, C.D., J.F. Keely, and W. Fish. Potential for solute retardation on monitoring well sand packs and its effect on purging requirements for ground water sampling. *Ground Water Mon. Rev.*, 7:40-47 (1987).
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- Fish, W. and F.M.M. Morel. Propagation of error in fulvic acid titrations. *Org. Geochem.*, 8:119-120, (1985).
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- Fish, W. and F.M.M. Morel. Characterization of organic copper-complexing agents released by *Daphnia magna*. *Can. J. Fish. Aquat. Sci.*, 40:1270-1277, (1983).
- Fish, W. and F.M.M. Morel. Effects of natural and synthetic chelators on toxic metal transport in a porous medium. Proceedings: N.E. Conference Waste Storage and Disposal & Groundwater Resources, June 28 - July 1, 1982, Richard P. Novitski and Gilbert Levine (eds.), USGS (1982).

## **CURRICULUM VITA**

### **GWYNN ROCHELLE JOHNSON**

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### **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.

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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.

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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 ft<sup>2</sup> 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% HNO<sub>3</sub>), 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.