

State of Washington Water Research Center Annual Technical Report FY 2002

Introduction

The mission of the State of Washington Water Research Center (SWWRC) is to:

- i) facilitate, coordinate, conduct, and administer water-related research important to the State of Washington and the region,
- ii) educate and train engineers, scientists, and other professionals through participation in research and outreach projects,
- iii) disseminate information on water-related issues through technical publications, newsletters, reports, sponsorship of seminars, workshops, and conferences as well as other outreach and educational activities.

The SWWRC has developed a multi-pronged approach to accomplish these goals. To promote research and outreach, the SWWRC has been organized into five program areas: Watershed Management, Water Resources and Biotic Systems, Groundwater Systems, Irrigated Systems, and Outreach and Education. These programs have helped prepare several multidisciplinary research proposals and provide better links between faculty and the SWWRC. The Center is also involved in international research and education activities.

The SWWRC is continuing its intensive efforts to reach out to agencies, organizations, and faculty throughout the State. Activities include presentations to watershed groups, participation in regional water quality meetings, and personal contacts. A new dynamic web page has been created to share information with stakeholders.

It is within this overall context that the USGS-funded project activities reported in this document must be inserted. These include the internally funded projects as well as the national proposals awarded to the Center. These projects provide a solid core to the diverse efforts of the SWWRC. Water quantity and quality issues continue to be a major concern in the State of Washington due to the endangered species act, population growth, industrial requirements, and agricultural activities. Emerging issues such as arsenic removal at small systems, water reuse, emergency response and vulnerability, and storm water runoff regulations are also beginning to raise concerns. All of these issues will be important drivers of the activities of the SWWRC in the foreseeable future.

Research Program

In accordance with its mission, the SWWRC facilitates, coordinates, conducts, and administers water-related research important to the State of Washington and the region. The Center supports competitively awarded internal grants involving water projects evaluated by the Joint Scientific Committee. The Center also actively seeks multidisciplinary research on the local and national levels. Meetings between stakeholder groups, potential funding agencies, and research faculty are arranged as

opportunities arise. Faculty are apprized of any opportunities. The Center also submits proposals on its own behalf.

Collaborative Research:Hydraulic and Geomorphic Controls on the Evolution of Cluster Bedforms in Gravel-Bed Streams

Basic Information

Title:	Collaborative Research:Hydraulic and Geomorphic Controls on the Evolution of Cluster Bedforms in Gravel-Bed Streams
Project Number:	2002WA12G
Start Date:	8/1/2002
End Date:	7/31/2004
Funding Source:	104G
Congressional District:	Washington Fifth
Research Category:	Engineering
Focus Category:	Sediments, Hydrology, Geomorphological Processes
Descriptors:	Restoration, Bedforms Migration, Stage-Discharge Relations
Principal Investigators:	Thanos N Papanicolaou, Lisa Louise Ely

Publication

Problem and Research Objectives

The overall objectives of this collaborative study are to investigate the specific hydraulic conditions that control the evolution of cluster bedforms in both laboratory and field settings and to investigate the corresponding effects of the clusters on near-bed turbulence and channel stability. A cluster microform is a grouping of sediment particles, usually around a larger anchor sediment particle, against which a stoss of imbricate clasts develops and behind which a wake tail grows. Cluster bedforms may play a significant role in delaying gravel transport through a stream and have been shown to provide important habitat for fish and stream invertebrates. Understanding the hydraulic conditions under which these bedforms develop and disintegrate is critical for managing, restoring and maintaining aquatic stream habitats in disturbed, natural and flow-regulated streams.

Lab Objectives

The overarching goal of the lab component is to advance current knowledge on cluster formation and evolution by tackling some of the aspects associated with cluster micro-topography. The specific objectives of the laboratory study are:

1. To identify the bed shear stress range in which clusters form from a non-clustered bed and subsequently the stress values at which clusters disintegrate;
2. To quantitatively describe the spacing characteristics and orientation of clusters with respect to flow characteristics;
3. To quantify the effects clusters have on the mean bedload rate in unsteady flow conditions;
4. To assess the effects of clusters on the pulsating nature of bedload.

Field Objectives

A field component has been added to the ongoing laboratory studies to compare the results from the laboratory flume with processes in natural streams. The main objectives for the field component of the project are:

1. To characterize the cluster bedform morphologies in natural streams and compare with the morphologies produced in the laboratory for uniform and non-uniform grain sizes.
2. To identify the field geomorphic settings conducive to creating and maintaining cluster bedforms similar to those formed in the laboratory.
3. To characterize the hydraulic parameters, such as velocity, shear stress and near-bed turbulence, necessary to form, maintain and disaggregate sediment clusters.
4. To determine the fate of individual sediment particles within and outside clusters during bed-mobilizing events.

Methodology

Lab Methodology

This research addresses two aspects associated with cluster development and evolution, namely, cluster microform geometric characteristics and the effects of clusters on bed stability and the statistical properties of the instantaneous bedload rate. These aspects were investigated in a laboratory flume with the use of uniform-size spherical glass particles to eliminate effects due to particle protrusion, size, shape, specific gravity and sediment gradation on cluster development.

Knowledge in cluster microtopography was further advanced by investigating two main experimental scenarios, referred to as test series A and B. All runs in test series A were initiated from a non-clustered bed since the objective of this scenario was to determine the flow conditions under which clusters form and record their spacing and orientation once a developed cluster bed is formed. Test series B, on the other hand, simulate conditions where clusters preexisted in the surface layer due to their establishment from a precursor event. A subset of a test series B, referred to as test series B-NC, was performed without the presence of clusters, to discriminate the effects of flow on bedload characteristics.

Several established experimental techniques (such as video camera, photoshop software) were employed to measure the instantaneous bedload rate, map the geometric characteristics of clusters and provide localized information about the interaction of clusters and the transported material. In addition, statistical tools (such as MINITAB) were used to develop autoregressive (ARIMA) models for predicting the instantaneous bedload rate for both test series A and B. The ARIMA models provide unique information about the mean statistical properties of bedload and allow a quantitative comparison between test series B and B-NC. The ARIMA analysis was complemented with a change-point analysis to identify the effects of clusters on bedload transport.

Field Methodology

The procedures to set up the first cluster monitoring site in Year 1 involved 1) identifying and marking the clusters, 2) describing and photographing each cluster, 3) surveying cluster locations, 4) surveying channel cross sections, 5) installing stage monitoring instrument, 6) measuring flow velocity at known stage. After each flow event that is large enough to entrain and transport gravel on the bed (i.e. spring snow melt), the change in the channel bed will be re-photographed and documented. Anticipated results include (1) comparison of the form and spacing of sediment clusters in the field and lab, (2) calculation of the bed shear stress values necessary to form, maintain and break apart the cluster bedforms in the field and lab, and (3) further understanding of the role of geomorphic channel form in the formation of sediment clusters.

A total of 77 clusters were identified and marked at Site 1 on the gravel bar and adjacent shallow stream bed in an area measuring approximately 20 meters x 5 meters. All of the clusters involved 3 or more particles. At some point all clasts are interacting to some degree with the adjacent sediment particles, only the clusters with obvious anchor particle(s) protruding above the average channel bed were marked. Each cluster number was written on the anchor clast in a subtle location on the downstream side with permanent marker.

Two photographs were taken of each cluster using digital camera. A ruler scale and number of the cluster written on masking tape was included in each photo (not always possible for submerged clusters). All photos were taken with the bottom of the photo toward the bank and the top oriented toward the stream.

-Photo 1: Widest angle setting on camera from a consistent height (same scale for all clusters).

-Photo 2: Zoom in on cluster to fill field of view (scale varied for different clusters).

For each cluster, the following characteristics were recorded to supplement the photographs:

- a. Cluster number
- b. Length of cluster
- c. Width of cluster
- d. Shape of cluster: triangle (with either upstream or downstream tail), diamond, ring, line, or rectangle.
- e. Orientation of cluster relative to flow direction
- f. Measurement of long, intermediate and short axis of anchor clast(s)
- g. Orientation of anchor clast relative to flow direction
- h. Number of particles in cluster
- i. Approximate d50 of non-anchor clasts in cluster
- j. Additional comments

The center point of each cluster was surveyed using a total-station laser theodolite in preparation for creating a detailed map of cluster location and spacing. The survey instrument station location was chosen at a point that had a clear view of the entire cluster site and channel cross sections and is not likely to be inundated or eroded away during high flows. The surveying station was monumented with a permanent stake in the ground, and several additional survey benchmarks were surveyed and monumented. The exact survey grid can be reoccupied and cluster locations resurveyed to monitor any changes in cluster locations.

Three channel cross-sections were surveyed at the upstream, downstream and middle of the gravel bar under study. The end points of each cross-section were monumented with stakes. The surveyed cross-sections will be used in flow modeling to determine discharge at the site.

A stage monitoring instrument and data recorder made by Global Water Instruments were installed to record the peak stage. The stage monitor was installed on the right bank of cross section 2, across the river from Cluster Site 1. This bank is vertical, which allows the monitor casing to be anchored to the bank. The pressure transducer was positioned below the water level, and the cable leading to the data logger was fed through electrical conduit pipe with 2 elbows that curved up and over the top of the bank. The pipe was anchored to fence posts that were pounded into the side and top of the bank. Velocity and stage at the time of the installation were recorded. Because the stage recorder is located right on a surveyed channel cross section, the stage can be directly related to water depth over the cluster site. The instrument will automatically record the stage every 30 minutes for up to several months. This instrument will be retrieved after the peak flow has occurred in mid- to late June, to avoid vandalism during the high-use summer season. The instrument will be reinstalled in late fall and left in place over the winter.

Principal Findings and Significance

Lab Studies

A major contribution of the WSU research team is a detailed documentation of the evolutionary cycle of clusters, i.e. formation through disintegration, during the rising limb of a hydrograph and identification of the bed shear stress condition that partial or complete break-up of individual clusters commences. This condition is defined as the threshold or critical condition for partial or complete cluster disintegration.

Figure 1 provides a unique depiction of the instantaneous bedload rate q_b time series. The bedload rate time series, expressed in kg/m/s, is shown with the solid pulsating line enriched with square symbols. The thick solid line, showing in Figure 1 in the form of a stepwise function, indicates the feed rate of sediment at different stress increments.

Figure 1 also offers a descriptive overview of the cumulative effects that clusters and flow may have on the pulsating nature of bedload. It is observed that at stresses less than $2.25 \tau_{cr}^*$ the disbandment of a whole cluster is rare, rather particles were removed from individual cluster as they went through their evolutionary cycle with respect to shape and size. At stresses equal to or greater than $2.25 \tau_{cr}^*$, partial or complete disintegration of individual clusters occurs causing significant spikes in bedload transport. These spikes are identified in Figure 1 as the black circles capping the significant peaks in the time series and the stress condition of $2.25 \tau_{cr}^*$ is considered here as the critical stress condition for cluster stability. For stress conditions ranging between $2.5 \tau_{cr}^*$ and $3.0 \tau_{cr}^*$, complete cluster breakup occurs throughout each of the stress increments resulting in elimination of organized cluster topography. The elimination of organized topography commences at $2.5 \tau_{cr}^*$, however, some individual clusters persist until $3.0 \tau_{cr}^*$.

Based on the above observations one can suggest that the instantaneous bedload transport of glass spheres through a clustered area can be classified into three phases, namely phase I, phase II, and phase III (Figure 1). Phase I corresponds to a stress range varying between $1.5 \tau_{cr}^*$ and $1.75 \tau_{cr}^*$ (8.5-70.5min); the peaks in bedload rate within phase I are smaller comparatively to the peaks appearing in phases II and III. Phase II corresponds to a stress increment of $2.0 \tau_{cr}^*$ to $2.25 \tau_{cr}^*$ (71-125.5min) and constitutes the transition or buffer region between phase I and III; in phase II, the commencement of complete or partial disintegration of individual clusters occurs. Finally, phase III occurs for a bed shear stress greater or equal to $2.5 \tau_{cr}^*$ (126-162.5min). In phase III, complete cluster disintegration transpires and causes significant fluctuations in the bedload transport rate.

Field Studies

Site Selection

One site was selected for field study, on the American River. Field reconnaissance was conducted on several tributaries in the Yakima River drainage basin on the East slopes of the Cascade Mountains in Fall, 2002 and early Spring, 2003. The goal of the reconnaissance was to identify gravel-bed streams draining the Cascade Mountains that best matched the criteria for site selection, including evidence of gravel clusters, lithology, grain size, gradient, discharge, accessibility for monitoring. Using maps and aerial photos, four rivers in the Yakima watershed were chosen for detailed field reconnaissance: the American River, Little Naches River, Taneum Creek and Teanaway River. Cluster bedforms were found on the American River and Teanaway River. All of these rivers are unregulated and therefore have a greater chance of bed-mobilizing high-flow events. The American River was deemed the most promising location to set up the first field monitoring site for this project based on the following attributes:

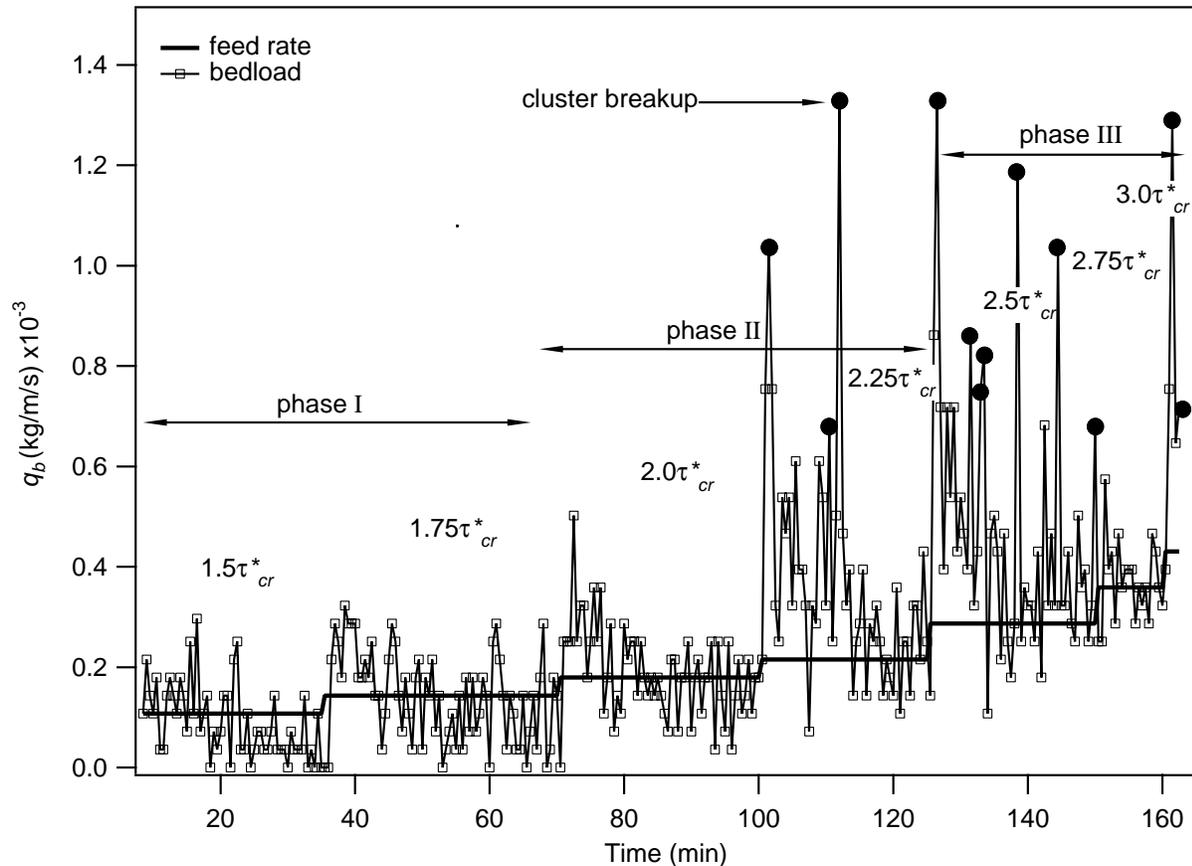


Figure 1. Bedload time series for cluster response to inflow hydrograph (test series B). In phase I ($1.25\tau_{cr}^*$ to $1.75\tau_{cr}^*$), clusters act as a sink to incoming particles so that the mean transport rate is lower than the mean feed rate. In phase II ($2.0\tau_{cr}^*$ to $2.25\tau_{cr}^*$), the buffer region, clusters do not affect the mean transport rate so that the bedload rate is equal to the feed rate. Phase III ($\geq 2.5\tau_{cr}^*$), depicts the region of bed shear stress where clusters act as sediment sources and not only add to the pulsating nature of bedload but also increase the mean transport rate so that it is greater than the feed rate.

- A well-developed suite of gravel clusters
- Watershed is relatively undisturbed by human activities such as logging, roads or mining.
- It is one of only 3 real-time USGS gaging stations (American River near Nile, Washington) with online access in the upper Yakima basin. Although the gaging station is several miles downstream from the cluster study site, it allows for remote monitoring of the hydrograph for timing and relative size of peak discharges.
- The study site near Pleasant Valley campground is also included in a recent study of geomorphic and hyporheic characteristics of salmon spawning habitat, conducted by Brooke Asbury, a graduate student at Central Washington University. The proximity of the two studies will broaden the potential applications of the current study by allowing a comparison or even an extension of the study on salmon habitat.
- Most reaches of the river are readily accessible in late spring through fall and are on U.S. Forest Service land.

Site Description

Cluster Site 1 on the American River is a gravel bar and adjacent channel bottom on the left bank of the river immediately downstream of the Pleasant Valley Campground at 46° 56' 45" N. Lat., 121° 19' 10" W. Long. The site is ~15 km upstream of the USGS gaging station on the American River at the junction with the Bumping River (USGS Amer. R. nr Nile, WA). The river at Site 1 is ~15 meters wide, highly sinuous, with a moderate gradient. The valley floor at this site is ~1.75 km wide. About 5 km downstream, the river enters the narrow, steep canyon that characterizes the lower reach of the American River. The gravel bar is on the downstream inside bank of a bend in the channel. The bar is partly to totally submerged during annual peak flows and is exposed during lower flows. The gravel bar contains numerous gravel clusters of 3 or more clasts, which become more sparsely scattered in the main flow channel.

Summary of Field Studies

As mentioned above, 77 clusters were identified and described at American River Site 1. The cluster morphologies fell into 6 forms: triangle (with either upstream or downstream tail), diamond, ring, line, or rectangle (Table 1). Two clusters were not described.

TABLE 1. Cluster morphologies at American River Site 1.

Triangle up	Triangle dn	Diamond	Ring	Line	Rectangle	Total
22	3	7	4	31	8	75

The line shape, consisting of an anchor clast with 2 or more imbricated clasts directly upstream or downstream of it, was the most common. The triangle shape consists of an anchor clast with the long axis transverse to the flow and an accumulation of smaller clasts either upstream or downstream. The triangle shape with an upstream tail of imbricated particles was the second most common. The other shapes all occurred at a much lower abundance. The diamond shape consists of one or more anchor clasts transverse to the flow with an accumulation of smaller clasts both upstream and downstream. The ring and rectangle shapes consist of multiple clasts that form either a ring or rectangle shape and collectively serve as an anchor against which smaller clasts accumulate.

The spacing of the clusters appeared to be more dense on the gravel bar than in the adjacent low-flow channel, but that relation has not yet been quantified at this site. Further field studies this summer at lower flows when a greater portion of the channel bed is exposed will seek to verify this initial observation. This pattern is supported by observations on other rivers, in which clusters are more common on gravel bars where the sediment is subject to fewer flows that are able to mobilize bed material, rather than in the thalweg channel where the sediment is better sorted (Ian Reid, written communication 2003; Hassan, & Reid, 1990).

References

Hassan, M.A. & Reid, I., 1990, The influence of microform bed roughness elements on flow and sediment transport in gravel bed rivers. *Earth Surface Processes & Landforms* 15, 739-750.

Using environmental tracers to improve prediction of nonpoint pollutant loadings from fields to streams at multiple watershed scales

Basic Information

Title:	Using environmental tracers to improve prediction of nonpoint pollutant loadings from fields to streams at multiple watershed scales
Project Number:	2002WA19G
Start Date:	8/1/2002
End Date:	7/31/2005
Funding Source:	104G
Congressional District:	Washington Fifth
Research Category:	Ground-water Flow and Transport
Focus Category:	Non Point Pollution, Nitrate Contamination, Hydrology
Descriptors:	Catchment Hydrology, Environmental Tracers
Principal Investigators:	C Kent Keller, Richelle Allen-King, Shulin Chen

Publication

1. Allen-King, R., 2003, Ground and Surface Water Contributions to Chemical Mass Discharge: Field to Basin Scales, Keynote Address, "in" Abstracts, 4th Symposium on the Hydrogeology of Washington State, April 8-10 2003, Tacoma, WA. (<http://www.ecy.wa.gov/events/hg/index.htm>)
2. Keller, C.Kent, 2003, Using environmental tracers to understand agrichemical transport pathways to Palouse surface water, Invited Presentation to WSU Water Quality Research and Extension Colloquium, April 24, 2003, Washington State University, Pullman, WA.

Problem and Research Objectives

The global N cycle has been massively perturbed in the past century by agricultural application of artificially fixed N to the terrestrial environment. Among the most serious consequences of this perturbation is N loading of terrestrial and coastal ocean waters with associated perturbations to water quality, aquatic and marine habitat and productivity, and other environmentally critical variables and processes. In the US, tens of thousands of river and shore reaches are considered impaired by the EPA, and many of these impairments are believed to be attributable to agricultural non-point sources. In this context Congress has mandated the EPA to implement the TMDL (Total Maximum Daily Load) program and it is estimated that around 40,000 TMDLs will be required nationwide. Given the magnitude of this undertaking, it is clearly important to develop sound scientific basis for TMDL determination. This in turn means understanding how agricultural practices are related to streamwater N loading, in various climate/cropping associations.

In this work we are studying how field-scale processes influence delivery of nitrogen (primarily as dissolved nitrate, NO_3) to streams. ***We have hypothesized that in our semiarid dryland farming region, stream NO_3 discharge, from field and small catchment to basin scales, is principally controlled by the response of field-scale flow and transport processes to drainage regime and strongly seasonal hydrology.*** The roles of biologic processes are rapid nitrification of fertilizer ammonia beneath bare fields in the fall, generating the NO_3 reservoir, and uptake of water and NO_3 by plants as the runoff season yields to the growing season. We are testing this hypothesis by (a) expanding our ongoing study of field-scale processes to include undrained settings, and (b) developing a spatially- and temporally-detailed ^{18}O data set which can be used, in parallel with geochemical data sets, for simultaneous isotope and geochemical hydrograph separations at multiple watershed scales. The isotope data are needed to identify water sources (“new” vs. “old”). Used in combination with pathway information from the geochemical tracers, they will help us understand how temporal evolution of soil NO_3 distributions is related to transport times to streams.

The concentration and mass discharge of an environmental tracer at a watershed gauging station are the averaged consequences of hydrologic processes across the entire watershed. The watershed-scale averaging property of stream discharge and streamwater isotope geochemistry has been used for decades to interpret variation of sources of streamflow over the course of hydrologic events. These signals, when combined with measurements internal to the watershed (such as monitoring at smaller catchment scales and inside catchments), can reveal the underlying processes and their spatial variation. Stream-gauge monitoring of nested watersheds thus generates measurements that appropriately and consistently (and naturally) provide information about spatial variability at each scale. We are taking this approach to address the following research objectives:

- a. ***Observe geochemical and isotopic composition of surface and subsurface water at the field scale.***
- b. ***Develop isotope hydrograph separation (IHS) models for a succession of catchment-to-basin watershed scales.***
- c. ***Compare IHS with geochemical hydrograph separation (GHS) models to identify processes and pathways of water and NO_3 delivery to streams.***
- d. ***Examine scaling trends of IHS and GHS models.***

Methodology

Our two field locations are located near Pullman, WA, within the Missouri Flat Creek watershed of the South Fork of the Palouse River. The Missouri Flat Creek drainage has a long record of study by USGS and WSU scientists. The fields are subject to typical farming practices and crop rotation, receiving ammonia fertilizer during fall and spring planting, and they represent typical bottom-slope, streamflow-generating locations. The undrained field exhibits intermittent winter-spring

surface runoff while the tile-drained field does not. These fields represent the principal settings we assume to control streamflow generation and NO_3 discharges.

The tile-drained location was instrumented in 2001 with suction lysimeters (operated at 0.5 bar) and zero-tension pan lysimeters. These samplers were installed horizontally in triplicate at 0.2, 0.5, and 1.0 m depths from a trench (to permit location of sampler intakes beneath undisturbed field soil). They allow us to sample subsurface-pathway events (pans) as well as resident porewater over a range of saturation conditions (suction). In addition, depth profiles of 5 thermistors and 5 TDR moisture probes were installed via the trench wall. Data from these instruments are logged continuously by the weather station (with precip gauge/sampler) located nearby. With this array, we monitor subsurface conditions above a tile drain which drains approximately 10 ha and outlets 10 m distant. At the undrained field, selected parallel instrumentation will be installed in fall 2003. Subsequently, we plan to collect multiple 1.5-m deep core samples in each of the fields, for detailed determination of ^{18}O and NO_3 depth distributions and their spatial variation, at least twice (to assess seasonal variation).

Pressure transducers and dataloggers have been deployed and rating curves developed that measure water discharge from nested 660–7000 ha watersheds.

Principal Findings and Significance

Water year 2002-2003 has been devoted to maintenance and refinement of surface-water flow logging and monitoring, and to development of sampling and analysis methods for dissolved cations, anions, and our new tracer ^{18}O . We have sampled precipitation and from three to five (depending on flow conditions) surface-water monitoring stations approximately 20 times since Fall 2002. Approximately 300 aliquots of water from these sampling events are in various stages of analysis.

Mass-spectrometric analysis for ^{18}O began in late fall 2002. Our backlog of surface-water samples from 00-01 and 01-02 has been run and the results (Figure 1) indicate definite seasonal responses, with different amplitudes at different basin scales. Analysis of 02-03 surface water and precipitation samples is ongoing.

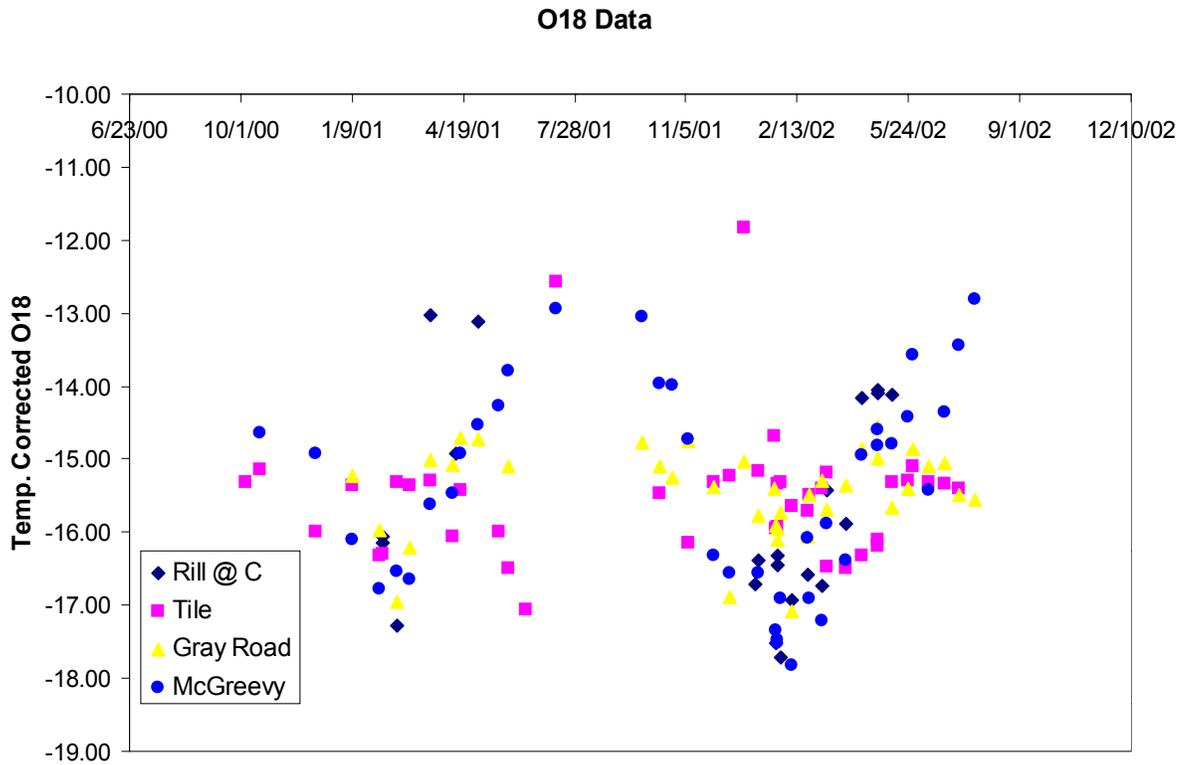


Figure 1. ^{18}O levels plotted vs. time for principal surface-water monitoring stations. List in legend is in order of increasing basin size. Ordinate values are δ (per mil). Note pronounced trough in data envelope associated with high-flow conditions in winter.

Surface and Subsurface Transport Pathways of Non-Point Agricultural Pollutants: Analysis of the Problem over Four Decades of Basin Scale

Project 1999WA0013G was not funded for FY2002.

Problem and Research Objectives

The purpose of this research is to use environmental tracers to quantify and predict the contributions of subsurface and surface runoff to observed loading of non-point pollutants to streams at multiple scales of study (field to basin) in a dryland agricultural setting near Pullman, WA. These loading contributions can ultimately be compared to predictions obtained employing a GIS-based solute transport model. The environmental tracer predictive model will use field-scale measurements to quantify source terms. Overall goals are to examine the scaling behavior of the observed loading, and to develop capability to model this behavior.

Methodology

Flow and Chemistry. The study area is the Missouri Flat Creek watershed, a 14,400 ha agricultural watershed. N-fertilizer is generally applied to fields in the fall or spring at rates up to ~125 kg/ha. Ground and surface water samples are collected at approximately two-week intervals from an ephemeral stream and a tile drain located in actively farmed and topographically constrained fields (~10 ha), and from seven stream-gauging stations located along Missouri Flat Creek. Surface water discharge is monitored continuously. Samples are routinely analyzed for two pesticides (the insecticide lindane or gamma-hexachlorocyclohexane (HCH) and the herbicide triallate, S-(2,3,3-trichloroallyl) diisopropylthiocarbamate), a nutrient (nitrate), and the tracers EC and silica. Lindane is applied as a seed coating on most spring and fall crops in the region. Triallate is used as a pre-emergent herbicide.

Surface water samples are collected using a DH-48 sampler. The samples are integrated vertically and horizontally, in accordance with USGS guidelines (Sheldon, 1994). The EC is measured using a temperature-compensated electrode. Dissolved silica is analyzed by a colorimetric method, and nitrate is determined using a continuous flow analyzer. Lindane and triallate are extracted using a solid-phase microextraction technique and analyzed using gas chromatography (Schaumloffel, 2000).

The EC and dissolved silica, which are environmental tracers, are used to separate the contributions of subsurface and surface runoff to streamflow. Two-component, ground and surface water, hydrograph separation are performed at each scale of observation. Tile drain and ephemeral stream tracer concentrations measured from field plots are used to represent time-dependent groundwater and overland flow component concentrations. Hydrograph separation is used to determine the components of stream flow with time. We employ two environmental tracers, EC and silica, along with stream discharge were used to solve the following set of mass balance equations to determine flow components ($Q_{k,t}$):

$$Q_{T,t} = Q_{OF,t} + Q_{SW,t} + Q_{GW,t} \quad (1)$$

$$Q_{T,t} C_{T,i,t} = Q_{OF,t} C_{OF,i,t} + Q_{SW,t} C_{SW,i,t} + Q_{GW,t} C_{GW,i,t} \quad (2)$$

where $Q_{T,t}$, $Q_{OF,t}$, $Q_{SW,t}$, $Q_{GW,t}$ are the flow in m³/day for total stream flow, overland flow, soil water, and groundwater, respectively at time t ; $C_{T,i,t}$, $C_{OF,i,t}$, $C_{SW,i,t}$, $C_{GW,i,t}$ are the concentrations of chemical i for observed stream flow, overland flow, soil water, and groundwater, respectively at time t . Agricultural chemical discharges are predicted via eq. (2) using the time-dependent flow

components determined through hydrograph separation along with the observed edge-of-field (ephemeral stream or tile drain) concentrations.

Spatial information. Based on the digital elevation model (DEM) of the Palouse River basin, a delineation of the sub watersheds within the basin was conducted. Three watersheds were selected to represent different scales ranging from field to small-size and large-size watersheds. The large-size watershed was selected to be the whole Palouse River Basin. The medium-size watershed was selected to be the Missouri Flat Creek watershed. A small watershed within the Missouri Flat Creek watershed represented a farm-scale watershed. The DEM was also used to calculate other important topographic functions (e.g. slope, aspect and hillshade) for the three selected watersheds. The Stream Network within the watersheds was generated using the EPA River Reach File 3 database. Land use and land cover information for the study area were obtained using the USGS 1:250,000 scale LULC maps. These data were organized and stored into ArcView GIS shapefiles.

Principal Findings and Significance

We have developed and compiled a geographic database for the Palouse River watershed in the State of Washington. The database contains soils information at three different hierarchical scales, ranging from a small farm-scale watershed (6.6 km²), a multiple-farm-scale watershed (70 km²), to a regional watershed (8,603 km²), which allows us to assess the variation of soil properties among the different watershed scales. Watershed attributes (climate, topography, sub-watershed delineation, land use, and soil types) are represented in the form of maps. Soil properties were represented as averaged depth-distributions to analyze the variation within and between the different watershed scales. Watershed attributes and soil properties of the two smaller watersheds were similar, allowing transition from one scale to the other. The largest watershed differed considerably from the smaller ones because of the increased spatial variability in pedological and geological features, due to the larger spatial extent of the watershed.

Using chemical hydrograph separation, the total stream flow within the 5000 ha watershed was quantified into three components: overland flow, soil-water, and groundwater flowpaths. This was accomplished using distinct time-dependent edge of field tracer concentrations to represent flowpath chemistry. From this separation, continuous pesticide mass discharge in surface water was estimated at three watershed scales. Mass discharge predictions incorporated available cropping information and observed spatial and temporal trends in flowpath chemistries. Seasonal trends and magnitudes of daily pesticide discharge were well represented by the predictive model. Continuous pesticide mass discharge overpredicted observed lindane and triallate mass discharges by a factor ranging from approximately 1.4 to 2.5 and 2.0 to 3.8, respectively, for the basin scales modeled (~150-5000 ha). Given the simplifying assumptions involved in these predictions, and the orders of magnitude variability in both stream flow and pesticide concentration, the predictions are considered to be quite reasonable and the method warrants further refinement. Removal processes (including volatilization, sorption to stream sediments, or biodegradation), non-distinct flowpath chemistry used in the hydrograph separation, and/or field-to-field chemical discharge or application variability may account for the model overpredictions.

Overland flow is the most important flowpath contributing to annual lindane and triallate mass discharge in the watershed based on the hydrograph separation. In the tile drained field, the lindane mass discharge per area is significantly reduced in comparison to a field drained by overland flow. Similar predictive modeling suggests that annual nitrate discharge is also dominated by the overland flow component, although the soil water pathway is much more significant for this nutrient than for

the pesticides studied. Importantly, the nitrate discharge via soil water may be an important contributor to the stream ecosystem in spring. Comparisons in mass discharge between field- and basin-scales imply that important removal processes (plant uptake and/or denitrification) occur in the near-field drainages features (e.g. drainage ditches and tributaries to Missouri Flat Creek) during the spring season.

This work demonstrates the potential for the application of time-dependent geochemical hydrograph separation modeling to predict seasonal and annual chemical mass discharges within the semi-arid Palouse watershed. Because the chemicals studied behave similarly to the selected tracers (e.g. behave essentially conservatively) during the winter, high flow and high chemical mass discharge portion of the year, the predictive modeling can be used to inexpensively provide order of magnitude estimates of annual discharge. Comparisons between observed and modeled chemical mass discharges at varying hierarchical scales of study allow us to identify the in-stream locations (environments where) where important removal processes occur. This study provides specific information pertinent to reducing agricultural chemical mass discharges to streams in the Palouse region as well as a tool to provide information to help reduce such discharges in other agricultural systems. We expect that this approach will be a useful tool in agricultural watersheds in different hydrologic settings and may be particularly helpful when combined with other information or modeling approaches.

A Watershed Scale Study on No-till Farming Systems for Reducing Sediment Delivery

Project 1999WA0014G was not funded for FY2002.

Problem and Research Objectives

This project addresses priority areas of water research in the Pacific Northwest. The increased listing of salmon species as threatened or endangered by the National Marine Fisheries Service, under provisions of the Endangered Species Act, has profound impacts upon agricultural practices and agriculture sustainability. The Northwest Wheat and Range Region (NWRR) located in Eastern Washington, Northern Idaho and Northeastern Oregon contains some of the most important salmon habitat, but also one of the highest soil erosion levels in the United States. Ground freezing and thawing cycles reduce soil particle strength making them easy to be detached and transported by runoff. In addition, traditional practice farming systems tend to leave the soil unprotected to rain energy, thus making the soil susceptible to erosion. Protecting fish habitat by controlling soil loss and associated sediment and chemical loading in the streams is a major challenge to the farmers in this region. No-till farming has been recommended to farmers as a conservation practice to reduce soil erosion. The effectiveness of this practice, however, has not been evaluated at a watershed scale. This project fits the USGS's interest in "determination of the effectiveness of best management practices (BMPs) at watershed scales of tens to hundreds of square miles".

Another important soil erosion-related issue is sediment delivery. It is critical to determine how much of the eroded soil will actually end up in the stream in order to assess the environmental impact of agricultural practices in the watershed. For the NWRR, which features steep rolling hills and freezing and thawing winter conditions, sediment delivery ratios have not been well studied. As a result, there is a lack of basic modeling tools for the purpose of planning, management, and policy development for these agricultural watersheds.

The objectives of this research are to:

1. Compare soil loss from no-till and traditional farming fields
2. Evaluate models for sediment delivery process under no-till and traditional farming conditions
3. Develop a model for predicting sediment delivery to the entire watershed

Methodology

The methodology used to achieve the above objectives included field data collection, field experiments, and mathematical modeling.

Runoff and infiltration study

The purpose of the runoff study is to investigate the difference between no-till and conventional tillage systems in terms of runoff produced from a comparable rainfall event. Less infiltration results in more runoff and higher erosion potential. One-square meter runoff plots with borders and runoff collectors were installed in the fields of different precipitation areas. These plots were installed for data collection in the 1999-2000, 2000-2001, 2001-2002, and 2002-2003 winter seasons. Initially, the watershed was divided into three different areas according to precipitation level: high, intermediate and lower precipitation rate, respectively. The results from the earlier seasons of the project indicated that the most significant activities occurred mainly in the high precipitation zone, although runoff plots were established in each of the areas. However, both the

intermediate and lower precipitation areas had such scarce activity in terms of runoff, that, in the 2002-2003 season, the runoff plots were concentrated in the high precipitation zone. This zone was divided in four sections according to tillage system and geographic orientation: no-till with north-facing orientation; no-till with south-facing orientation; conventional tillage with north-facing orientation; and conventional tillage with south-facing orientation. Four runoff plots were installed in each of the areas, totaling 16 runoff plots in the watershed. These areas were located in the Columbia Center/Mountain Road area of Garfield County. In addition to the runoff plots, a frost tube was placed in each of the four areas of the high precipitation zone. Also, soil moisture and soil temperature of each area were recorded every 15 minutes using soil moisture probes and thermocouples, installed at 0, 10, 20 and 30 cm of depth in the soil profile. An automatic weather station was also installed in the high precipitation zone with additional manually read precipitation gauges available across the watershed and operated by the conservation district.

Another measurement made on soil infiltration capacity of different tillage systems is permeability. This measurement was performed during the report period on a monthly base in the field using a Guelph permeameter.

Plot service consisted of monitoring the volume of water in the collectors attached to the plots, as well as checking and correcting the plot borders for frost heaving, overflow, or underflow conditions. In addition, soil moisture and thermocouple data were downloaded and frost tubes were checked periodically.

Sediment delivery study

Monitoring systems were implemented in the Pataha Watershed to measure the sediment delivery from sub-watersheds. Two sub-watersheds were selected, one with primarily no-till practice and the other with mostly a conventional tillage system. Instrumentation installed consisted of water level recorders, automated water samplers, a recording precipitation gauge, and manually read precipitation gauges. Similar settings were established in another watershed located close to the university. In this watershed, the main activity has been focused on study of rill formation with periodic observations being made to record any rill development.

Hydrological and sediment delivery modeling

An integrated watershed hydrological model framework was developed that includes an overland flow model and a channel routing model. A sediment transport model is currently being developed for a sub-watershed located near the town of Pomeroy for predicting sediment delivery to the main channel. The model will be verified with data from sub-watersheds that were instrumented to collect the following data:

- Flow sequence in response to a storm, by flumes and flow meters.
- Rainfall intensity sequence, by a recording rain gage.
- Infiltration sequence, by taking the difference between rainfall and flow in the runoff plots.
- Sediment production sequence (transported by main channel), by automated samplers.

A process-based hydrologic modeling framework using Saint-Venant equations has been developed. Saint-Venant equations include a continuity equation and a momentum equation. For the study

region, with low precipitation intensities, the momentum equation is replaced by the Chezy equation.

The continuity equation is represented as

$$\frac{\partial h}{\partial t} + \frac{\partial q}{\partial x} = r - f$$

where the first term is the variation of the flow water depth 'h' with respect to the variation of time 't'; the second term represents the variation of the flow rate 'q', with respect to the change in distance 'x'; and the term on the right-hand side corresponds to the rainfall excess, represented as the difference between rainfall intensity 'r' and infiltration rate 'f'.

The Chezy equation is represented as:

$$h = \left(\frac{q}{\alpha} \right)^{\frac{1}{\beta}}$$

in which $\alpha = Cs^{\frac{1}{2}}$; $\beta = \frac{3}{2}$; s = slope of channel, and C = roughness coefficient.

Complete development of the equation is presented elsewhere (Wang et al, 2002).

Other activities for the report period included the development of a channel routing model and the model simulation using the Revised Universal Soil Loss Equation (RUSLE). The channel routing equations are derived from the complete Saint-Venant equations. The Mixing-cell method was used to make the equation discrete in space and to reduce it to a first-order nonlinear ordinary differential equation. The equation was then integrated to obtain a semi-analytical solution.

In a separate simulation study, ArcView GIS and RUSLE were used to estimate soil erosion and its response to no-till practice in the Pataha Creek Watershed. With the aid of GIS and appropriate formula specific designs for the Northwest Pacific Region, the L and S factors can be easily calculated from DEM and the R_{eq} factor from precipitation maps. K factor was ascertained directly from the national SSURGO database, and C factor was calculated from RUSLE using crop rotation and land use maps. Soil erosion from each cell was obtained with these factors in the GIS environment. The Sediment Delivery Distributed (SEDD) Model integrated with GIS was employed to determine the transport of eroded soil to river channel at the watershed scale. Channel erosion was not included in this study. The impacts of no-till practices on soil loss and sediment yield to river channel at the Pataha Creek Watershed were then studied by running the RUSLE under a scenario consisting of all the agricultural land adopted no-till practices.

Principal Findings and Significance

The weather conditions in the report year were not favorable for gathering field data in terms of runoff and soil loss. The winter was mild, with less than normal precipitations. In addition, most of

the freezing and thawing cycles showed just diurnal variation with a shallow and short-lasting frozen depth. Moreover, precipitation events were of low intensities and occurred when the soil was not frozen. Consequently, both the snowmelt and rainfall events were not capable of producing runoff in any of the plots installed in the field. For this reason, we can assume a null erosion event in the studied areas of Pataha watershed in the 2002-2003 season. The results can certainly be considered an issue for modeling purposes, but also demonstrates that the process of soil freezing and thawing has a critical effect on soil erosion. Similar features were found in the small watershed close to Pullman where most of the precipitation events were of low intensity and occurred also when the soil was not under a freeze-thaw process. Although there were some precipitation events over frozen soil, the low intensity was not enough to exceed the infiltration capacity of the soil, thus runoff was not produced. However, some events caused exfiltration processes in localized downslope areas of the watershed, and the exfiltration generated some minor rill erosion. Exfiltration started at the end of January 2003 after the soil had infiltrated a little more than 21 mm of rain in a three-day event. At that time, the soil profile had an average volumetric soil moisture of about $0.35 \text{ m}^3/\text{m}^3$ and more than $0.4 \text{ m}^3/\text{m}^3$ at the surface, with the soil surface temperature having risen to more than $3 \text{ }^\circ\text{C}$. In the Pataha watershed, the soil moisture did not reach such high levels during the season.

The conventional tillage areas of the Pataha watershed had higher frequency of soil temperature under freezing point than the Airport watershed, with the low temperature being observed deeper in the profile. On the other hand, the conservation tillage field of the Pataha Watershed showed less and more shallow freezing events, which clearly demonstrates the protective effects of tillage residues.

The results of the RUSLE simulation for the watershed showed that the average cell soil loss is about $11.09 \text{ t/ha}\cdot\text{yr}$ in the Pataha Creek Watershed with the current land use pattern. The Sediment Delivery Distributed (SEDD) Model simulation result showed that the average cell sediment yield to the river channel was $4.71 \text{ t/ha}\cdot\text{yr}$, or about 42.4% of the total soil loss. If all the agricultural lands adopted no-till practices, the average cell soil loss would decrease from $11.09 \text{ t/ha}\cdot\text{yr}$ to $3.10 \text{ t/ha}\cdot\text{yr}$ for the whole watershed and from $17.67 \text{ t/ha}\cdot\text{yr}$ to $3.89 \text{ t/ha}\cdot\text{yr}$ for croplands under no-till scenario. The average cell sediment yield to river channel decreased from $4.71 \text{ t/ha}\cdot\text{yr}$ to $1.49 \text{ t/ha}\cdot\text{yr}$ for the entire watershed and from $7.11 \text{ t/ha}\cdot\text{yr}$ to $1.55 \text{ t/ha}\cdot\text{yr}$ for cropland under no-till scenario. The contribution of cropland would decrease from 92.4% to 72.8% for soil loss and from 87.4% to 60.1% for sediment yield to the river channel if all the cropland in the Pataha Creek Watershed adopted no-till practice. These model results were consistent with other studies in the region.

The other major accomplishments of the research team in the report period were the development of the models for describing surface runoff on a hill slope and for channel routing. The surface runoff model paper was published and the channel routing paper was submitted. In this research, a much simpler procedure will be used to solve the first-order nonlinear ordinary differential equation based on a four-point finite difference method. This method makes it possible to obtain an implicit nonlinear algebraic equation from the first-order nonlinear ordinary differential equation for calculating outflow discharge at any time and location.

Facilitated Transport of Pesticides by Organic Colloids

Basic Information

Title:	Facilitated Transport of Pesticides by Organic Colloids
Project Number:	2002WA12B
Start Date:	3/1/2002
End Date:	2/28/2003
Funding Source:	104B
Congressional District:	Washington Fifth
Research Category:	Water Quality
Focus Category:	Non Point Pollution, Solute Transport, Groundwater
Descriptors:	Groundwater Quality, Solute Transport, Colloids, Pesticides
Principal Investigators:	Markus Flury, Richelle Allen-King, Claudio Osvaldo Stockle

Publication

1. Flury, Markus, Claudio O. Stockle, and Richelle Allen-King, 2003, Facilitated Transport of Pesticides by Organic Colloids, State of Washington Water Research Center, Washington State University, Pullman, Washington, State of Washington Water Research Center Report WRR-13, 25 pp.

Problem and Research Objectives

The presence of pesticide in ground water is of great concern for groundwater quality. National monitoring programs have found pesticides in shallow and confined aquifers. For instance, the National Water Quality Assessment (NAQWA) reported that 48.4% of the 2,485 wells sampled in the United States contained evidence of pesticides. Atrazine is the most common pesticide reported in groundwater in the United States and Europe. This pesticide is widely used in both agricultural and industrial land for the control of weeds.

There are several studies that link the presence of colloids with the enhancement of pesticide mobility, under both laboratory and field conditions. In addition, there is direct evidence that the presence of colloids enhances the movement of atrazine. But due to the large amount of different colloids, the current information allows only general conclusions that cannot be used in the assessment of the overall movement of pesticides.

One kind of colloid that is particularly important is natural and artificial organic matter that possesses great affinity with pesticides. As the use of wastewater irrigation increases and addition of organic amendments to agricultural soil becomes more and more popular, it becomes necessary to establish the conditions under which the interaction of organic colloids and pesticides pose a threat for the groundwater.

The objectives of the present research are to:

- Elucidate the mechanism of mobilization and transport of organic colloids.
- Investigate the transport of atrazine as facilitated by various well-characterized organic colloids.
- Develop a conceptual model for colloid-facilitated transport.

Methodology

The study was done with 4 different types of porous media: silica sand, iron-coated silica sand, clay-mineral-coated silica sand, and humic-material-coated silica sand. Procedures were worked out to coat the silica sand with the different materials and to characterize the coated sands. Column transport experiments were carried out to characterize column packings and stability of the coatings on the sand. No experiments with atrazine have been carried out to date, but will be conducted in summer 2003.

Silica Sand

Silica sand (J. T. Baker) was sieved and cleaned with citrate-dithionite to remove iron and treated with H₂O₂ to remove organic matter.

Iron Oxide

Ferrihydrite was synthesized with a methodology proposed by Schwertmann and Cornell (2000)¹. Briefly, 2000 ml of warm water (75°C) was added to 20 g of Fe(NO₃)₃·9H₂O.

¹ Schwertmann, U. and Cornell, R. M. 2000. Iron oxide in the laboratory. Willey-VCH 2nd edition, 181 p.

The mixture was stirred and put back in the oven for 10 to 12 minutes and cooled down in ice (0.5 to 1⁰ C). The material was then dialyzed until the EC of the water reached a value less than 5 μ S/m.

Extensive tests were carried out to evaluate the ferrihydrite concentrations and the pH at which a homogeneous and extensive coating of the sand was obtained. The coating on the silica sand was done with a modification of the methodology developed by Scheidegger et al. (1993)². Briefly, the procedure was done in a 50 ml polyethylene tube, initial pH was 6.5; after 24 hours the pH was increased to 7.0 for 24 hours and finally to 7.5 for 24 for hours. The pH modification was done with fresh 0.001 M NaOH. Vigorous stirring ensured uniformity of the pH in the solution. The uniformity and extend of the coating was evaluated with SEM.

Humic Material

Coating of humic material over the sand surface was done following the methodology developed by Kopal et al. (1997)³ and Yang and Koopal (1999)⁴. The procedure consists in a modification of the sand surface to aminopropil silica and the coating of the humic material over the sand.

First, the humic material was purified. Ten grams of Aldrich humic acid were dissolved in NaOH at pH 11, stirred overnight and centrifuged to remove precipitated undissolved material. Then the supernatant was brought to pH 2 with 1 M HCl, stirred for 24 h and centrifuged at 12,100g in a Beckman centrifuge. The precipitate was rinsed with 0.01 M HCl several times to convert the humic acid to its proton form.

Second, the silica sand surface was modified with 3-aminopropyl-dimethyl-methoxysilane (Silar Laboratory). Sixty grams of clean sand was added to 2% (w/w) of the 3-aminopropyl-dimethyl-methoxysilane in toluene solution for 1 h, using a CaCl₂ guard tube to exclude CO₂. The modified sand was then transferred to a vacuum oven and cured at 150⁰C for 20 h.

300 ml of the purified humic acid was mixed with 60 g of aminopropyl sand and stirred for two hours at room temperature. Then the sand was separated form the humic acid solution and cleaned with deionized water until the supernatant was colorless.

Column Experiments

The experiments were carried out under water-saturated conditions. The columns were pre-wetted from the bottom with the same solution that was used in the experiment. The reason for this was to avoid air entrapment in the column. The solutions used in the column studies were prepared to mimic the ion composition in soil pore water, and had

² Scheidegger, A., Borkovec, M. and Sticher H. 1993. Coating of silica sand with goethite: preparation and analytical identification. *Geoderma*, 58:43-65.

³ Kopal, L. K., Yang, Y., Minnaard, A. J., Theunissen, P. L. M., Van Riemsdijk, V. H. 1997 Chemical immobilization of humic acid on silica. *Colloids Surf. Physicochem. Eng. Aspects*. 141:385-395.

⁴ Yang, Y and Koopal, L. Immobilization of humic acids and binding of nitrophenol to immobilized humics. *Colloids Surf. Physicochem. Eng. Aspects* .151:201-212

ionic strength of 15.4 mmol/L. The characteristic of the pore water solution of the Palouse soil was obtained from the National Soil Database (www.statlab.iastate.edu/soils/nsdaf/). Sodium nitrate was used as a conservative tracer to monitor the column properties. Nitrate was measured with a UV/VIS spectrophotometer at 220 nm (Hewlett Packard, model 8452A).

Column studies were carried out to evaluate the potential mobility of the different organic colloids fraction obtained in the previous phase of the research. The mobility of Atrazine will be studied in the presence and absence of the different organic colloids fractions. These experiments with Atrazine will be conducted in summer 2003.

Conceptual Model for Colloid-facilitated Transport

A conceptual model for colloid-facilitated pesticide transport was developed. The model was based on literature findings and hypothesized mechanisms of pesticide-organic matter-porous material interactions.

Principal Findings and Significance

Ferrihydrite Synthesis and Coating

The synthesis of ferrihydrite produced 6-L ferrihydrite as verified XRD measurement. Ferrihydrite concentration in solution after the dialysis was 192 mg/100 ml. This value was closely correlated with expectations based on stoichiometric calculations.

Extensive experiments were done to characterize the coating. At pH 7.8 a large amount of ferrihydrite was coated (143 mg Fe/g sand) but SEM analysis showed that the coating was irregular and with large particle size (Figure 1a) and at pH 5 the amount of iron coated was very low (1.99 mg Fe/g sand). Therefore a different approach was chosen to coat the sand; the pH was changed gradually over three days starting at pH 6.5 and increased in 0.5 pH units until reaching a pH 7.5 at the third day. This methodology is referred as a three-day coating (Figure 1b). With this methodology the coating was more uniform. Currently, we are determining the surface area of the coated sands using gas absorption techniques.

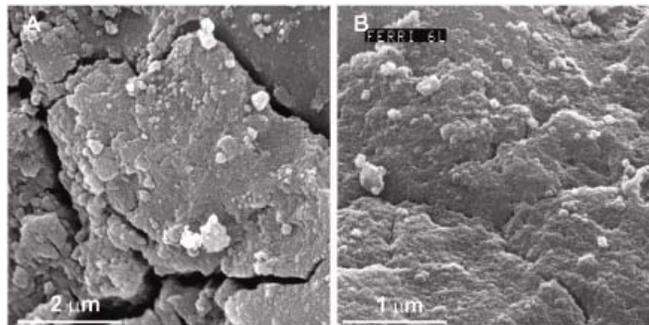


Figure 1. Ferrihydrite-coated sand surface. (a) coated at pH 7.8 (b) 3-day procedure

A second experiment, conducted with a different initial ferrihydrite concentration and a 10 mM NaNO₃ background showed that the uniformity and the amount of coating is concentration dependent (Table 1). We found that the amount of ferrihydrite coated over the sand was higher than reported by Scheidegger et al. (1993)⁵ and Lo and Chen (1997)⁶ and similar to that reported by Benjamin et al. (1996).

Table 1. Ferrihydrite coating over silica sand as a function of initial ferrihydrite concentration in suspension.

Initial Ferrihydrite concentration (mg Fe/100 ml)	Fe coated on sand (mg Fe/g sand)			
	Rep 1	Rep 2	Rep 3	Mean
153.6	19.46	19.80	26.24	21.83
76.8	11.59	10.96	10.31	10.95
38.4	5.79	5.61	6.17	5.86
19.2	4.58	4.50	4.34	4.47

Humic Material

Humic material was successfully coated over the sand, but the main limitation was the low amount coated over the sand when we tried to coated monolayer of humic acid. The reason for this result can be related to the low silanol concentration on the sand surface (8 $\mu\text{mol}/\text{m}^2$). Because the sand has very low surface area (in order of 0.01 m^2/g) the number of silanol groups on the sand surface was low and therefore the amount of humic acid that can be coated is limited. To increase the amount of coating, we chose to coat multilayers of humic acids over the sand. The amount of humic material of the multilayer was pH dependent.

Clay Material

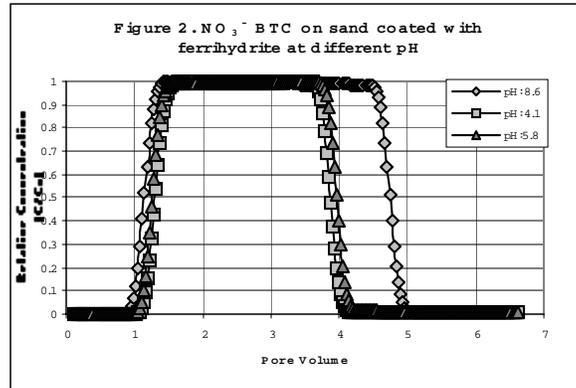
We found that clay coated sand methodology presented some stability problems; therefore, some preliminary experiments are under way to improve the stability under different pH conditions.

Column Experiments

Several column experiments with nitrate indicated that NO₃ in the ferrihydrite system did not behave as conservative tracer. At low pH the retardation of the breakthrough was more evident than at higher pH. It was surprising that even at pH 8.5 (higher than the point of zero charge of the ferrihydrite) it was still possible to observe retardation in the breakthrough of nitrate (Figure 2).

⁵ Scheidegger, A., Borkovec, M. and Sticher H. 1993. Coating of silica sand with goethite: preparation and analytical identification. *Geoderma*, 58:43-65.

⁶ Lo, S. and Chen, T. 1997. Adsorption of Se(IV) and Se(VI) on an iron coated sand from water. *Chemosphere* 35:919-930.



Conceptual Model for Colloid-facilitated Transport

The conceptual model for colloid-facilitated atrazine transport was developed based on a literature review and is schematically depicted in Figure 3.

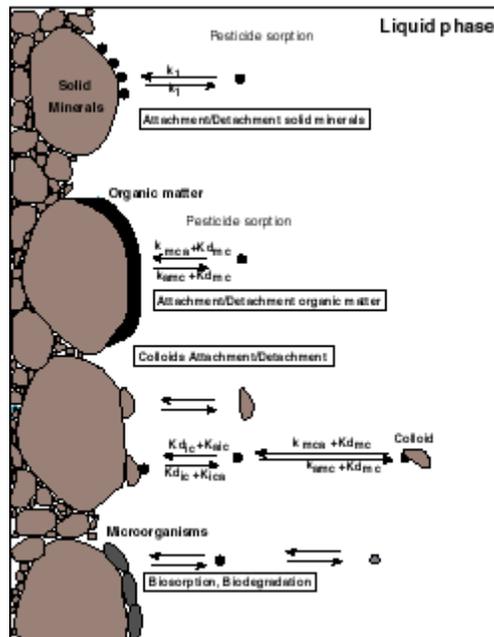


Figure 3. Conceptual model of colloid facilitated transport

Integration of Surface Irrigation Techniques to Reduce Sediment and Nutrient Loading in the Yakima River Basin

Project 2000WA4G was not funded for FY2002.

Problem and Research Objectives

Surface (rill) irrigation has been identified as one of the main sources of excess sediment in the Yakima River Basin. In turn, it is this source of water quality degradation that is thought to be one of the causes for declining salmon runs in the Yakima River. The Washington Department of Ecology has set a sediment limit for irrigation return flows of 25 NTUs (56 mg/l). Some irrigators are converting their rill irrigation systems to either sprinklers or drip irrigation at a cost of \$300 to \$1000 per acre. In some cases, this large capital investment in improved irrigation systems is being offset by cost share and low interest loan programs. However, there is not enough cost share money to match the rill acreage and many irrigators cannot afford to convert their irrigation systems even if cost share were available to everyone. Therefore, many rill irrigators are attempting to improve their existing systems in order to keep their operations as profitable as possible. Many rill irrigators are applying Polyacrylamide (PAM) and successfully decreasing sediment loads from furrows by 80 to 90 percent. Unfortunately, this cleaner water often erodes sediment from the tailwater ditch causing elevated NTU levels still too high to be returned to irrigation district canals and drainage ditches. The focus of this research is on inexpensive methods to further reduce sediment and nutrient loads from rill irrigation. Sediment loads are being evaluated for PAM (\$20/ac per year) used with Surge irrigation (\$125/ac), tailwater drains (\$75/ac), tailwater checks (\$25/ac), and grass-lined tail ditches (\$25/ac).

Methodology

The five treatments are: Treatment 1) PAM alone as the control, Treatment 2) PAM and Surge irrigation, Treatment 3) PAM and closely spaced surface drains in the tailwater ditch, Treatment 4) PAM with a grass-lined tailwater ditch, and Treatment 5) PAM and tailwater checks. The treatments were installed at two locations during the 2001 and 2002 growing season. Data was collected during 5 irrigation events in 2001 and 11 irrigation events in 2002. The treatments were randomized at each site and the treatments were large enough to allow 24 to 16 furrows to flow into the tailwater ditch depending upon the site.

Each treatment was monitored for inflow, outflow, soil moisture, sediment load, nutrient concentration. Inflows was estimated by measuring the time needed to full a bucket of a known volume. Outflow from each treatment was measured by a flow meter that received water from a collection sump and sump pump. Soil moisture was monitored with the neutron probe and access tubes. Average advance time was also recorded. Sediment samples were collected at periodic intervals during irrigation runoff events. These samples were analyzed with an NTU meter and gravimetrically with filter paper.

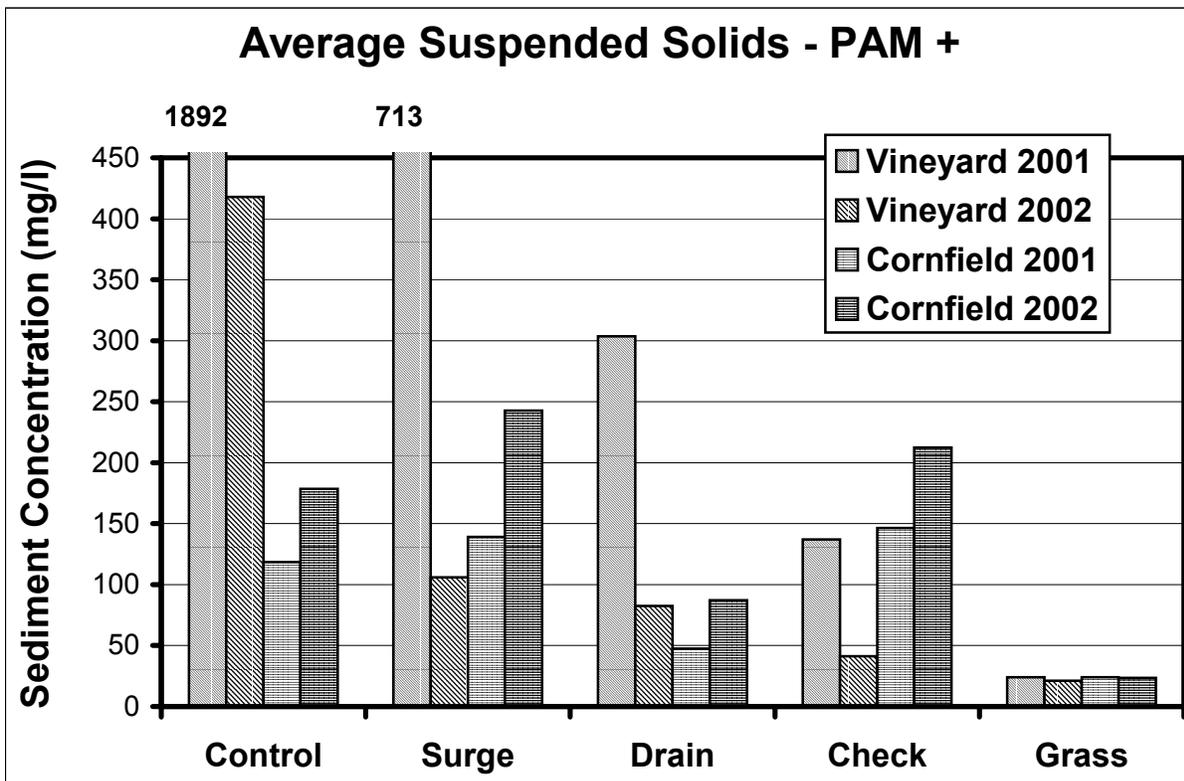
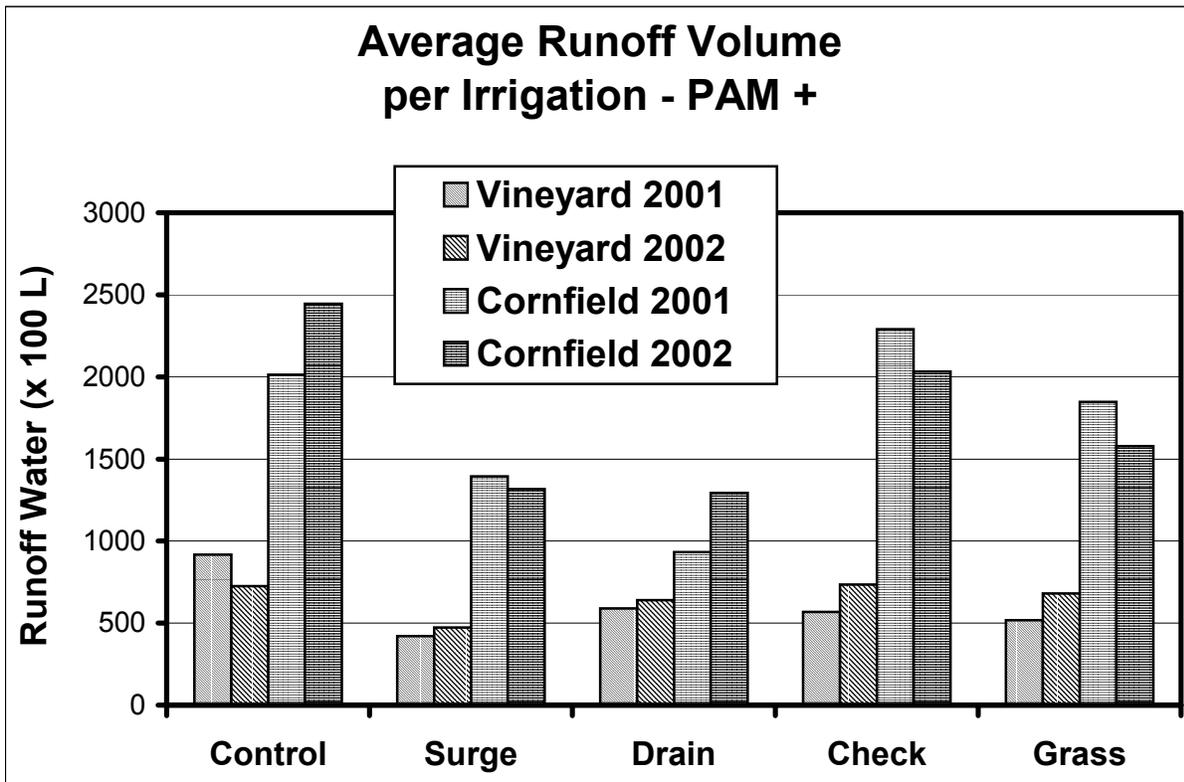
Composite samples were also collected from irrigation runoff events for nutrient analysis. Samples were taken as water fell into the tailwater sumps. Samples were kept at 4 °C until chemical analyses. All water quality analyses were performed using EPA methods (U.S. EPA, 1983). Soluble compounds were determined in samples filtered with a 0.45µm pore-size membrane and analyzed for ammonium-nitrogen, nitrate-nitrogen, and soluble reactive phosphorus. Unfiltered samples were analyzed for total Kjeldahl nitrogen, and total phosphorus.

After outflow was measured, the tailwater effluent was delivered to a sediment trapping boxes consisting of slotted apple crates lined with filter fabric to retain sediment. The number of boxes was dependant on the expected tailwater flow. The depth of sediment added to the boxes was measured at the end of the irrigation season.

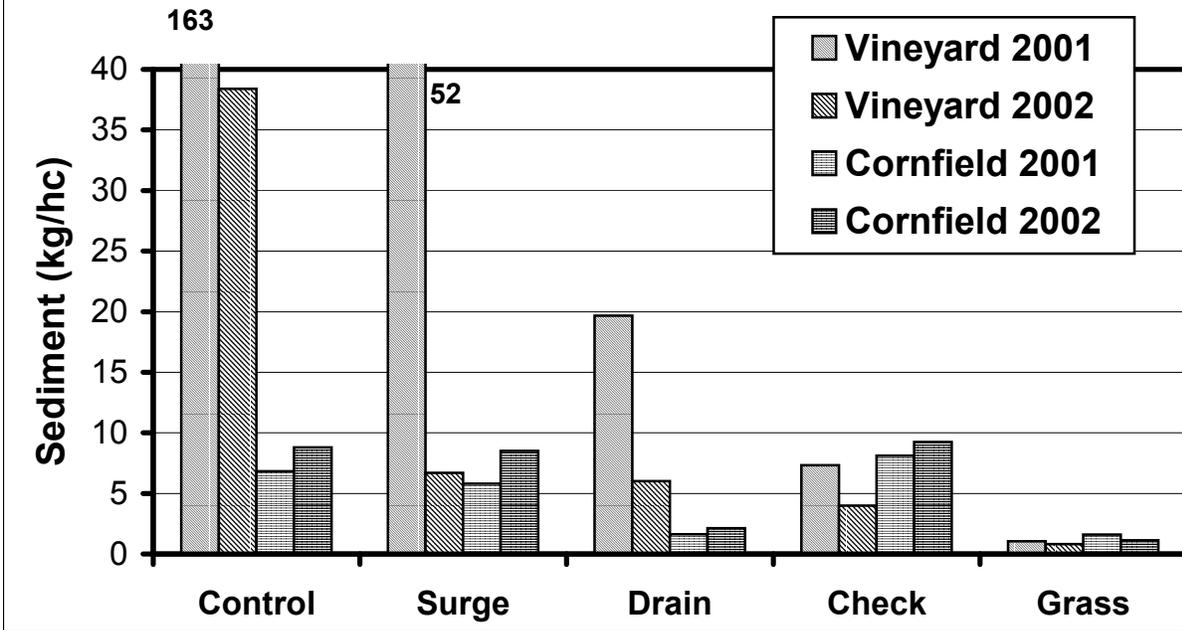
PAM was applied to all the furrows just below the point of water delivery and at the time when the furrow soil had been disturbed by field operations. Similarly, all other cultural practices such as weed control and fertilization was held constant between treatments according to standard production practices.

Principal Findings and Significance

- Formed a project management/oversight team comprised of members from a cross section of Tribal Offices and Government Agencies.
- Two “on-farm” experiments/demonstrations were installed on cooperating farms. Billy Korstad (2001 & 2002) in the Wapato Irrigation District cooperated on a 40-acre, rill irrigated, grain corn field with 1300 foot runs and a 0.2% slope on the tailwater ditch. Ken Lewis (2001) and Wycoff Farms (2002) of the Roza Irrigation District cooperated on a 30-acre, rill irrigated, Concord grape field with 800 foot runs and a 1.2% slope on the tail water ditch. Five data collection runs were completed on these fields during the 2001 growing season and 11 during the 2002 growing season. The results of these experiments are still being analyzed. However, runoff volume, average sediment concentration, and sediment lost per land area are shown in Figures 1, 2 and 3, respectively.



Average Erosion/Sediment Load per Irrigation - PAM +



Development of a Comprehensive Monitoring Protocol to Characterize the Concentration and Associated Health Risk of Salmonid Pathogens Suspended in Water

Basic Information

Title:	Development of a Comprehensive Monitoring Protocol to Characterize the Concentration and Associated Health Risk of Salmonid Pathogens Suspended in Water
Project Number:	2002WA15B
Start Date:	3/1/2002
End Date:	2/28/2003
Funding Source:	104B
Congressional District:	Washington Fifth
Research Category:	Water Quality
Focus Category:	Methods, Water Quality, Education
Descriptors:	Salomonid Pathogens, Polymerase Chain Reaction, Nucleic Acid Arrays, Inhibition, Recovery, Fish Hatcheries, Surface Water Quality
Principal Investigators:	Douglas Ruben Call, Ken Cain, Rollin H Hotchkiss, Frank Jean Loge

Publication

1. Wallace, Brandi J., 2002, Assessment of the occurrence and relative concentrations of salmonid pathogens in fish hatcheries from Washington state. MS Thesis, Department of Civil and Environmental Engineering, Washington State University, Pullman, Washington, 16 pp.
2. Call, Douglas R., Rollin H. Hotchkiss, Kenneth D. Cain, and Frank J. Loge, 2003, Development of a Comprehensive Monitoring Protocol to Characterize the Concentration and Associated Health Risks of Salmonid Pathogens Suspended in Water, State of Washington Water Research Center, Washington State University, Pullman, Washington, State of Washington Water Research Center Report WRR-14, 9 pages.

Problem and Research Objectives

Fisheries management involves activities such as propagation of hatchery fish and collection, transport, and release of indigenous and hatchery fish to bypass water control structures. Propagation and transport practices place a high density of fish in a relatively small volume of water, an environment conducive to reproduction and dissemination of etiological agents responsible for a range of fish diseases. The occurrence of salmonid pathogens in hatcheries, in transport vehicles (e.g., barges and trucks) and in waters receiving fish supplementation is rarely evaluated. The subsequent fate and transport of pathogens in downstream receiving waters is poorly understood.

While fisheries biologists have always been cognizant of the potential detrimental effects of fish pathogens on salmonid populations, there has been no comprehensive monitoring protocol suitable for detecting a broad range of fish pathogens suspended in the water column. Consequently, it has been virtually impossible to evaluate how disease agents are impacted by management practices. The development of a comprehensive monitoring protocol would aid a variety of local, state, and federal agencies and organizations, including the Army Corps of Engineers, the Bonneville Power Administration, the Washington Department of Fish and Wildlife, state and national fish hatcheries, and organizations such as the Whirling Disease Foundation. With suitable monitoring methods, these regulatory and management entities would be able to consider prevalence, incidence and disease outcome when developing and implementing management and control practices to insure the health and maintenance of indigenous fish populations in Washington State.

Molecular techniques have been employed in a broad range of environmental habitats to monitor the occurrence of specific organisms. Molecular techniques have included polymerase chain reaction (PCR), nucleic acid probes (e.g., gene probes), and fluorescent antibodies. When these techniques are used to identify pathogens within aquatic environments, generally a large quantity of water (e.g., 1,000 L) must be concentrated to a relatively small volume (e.g., 0.1 mL) because pathogens typically occur at low concentrations on an intermittent basis. The most common method to concentrate a large quantity of water is filtration. The targeted organisms are then eluted from the filter, the nucleic acid is extracted, and an appropriate molecular technique is used to identify the presence or absence of the target sequence. The above steps constitute a monitoring protocol.

Two principal factors must be accounted for in a molecular-based monitoring protocol before using the results in management and control of engineered and natural systems. First, the detection limit of the molecular-based monitoring protocol must be established. The detection limit is influenced by the percent recovery of organisms off the filter, the extent of PCR-inhibition associated with compounds co-eluted from the filter (e.g., humic acids), and the overall sensitivity of the PCR assay (e.g., number of organisms necessary to produce a positive result). Second, an explicit statement of the health risks associated with positive or negative PCR results must be developed. The health risks should then be characterized with a dose-response model, a mathematical expression that relates the probability of death (infection and illness can also be used as endpoints) to a specified level of exposure to an etiological agent. All previous studies that used molecular-based protocols to monitor environmental samples for specific organisms report results in a +/- reporting scheme. There have been no explicit statements of detection limits, sources of variation, or the health risks associated with a positive or negative result (3, 5). Recently, a comprehensive framework was developed for quantifying the detection limit of PCR-based

monitoring protocol and the health risks associated with positive and negative results (6). The framework was used to evaluate the human health risks associated with recreational contact in waters polluted with non-point source runoff.

We proposed to adapt this risk-based framework to a novel methodology designed to simultaneously detect multiple fish pathogens in the water column. This framework would permit evaluation of the health risks associated with positive and negative assay results. The specific objectives were to: (1) develop a DNA microarray to be coupled with PCR for multiplex detection of salmonid pathogens; (2) quantify the detection limit of the PCR-based monitoring protocol, and (3) perform a cursory evaluation of the occurrence and associated health risks of fish pathogens in hatcheries, transport vehicles, and surface waters within Washington State. A fourth objective involved developing and instructing a new course on the ecological aspects of fish management and control in the Pacific Northwest, but administratively imposed limitations on grant duration eliminated this objective.

Methodology

Sample Collection and Preservation. Water samples were collected from 21 fish hatcheries in Washington State during the summer of 2002. As per sampling agreement, the hatcheries are referenced herein with alphabetical letters A-U to maintain anonymity. At each location, water samples were collected from the inlet and outlet for analyses of hardness, suspended solids, total and fecal coliforms, and enterococci as per Standard Methods, 20th edition (2), methods 2340C, 2540D, 9221B, 9221E, and 9230B, respectively. In addition, 4-204 L were filtered from the hatchery influent and effluent for analysis of selected pathogens. These samples were concentrated on-site by pumping the water (stainless steel progressive cavity pump, Ryan-Herco Products Corp, Sacramento, CA) through a 0.45 µm pore size, 293 mm FALP filter (Millipore, Bedford, MA). The 1-L water samples and filters were transported on ice to Washington State University for processing. Filters were eluted and concentrated immediately upon arrival and the resulting solutions stored at -20 °C. The 1-L water samples were processed within 24 hours for the specified water quality characteristics.

Filter Elution, Nucleic Acid Extraction, and Purification. The 293 mm FALP filters was folded in half and laid flat in a sterile Pyrex glass dish containing 200 mL of elution buffer: 1.5% (w/v) beef extract in 1X PBS (137 mM NaCl, 2.7 mM KCl, 10 mM Na₂HPO₄, 2 mM KH₂PO₄, pH 7.4). The filter was eluted by scrubbing the surface with a sterile nylon bristle brush for 10 minutes. Extracts were collected in 250 mL centrifuge tubes; the brush was rinsed with elution buffer and the liquid pooled with the extracts. The tubes were centrifuged at 6,000 x g for 10 minutes. After removing the supernatant, the pellet was weighed and distributed to 10 mL screw-capped microcentrifuge tubes. The maximum mass allowed per tube was 1g; nucleic acid was extracted from the FALP pellet and purified using a commercially available Ultraclean™ Soil DNA Isolation Kit (MO BIO Laboratories, Inc., Solana Beach, CA).

Pathogen Detection. We screened samples for 15 bacterial pathogens using a combination of PCR and microarray detection. Primers were designed to target conserved sequences from the 16S rDNA gene (179 bp total length). Target sequences were amplified using a standard protocol (initial denaturation at 95°C for 5 min; 30 cycles consisting of 95°C for 30 sec, 60°C for 60 sec, and 72°C for 60 sec; and a final extension step at 72°C for 10 min). Reaction constituents included 1X reaction buffer, 5 mM dNTPs, 25 mM MgCl₂, 2 U AmpliTaq Gold (Applied Biosystems, Foster City, CA) and 20 uM 16srDNA primers. For each PCR assay, positive and negative controls were included. The PCR products were identified on a DNA microarray as follows. PCR products were

automatically tagged with biotin by including a 5' biotin conjugate on each PCR primer. The 179 bp products from each sample were verified by agarose gel electrophoresis before adding 5 µl of PCR product to 35 µl hybridization buffer (4X SSC and 5X Denharts). Each PCR product was heat denatured by boiling 2 min and then aliquoted into two wells of a 12-well Teflon masked microarray slide. Each well included oligonucleotide probes complementary to DNA sequences for 15 pathogenic fish bacteria and 3 controls (*E.coli*, *S. aureus*, and *V. phosphoreum*). After overnight hybridization at 60°C, PCR products were removed and the arrays were washed and detected as described by Call et al. (2003). Microarrays were then scanned images processed using an ArrayWoRx scanner (Applied Precision, Issaquah, WA). "Spots" on the array signified hybridization of a PCR product with a specific pathogen probe. Spots with intensity values greater than non-hybridizing probes were considered positive for this analysis.

Baseline Sensitivity and inhibition of PCR. The sensitivity of the PCR/microarray assay was shown to be equivalent to less than 10 colony forming units. The relative impact of inhibitory substances on PCR was evaluated for each location. An aliquot of the filter extract obtained from the FALP filter was spiked with ca. 100 cells of *S. aureus* prior to purification. The level of inhibition was determined by amplifying 10-fold serial dilutions of the purified samples and visualized by gel electrophoresis. For example at positive PCR band at the second 10-fold dilution would be have a concentration of 1,000 cfu in the original undiluted filter extract.

Recovery from FALP Filters. An overnight culture of *E. coli* K-12, grown in nutrient broth (Difco), was prepared in dechlorinated tap water. The initial titer of viable *E. coli* was enumerated on nutrient agar plates incubated overnight at 37°C. The solution was filtered through three separate 293 mm FALP filters pre-wetted with methanol. The concentration of viable *E. coli* cells was enumerated in the filter eluate to assess bacterial recovery and the experiment was replicated three times. Based on findings from a previous study (1) the mean recovery established in this *E. coli* recovery experiment was assumed to correspond to all field samples.

Quantification of the detection limit. The detection limit of the overall assay was quantified using the following equation (1):

$$\text{Detection limit} \left(\frac{\text{cfu}}{\text{L filtered}} \right) = \frac{(I)(S)}{(V_f)(\%V_p)(R_e)} = \frac{I}{(R_e)(V_f)} \cdot \frac{S}{\%V_p} = \frac{RI}{V_f} \cdot \frac{S}{\%V_p} \quad (1)$$

where S is the sensitivity of the PCR assay, V_f is the volume of sample processed through the filters, R_e is the recovery of organisms from FALP filters, I is inhibition of PCR assays, and $\%V_p$ is the fraction of concentrated sample analyzed with PCR.

Principal Findings and Significance

Standard Water Quality Indices. The concentration of total suspended solids was below the state regulatory requirement of 15 mg/L in all 21 hatchery effluents sampled in this study. With the exception of one hatchery, the total suspended solids concentration was below the EPA recommended value of 6 mg/L for hatcheries with an offline sedimentation basin. The influent concentration of fecal coliform and enterococci at each hatchery varied considerably, with values ranging from <2 to 300 and <2 to 49 MPN/100mL, respectively. Relative to influent concentrations, 30% of the hatcheries had a statistically significant increase in the concentration of fecal coliform in the effluent, and 40% had a similar increase in the concentration of enterococci. Conversely, 24% of the hatcheries produced a net reduction in the concentration of fecal coliform, and 19% had a similar decrease in the concentration of enterococci. Hence based on a single sampling event the

hatchery environment does not appear to constitute a significant reservoir for the propagation of standard indicator organisms.

Detection and Implication of Salmonid Pathogens. Assay sensitivity and inhibition are important considerations when detecting pathogens. If a pathogen is detected, then some quantitative estimate is needed to understand the potential biological significance. If, however, no pathogens are detected, we need to know what the minimum sensitivity of the assay is before we can draw any conclusions. That is, if a sample is negative but has very low sensitivity, then there is little confidence in the negative result. The sampling strategy described here provides a means to estimate the minimum concentration that could be detected when all of the variables in equation 1 are considered. Overall 23 of 38 (60%) of the water samples had detectable concentrations of fish pathogens. In eight cases (21%) we detected no pathogens and there was no inhibition detected for the assay suggesting that these samples were truly negative within the constraints of entire assay. The remaining 19% of samples were also negative, but some inhibition was present that reduced assay sensitivity. In general, the water samples from the fish hatcheries were amenable to our sampling strategy when compared with other environmental samples (1).

Both influent and effluent samples were available for 15 of the 21 sampled hatcheries. Six of the 15 bacterial species were detected in the influent and effluent of the hatcheries. There was no correlation between influent water source, whether it was river, well, or a spring, and the detected pathogens. The predominant organism was *Aeromonas* spp.; 79% of the influent samples contained a detectable concentration suggesting that these organisms are fairly ubiquitous in the aquatic environment. Motile aeromonad septicaemia causes haemorrhagic ulceration and lesions on and around the fins, and haemorrhaging of internal tissues leading ultimately to the demise of the infected fish (4).

Within the constraints of this study (only one sampling visit per hatchery), the hatcheries do not appear to serve as a reservoir to further propagate pathogens in the effluent. This conclusion is based on the observation that in 46% of hatcheries where both influent and effluent samples were available, one or more pathogens was detected in the influent, but not the effluent and there was no relationship with assay inhibition that could otherwise explain this result. In only one case were pathogens detected in effluent, but not the influent.

In three cases, *Mycobacterium* (*M. chelonae* or *M. fortuitum*) was detected in effluent samples. Mycobacteriosis is a disease that affects a large number of fish species and is manifested by chronic systemic disease with granulomas forming throughout the internal organs. *M. chelonae* and *M. fortuitum* are both capable of causing disease in humans (4). *Yersinia ruckeri* was detected in both the influent and effluent of one hatchery, which was the only acclimation pond sampled in the study. This organism causes enteric redmouth disease in trout that is manifest by severe haemorrhagic septicaemia and high mortality (4). Several hatcheries reported active cases of cold water disease (*Flavobacterium psychrophilum*) during the time that samples were collected, but no species from this genus were detected in the hatchery water. Failure to detect any *Flavobacterium* despite good assay performance suggests that either the microarray detector needs to be improved or that we sampled at an inopportune time to detect these organisms. It would be reasonable to expect all three *Flavobacterium* species to be found in a planktonic state. *S. aureus* was also detected in some samples, but this latter organism is not a fish pathogen and may represent a nonspecific detection of a closely related organism.

The health risks associated with the relative concentrations of pathogens detected in this study are not readily quantifiable due to the lack of dose/response data. The occurrence of salmonid

pathogens in the hatchery influent, while not surprising does raise potential health concerns for both hatchery stock and potentially for native stocks receiving effluent waters. Findings from this study support the need to further study the ecology of planktonic salmonid pathogens. Bacterial salmonid pathogens can clearly survive within the aquatic environment, but the factors influencing the rates of growth and decay, and the corresponding health risks, are poorly understood. The fact that the majority of effluent samples were biologically "cleaner" than the influent samples suggests that there are effective management practices already in use at most facilities. Further work is needed to determine if these encouraging results are applicable at other sampling times and to identify which management practices are most effective for controlling biological quality of hatchery effluent.

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Reactive Transport of Reducible Metal Ions: Reaction Kinetics, Column Experiments, and Transport Modeling

Basic Information

Title:	Reactive Transport of Reducible Metal Ions: Reaction Kinetics, Column Experiments, and Transport Modeling
Project Number:	2002WA16B
Start Date:	3/1/2002
End Date:	2/1/2003
Funding Source:	104B
Congressional District:	Washington Fifth
Research Category:	Water Quality
Focus Category:	Hydrogeochemistry, Models, Toxic Substances
Descriptors:	Chromium, groundwater, reactive transport model
Principal Investigators:	James Niels Petersen, Brent Michael Peyton, Hanxue Qiu, Sridhar Viamajala

Publication

1. Viamajala, S., B. M. Peyton, and J. N. Petersen. Modeling chromate reduction in *Shewanella oneidensis* MR-1: Development of a novel dual-enzyme kinetic model. *Biotechnology and Bioengineering*. (Accepted for Publication)
2. Qiu, H.; M. Alam; S. Viamajala; B. M. Peyton; J. N. Petersen; D. Yonge. Microbially-mediated chromate reduction in 1-D soil columns: Experimental results and numerical modeling. (In preparation)
3. Qiu H., S. Viamajala, M. Alam, B.M. Peyton, J.N. Petersen, D.R. Yonge. 2002. Reactive Transport Modeling of Microbially-Mediated Chromate Reduction in 1-D Soil Columns. Poster presented at the American Geophysical Union Fall Meeting, San Francisco, California. December 6-10, 2002.

Problem and Research Objectives:

Chromium is the second-most common inorganic contaminant at hazardous waste sites in the US. It is found at many locations in the Pacific Northwest such as the U.S. Department of Energy's Hanford Site located in Southeastern Washington State, the Pacific Sound Resources site (formerly the Wyckoff Wood Treatment Facility), the U.S. Naval Submarine Base (Subbase) at Bangor in the Puget Sound region, the Midnite Mine (located on the Colville Indian Reservation), the Silver Bow Creek / Butte Area of Montana and at Lake Coeur d'Alene. In its oxidized form, Cr(VI) presents significant health hazards and is a soluble, highly mobile species. Therefore, it is imperative that technologies be developed to remediate sites contaminated with this compound. Moreover, chromium can serve as an example of other reducible metal ions, such that knowledge gained learning how chromium interacts with the environment will provide insights into how other reducible metals, such as uranium and technetium, are transported through the environment. The primary objective of our current research was to integrate experimental and numerical tasks to gain a better understanding of the complex biogeochemical interactions that dictate the transport of Cr(VI). In particular, we proposed that we would develop general reactive transport modules to describe the reactive transport of chromium, biomass, and nutrients in bench-scale laboratory columns. We further proposed that the developed modules would be embedded into RT3D, a widely used 3-D mass transport model. RT3D is especially focused on organic contaminants, such as BTEX, PCE/TCE, and other sequential decay reactions and addition of Cr(VI) reactive transport modules would enhance the capabilities of the RT3D software package to describe reducible metal transport. The module development would be based on kinetic parameters obtained from batch experiments and would be calibrated with data from bench-scale soil columns.

Methodology:

1. The batch tests:

The purpose of this study was to develop and test a kinetic model that would describe Cr(VI) reduction by anaerobic stationary phase MR-1 cultures grown under different conditions. Cr(VI) reduction tests were performed with stationary phase cultures grown on fumarate as the terminal electron acceptor. The cultures were incubated for 36 hours until fumarate was consumed and the cultures reached stationary phase. After 36 hours of incubation, serum bottles containing the cultures were transferred to an anaerobic glove box (Model 1025, Forma Scientific Inc., OH; gas mix – 90% N₂, 5% H₂ and 5% CO₂) and opened where Cr(VI) reduction experiments were performed. For this purpose, batch reactors containing 2mL of culture were established in sterile 24-well tissue culture plates (Corning Inc., NY) inside the anaerobic glove box. Cr(VI) reduction was tested with five different initial Cr(VI) concentrations ranging from 0.04-0.12 mM. Required Cr(VI) concentrations were achieved in the reactors by adding K₂CrO₄ from anaerobic sterile stock solutions that were 100 times more concentrated than the target concentration. Each initial Cr(VI) concentration was tested at least in duplicate and some tests were repeated (in duplicate) with cultures from a different serum bottle. Cell protein, cell numbers and optical density were measured at the beginning of the experiment and assumed to be constant since the cultures were at stationary phase and the duration of the experiment was short.

2. The column tests

Soil column experiments were performed to provide data for calibration of the numerical model and for validation of modeling results. Stainless steel high pressure liquid chromatography columns (2.5 cm (ID) x 15 cm), containing quartz sand as the porous media matrix, were used for the

experiments. The columns were inoculated with a well-known metal reducing bacterium, *Shewanella oneidensis* MR-1, which served as a model microorganism in these tests. Before inoculation of the columns, MR-1 cultures were grown aerobically in simulated groundwater (SGW) amended with lactate. To ensure a uniform initial biomass distribution in the column, quartz sand was mixed with log phase culture broth ($\sim 10^8$ CFUs/mL) and the resulting slurry was loaded and packed into the column. After inoculation, the column was flushed overnight with substrate-free SGW at a flow rate of 1mL/h (Darcy velocity ~ 1 ft/day), to wash out unattached biomass. This flow rate approximates natural groundwater flow velocity. Thereafter, Cr(VI) and substrate were added simultaneously to the column to stimulate both bacterial growth and Cr(VI) reduction to Cr(III). Concentration of Cr(VI), lactate and fumarate in the feed stream were 2mg/L, 15mM and 2mM respectively. The parameters measured in these experiments include 1) concentrations of nutrients (lactate and fumarate) in the column influent and effluent, 2) Cr(VI) and Cr(III) concentrations in both the column feed and effluent, 3) effluent biomass concentration (cell count and protein), 4) hydraulic conductivity (pressure drop), and 5) pH. Each column experiment was replicated to insure repeatability. Un-inoculated columns were used as abiotic controls and for residence time distribution studies using a bromide tracer. Column feed was delivered with syringe pumps.

At the completion of the test, the column was cored, and the attached biomass concentration was determined by performing protein assays using the Pierce Micro Bradford Protein Assay Kit. Data from these soil column experiments was compared to results predicted using the modified RT3D code described below. Comparing observed data to reactive flow and transport model predictions has allowed the evaluation and verification of numerical processes descriptions developed in this project.

3. Numerical module development and coding

To describe results from columns experiments, numerical models were developed using RT3D, a commercially available and widely-used flow and transport code. Modules were developed to describe kinetics of biotransformation of Cr(VI), biomass growth, and substrate utilization and incorporated into RT3D. Thus, the numerical code could simulate Cr(VI) reduction results in the column by taking into account convection, dispersion and microbial reduction.

For numerical modeling purposes, the column was considered to be a one-dimensional system with constant flow. For such a system, the mass balance equation for a transported species is written as:

$$\frac{\partial}{\partial t}(nc) = \frac{\partial}{\partial z}(\alpha q \frac{\partial c}{\partial z}) - \frac{\partial}{\partial z}(qc) - R_{ba} - R_{bs} \quad (1)$$

where c is the aqueous phase macroscopic averaged concentration of the transported species [ML^{-3}], n is the porosity, α is the dispersivity [L], q is the Darcy flux [MT^{-1}], R_{ba} is the microbial reaction rate that describes the mass of the contaminant biotransformed per unit of bulk porous media volume per unit time [$\text{ML}^{-3}\text{T}^{-1}$], and R_{bs} is the volume-specific rate of contaminant removal that results from surface-associated biotransformation [$\text{ML}^{-3}\text{T}^{-1}$].

This model ignores variations in porosity values due to changes in biomass concentration because numerical simulations in a variable porosity model indicated that accounting for porosity changes had little effect on nutrient and biomass profiles in one-dimensional constant flow systems.

Assuming constant porosity and dispersivity values, Equation (1) can be rewritten as:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z} - r_{ba} - r_{bs} \quad (2)$$

where $v = q/n$ is the pore velocity [LT^{-1}], $D = \alpha q/n$ is the dispersion coefficient [L^2T^{-1}], and the r_i are the various reaction rates that describe the mass of contaminant reacted or sorbed/desorbed per unit liquid volume per unit time [$ML^{-3}T^{-1}$].

In addition to nutrient concentrations, we were also interested in predicting the growth and accumulation of biomass in the system. Mass balance expressions that describe growth and transport of aqueous phase biomass, and growth and accumulation of attached biomass are expressed as:

$$\frac{\partial X_a}{\partial t} = \frac{\partial}{\partial x_i} (D_{ij} \frac{\partial X_a}{\partial x_j}) - \frac{\partial}{\partial x_i} (v_i X_a) + \hat{r}_X X_a - r_{att} + \frac{r_{det} \rho_k}{n} - K_{de} \cdot X_a \quad (3)$$

$$\frac{dX_s}{dt} = \hat{r}_X X_s - r_{det} + \frac{n r_{att}}{\rho_k} - K_d \cdot X_s \quad (4)$$

where \hat{r}_X is the specific bacterial growth rate [T^{-1}], X_a is the concentration of biomass in the aqueous phase [ML^{-3}], X_s is the solid phase biomass concentration per unit mass of porous media solids [MM^{-1}], and ρ_k is the bulk density of porous media [ML^{-3}]. r_{att} is the rate at which suspended cells attach to the solid phase (mass of attached cells per unit liquid volume per unit time [$ML^{-3}T^{-1}$]), and r_{det} is the rate at which cells detach from the solid phase (mass of detached cells per unit bulk mass of porous media solids per unit time [$MM^{-1}T^{-1}$]).

Attachment and detachment of microbial cells were described as non-linear processes and the kinetic rates of attachment and detachment can be written as:

$$r_{att} = K_{att} \cdot \lambda \cdot X_a \quad (5)$$

$$r_{det} = \frac{K_{det}}{\lambda} \cdot X_s \quad (6)$$

where K_{att} is the attachment coefficient [T^{-1}], and K_{det} is the detachment coefficient [T^{-1}], and λ is the limiting factor for biomass growth and can be defined as

$$\lambda = \frac{X_{s_{max}} - X_s}{X_{s_{max}}} \quad (7)$$

This definition of λ is based on a maximum retention capacity such that when X_s is much less than the maximum retention capacity, $X_{s_{max}}$, the attachment will be high and when X_s approaches $X_{s_{max}}$, the attachment will approach zero.

Cr(VI) reduction kinetics by *Shewanella oneidensis* MR-1 was described by the dual enzyme kinetic model that was developed using batch kinetic data from experiments described above. The dual-enzyme kinetics is based on the hypothesis that Cr(VI) reduction in MR-1 occurs via two parallel and independent mechanisms – 1) a rapid mechanism that is susceptible to Cr(VI) and is deactivated during chromate reduction (“deactivating enzyme”) and (2) a slower mechanism that is resistant to Cr(VI) and the activity of which remains stable during chromate reduction (“stable enzyme”). Kinetic expressions for Cr(VI) reduction and substrate consumption were included in the mass balance equations (Eq. 2). A set of seven simultaneous differential equations were obtained after mass balance for biomass, substrate and Cr(VI) in the solid and aqueous phases. These equations were solved using GMS3.1 with RT3D as a modular computer code which allows for development of user defined kinetic modules by providing solvers to solve the governing equations. To solve the reactive transport portion of the model, we selected Runge-Kutta and General Gear Solver since both can give a reliable solution when proper time steps and spatial discrepancy are

adopted. Hybrid MOC method was chosen to solve the convection term. A very fine grid (300 grids for a total column length of 15 cm) was used and transport step $\Delta t=0.001\text{h}$ was selected via precision test. The solver provide a default transport step length based on Peclet and Courant number constraints but we found this default transport step can not guarantee a reliable model precision(data not show). Trial and error method is used to calibrate the parameters on the basis of initial parameter estimation.

Principal Findings and Significance

During this study, a series of batch and soil column experiments were performed in concert with reactive flow and transport numerical modeling. First, kinetic experiments conducted in batch reactors were used to develop Cr(VI) reduction kinetics for *Shewanella oneidensis* MR-1. Since Cr(VI) reduction in MR-1 could not be described using kinetics previously developed for other microorganisms, we developed a novel dual-enzyme kinetic model. This model takes into account multiple parallel Cr(VI) reduction pathways that exist in MR-1 and is therefore different from previous models that assumed a single Cr(VI) reducing enzyme. To elicit information on the complex interactions between soil, indigenous microbes, nutrients and Cr(VI), column experiments were performed. In these experiments, Cr(VI) and nutrient were fed to the column simultaneously, to simulate a nutrient-fed bioremediation system. Under these conditions it was observed that when the influent Cr(VI) concentration was less than 1mg/L, the column was able to sustain Cr(VI) reduction for more than 1 month, while when Cr(VI) feed concentration was increased to 2mg/L, the breakthrough occurred in 3-4 days. The reactive transport model developed by incorporating dual-enzyme Cr(VI) reduction kinetics was accurately able to describe the non-linear Cr(VI) breakthrough behavior in the column.

Information Transfer Program

The State of Washington Water Research Center continues to believe that Outreach and Education are important components to its mission. The primary goal is to facilitate information exchange by providing opportunities for combining the academic work of research universities in the state with potential users and water stakeholders. This process occurs through a variety of activities, formal and informal, that raise the visibility of university research results throughout the Pacific Northwest. Federal, state and local agencies, non-governmental organizations, watershed groups, consulting firms, and concerned citizens are in need of interpreted science that can be applied to solving the region's water problems. The Center makes substantial efforts to facilitate this process.

Information Transfer

Basic Information

Title:	Information Transfer
Project Number:	2002WA4B
Start Date:	3/1/2002
End Date:	2/28/2003
Funding Source:	104B
Congressional District:	Washington Fifth
Research Category:	None
Focus Category:	Management and Planning, Education, None
Descriptors:	None
Principal Investigators:	Michael Ernest Barber

Publication

The following items constitute the core of the technology transfer activities of the SWWRC.

After the February 2002 regional water quality conference, a considerable amount of effort went into putting the proceedings on our WEB page and analyzing the responses to program questionnaires in order to improve our next conference. To maximize the impact, the WEB page was available to everyone whether or not they attended the conference.

Planning began for our next conference on TMDL implementation. This conference will be held in October 2003 in conjunction with the Washington Department of Ecology and the US EPA. A steering committee was organized comprised of a number of regional experts in water resources. A number of telephone conference calls were conducted and one, face-to-face meeting was held in Yakima. Plans for the conference and a pre-conference workshop were developed.

Continued funding for the USDA-CSREES grant was received. The project helps coordinate research and extension activities of the Water Research Institute and Cooperative Extension Services in Alaska, Oregon, Idaho, and Washington with EPA Region 10. Bi-monthly meetings were held, and communication between researchers and government agencies is expanding rapidly.

Three meetings with the Spokane/Rathdrum Prairie aquifer committee were attended to discuss Idaho and Washington Water Institute involvement with a potential project near Spokane. The project would be a joint venture between the USGS and the States of Washington and Idaho.

Our WEB page underwent a major upgrade during the last year. This is an important avenue for us to present information about the activities of the Center and the research faculty in the state as well as news and events, research reports, and opportunities for research funding. This media requires nearly continuous work to ensure that the material is current and the look of the page is up to date. Last year, we totally changed our WEB site moving from a HTML-based system to one based on Dream Weaver. All of our links were verified and reorganized as a number were no longer applicable, new links were added, and we began the process of making future research reports available for download via PDF format rather than mailing of paper copies.

Our database of interested stakeholders is constantly being updated. Currently, over 2,200 names are included with the number constantly increasing.

Participation in a University of Washington seminar for Journalists interested in technical background for water-related articles. This has led to several telephone interviews from journalists from Montana, Oregon and Washington.

A variety of other small activities were conducted during the year such as a) addressing questions related to the Eastern Washington Stormwater Manual, b) presentations to watershed groups, c) service in response to telephone and e-mail requests from users, and d) attendance at extension and agency meetings.

USGS Summer Intern Program

Student Support

Student Support					
Category	Section 104 Base Grant	Section 104 RCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	0	7	0	0	7
Masters	2	4	0	0	6
Ph.D.	2	3	0	0	5
Post-Doc.	1	1	0	0	2
Total	5	15	0	0	20

Notable Awards and Achievements

The SWWRC Program Director for Groundwater Systems, Dr. Richelle Allen-King, was selected as the 2003 Darcy Lecturer. Dr. Allen-King has been actively involved in SWWRC activities and has been funded by USGS awards at the national level.

Publications from Prior Projects

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