

**Water Resources Research Center  
Annual Technical Report  
FY 2006**

## Introduction

This report covers the period March 1, 2006 to February 28, 2007, the 41st year of the Massachusetts Water Resources Research Center (WRRC). The Center is under the direction of Dr. Sarah Dorner, who holds a joint appointment as Director of the WRRC and as Research Assistant Professor in the Department of Civil and Environmental Engineering at the University of Massachusetts Amherst.

Dr. Stephen Mabee of the UMass Amherst Department of Geosciences continued work on a three-year 104G USGS grant to look at *A Regional Approach to Conceptualizing Fractured-Rock Aquifer Systems for Groundwater Management*. This is the third year of the study, but due to a late start, a no-cost extension was requested to continue the research until May 2008.

At the University of Massachusetts Dartmouth, Dr. Yuegang Zuo of the Chemistry and Biochemistry Department continued a two-year project on *Monitoring Estrogenic Hormones Undesired Fish Contraceptives, and Investigating Their Sources, Transportation and Fate in Buzzards Bay, Massachusetts*. This project is also extended, until December 2007.

A new two-year project, led by Piotr Parasiewicz of the University of Massachusetts Amherst, is researching *Using Hydromorphological Signatures to Determine Flow Related Habitat Thresholds for Instream Communities*.

Finally, a graduate student grant was awarded to Ashish Sahu of the University of Massachusetts Amherst Civil and Environmental Engineering Department to study *Perchlorate Reduction in Groundwater Using Elemental Sulfur*.

Other projects conducted at WRRC include the Massachusetts Water Watch Partnership, the Acid Rain Monitoring Project, and continued collaboration with UMass Extension on a stream continuity project. A new project, to continue work on a Clearinghouse for innovative stormwater Best Management Practices in Massachusetts, was awarded to WRRC by the MA Dept. of Environmental Protection.

Though we did not hold a Water Conference during this reporting period, much work was accomplished to prepare the conference held at UMass on April 9, 2007.

**Research Program**

# A Regional Approach to Conceptualizing Fractured-Rock Aquifer Systems for Groundwater Management

## Basic Information

<b>Title:</b>	A Regional Approach to Conceptualizing Fractured-Rock Aquifer Systems for Groundwater Management
<b>Project Number:</b>	2003MA19G
<b>Start Date:</b>	9/30/2004
<b>End Date:</b>	9/29/2007
<b>Funding Source:</b>	104G
<b>Congressional District:</b>	1st District of MA
<b>Research Category:</b>	Ground-water Flow and Transport
<b>Focus Category:</b>	Water Supply, Groundwater, Water Quantity
<b>Descriptors:</b>	fracture characterization, domain analysis, well yield, fractured rock aquifers, groundwater availability, groundwater mapping, borehole geophysics
<b>Principal Investigators:</b>	Stephen B. Mabee, Michele Cooke

## Publication

1. Manda, A.K; S.B Mabee, D.U. Wise, In prep, Influence of rock fabric on fracture attribute distribution and implications for groundwater flow in the Nashoba Terrane, Eastern Massachusetts, to be submitted to Journal of Structural Geology.
2. Manda, A.K, S.B. Mabee and D.F. Boutt, 2006. Characterizing fractured crystalline bedrock aquifers using hydrostructural domains in the Nashoba terrane, eastern Massachusetts. Geological Society of America Annual Meeting, Philadelphia, Abstracts with Programs, v.38, no.7, p.25.
3. Diggins, J.P., D.F. Boutt, A.K. Manda and S.B. Mabee, 2006. Estimating bulk permeability of fractured rock aquifers using detailed outcrop data and discrete fracture network modeling. Geological Society of America Annual Meeting, Philadelphia, Abstracts with Programs, v.38, no.7, p.223.
4. Boutt, D.F., A.K. Manda, S.B Mabee, J.P. Diggins, 2006, Characterizing fractured crystalline bedrock aquifers using discrete fracture networks in the Nashoba Terrane, Eastern Massachusetts, Eos Transactions, American Geophysical Union, v. 87, no. 52, Fall Meeting Supplement, Abstract H13D-1429.
5. Manda, A.K., S.B. Mabee and S.A. Hubb,. 2005. Field mapping and fracture characterization techniques predict groundwater preferential flow paths in fractured bedrock aquifers, Nashoba terrane, MA. EOS Transactions, American Geophysical Union, v.86, no. 52, Fall Meeting Supplement, Abstract H23E-1477.

## **Problem Statement**

The use of fractured-bedrock aquifers to meet private, public and commercial water supply needs is increasing in the New England region. Municipalities and water suppliers are finding it increasingly difficult to locate and develop water supplies in overburden aquifers because of contamination and a lack of suitable sites. In addition, recent droughts in the northeast have forced many communities and homeowners to drill new wells. As a result, water suppliers are going deeper into bedrock aquifers. Yet information on the factors that influence the availability and recharge characteristics of fractured bedrock aquifers in highly deformed crystalline metamorphic rocks is limited.

The availability of water in fractured rock aquifers is particularly critical in New England because growth and development along the coast, major transportation corridors and in rural communities adjacent to large metropolitan areas is rampant. For example, the I-495 corridor in Massachusetts, a circumferential highway 30 miles west of Boston, has become the focus of recent growth. Professional office buildings, research and development parks associated with the computer industry, warehouses and light industry are springing up along this corridor, as are housing and condominium developments. Municipalities and water suppliers are simply unprepared for the onslaught of development and need help in understanding the complex dynamics of the ground water system.

Sustaining and managing ground water resources in fractured bedrock requires an evaluation of 1) the availability of water, 2) the source and vulnerability of recharge to water supply wells and 3) the impact of water withdrawals from the bedrock on streams, wetlands and unconsolidated aquifer systems that overlie the bedrock. These evaluations all require basic information on the physical characteristics of the ground water system.

## **Objectives**

The objectives of this project are to gather regional bedrock characteristics that relate to the occurrence and movement of ground water in bedrock and use this information to begin constructing regional conceptual models of the fractured-rock aquifers in the Nashoba terrane in Massachusetts. The approach utilizes existing information augmented by the collection of low-cost field data to develop regional conceptual models of the ground water flow system. Water managers can then use these conceptual models as an initial framework for formulating an understanding of bedrock flow behavior and recharge characteristics.

Specific tasks of this project involve: 1) Fracture Characterization and Domain Analysis - collection and synthesis of fracture characterization data over the region and mapping of the spatial distribution (domain analysis) of fracture sets and their characteristics, 2) Compilation and Analysis of Existing Well Data - compilation and statistical analysis, including variography, of available well data to link spatial continuity of well yields to characteristics of the fractured rock system, 3) Borehole Geophysics - collection of optical and acoustic televiwer data from selected boreholes to verify sheeting joints, 4) Compilation of Regional Litho-Group Map - development of a mapping classification system that uses the notion of "litho groups" to characterize bedrock units in terms of their fracture characteristics, physical properties and

geologic setting (eg., overburden type and thickness) and 5) Conceptual Model - preparation of a qualitative conceptual model of ground water flow behavior in each litho group category.

### Relationship of Project to USGS and Other Activities

This project is part of a much larger, more comprehensive study being conducted by the USGS WRD Northborough office on the Geohydrology of the Nashoba Terrain, Massachusetts. This larger scale project involves the collection of data at three scales: regional, quadrangle and the local well-field scale. Recent work by the USGS in Connecticut and New Hampshire indicates that an understanding of ground water occurrence and movement in fractured rock aquifers can be made by combining the results of 1) fracture, geologic, well, and geophysical analyses performed at the regional level, 2) detailed mapping of bedrock lithology and physical characteristics that affect water occurrence and flow at the quadrangle scale, and 3) hydrogeologic and geophysical investigations at the well-field scale. This larger scale project is a joint effort that involves the participation of USGS scientists from the Water Resources Discipline, USGS mappers from the BRASS (Bedrock Regional Aquifer Systematics Study) program, the Office of the Massachusetts State Geologist, and University of Massachusetts scientists (this project). Table 1 describes the tasks that each agency will perform and shows how the work will be coordinated.

Table 1. Coordination Plan and Approximate Timetable

<u>Task</u>	<u>Activity</u>	<u>Timetable</u>	<u>Responsible Party</u>
Existing Data (Regional Scale)	Base map	2003	USGS <sup>1</sup>
	Geologic map	2003	USGS
	Imagery	2003	USGS
	Fracture data/analysis	completed	This Project <sup>2</sup>
	Existing well data/analysis	completed	This Project
	Add'l well data in field	completed	This Project/USGS
	Borehole fracture data	underway	This Project/USGS
	Litho-group map	completed	This Project
Geologic & Fracture Data (Quadrangle Scale)	Map Quad #1-Grafton	completed	USGS BRASS <sup>3</sup>
	Map Quad #2-Marlboro	completed	State Geologist <sup>4</sup>
	Map Quad #3-Nashua S.	completed	USGS BRASS <sup>3</sup>
	Map Quad #4-Hudson	completed	State Geologist <sup>4</sup>
	Map Quad #5-Ayer	completed	State Geologist <sup>4</sup>
	Map Quad #6-Milford	underway	
Conceptual Model Devel.		completed	This Project/USGS
Test and Verify Model (Well Field Scale)		underway	This Project/USGS
Prepare and Publish Reports		Late 2007	This Project/USGS

<sup>1</sup> Start date of USGS cooperative project is March 2003, Bruce Hansen, USGS

<sup>2</sup> Start date of this project is September 30, 2004 (no cost extension granted)

<sup>3</sup> USGS BRASS = Bedrock Regional Aquifer Systematics Study project, Greg Walsh, USGS, began mapping in summer 2004; finishing Nashua South quadrangle in 2007

<sup>4</sup> State Geologist – Mapping funded by the STATEMAP component of the National Cooperative Geologic Mapping Program, Marlboro completed in June 2004, Hudson preliminary map completed in June 2005, Ayer quadrangle completed 2006, Milford will be finished in fall 2007.

Please note that although the USGS portion of the work was supposed to start in 2003, funding did not become available for the project until spring of 2007. The University of Massachusetts and the USGS are working collaboratively on the collection of borehole geophysical data on selected wells in the Nashoba terrane. We are collecting fluid resistivity, temperature, gamma, electromagnetic induction, acoustic and optical televiwer and heat pulse flowmeter data. These data, along with well field pumping test data, will be used to verify the conceptual models.

### **Work Accomplished on *This Project* in Past Year**

Work completed during the period March 1, 2006 to February 28, 2007:

1. Tasks 1 (Fracture Characterization and Domain Analysis), 2 (Compilation and Analysis of Existing Well Data) and 4 (Compilation of Regional Litho-Group Map) are complete.
2. Task 5 (Conceptual Model) is underway. Discrete fracture network models are being run for individual outcrops to test the concept of hydrostructural domains. Model results will be compared with well field pumping test data and the borehole geophysical data. Existing pumping test data has been collected and is being analyzed.
3. Task 3 (Borehole Geophysical Surveys) is underway during the summer of 2007.
4. Currently building discrete fracture network models of individual outcrops and assigning hydraulic conductivity values to several domains for testing against well-field scale pumping test and borehole geophysical data.

Although the project ends on September 29, 2007, Alex Manda will be continuing the model validations through the 2007/2008 academic year in order to complete his Ph.D.

### **Work Accomplished by Collaborators (Table 1)**

**USGS** – The USGS WRD Northborough office was finally funded in spring 2007. The scope of services has changed slightly. In addition, to assisting with the borehole geophysical data collection, the USGS will also be conducting a statistically based yield probability study for the Nashoba terrane. They will use the fracture data collected in this study and in the quadrangle scale mapping completed by the Office of the Massachusetts State Geologist.

**Office of the Massachusetts State Geologist** – The office of the Massachusetts State Geologist has contributed in the following way using funds supplied by the National Cooperative Geologic Mapping STATEMAP and EDMAP programs and from the Massachusetts Department of Environmental Protection.

1. A preliminary bedrock geologic map and a fracture characterization map is currently being prepared for the Milford quadrangle. These maps provide detailed lithologic and fracture characterization data as well as information on the distribution of permeable

overburden deposits at the quadrangle scale. These data will be used as a test for the regional scale and quadrangle scale hydro-structural domain maps to be prepared under this project. We now have new bedrock and fracture characterization maps for three quadrangles that provide a north south transect across the Nashoba terrane.

2. We have also begun bedrock geologic mapping in the Westford and Blackstone quadrangles.
3. A fracture characterization map is being prepared for the Wilmington quadrangle.
4. In addition, using funds from the EDMAP component of the National Cooperative Geologic Mapping Program, we have new bedrock and fracture characterization maps for the Concord quadrangle, which completes an east-west transect across the Nashoba terrane.
5. A well database consisting of over 1000 wells has been assembled for the Milford quadrangle.

**USGS BRASS Program** – Greg Walsh from the USGS BRASS program completed bedrock and fracture mapping in the Nashua South quadrangle. Greg is finalizing the map in summer 2007.

## **Summary of Results**

The following is a description of results, achievements and goals related to this project. The specific objective is first stated before a description of the status of that objective is given. Highlighted below are both the goals that have been achieved and those that are still pending. Note that this grant has supported Alex Manda, Ph.D. candidate, for the previous 2.5 years.

- 1) Fracture Characterization and Domain Analysis - collection and synthesis of fracture characterization data over the region and mapping of the spatial distribution (domain analysis) of fracture sets and their characteristics. Completed (see previous annual reports).
- 2) Compilation and Analysis of Existing Well Data - compilation and statistical analysis, including variography, of available well data to link spatial continuity of well yields to characteristics of the fractured rock system. Completed (see previous annual reports).
- 3) Borehole Geophysics - collection of optical and acoustic televiwer data from selected boreholes to verify sheeting joints.

Borehole geophysical data is currently being collected at selected wells in the Nashoba terrane. Patrick Diggins, MS candidate at the University of Massachusetts and Jason Sorenson, a USGS employee, are working together to collect this data. Dr. David Boutt (Hydrogeology professor at the University of Massachusetts), Dr. Stephen Mabee (MA State Geologist) and Bruce Hanson (formerly of USGS and now with the MA Department of Conservation and Recreation) are assisting with data collection. In addition to optical and acoustic televiwer logging, we are also collecting fluid resistivity, gamma, temperature, electromagnetic induction and heat pulse flowmeter data. This will identify how much and which fractures are producing water in the borehole. These data will be compared to outcrop fracture characterization data and

model results. As of this writing, three wells have been logged. We have use of the geophysical equipment until the end of August 2007. The goal is to log 25 to 30 wells during this time.

4) Compilation of Regional Litho-Group Map - development of a mapping classification system that uses the notion of “litho groups” to characterize bedrock units in terms of their fracture characteristics, physical properties and geologic setting (e.g., overburden type and thickness).

This task is completed. We have substituted the term, ‘hydrostructural domain’ in place of ‘litho group’ to describe assemblages of rocks that have similar physical properties and hence similar hydraulic characteristics. Major criteria for determining hydrostructural domains are rock type, number and distribution of fracture sets, type of fractures present or absent, degree of fracture development, fracture spacing and nature of fracture termination. See previous annual reports for details.

5) Conceptual Model - preparation of a qualitative conceptual model of ground water flow behavior in each litho group category.

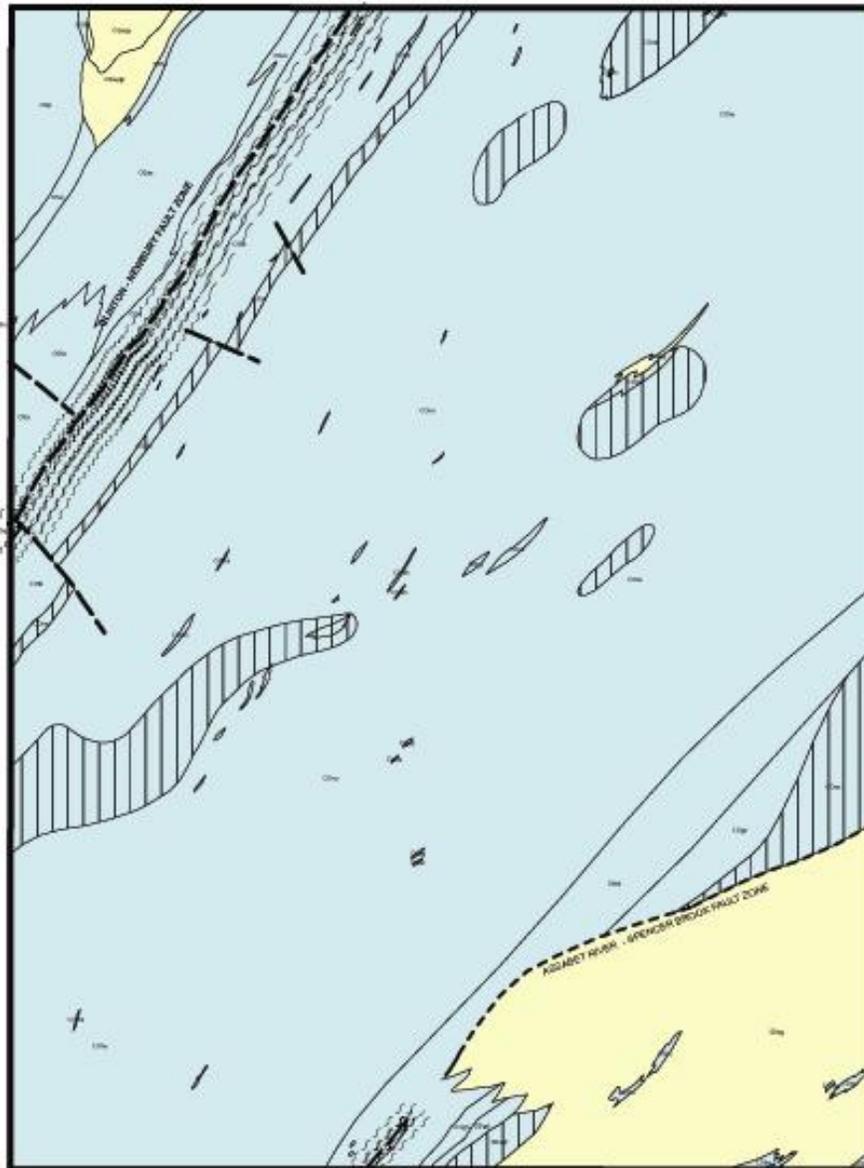
Most of the work in the previous year has focused on this task. We have extended our work beyond the conceptual model phase and are now performing numerical modeling to test and validate the conceptual model and the notion of “hydrostructural domains”. A summary of this work follows.

Hydrostructural domains are packages of rocks that have similar fracture intensities and thus are likely to possess comparable hydraulic properties. However, this study has identified that other than fracture intensity, fracture trace length and the number of fracture sets also influence the hydraulic properties of rocks. Thus, the number of fracture sets and fracture trace lengths have been included in identifying hydrostructural domains for the regional study of the Nashoba terrane. A hydrostructural domain map of the Nashoba terrane that shows how fracture attributes that influence the transmissive properties of rock units vary within the Nashoba terrane was created.

Numerical simulations of groundwater flow in the hydrostructural domains for the Nashoba terrane were conducted using discrete fracture networks in 10 m<sup>3</sup> box regions with sides that had either specified heads or fluxes. However, these simulations were unsuccessful because the parameters required for building discrete fracture networks exceeded the maximum threshold for model running. The groundwater flow code MAFIC was incapable of simulating flow in fracture networks created from the fracture data of the Nashoba terrane. In spite of the inability to simulate flow in the fracture networks representing hydrostructural domains at the regional scale, it was apparent that the number of outcrops used to create domains was insufficient to adequately capture the true hydraulic character of the discrete fracture networks; spatial heterogeneity of fractures was not adequately captured at this scale.

To overcome the problems encountered with the Nashoba regional study, fracture characterization and numerical model simulation were conducted at the quadrangle scale. A hydrostructural domain map for the Hudson quadrangle was created where the density of stations was higher per square mile than that at the regional scale. Also different criteria were used to

define the hydrostructural domains at this scale so as not to encounter the same problems as those in the regional study. Three domains were delineated: steeply dipping layered rocks (SDLR), steeply dipping layered rocks with strong tendency to part parallel to foliation (SDLRSPPF), and massive rocks (MASSIVE) (Fig. 1, Tables, 1, 2 and 3). Numerical models of groundwater flow in fracture networks were derived from outcrop-scale field data and simulated as 10 x 10 x 10 meter cubes. Flow was calculated in an east west, north-south, and vertical direction (top to bottom) by controlling boundary conditions. Results showed that the most transmissive domain in the E-W and N-S directions was MASSIVE, whereas in the top to bottom direction the most transmissive domain was SDLRSPPF (Fig. 2). The least transmissive domain in the N-S and top to bottom directions was SDLR, whereas in the E-W direction the least transmissive domain was SDLRSPPF (Fig. 2). This analysis was conducted on fracture networks that were assumed to have similar fracture apertures.



Photography from aerial 1:50,000 scale interpretation  
Topographic, cultural features overlaid on aerial photograph  
Map of 1:50,000 scale, 1988  
Rock color legend: 1:50,000 scale, 1988  
Scale of 1:50,000



Map of 1:50,000 scale, 1988  
Scale of 1:50,000

EXPLANATION OF HYDROSTRUCTURAL DOMAINS

- Massive Rocks - Rocks exhibiting no foliation or occasional weak foliation.
- Steeply-Dipping Layered Rocks - Foliated rocks exhibiting dips greater than 60°. Sheeting is generally not well developed except in a few isolated locations.
- Steeply-Dipping Layered Rocks with strong Partings Parallel to Layering - Partings are pervasive, generally through-going and generally extend across the outcrops.

Figure 1. Hydrostructural domain map of the Hudson quadrangle, eastern Massachusetts.

Table. 1 Fracture statistics for MASSIVE<sup>1</sup> hydrostructural domain

Fracture Set	Strike and dip of fracture set	Median Spacing (m)	Median Trace Length (m)
1	150/83	0.60	0.80
2	089/51	0.25	2.10
3	027/68	0.85	2.00
4	193/66	0.20	1.75

<sup>1</sup>Massive rocks with no or little foliation

Table. 2 Fracture statistics for SDLR<sup>2</sup> hydrostructural domain

Fracture Set	Strike and dip of fracture set	Median Spacing (m)	Median Trace Length (m)
1	123/86	1.35	1.10
2	034/70	0.60	1.60
3	246/81	0.20	1.80
4	022/05	0.50	2.00

<sup>2</sup>Steeply Dipping Layered Rocks

Table. 3 Fracture statistics for SDLRSPPF<sup>3</sup> hydrostructural domain

Fracture Set	Strike and dip of fracture set	Median Spacing (m)	Median Trace Length (m)
1	142/73	0.5	1.1
2	226/71	0.2	1.5
3	015/75	1	1.6
4	007/11	0.35	2.9
5	219/74	0.3	1.5

<sup>3</sup>Steeply Dipping Layered Rocks with Strong tendency to Part Parallel to Foliation

The results suggest that foliated rocks showing a strong tendency to part parallel to foliation have a significant influence on flow because the features are penetrative, through-going and pervasive in the outcrop (note the high vertical transmissivity). In contrast, strongly foliated rocks that do not tend to part parallel to foliation and which are annealed, do not show as strong a vertical flow. In such rocks, the presence of cross joints (E-W flow direction) is equally important in controlling flow. Massive rocks have good flow characteristics because in the field they tend to have better developed sheeting joints providing greater connectivity. Also note that E-W flow in all three domains are very similar suggesting that these fractures have similar properties that are independent of the domain.

The results appear also to be surprising. The most transmissive domain, based on the assessment of fracture attributes and observed number of fracture sets, is predicted to be SDLRSPPF (Table 3). This domain has comparable fracture trace length and spacing to MASSIVE domain (Table 1).

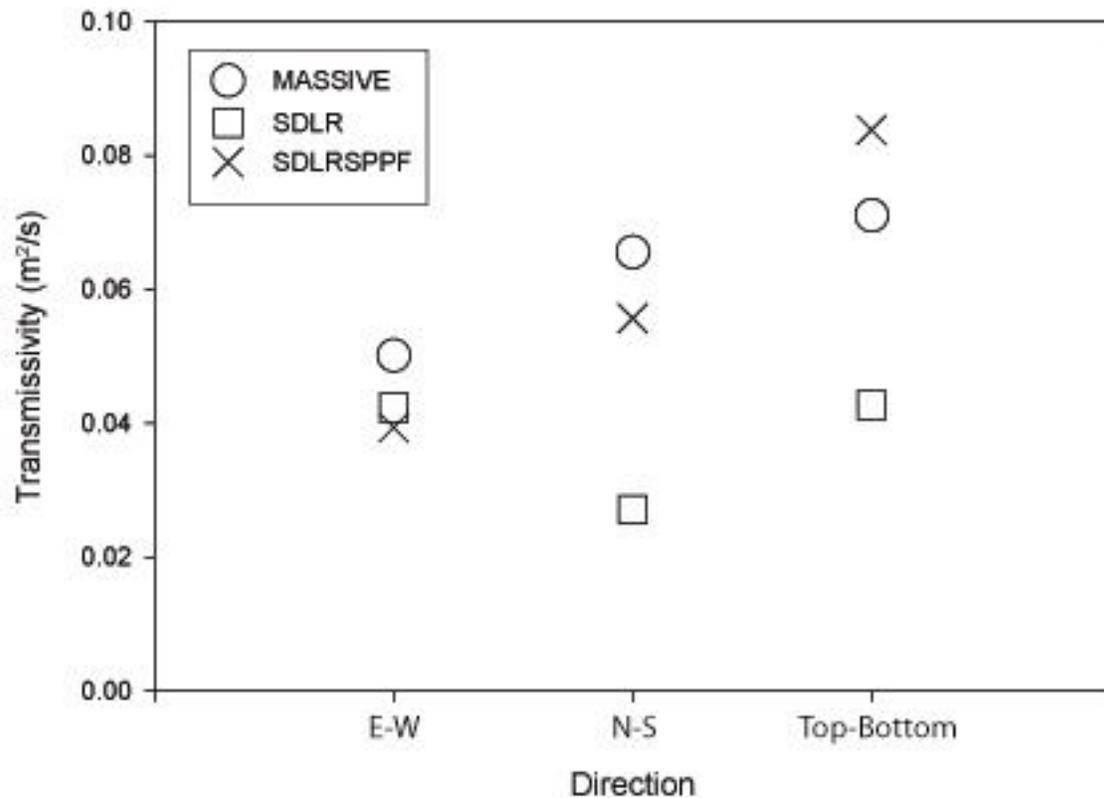


Figure 2. Plot showing the transmissivity derived from different domains in different directions.

However, the SDLRSPPF domain has more fracture sets that have markedly varying orientations suggesting that this domain should be more conductive because it has higher fracture connectivity than the MASSIVE domain. In reality, as the simulation results reveal, the MASSIVE domain is more conductive in two of the three directions in which the simulations were conducted.

The SDLRSPPF domain is not the most transmissive unit in the E-W and N-S flow directions. In fact, SDLRSPPF is the least transmissive domain in the E-W direction. Even though fracture trace length and fracture intensity for SDLRSPPF and MASSIVE domains appear to be comparable, there are subtle differences in the total number of fractures present in each model, and hence the total volume that fractures take up in each model. The MASSIVE domain has more fractures and hence a higher fracture volume than the SDLRSPPF. This increases the potential permeability of the domain thereby imparting a higher transmissivity on the MASSIVE domain.

The qualitative assessment of the hydrostructural domains needs to be validated with hydraulic data from the field area. Unfortunately, well yield data that is currently available at the regional and quadrangle scales is not sufficient to characterize the transmissive properties of fractured crystalline rocks. An ongoing USGS/UMASS collaborative project will collect

hydraulic data that will be used to validate the numerical simulation results of this study. When these data are available, validation of the hydrostructural domains at the quadrangle scale will continue.

### **Recommendations from data analysis and numerical model simulations**

The following recommendations are provided to help with collecting robust data sets in the future that can adequately capture the transmissive properties of discrete fracture networks in numerical models:

- Aperture data needs to be collected from outcrops using feeler gauges or other measuring devices. An estimate of fracture aperture derived from outcrops will help to constrain numerical models so that they match natural fracture networks.
- The proportion of fractures that have a particular termination style needs to be determined at the outcrop. This can be done by counting the total number of fractures along either the entire outcrop or along sections of the outcrop (e.g. 10 m sections) and counting fractures that have particular termination styles along that particular section. Results from this procedure will then be used to help determine the connectivity of the fracture network.
- Fracture sets that terminate against other sets need to be documented in the field. This information required during model building to accurately replicate the natural fracture network, affects the conductivity of the fracture networks.
- The proportion of fractures that are conducting within particular fracture networks needs to be determined. Data that can be used to determine the proportion of conducting fractures within a particular fracture network include detailed well drillers' reports or conducting new well tests.
- The proportion of fractures that belong to a particular fracture set needs to be determined.

# Monitoring Estrogenic Hormones Undesired Fish Contraceptives, and

## Basic Information

<b>Title:</b>	Monitoring Estrogenic Hormones Undesired Fish Contraceptives, and
<b>Project Number:</b>	2005MA47B
<b>Start Date:</b>	3/1/2005
<b>End Date:</b>	2/28/2007
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	3rd Massachusetts
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Water Quality, Toxic Substances, Geochemical Processes
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Yuegang Zuo

## Publication

1. Zuo Yuegang; Yuejuan Lin, 2007, Solvent effects on the silylation-gas chromatography-mass spectrometric determination of natural and synthetic estrogenic steroid hormones, *Chemosphere*, (in press)
2. (2) Zuo Yuegang; Kai Zhang, Yuejuan Lin, 2007, Microwave-accelerated derivatization for the simultaneous gas chromatography-mass spectrometric analysis of natural and synthetic estrogenic steroid hormones. *J. Chromatography A* 1148, 211-218.
3. Zuo Yuegang; Kai Zhang, Yiwei Deng, 2006, Occurrence and photochemical degradation of 17 $\beta$ -ethinylestradiol in Acushnet river estuary. *Chemosphere* 63, 1583-1590.
4. Zuo Yuegang; Kai Zhang, 2005, Discussion: Suitability of N,O-bis(trimethylsilyl)trifluoroacetamide as derivatization reagent for the determination of the estrogens estrone and 17 $\beta$ -ethinylestradiol by gas chromatography-mass spectrometry. *J. of Chromatogr. A* 1095, 201-202.
5. Zhang Kai; Yuegang Zuo, 2005, Pitfalls and solution for simultaneous determination of estrone and 17 $\beta$ -ethinylestradiol by gas chromatography mass spectrometry after derivatization with N,O-bis(trimethylsilyl)trifluoroacetamide. *Anal. Chim. Acta* 554, 190-196.
6. Lin Yuejuan; Yuegang Zuo, 2007, Ion-pair HPLC Determination of estrogens and their Conjugates in Water Samples. 7th Csaba Horvath Medal Award Symposium, April 19-20, 2007, Hartford Convention Center, Hartford, Connecticut.
7. Zuo Yuegang, 2007, Estrogenic Steroid Hormones in Aquatic Ecosystems, Their Effects on Fish Population and Their Environmental Fate. The Department of Chemistry Seminar at Kansas State University, Feb. 1, 2007 (invited).
8. Lin Yuejuan; Yuegang Zuo, 2007, Determination of estrogens and their Conjugates by Ion-pair HPLC. University of Massachusetts Dartmouth Thirteenth Annual Sigma Xi Research Exhibit, April 24-25, 2007, North Dartmouth, MA.
9. Wang Chengjun; Jiping Zhou, Vanessa Ruelos, Amita Sachdeva, Yuegang Zuo, 2007, Simultaneous Determination of Creatinine and Uric Acid in Human Urine Samples by High Performance Liquid Chromatography. University of Massachusetts Dartmouth Thirteenth Annual Sigma Xi Research Exhibit, April 24-25, 2007, North Dartmouth, MA
10. Zuo Yuegang, 2007, Incorporation of authentic chemical separation research projects into analytical chemistry curriculum. 233rd ACS National Meeting, Chicago, IL, March 25-29, 2007.
11. Zhang Kai; Yuegang Zuo, 2006, Occurrence, Microbial and Photochemical Degradation of Endocrine Disrupting Estrogens in Surface Waters. University of Massachusetts Lowell, Dept. of Chemistry Seminar Series, Oct. 18, 2007.
12. Zuo Yuegang, 2006, Bioeffects and fate of estrogenic steroid hormones in fresh and coastal marine waters. International Workshop on water contaminants and Health Effects. Edmonton, Alberta, Canada, July 5-9, 2006 (invited).
13. Zuo Yuegang, 2006, Improved gas chromatography-mass spectrometry determination of estrogenic hormone steroids in aquatic environments. 37th ACS Central Regional Meeting, May 16-20, 2006. Frankenmuth, MI.
14. Wu Jingping; Yuegang Zuo, 2006, GC determination of phthalate esters and their photodegradation in natural water. University of Massachusetts Dartmouth Twelfth Annual Sigma Xi Research Exhibit, April 25-26, 2006, North Dartmouth, MA.
15. Zhang Kai ; Yuegang Zuo, 2006, Pitfalls and solution for simultaneous determination of estrone and

17alpha-ethinyestradiol by GC-MS after derivatization with N.O-Bis(trimethylsilyl) trifluoroacetamide. University of Massachusetts Dartmouth Twelfth Annual Sigma Xi Research Exhibit, April 25-26, 2006, North Dartmouth, MA

16. Lin Yuejuan; Yuegang Zuo, 2006, Analysis of free-form estrogen steroid hormones and their conjugates in urine and natural water using HPLC. University of Massachusetts Dartmouth Twelfth Annual Sigma Xi Research Exhibit, April 25-26, 2006, North Dartmouth, MA.
17. Zuo Yuegang; Kai Zhang, 2006 Pitfalls and solution for simultaneous determination of estrogenic steroids using silylation-gas chromatography-mass spectrometry. The 231st ACS National Meeting and Exposition, Atlanta, GA March 26-30, 2006.

The occurrence of estrogenic compounds in aquatic environment has become of increasing concern during the past decade due to their endocrine disruption potential. Among these estrogenic chemicals, a group of synthetic steroids, such as 17 $\alpha$ -ethinylestradiol, is of particular concern. This concern arises in part from the increasing use of birth-control pills, formulated with exogenous estrogenic and progestational chemicals that show high physiological activity at very low concentrations and have been associated to certain alarming effects on reproduction and developmental processes such as feminization, decreased fertility or hermaphroditism. The Buzzards Bay receives stormwater runoff, effluents from wastewater treatment facility of New Bedford, Fairhaven, Fall River and other surrounded towns. This leads to direct input of many different classes of pollutants, including endocrine-disrupting estrogenic hormones, through the sewage effluents and industrial wastewater. The combination of these estrogenic compounds and other pollutants can adversely affect plankton, and fish, and could be related to the declines in lobster abundance in Buzzards Bay. The objectives of this research project are (1) to develop an SPE-GC-MS analytical method for the separation and quantitation of estrogenic hormones: estrone, 17 $\beta$ -estradiol, 17 $\alpha$ -ethinylestradiol and mestranol; (2) to employ the analytical methods developed in this project to monitor estrogenic hormones: estrone, 17 $\beta$ -estradiol, 17 $\alpha$ -ethinylestradiol and mestranol in New Bedford Harbor and Buzzards Bay Water; (3) to assess the microbial and photochemical fate of estrogenic hormones in the Buzzards Bay; (4) To train graduate and undergraduate students to use the techniques developed in this project to monitor and protect our aquatic environment.

In the first stage of this project, our research had been focused on developing a Solid-Phase Extraction (SPE) GC-MS analytical method for the separation and quantitation of estrogenic hormones and other endocrine disrupting compounds. These included developing a new silylation solution to prevent the formation of undesired multiple derivatization products and conversion of trimethylsilyl derivatives of EE2 formed to their respective E1 derivatives reported in previous studies, and integrating an SPE method into GC-MS analysis, as well as the effects of solvent, temperature, and reaction time on the derivatization of EE2. To shorten the derivatization time of estrogenic steroids, we have developed a microwave-accelerated derivatization method for the simultaneous gas chromatography-mass spectrometric analysis of natural and synthetic estrogenic steroid hormones. We have also validated an HPLC method for the simultaneous determination of free and conjugate steroid hormones.

With the newly developed analytical techniques, we have determined the estrogenic hormones in seawater around Acushnet river estuary in Buzzards Bay and examined their possible sources, effluents from wastewater treatment plants. We have also carried out some preliminary studies on the microbial and photochemical degradation of estrogenic steroid hormones in Buzzards Bay seawater.

We presented our research results obtained in the project in professional conferences, published five papers in peer-reviewed international scientific journals, and are preparing two more manuscripts for publication soon.

For the educational component, I supervised five graduate students (one supported by this grant and the others by other UMass Dartmouth funds as the match) under this environmental estrogenic steroid research project. One of them, Kai Zhang, has completed his Ph.D. dissertation defense. Another, Yuejuan Lin, is planning to have

her M.S. thesis defense in August, 2007. The third student, Chengjun Wang, is working on his dissertation research.

## **9. Project Findings:**

1. The determination of estrogenic steroids, particularly in natural water systems, have been an analytic challenge for chemists due to the extremely low concentration of estrogenic steroids and interference from the sample matrices. Many immunoassay, gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), liquid chromatography (LC), and liquid chromatography-mass spectrometry (LC-MS) techniques have been developed for the determination of estrogenic steroid hormones in aquatic environments. GC-MS has been a preferred approach for simultaneous analysis of both synthetic and natural estrogenic steroids because of its superior separation and identification capabilities. In order to employ high-resolution GC for the analysis of estrogenic steroids, derivatization is required to increase analyte volatility and thermal stability and thus improve chromatographic separation. Many reagents are available for this purpose. Trimethylsilyl (TMS) derivatives are probably the most widely employed. The combination of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) + trimethylchlorosilane (TMCS) is amongst the most popular silylating reagents used for the identification and quantification of estrogenic steroid hormones in water samples. However, several research groups reported on the formation of different derivatization products of EE2 with this silylating reagent [Shareef et al., 2004; Zuo and Zhang, 2005, Zhang and Zuo, 2005]. And thus suggested that derivatization with BSTFA + TMCS might not be suitable for the determination of EE2 by GC-MS under the previously reported conditions. In this project, we have developed a new silylation mixture (BSTFA:TMCS:pyridine = 49.5:05:50 (v/v/v)), overcome these pitfalls and generated a single product of di-TMS derivative of EE2 (Zuo and Zhang, 2005; Zhang and Zuo, 2005). We have also established a microwave-accelerated derivatization method for the simultaneous gas chromatography-mass spectrometric analysis of natural and synthetic estrogenic steroid hormones (Zuo et al., 2007). We have also validated an HPLC method for the simultaneous determination of free and conjugate steroid hormones (Lin et al. 2006).

2. We have successfully applied our developed analytical procedure in the simultaneous determination of both natural and synthetic estrogenic steroids (estrone and 17 $\alpha$ -ethynylestradiol) in Acushnet River estuarine seawater (Zuo et al., 2004, 2006). Our results have shown that the concentration of three common estrogenic hormones, 17 $\alpha$ -ethinylestradiol, estrone and 17 $\beta$ -estradiol, could be over 4.7, 1.2 and 0.83 ng/L, respectively, during the summer, which can certainly cause fish feminization in the Bay and may responsible for the significant decline in lobster population in Buzzards Bay. To further identify the sources of estrogenic hormones in the Bay, we have examined both influents and effluents of New Bedford Wastewater Treatment Plant with the GC-MS and HPLC methods developed in this projects and found significant amount of conjugate and trace free steroid hormones.

3. Our preliminary study has shown that EE2 can undergo a rapid photodegradation in estuarine seawater under natural sunlight irradiation, with a half-life of less than 1.5 days in spring sunny days. Our studies have also shown that natural estrogenic compound E2 can be oxidized to E1 by microorganisms in natural river water

with half-lives of 0.2-9 days at 20 °C, and E1 is then further degraded at rates consistent with previous investigations. Compared to E2, synthetic EE2 is much more resistant to biodegradation in natural water. Although EE2 is relatively resistant to microbial degradation, EE2, like other estrogenic steroids, contains a phenolic functional group, which is susceptible to photodegradation. To study the photochemical degradation of EE2 in seawater, EE2 was dissolved into seawater collected from Buzzards Bay and Acushnet River Estuary and irradiated under natural sunlight or simulated solar source in cylindrical quartz tubes (20 cm long x 1.4 cm i.d.). The results obtained indicate that the photochemical transformation represents a major fate of estrogenic steroids in natural surface water.

4. Five graduate students have trained in this project to use the techniques developed to monitor and protect our aquatic environment from estrogenic pollutants.

# Perchlorate Reduction in Groundwater Using Elemental Sulfur

## Basic Information

<b>Title:</b>	Perchlorate Reduction in Groundwater Using Elemental Sulfur
<b>Project Number:</b>	2006MA58B
<b>Start Date:</b>	3/1/2006
<b>End Date:</b>	2/28/2007
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	1st
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Nitrate Contamination, Toxic Substances, Water Quality
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Ashish K. Sahu, Sarina Ergas

## **Publication**

1. Conneely T., A.K. Sahu, S.J Ergas, and K. Nüsslein, Investigation of Sulfur Dependent Perchlorate-Reducing Consortia, (In preparation for Applied and Environmental Microbiology).
2. Sahu, A.K; S.J. Ergas, Perchlorate Reduction Using Elemental Sulfur, In preparation for Environmental Science and Technology.

## 1. Problem and Research Objectives

Perchlorate ( $\text{ClO}_4^-$ ) release in groundwater has affected drinking water to over 15 million people in the south west of the United States and groundwater contamination has been recorded in over 40 US states (Urbansky, 2000, MADEP, 2006). Perchlorate is used in the manufacture of missiles, fireworks, leather industries (US Environmental Protection Agency (USEPA), 2005). Trace levels of  $\text{ClO}_4^-$  has known to affect uptake of thyroid hormone in the thyroid glands and other health effects have also been recorded (Zoeller, 2005). Since  $\text{ClO}_4^-$  is an extremely stable and soluble anion in water, it readily transports with water and is difficult to remediate using conventional treatment technologies. Present full scale technologies for  $\text{ClO}_4^-$  remediation include Ion Exchange (IX), Granular Activated Carbon (GAC) adsorption, and biological reduction (USEPA, 2005).

The USEPA has addressed  $\text{ClO}_4^-$  as an emerging contaminant but no national standards have been established (USEPA, 2002). The Commonwealth of Massachusetts has adopted a perchlorate standard of 2  $\mu\text{g/L}$   $\text{ClO}_4^-$  (MADEP, 2006) and other states (eg: CA, TX) have set an advisory levels of 4-18  $\mu\text{g/L}$   $\text{ClO}_4^-$  (USEPA, 2005).

This study investigated biological  $\text{ClO}_4^-$  reduction using elemental sulfur as an electron donor by sulfur oxidizing bacteria. Elemental sulfur is a waste byproduct of oil industries, is inexpensive and serves as an excellent packing material both in bioreactors and for *in situ* groundwater treatment in permeable reactive barriers (PRBs).

The objectives of this research were to:

1. Quantify  $\text{ClO}_4^-$  reduction using batch cultures.
2. Operate a series of bench scale packed bed reactors using realistic  $\text{ClO}_4^-$  concentrations.
3. Reduce the empty bed contact times (EBCT) and investigate the reactors for effects of recirculation rates, presence of dissolved oxygen.
4. Investigate  $\text{ClO}_4^-$  reduction by sulfur oxidizing bacteria in the presence of co-contaminants such as  $\text{NO}_3^-$ -N and TCE.

## 2. Methodology

Batch cultures for  $\text{ClO}_4^-$  reduction were enriched from denitrification zone of a wastewater treatment plant containing elemental sulfur (4 mm) as an electron donor, oyster shells as an alkalinity source and 5 mg/L  $\text{ClO}_4^-$  with trace elements. Synthetic feed was prepared from a groundwater collected from a nearby farm. On acclimatization, these enriched cultures were inoculated in one liter acrylic column bench scale reactors. The reactors contained elemental sulfur and oyster shells in the volume ratio of 3:1. The reactors were designed with side ports at intervals of 10 cm to obtain sample for concentration profiles. The synthetic feed water to the reactor was sparged with nitrogen to maintain anoxic conditions in the bioreactor, this was quantified using Resazurin, a chemical that changes color in the presence of oxygen.

Perchlorate was monitored using the standard USEPA 314.0 method using an Ion Chromatograph with detection limits of 4  $\mu\text{g/L}$   $\text{ClO}_4^-$  (USEPA, 1999). pH and sulfate were also monitored on a periodic basis.

### 3. Principal Findings and Significance

#### Batch cultures

Enriched batch cultures showed that 5 mg/L  $\text{ClO}_4^-$  could be reduced to less than 0.5 mg/L  $\text{ClO}_4^-$  in 20 days; this trend was observed after repeated spiking with fresh perchlorate solution for more than one year. These enriched cultures were termed SUPeRB (Sulfur Utilizing Perchlorate Reducing Bacteria) by the research team. Perchlorate reduction by SUPeRB was investigated using other electron donors (acetate, elemental iron, ferrous iron, hydrogen). In addition, the effect of salinity, aerobic conditions, and inoculum source on perchlorate reduction was investigated. The results showed that SUPeRB could use other electron donors including acetate and ferrous iron for  $\text{ClO}_4^-$  reduction but could not reduce  $\text{ClO}_4^-$  using  $\text{H}_2$  and elemental iron as sole electron donors. SUPeRB also showed the potential to reduce high levels of  $\text{ClO}_4^-$  (5-20 mg/L) at salt concentrations in the range of 30-45 g/L. The cultures did not reduce  $\text{ClO}_4^-$  under aerobic conditions. The inoculum source (mixed liquor from the denitrification zone of a wastewater treatment plant) was re-tested for and showed reproducible results. Autoclaved controls showed no  $\text{ClO}_4^-$  reduction.

To further investigate the characteristics of SUPeRB, bacterial community analysis using PCR and isolation of a sulfur oxidizing perchlorate reducing strain was accomplished in collaboration with Dr. Klaus Nüsslein and Teresa Conneely of the Department of Microbiology. The isolation of SUPeRB showed the bacteria belongs to the *Delftia sp.* Further characterization of this isolate is ongoing.

The batch culture results showed that SUPeRB can be enriched from a wastewater seed using elemental sulfur as an electron donor and perchlorate as an electron acceptor. These bacteria are autotrophs and are slow growing and hence produce very little sludge. There is no addition of carbon substrate needed since they use inorganic carbon as their carbon source. The salinity results show that SUPeRB can be used for treatment of IX brines which have high  $\text{ClO}_4^-$  concentrations. The brine concentrations chosen in this study are similar to IX brines used commercially. IX technology has become a cost effective method for treatment of perchlorate contaminated drinking water since the process is relatively inexpensive, can be done in a smaller reactor volume than biological process, (Martin *et al.*, 2006) and there are no biological residues carried over to the product water. The problem arises when these resins are regenerated with brine solution, as these brines cannot be disposed of in wastewater treatment plants as high brines lead to upsets in wastewater operations, require higher doses of coagulant for settling and the effluent contains high brine which cannot be leached into the open fields. SUPeRB cultures can be inoculated in a hybrid system with IX and a packed bed reactor to treat these brines.

## Bioreactor Performance

SUPeRB cultures were inoculated in one liter continuous bench scale bioreactors operated in upflow mode. At high concentrations (5-8 mg/L  $\text{ClO}_4^-$ ) and with intermittent recirculation,  $\text{ClO}_4^-$  was reduced to less than 0.5 mg/L. EBCT was reduced from 100 hours to 13 hours over a period of 120 days. Average  $\text{ClO}_4^-$  removal efficiency was 88%. The contents of this reactor were divided to form two new bioreactors to treat  $\text{ClO}_4^-$  concentrations in the range of 80-100  $\mu\text{g/L}$ . Reactor performance was investigated at varying EBCT, recirculation rates and with the presence of the co-contaminant,  $\text{NO}_3^-$ . EBCT was reduced from 30 hours to 8 hours with an average removal efficiency of 96%. Reactor operation with little or no recirculation showed the best  $\text{ClO}_4^-$  removal than at higher recirculation ratios. The presence of  $\text{NO}_3^-$ -N did not inhibit  $\text{ClO}_4^-$  reduction. Concentration profiles showed that both  $\text{ClO}_4^-$  and  $\text{NO}_3^-$ -N reduction was occurring in the first 10 cm of the reactor. The presence of dissolved oxygen in the feed water did not inhibit  $\text{ClO}_4^-$  reduction or bioreactor removal efficiency.

Perchlorate can be treated in *ex-situ* processes such as packed bed bioreactors with little recirculation. A little recirculation may be needed during the initial stages of operation of the reactor to improve mass transfer of  $\text{ClO}_4^-$  to the biofilm. Higher recirculation rates could scour off the biofilm which leads to decrease in  $\text{ClO}_4^-$  removal efficiencies as these bacteria take a longer time to grow. High  $\text{ClO}_4^-$  concentrations (5-10 mg/L) have been recorded in military ranges while low ranges of  $\text{ClO}_4^-$  (80-100  $\mu\text{g/L}$ ) have been found at many local and industrial sites (USEPA, 2005). These ranges of  $\text{ClO}_4^-$  concentrations could be reduced by SUPeRB at EBCTs ranging from 8-13 hours. Both  $\text{ClO}_4^-$  and  $\text{NO}_3^-$ -N have been found at many military sites as co-contaminants (Clausen, 2006). This is one of few studies to show both  $\text{ClO}_4^-$  and  $\text{NO}_3^-$ -N can be reduced simultaneously.

Based on the above results and findings,  $\text{ClO}_4^-$  reduction using elemental sulfur as an electron donor is a promising technology for  $\text{ClO}_4^-$  treatment in groundwater. Further tests will be required at pilot scale to prove its treatment potential and commercial aspect of the technology. The elemental sulfur pellets can also be used as a packing material for permeable reactive barriers (PRBs). Though this project did not investigate any PRBs, the researchers envision the use of SUPeRB in PRB for *in situ* groundwater remediation.

# USING HYDROMORPHOLOGICAL SIGNATURES TO DETERMINE FLOW RELATED HABITAT THRESHOLDS FOR INSTREAM COMMUNITIES

## Basic Information

<b>Title:</b>	USING HYDROMORPHOLOGICAL SIGNATURES TO DETERMINE FLOW RELATED HABITAT THRESHOLDS FOR INSTREAM COMMUNITIES
<b>Project Number:</b>	2006MA60B
<b>Start Date:</b>	3/1/2006
<b>End Date:</b>	2/29/2008
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	1st
<b>Research Category:</b>	Biological Sciences
<b>Focus Category:</b>	Hydrology, Ecology, Management and Planning
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Scott D Jackson, Christina Cianfrani, Piotr Parasiewicz

**Publication**

## INTRODUCTION

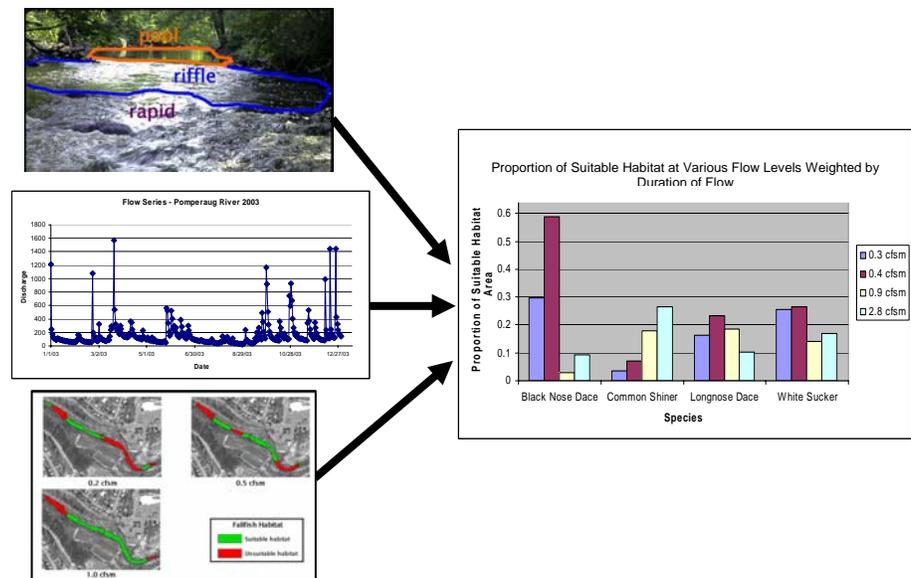
Field measurements from the existing database of streams in the northeastern United States were used to evaluate the feasibility of using hydromorphological (HMU) signatures in determining fish communities as part of an overall methodology for quantifying instream flow requirements and habitat thresholds. The results of this research may lay the foundation for using HMU signatures to identify thresholds of change in aquatic communities as a result of changes in hydrologic regime due to water withdrawals/alterations. These thresholds could then begin to provide the scientific basis for determining acceptable limits of hydrologic change within river systems to protect ecological integrity.

Our project builds upon a newly developed French method (Le Coarer, 2005) of using hydraulic (velocity and depth) distribution score-cards, called “Hydrosignatures,” as a habitat metric. We apply this concept to represent the distribution of HMUs in the stream for different flow conditions (e.g. high, medium, low). We then attempt to use these HMUs to create templates that can be used with fish habitat models in an attempt to predict the probable composition of fish communities associated with these patterns. This project update presents the preliminary results from the first year of the study (Phase I), and the future directions of the research for year 2 (Phase II).

## PHASE I (Year 1)

The purpose of Phase I of this project was to use existing data to show proof of concept of a method to: 1) identify and map HMU signatures for river sections under different flow conditions; and 2) relate the HMU signatures to physical habitat. To accomplish this, data including habitat and HMU mapping, flow-duration curves, and fish habitat models (generated using MesoHABSIM) were used to compute the relative area available for habitat for individual species under varying flow conditions (high, medium, and low summer flows) (Figure 1). This was completed for both existing summer flow durations as well as modeled pristine flow conditions.

Figure 1. Basic methodology to create habitat probability models under various flow conditions.



*Hydraulic and Fish Data*

As part of previous projects, HMUs were mapped in the field for 10 rivers in Connecticut, Massachusetts, New Hampshire, and New York. Each HMU was mapped using a personal digital assistant (PDA) and ArcPad software (ESRI, Redlands, CA). Aerial photographs uploaded to the PDA were used to help identify river locations. Eleven HMU categories were used when mapping with definitions taken from Parasiewicz (2001): 1) backwater; 2) pool; 3) plungepool; 4) glide; 5) run; 6) fastrun; 7) rapids; 8) sidearm; 9) cascade; 10) ruffle; and 11) riffle. Within each HMU, random velocity and depth measurements were taken.

Fish were collected using a backpack electro-shocker and a grid technique described by Bain et al. (1985). Sampling occurred in representative HMUs at each site on each river to ensure each type of habitat was appropriately represented. Fish were measured and identified to species.

Considerable effort was spent in year 1 of the project mining data from existing projects. Specific river sections were chosen according to project criteria. Data was then formatted for compatibility.

*Habitat Suitability*

Sites on the Quinebaug and Pomperaug Rivers were used to test the ability of the technique to detect differences in suitable habitat availability based on changes in flow regimes. Using four key species (as defined by the target fish community identified for the Quinebaug River), changes in habitat availability were modeled for four summer flow levels under two flow regimes, measured and 'pristine' (Figure 2). The regimes differed in percent duration of low, medium, and high flows.

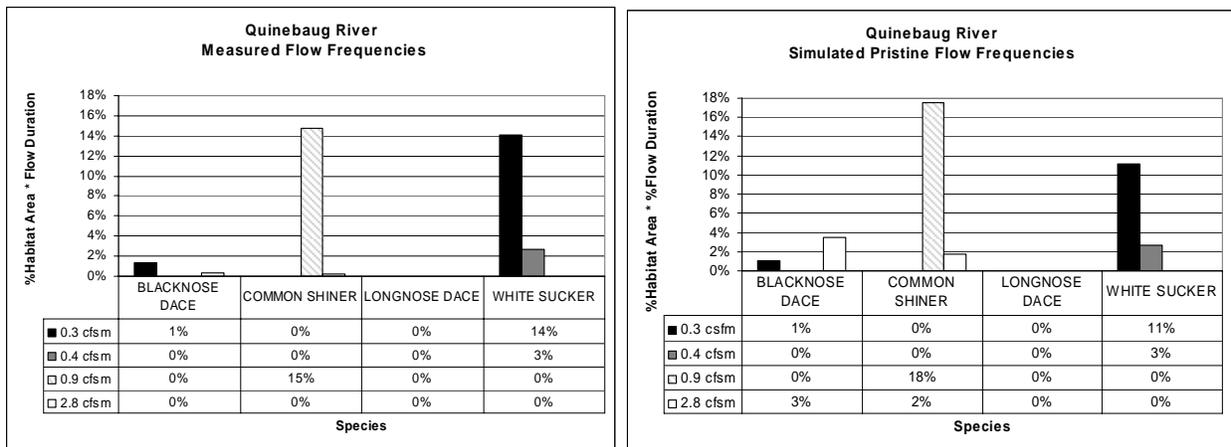


Figure 2. Available habitat (as percentage of total wetted width) for the Quinebaug River under two flow regimes weighted for duration during the summer.

The amount of available habitat was not sensitive to significant changes in flow regimes using this technique. Further analysis is needed to determine which component(s) may need adjustment in order to detect the differences. For example, research as part of another project has shown the choice of fish habitat model can have a significant impact on overall results. This study compared the predictive capability of models developed using: 1) three rivers individually (each

with differing levels of impairment); 2) a regional model using significant parameters from of all three rivers; and 3) a global model using all field collected data for all rivers. Such considerations will be explored as the model is refined.

#### *HMU Classification*

We are exploring the possibility of reducing the number of HMUs through cluster analysis. We are also analyzing trends among the high, medium, and low flow data of the HMUs used in the field mapping protocol. We aim to develop a standardized characterization, or template, of depth and velocity for each HMU to use in fish habitat models. If templates can be developed based on HMUs, field work effort could be reduced significantly (i.e. one would only have to map the HMU and take a minimal number of depth and velocity measurements). More than one potential “template” may result if distributions vary for different flow levels.

Preliminary k-means hierarchical cluster analysis (McGarigal, et al, 2000) was used to reduce the number of HMUs. The analysis using depth and velocity measurements showed a reduction was possible in the number of HMUs from 11 to 8. This analysis resulted in the following HMUs: 1) backwater; 2) pool; 3) glide/run; 4) plungepool; 5) sidearm; 6) cascade; 7) ruffle/riffle; and 8) fastrun/rapids

For the second part of this analysis, histograms for the depth and velocity measurements for each HMU for each flow (high, medium, low) were created. Bins were predetermined as per NEIHP protocol with bin size for depth equal to 25 cm and for velocity equal to 15 cm/s. The histograms were standardized and plotted to inspect for visual trends (Figure 3). Visual inspection was followed with Kolmogorov-Smirnov tests (Davis, 2002) in a pairwise fashion for all combinations of the three flow data sets within each HMU (i.e. low vs medium, medium vs high and high vs low). This test was used to determine which data sets could be combined. This was repeated for both depth and velocity data. Preliminary results show that few data sets can be combined and that templates for each HMU for each flow will most likely be necessary.

#### PHASE II (Year 2)

In the second year of the project, we will continue to evaluate the modeling approach outlined in Phase I. We will also build on Phase II work by applying the MesoHABSIM habitat model to the new, reduced set of HMUs. Models previously developed using forward stepwise logistic regression applied to fish collection data for five rivers in New England will be applied to predict probability of presence and abundance of fish species using the simplified HMU set. We will also replace the actual depth and velocity data recorded at the time of fish sampling with the determined histogram distribution (template) for the appropriate HMU. The results will be compared with original MesoHABSIM models (using the full HMU set and measured velocity and depth). If the fish community shows no predictable change between the detailed measured depth and velocity data and the replacement template, we will assume that these characteristic distributions can be used for these HMUs in future modeling efforts. The final step for this project will be to use the models to predict the thresholds of change in the fish communities as a function of change in the hydraulic variables.

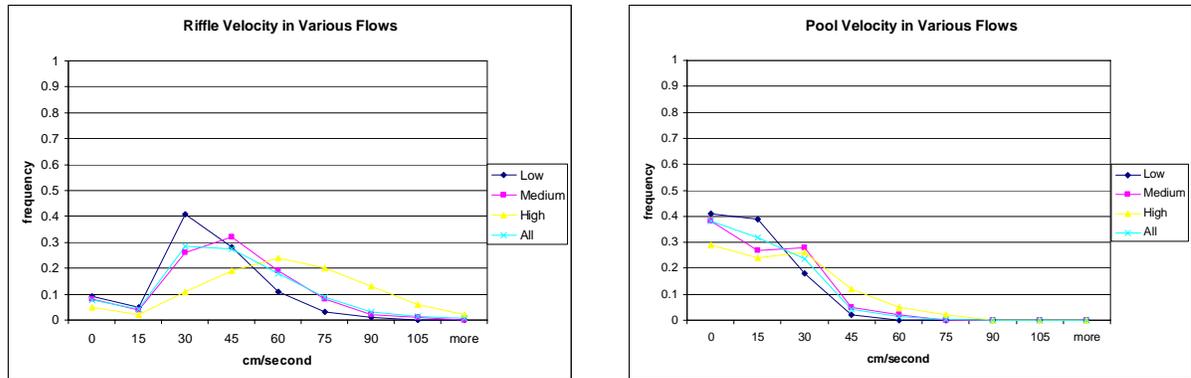


Figure 3. Frequency plots of riffle and pool velocity distributions for high, medium, low and average flows.

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# **Information Transfer Program**

## Student Support

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	5	0	0	0	5
Masters	7	0	0	0	7
Ph.D.	3	1	0	0	4
Post-Doc.	0	0	0	0	0
<b>Total</b>	15	1	0	0	16

## Notable Awards and Achievements

The project "Perchlorate Reduction in Groundwater Using Elemental Sulfur", by Doctoral Candidate Ashish K Sahu and his advisor Dr. Sarina J. Ergas. at the Civil and Environmental Engineering Department of the University of Massachusetts, Amherst, resulted in the following achievements. 1) Ashish Sahu won numerous prizes for this research at various conferences, these are listed below.

First prize for student paper competition award for A Novel Bioreactor for Perchlorate Reduction Using Elemental Sulfur, (2006) at the Air and Waste Management Association, November 3, Westborough, MA. Adventus Americas Award for Best Student Platform Presentation for Perchlorate Reduction in a Packed Bed Bioreactor Using Elemental Sulfur, (2006) at the 22nd Annual International Conference on Soils, Sediments and Water (UMassSoils), October 16-19, Amherst, MA. Student paper competition award for Biological Reduction of Perchlorate Contaminated Waters Using Elemental Sulfur (2006) at the International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Battelle, May 22-25, Monterey, CA.

To commercialize the project and to gather industrial collaboration, a protection of intellectual property (patent) was filed with help of Commercial Ventures and Intellectual Property (CVIP) at UMass-Dartmouth. The patent is still pending.

Sengupta, S., Ergas, S.J., Nüsslein, K. and Sahu, A.K. (2006) Process for autotrophic perchlorate reduction using elemental sulfur and mollusk shells US Patent Pending Application No: 11/645,152.

Involving high school students for internships gave this project a great learning experience and also media attention. Teresa Conneely and Thach Chu made a presentation on interesting science at WGBY in the program Making It Here Teen Style. Also, Thach Chu applied for the Junior Stockholm Water Prize and presented a poster at the Institute of Cellular Engineering while working on this research.

## **Publications from Prior Projects**

1. 2003MA8B ("Copper Removal by Biofilms") - Articles in Refereed Scientific Journals - Zhang, X., K. Brussee, and J. Rooney-Varga, 2006, Impacts of Chemical Stress Induced by Copper: Examination of a Biofilm System. *Water Science and Technology* 54 (9), 191-199.
2. 2003MA9B ("Potential Movement of Pesticides Related to Dissolved Organic Matter from Organic Fertilizer Application on Turf") - Dissertations - Heymann, Karen, 2007, Characterization and Sorption Behavior of Dissolved Organic Matter from Fertilizers and their Environmental Impact on Turfgrass Soil Leachates, MS Thesis, Plant, Soil, and Insect Sciences, University of Massachusetts, Amherst, MA, 119pp.