MA Water Resources Research Center

Annual Report FY 2006

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This report is available on line:
http://www.umass.edu/tei/wrrc/WRRC2004/WRRCpublications.html

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Introduction

This report covers the period March 1, 2006 to June 30, 2007[1], 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.

The fourth annual water resources research conference, *Sustainable Waters in a Changing World: Research to Practice*, was held at UMass on April 9, 2007.

[1] The USGS reporting year covers March 1 to February 28, while the University of Massachusetts and the Commonwealth of Massachusetts fiscal years run from July 1 to June 30. Projects funded by the State are reported for the period July 1 2006 - June 30, 2007.

Research Program

Four research projects were conducted this fiscal year: one research project funded through the USGS 104B program continued for a second year and is slated to complete in December 2007; another 104B funded two-year project was initiated this year, as well as a new one year student project. Finally, one project funded through the 104G Program continued its third year of research; Progress reports for all four projects follow:

1. A Regional Approach to Conceptualizing Fractured-Rock Aquifer Systems for Groundwater Management (USGS 2003MA19G)

Principal Investigators: Stephen B. Mabee, State Geologist, UMass Amherst and Michele Cooke, Professor, UMass Amherst Geosciences
Start Date: 9/30/2004
End Date: 9/29/2007 (extension requested through May 2008)
Research Category: Groundwater Flow
Focus Category: Water Supply, Groundwater, Water Quantity
Descriptors: Fracture Characterization, Domain Analysis, Well Yield, Fractured Rock Aquifers, Groundwater Availability, Groundwater Mapping, Borehole Geophysics

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 televiewer 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 (e.g., overburden type and thickness); and
5. Conceptual Model - preparation of a qualitative conceptual model of ground water flow behavior in each litho group category.

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.

Students Supported:
1 PhD student in Geosciences Department at University of Massachusetts.

Publications and Presentations:

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.

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.

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.

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.

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.

Manda, A.K., 2005, Characterizing the fractured bedrock aquifer of the Nashoba Terrane, Massachusetts, Mass. Water Resources Research Center/UMass Extension 3rd Annual Conference, Research to Practice: Science for Sustainable Water Resources, Amherst (Poster).

2. Monitoring Estrogenic Hormones – Undesired Fish Contraceptives, and Investigating Their Sources, Transportation and Fate in Buzzards Bay, Massachusetts (USGS 2005MA47B)

Principal Investigator: Yuegang Zuo, Ph.D., Associate Professor, Department of Chemistry and Biochemistry, Graduate School of Marine Sciences and Technology University of Massachusetts Dartmouth
Start Date: February 1, 2005
End Date: February 28, 2007
Focus Categories: Water Quality, Toxic Substances, and Geochemical Processes
Keywords: Estrogenic Hormones, mestranol, 17α-ethinylestradiol, estrone, 17beta-estranol, Buzzards Bay, Natural Water, Microbial Degradation, Photodegradation

Problem Statement:
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 17α-ethinylestradiol, is of particular concern. This concern arises in part from the increasing use of birth-control pills, formulated with exogeneous 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.

Project Objectives:
1. Develop an SPE-GC-MS analytical method for the separation and quantitation of estrogenic hormones: estrone, 17β-estradiol, 17α-ethinylestradiol and mestranol;

2. Employ the analytical methods developed in this project to monitor estrogenic hormones: estrone, 17β-estradiol, 17α-ethinylestradiol and mestranol in New Bedford Harbor and Buzzards Bay Water;

3. Assess the microbial and photochemical fate of estrogenic hormones in Buzzards Bay;

4. Train graduate and undergraduate students to use the techniques developed in this project to monitor and protect our aquatic environment.

Work Completed:
1. 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.

2. 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.

3. 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.

4. We have also carried out some preliminary studies on the microbial and photochemical degradation of estrogenic steroid hormones in Buzzards Bay seawater.

Project Findings:
1. The determination of estrogenic steroids, particularly in natural water systems, has 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, 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. We have also established 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 (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 17α-ethynylestrodiol) in Acushnet River estuarine seawater. Our results have shown that the concentration of three common estrogenic hormones, 17α-ethinylestradiol, estrone and 17beta-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^{o}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.

Students Supported:
2 MS students in Chemistry at UMass Dartmouth
1 MS student in Marine Science and Chemistry at UMass Dartmouth
1 PhD student in Chemistry at UMass Dartmouth
1 PhD student in Marine Science and Chemistry at UMass Dartmouth

Publications and Presentations:
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).

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.

Zuo Yuegang; Kai Zhang, Yiwei Deng, 2006, Occurrence and photochemical degradation of 17α-ethinylestradiol in Acushnet river estuary. Chemosphere 63, 1583-1590.

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 α-ethinylestradiol by gas chromatography-mass spectrometry. J. of Chromatogr. A 1095, 201-202.

Zhang Kai; Yuegang Zuo, 2005, Pitfalls and solution for simultaneous determination of estrone and 17α-ethinylestradiol by gas chromatography – mass spectrometry after derivatization with N,O-bis(trimethylsilyl)trifluoroacetamide. Anal. Chim. Acta 554, 190-196.

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.

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).

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.

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.

Zuo Yuegang, 2007, Incorporation of authentic chemical separation research projects into analytical chemistry curriculum. 233rd ACS National Meeting, Chicago, IL, March 25-29, 2007.

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.

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).
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.

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.

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.

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.

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.

3. Using Hydromorphological Signatures to Determine Flow Related Habitat Thresholds for Instream Communities (USGS 2006MA60B)

Principal Investigators: Piotr Parasiewicz, Department of Natural Resources Conservation, University of Massachusetts Amherst; Christina M. Cianfrani, School of Natural Science, Hampshire College; and Scott Jackson, Department of Natural Resources Conservation, University of Massachusetts Amherst
Start Date: February 1, 2006
End Date: February 29, 2008
Focus Categories: Hydrology, Ecology, Management and Planning

Problem Statement:
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 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.

Project Objectives:
1. Identify and map HMU signatures for river sections under different flow conditions; and

2. Relate the HMU signatures to physical habitat

Project Findings:
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.

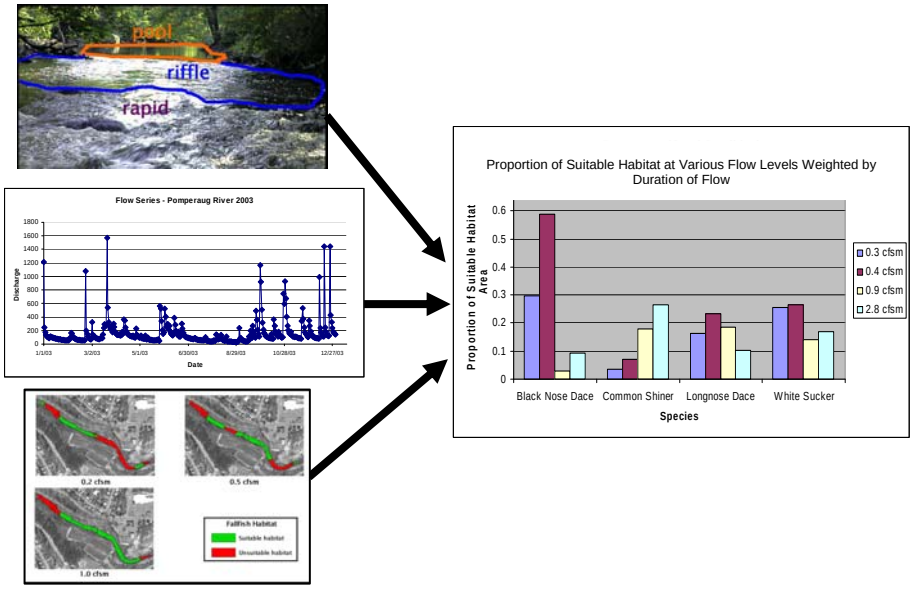


Figure 1. Basic methodology to create habitat probability models under various flow conditions.

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.

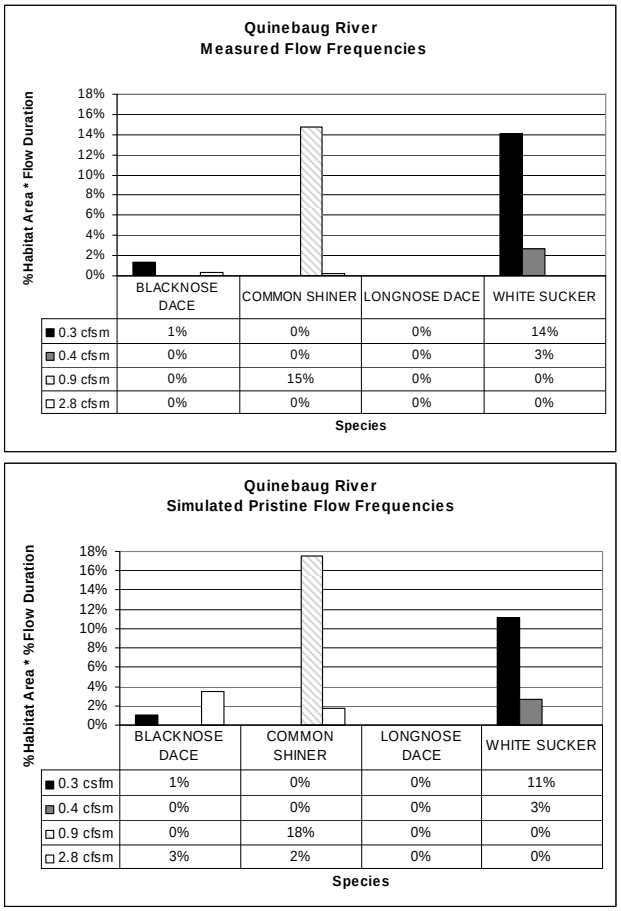


Figure 2. Available habitat (as percentage of total wetted width) for the Quinebaug River under two flow regimes weighted for duration during the summer.

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 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 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.

Students Supported:
2 BS students in Natural Resources Conservation at UMass Amherst
1 BS student in Environmental Science at Hampshire College
1 BS student in Freshwater Ecology and Outdoor Writing at Hampshire College
1 BS student in Water Science and Policy at Hampshire College
1 MS student in Natural Resources Conservation at UMass Amherst
3 MS students in Forestry and Environmental Engineering at Madrid Polytechnic, Spain

Publications and Presentations:
Cianfrani C., P. Parasiewicz, D. Walden, J. D. Legros and M. J Wirth, 2007, Using Hydromorphological Signatures to Determine Flow Related Habitat Thresholds for Instream Communities, Ecohydraulics conference, Christ Church, New Zealand.

Cianfrani, C., P. Parasiewicz, J. Legros, M. Wirth, 2007, *Using Hydromorphological Signatures to Determine Flow Related Habitat Thresholds for Instream Communities*. Poster presented by Christina M. Cianfrani, School of Natural Science, Hampshire College at the 4th Annual MA Water Resources Research Center Conference, *Sustainable Waters in a Changing World: Research to Practice*, April 9, 2007, University of Massachusetts, Amherst, Massachusetts.

4. Perchlorate Reduction in Groundwater Using Elemental Sulfur (USGS 2006MA58B)

Principal Investigators: Ashish K Sahu and Sarina J. Ergas. Civil and Environmental Engineering, University of Massachusetts Amherst

Start Date: February 1, 2006
End Date: February 28, 2007
Focus Categories: Nitrate Contamination, Toxic Substances, Water Quality

Problem Statement:

Perchlorate (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. Perchlorate is used in the manufacture of missiles, fireworks, leather industries. Trace levels of ClO_4^- has known to affect uptake of thyroid hormone in the thyroid glands and other health effects have also been recorded. Since 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 ClO_4^- remediation include Ion Exchange (IX), Granular Activated Carbon (GAC) adsorption, and biological reduction (USEPA, 2005).

The USEPA has addressed 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 µg/L ClO_4^- and other states (eg: CA, TX) have set an advisory levels of 4-18 µg/L ClO_4^-.

This study investigated biological 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).

Project Objectives:

1. Quantify ClO_4^- reduction using batch cultures.
2. Operate a series of bench scale packed bed reactors using realistic 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 ClO_4^- reduction by sulfur oxidizing bacteria in the presence of co-contaminants such as NO_3^--N and TCE.

Methodology:

Batch cultures for 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 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 µg/L ClO_4^-. pH and sulfate were also monitored on a periodic basis.

Principal Findings and Significance:

Batch cultures

Enriched batch cultures showed that 5 mg/L ClO_4^- could be reduced to less than 0.5 mg/L 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 ClO_4^- reduction but could not reduce ClO_4^- using H_2 and elemental iron as sole electron donors. SUPeRB also showed the potential to reduce high levels of ClO_4^- (5-20 mg/L) at salt concentrations in the range of 30-45 g/L. The cultures did not reduce 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 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 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 ClO_4^-) and with intermittent recirculation, 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 ClO_4^- removal efficiency was 88%. The contents of this reactor were divided to form two new bioreactors to treat ClO_4^- concentrations in the range of 80-100 □g/L. Reactor performance was investigated at varying EBCT, recirculation rates and with the

presence of the co-contaminant, 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 ClO_4^- removal than at higher recirculation ratios. The presence of NO_3^--N did not inhibit ClO_4^- reduction. Concentration profiles showed that both ClO_4^- and 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 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 ClO_4^- to the biofilm. Higher recirculation rates could scour off the biofilm which leads to decrease in ClO_4^- removal efficiencies as these bacteria take a longer time to grow. High ClO_4^- concentrations (5-10 mg/L) have been recorded in military ranges while low ranges of ClO_4^- (80-100 □g/L) have been found at many local and industrial sites (USEPA, 2005). These ranges of ClO_4^- concentrations could be reduced by SUPeRB at EBCTs ranging from 8-13 hours. Both ClO_4^- and NO_3^--N have been found at many military sites as co-contaminants (Clausen, 2006). This is one of few studies to show both ClO_4^- and NO_3^--N can be reduced simultaneously.

Based on the above results and findings, ClO_4^- reduction using elemental sulfur as an electron donor is a promising technology for 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.

Student Support:
1 PhD student in Civil and Environmental Engineering at UMass Amherst

Publications and Presentations:
Platform Sessions:

- Ergas, S.J., Sahu, A.K., Conneely, T., Nüsslein, K (2007) Perchlorate Remediation Using a Novel Autotrophic Perchlorate Reducing Microbial Community. Presented at University of Manchester, UK. May 25.
- Conneely, T., Sahu, A.K., Nüsslein, K. and Ergas, S.J. (2007) Perchlorate remediation using a novel autotrophic perchlorate reducing microbial community. Abstract accepted at the 23rd Annual International Conference on Soils, Sediments and Water, University of Massachusetts, Amherst, MA.
- Conneely, T., Sahu, A.K., Nüsslein, K. and Ergas, S.J. (2007) A Novel Bioreactor for Perchlorate Removal Using Elemental Sulfur as an Electron Donor, *Proceedings of the annual 4th Water Resources Research Conference* (WRRC), University of Massachusetts, Amherst, MA. April 9.
- Conneely, T., Sahu, A.K., Nüsslein, K. and Ergas, S.J. (2006) A Novel Bioreactor for Perchlorate Removal Using Elemental Sulfur as an Electron Donor, *Proceedings of the Water Quality Technology Conference and Exposition* (WQTC), Denver, CO. November 5-9.
- Sahu, A.K. and Ergas, S.J. (2006) Perchlorate Reduction in a Packed Bed Bioreactor Using Elemental Sulfur, *Proceedings of the 22nd Annual*

International Conference on Soils, Sediments and Water, University of Massachusetts, Amherst, MA. October 16-19.

- Sahu A. K. and Ergas, S.J. (2005) Autotrophic Biological Perchlorate Reduction Using Elemental Sulfur, *Proceedings of the Water Resources Research Conference* (WRRC), UMass, Amherst, MA. October 21.

Poster Sessions:

- Conneely, T., Sahu, A.K., Nüsslein, K. and Ergas, S.J. (2007) Investigation of a Novel Perchlorate Reducing Microbial Consortium. *Proceedings at the 107th General Meeting American Society of Microbiology*, Toronto, Canada. May 21-25.
- Sahu, A.K. and Ergas, S.J. (2006) Autotrophic Perchlorate Reduction Using Elemental Sulfur, *Proceedings of the Strategic Environmental Research and Development Program* (SERDP), Washington D.C. November 28-30.
- Chu, T., Mo, Y., Sahu, A.K. and Ergas S.J. (2006) Perchlorate Reduction by Sulfur Oxidizing Bacteria at High Salt Concentration, Poster at the First Annual Conference on Cellular Engineering, UMass, Amherst, MA. May 10.
- Rivera-Negrón, J.R. and S.J. Ergas (2006) Behavior of Autotrophic Perchlorate Reducing Bacteria and Analysis of Research Department Explosive [RDX] in Water by High Performance Liquid Chromatography, HPLC/UV, *Proc. American Institute of Chemical Engineers (AIChE) 2006 Annual Meeting*, San Francisco CA. Nov. 12-17.
- Sahu A.K. and Ergas, S.J. (2006) Batch Culture Studies on Biological Nitrate Reduction in Ion Exchange Brines by Hydrogenotrophic Bacteria, Poster at the First Annual Conference on Cellular Engineering, UMass, Amherst, MA. May 10.
- Sahu, A.K. and Ergas, S.J. (2006) Biological Reduction of Perchlorate Contaminated Waters Using Elemental Sulfur, *Proceedings of the 5th International Conference* on Remediation of Chlorinated and Recalcitrant Compounds, Battelle, Monterey, CA. May 22-25.

Publications in Preparation:

Sahu, A.K; S.J. Ergas, Perchlorate Reduction Using Elemental Sulfur, In preparation for Environmental Science and Technology.

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).

5. Acid Rain Monitoring Project (MADEP)

Principal Investigator: Marie-Françoise Walk, MA Water Resources Research Center, UMass Amherst
Start Date: July 1, 2006
End Date: June 30, 2007
Keywords: Acid Deposition, Surface Water Quality, Volunteer Monitoring

The Acid Rain Monitoring project continued for the 6th consecutive year after an 8 year hiatus preceded by 10 years of consecutive sampling. About 150 sites (mostly

streams) were sampled by volunteer collectors and tested for pH and alkalinity by volunteer labs. Of those, 26 long-term sites were analyzed for the full suite of major cations and anions. The data from 1983 to 1993 were previously analyzed for trends relevant to acid rain control. With sufficient new data on lakes and streams collected over the past 4 years, changes resulting from passage of state and federal clean air act revisions can be evaluated. These analyses are in process and should provide important evidence in the ongoing debate about clean air standards.

The more than 43,000 records of water chemistry for Massachusetts' lakes and streams, now covering 1983-2007, are posted on a web site in a searchable and downloadable form so that additional data analyses specific to the user may be conducted (http://umatei.resuo.ads.umass.edu/armproject1/).

The 1986 WRRC, *Acid Rain in Massachusetts*, is still being updated to include the past two decades, as well as the results of the trend analysis and their relevance to the current national debate on clean air act standards. Publication of the revised edition is planned for summer 2007.

An additional task was added to the project this year: The WRRC convened regional experts on acid deposition to a summit held at the University of Massachusetts in January 2007, in order to review current knowledge on acid deposition in Massachusetts, identify knowledge gaps, and recommend areas for future research to MADEP.

Students Supported:
1 BS student in Biology at UMass Amherst.

6. Blackstone River Assessment of Water Quality, Ecological Health, and Ecological Risk through Data Collection and Modeling – Phase I (UMass)

Principal Investigator: Paula Rees, Dept of Civil and Environmental Engineering, UMass Amherst
Start Date: July 1, 2006
End Date: June 30, 2007
Keywords: Surface Water Quality, Non-Point Source Pollution, QAPP

WRRC Staff assisted PI Paula Rees in her Blackstone River Watershed Assessment Study. The study is aimed at finalizing a watershed management study of the Blackstone River Basin in Massachusetts and Rhode Island by identifying cost-effective limits or controls for phosphorus, nitrogen and bacteria, as well as flow management opportunities with existing hydraulic structures, so that water quality and aquatic habitat can be improved throughout the basin. The role of WRRC staff was to review quality assurance/quality control steps and results for the water quality monitoring program.

Information Transfer Program

1. Massachusetts Water Watch Partnership: Monitoring Assistance for Volunteer Water Quality Monitoring (UMEXT)

Principal Investigators: Jerry Schoen, Marie-Françoise Walk, MA Water Resources Research Center
Start Date: 3/1/2006
End Date: 2/28/2007
Descriptors: Citizen Monitoring, Non-point Pollution, Monitoring, Volunteer, Quality Control

The Massachusetts Water Watch Partnership (MassWWP) was formed in 1990 to empower citizens to collect, evaluate, and act on scientifically credible water quality information for the Commonwealth's surface waters. The program relies on building a partnership with government, industry, educators, conservation organizations and the general public, who lend their respective talents to this effort to achieve practical solutions to water quality problems.

MassWWP funding was further reduced this year, limited to support received via a memorandum of understanding with UMass Extension, which allowed to provide basic assistance to volunteer monitoring groups throughout the state. A training session was offered on river benthic macroinvertebrate sampling and identification.

MassWWP continued to manage a listserv of about 135 members to facilitate communications in the Massachusetts watershed monitoring community. The website www.masswwp.org was also updated with the latest news and technical information.

Under this memorandum of understanding, UMass extension also supported WRRC staff to coordinate volunteers and manage the database for the Stream Continuity Project, a study looking at stream crossings and their status at creating barriers for fish and wildlife passage.

Students Supported:
1 BS student in Economics at UMass Amherst.

2. Generic Quality Assurance Project Plan Project (MAEOEA)

Principal Investigators: Jerry Schoen, MA Water Resources Research Center
Start Date: 1/1/2007
End Date: 6/30/2007
Descriptors: Citizen Monitoring, Quality Assurance Project Plans

MassWWP produced of a generic guide to Quality Assurance Project Plans, a template for associated Sampling and Analysis Plans, and a guide to writing these documents for a target audience of volunteer and community water monitoring groups, and offered two training courses in the spring of 2007 in eastern and central Massachusetts. This was conducted under contract with the Executive Office of Environmental Affairs.

3. Water Resources Conference 2007

Principal Investigators: Sarah Dorner, Director, and Marie-Françoise Walk, MA Water Resources Research Center, UMass Amherst
Start Date: 3/1/2006
End Date: 4/30/2007
Descriptors: Conference, Water Resources, New England

The Water Resources Research Center organized a fourth annual Water Resources Research Conference: *Sustainable Water in a Changing World: Research to Practice.* Though the conference took place after this reporting period, on April 9, 2007, a great deal of work took place during this fiscal year to prepare the conference. The Cooperative State Research, Education, and Extension Service New England Regional Program again cooperated in planning the conference. Eight co-sponsors helped underwrite the cost of the conference. Despite this support, attendance was down from 200+ to 134 participants this year. Whether the change in time of year (fall to spring) was responsible for the decrease, or the theme (more global than regional this year) was less attractive remains to be determined, but the steering committee felt that a large sponsor would allow more scholarships and would increase attendance.

Twenty posters were presented and there were 36 paper platform presentations in three concurrent sessions. The presentations were grouped into four tracks subdivided into three sessions each:

Water, Climate, and Ecosystems
- Aquatic Ecosystems
- Planning for Climate Change
- Modeling Tools for Decision-Making

Transboundary Waters
- Integrated Watershed Mgt: Challenges for Scientists and Policymakers
- Hydrodiplomacy
- Perspectives on Global Governance

Managing Water Resources for Sustainability
- Policy Responses for Sustainable and Safe Water
- Urban Water Management
- Remediation of Water Pollutants

Scientific and Watershed Community Collaborations
- Place, Season, & Landscape Perceptions
- Technology Tools for Community Science
- Incorporating IT in Community Projects

The Keynote Address was given by Dr. Evan Dollar, Senior Researcher, Division of Natural Resources and the Environment, Council for Scientific and Industrial Research, South Africa, on *Balancing Use and Protection of Water Resources: Democratizing Water Management in South Africa.* A followup workshop on that topic was held the next day for interested faculty and NGO staff.

Students Supported:
1 BS student in Biology at UMass Amherst.

4. Innovative Stormwater Technology Transfer and Evaluation Project (MADEP)

Principal Investigators: Sarah Dorner and Jerry Schoen, MA Water Resources Research Center
Start Date: 1/1/2007
End Date: 6/30/07
Descriptors: Stormwater, Water Quality, Non-point Source Pollution

MADEP awarded WRRC a two and a half year grant to continue a previous project WRRC staff had contributed to in FY'05 and FY'06. The goal of this project is to provide technology transfer information about innovative stormwater Best Management Practices (BMP) to MADEP, conservation commissions, local officials, and other BMP Users. The project maintains and updates the database already in place (www.mastep.net) and will continue to expand the database by adding information pertaining to at least twenty new proprietary BMPs and at least ten conventional and ten Low Impact Development BMPs. In the first six months of this project, WRRC staff met with the Massachusetts Stormwater BMP working group to get input on revision of BMP category rating system and redesigned the rating system.

Timeline priorities for year 1 of the project were also identified with the help of DEP, EOEA staff and external advisors (e.g. Mass Highways staff, vendors).

5. Other Information Transfer/Outreach

WRRC maintains a web site at www.umass.edu/tei/wrrc and a listserv of 1044 members to inform the public of latest water resources research news. An electronic newsletter was created in March 2007 and distributed through the listserv.

Other Activities

1. Environmental Analysis Laboratory

The Environmental Analysis Laboratory (EAL) was created in 1984 by WRRC to assist the Acid Rain Monitoring Project (ARM) by analyzing more than 40,000 samples for a suite of 21 parameters. Since 1988, the Lab has provided services to a wide range of off-campus and on-campus researchers. EAL provides chemical, physical, and microbial analysis of water, soils, tissue, and other environmental media for University researchers, public agencies, and other publicly-supported clients. Staffed with professional chemist Peter Kerr assisted by part-time students, the EAL conducts a wide variety of analyses to support environmental research, management, and monitoring activities, and has a particular strength in water-related analyses requiring substantial numbers of samples. EAL provides high quality analytical services for inorganic substances in water including nutrients, inorganic anions, and metals and has especially distinguished itself in the analysis of trace levels of phosphorus. More recently, the EAL has expanded its scope of services into the area of microbial analysis.

In this past year, EAL continued to provide laboratory support for the Acid Rain Monitoring Project, including a quality-control program for pH and alkalinity and analytical determinations for a suite of 15 parameters. The quality-control program for volunteer-monitoring groups continued for pH, alkalinity and dissolved oxygen. Analytical services were provided for ten Massachusetts and Connecticut volunteer

groups, the town of Barnstable, three university researchers, the Department of Environmental Health and Safety and Lycott Environmental, Inc. Collaboration with the Department of Civil and Environmental Engineering continued through the end of the Mass. Highways road-salt project.

2. External Advisory Board

The External Advisory Board (EAB) met December 11, 2006 at UMass Amherst for an update on WRRC activities and discussion of resources research priorities in Massachusetts.

3. Working Groups

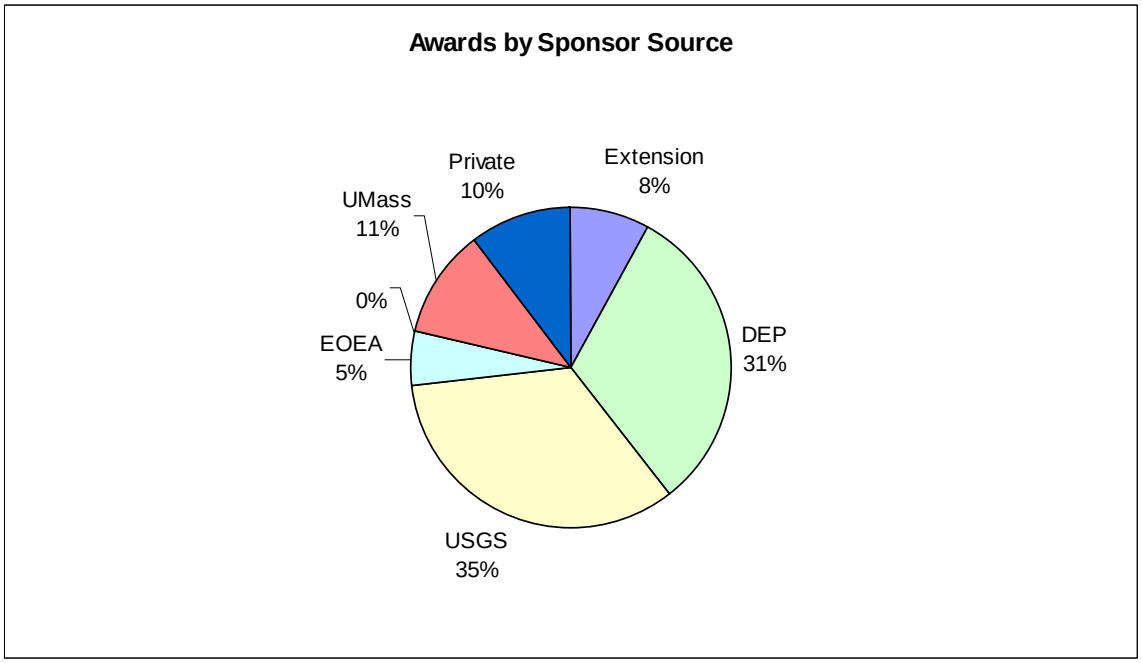
The WRRC has been participating in the coordination of interdisciplinary working groups on themes such as "Water" and "Environmental Contaminants." The working groups coordinate seminars, and have written proposals to fund interdisciplinary research.

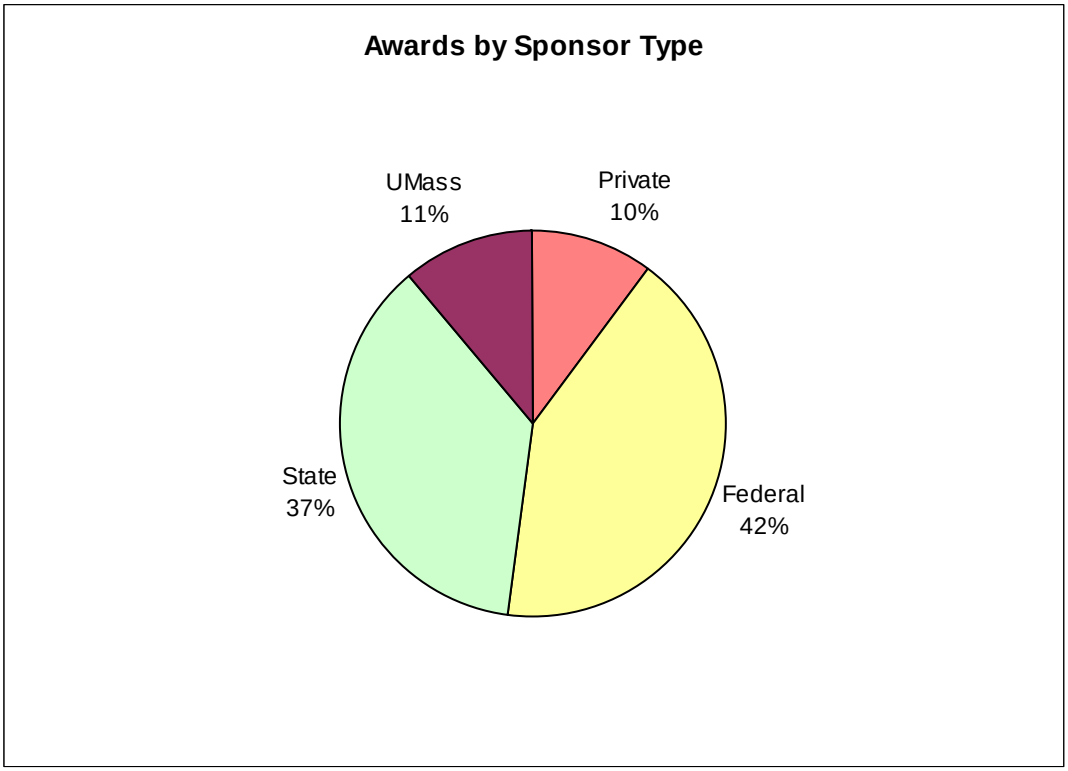
Financial Overview

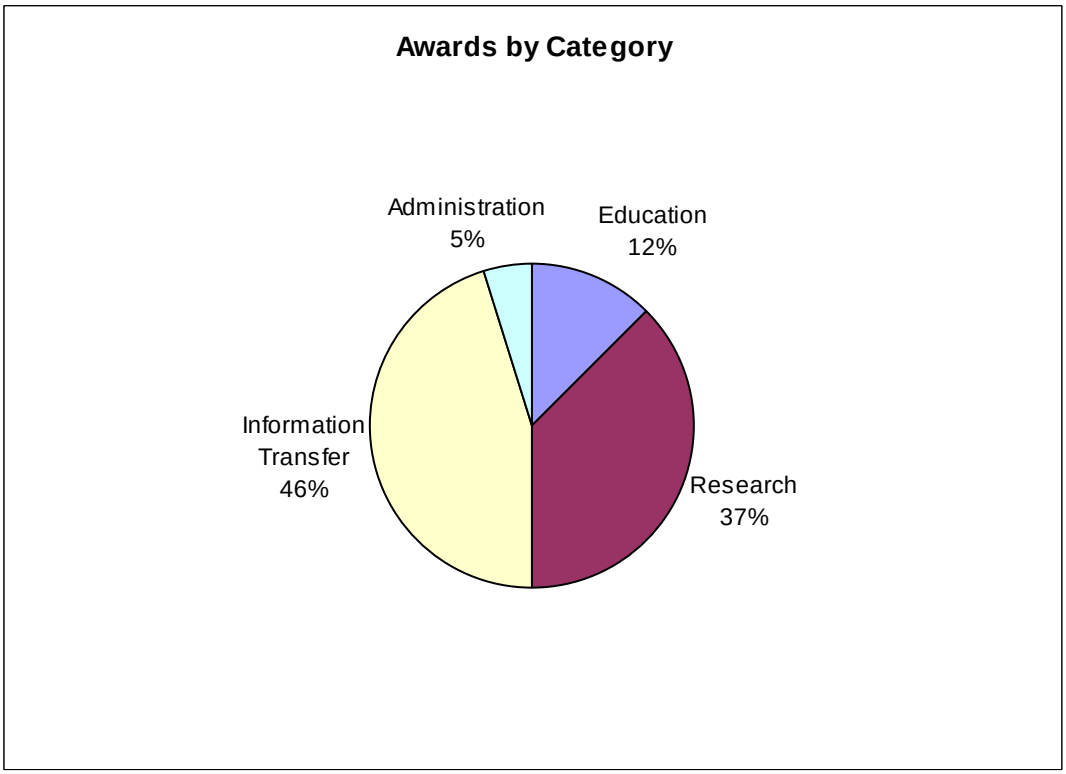
Center revenues come strictly from grants and contracts. The University of Massachusetts supports the half-time Director's salary and also provides physical facilities.

Total revenues amounted to $379,025:

USGS 104B:	$92,335 broken down as follows: $25,000 Zuo research project $24,898 Parasiewicz research project $5,000 Sahu research project $16,847 Administration $20,590 Information Transfer
USGS 104G	$30,667 (third of three year project)
Extension (MassWWP)	$30,000 Extension-WRRC MOU
DEP (Stormwater Project)	$45,000
DEP (Acid Rain Project)	$70,000
DEP (QAPP project)	$20,000
UMass (Director)	$30,000
UMass CEE (Blackstone)	$11,000
Lab Revenues (EAL)	$37,551
Conference Revenues	$12,471




Awards by Sponsor Type
UMass
11%
Private
10%
State
37%
Federal
42%


Awards by Category
Administration
5%
Education
12%
Information
Transfer
46%
Research
37%