Auburn University Environmental Institute
Annual Technical Report
FY 2004

Introduction

Alabama's Water Resources Research Institute was established at Auburn University in 1964 to assist in assuring that the State and Nation at all times have an abundance of good quality water to serve the needs of people and their cities, industries and agriculture. Alabama's water problems have been, and likely will continue to be, principally in the areas of water quality management and protection, water resources planning, water cycle, water quantity management and control, and nature of water.

The program of the Institute centers on the development, execution, marketing and funding of a research, outreach and instructional program that facilitates the better use, management and preservation of environmental and natural resources in Alabama, the Southeast and beyond.

The mission of the Institute has been to serve the State, Nation and global community by providing leadership and cohesion in areas of research, instruction and outreach. The goal of the Institute is to promote, coordinate and implement multi-disciplinary programs and activities to meet the environmental needs of the State, it's Universities, and the Nation.

Research Program

Nitrogen Cycling in Alabama Rivers: Effects of Nutrient Addition on the Composition of Functional Microbial Communities

Basic Information

Title:	Nitrogen Cycling in Alabama Rivers: Effects of Nutrient Addition on the Composition of Functional Microbial Communities
Project Number:	2004AL24B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	7th
Research Category:	Not Applicable
Focus Category:	Surface Water, Management and Planning, None
Descriptors:	
Principal Investigators:	Julie Beth Olson, Perry F. Churchill, Amelia K. Ward

Publication

Synopsis of Research

Project Title: Nitrogen Cycling in Alabama Rivers: Effects of Nutrient Addition on the Composition of Functional Microbial Communities

Principal Investigators: Julie B. Olson, Perry F. Churchill, and Amelia K. Ward, University of Alabama, Department of Biology, Tuscaloosa, AL 35487

a. Statement of the Problem and Research Objectives

Many of Alabama's freshwater ecosystems have been or are continuously exposed to conditions that degrade water quality. These range from increased sedimentation to addition of excess nutrients, either from agricultural run-off or point and non-point source contamination. Wastewater treatment plants are responsible for point-source pollution that results in the degradation of Alabama's rivers and streams. While effluent standards have been created and enforced for designated pollutants, numerous other compounds and pollutants are unregulated. These include nitrate and phosphate introduced into the system via tertiary treated wastewater released directly into Alabama's rivers and streams. Since nitrate is a biologically-available form of nitrogen, its impact on the natural communities inhabiting these ecosystems must be examined.

This proposal examines two sites in the Upper Watershed of the Cahaba River, one that is relatively pristine and one that is heavily impacted by effluent from a nearby municipal wastewater treatment plant. While macroscopic changes in the vegetation can be readily seen between the sites, almost nothing is known about changes in the microbial communities that are responsible for cycling nitrogen. We propose to examine the overall microbial biodiversity at each site and the bacterial taxa richness of those microorganisms that are capable of carrying out the various processes of nitrogen transformation. If, as predicted, significant differences in the microbial communities are found, this suggests that water quality is not being maintained and that community shifts are occurring at a process (or functional) level. The methods outlined in this proposal can be utilized as an additional or alternate method to more effectively monitor water quality within Alabama's freshwater ecosystems.

The primary objective of this research is to determine the presence and genetic diversity of the overall microbial community and of organisms capable of each process within the N cycle in a riverine ecosystem.

b. Research Methodology

Sampling

Water and sediment samples were collected during June 2004 from 2 selected sites on the Cahaba River. The two sampling sites along the Cahaba River were selected based on specific, documented land use patterns. One site is located 200 m north of a wastewater treatment outflow (considered for our purposes the pristine environment) and the second is immediately (<20 m) south of the wastewater treatment plant outflow into the main channel of the Cahaba River (considered the impacted site). From previous water chemistry measurements, these sites have been shown to be critical locations within the river system for nutrient enrichment and

utilization. Multiple 10cc syringe corers were used to take sediment samples. Water samples were taken for water chemistry analyses.

Water Chemistry Measurements

Surface water samples were collected in acid-washed polyethylene bottles, placed in ice within coolers, and transported to the laboratory, where water was immediately filtered through 0.7 μm GF/F filters. A portion of the filtrate was acidified and analyzed for dissolved organic carbon (DOC) on a Shimadzu T5000 Total Organic Carbon Analyzer (Wetzel and Likens 2000). A additional portion of the filtrate was analyzed for ammonium (NH_4-N), nitrate (NO_3-N), nitrite (NO_2-N), and soluble reactive phosphorus (SRP) by flow injection analysis using a QuickChem Automated Ion Analyzer (Lachat Instruments). Dissolved organic nitrogen (DON) was determined by a modified persulfate autoclave method (Dafner et al. 1999; Schaefer 2001) in which the final end-product is nitrate; DON concentration is determined from the post-digestion nitrate concentration minus the sum of the initial ammonium, nitrate, and nitrite concentrations.

DNA Extraction

DNA was extracted from the sediment samples using the method of Zhou et al. (1996), involving grinding in liquid nitrogen, freeze-thawing, high salt, and sodium dodecyl sulfate-extended heating. The resulting solution was extracted with an equal volume of phenol:chloroform (1:1), precipitated in isopropanol, and resuspended in Tris-EDTA (TE) buffer (used effectively in Jackson et al. 2001). Samples showing signs of humic contamination, (usually designated by a yellow-brown color) were purified using Sepharose 4B columns (Jackson et al. 1997).

PCR Amplification

Samples of sediment DNA were used to amplify 16S rRNA genes and genes specific for organisms with the capacity for nitrogen fixation, nitrification, and denitrification. Multiple amplification reactions (3 per sample) were run to ensure that DNA representative of the entire microbial community was used. Functional gene primer sets used included: nitrification- ammonia oxidizer partial 16S rRNA gene, *Nitrobacter* partial 16S rRNA gene; nitrogen fixation- *nifH* gene; denitrification- nitrite reductase *nirS* gene, nitrous oxide reductase *nosZ* gene.

Clone Library Formation

Amplified PCR products were ligated into pGEM (Promega Corporation) vectors and transformed into chemically competent *E. coli* cells. Resulting colonies were screened for successful insertion of the PCR product. PCR was used to amplify the insert and cloning was conducted by Macrogen (Korea).

Phylogenetic Analyses

Sequencher was used to align the resulting sequences. PAUP* will be used to perform phylogenetic analyses to determine if different communities are present at the two sites.

c. Principal Findings and Significance

Water Chemistry Data from June 21, 2004

Site	Total N (μgN/L)	NH_3-N (μg/L)	NO_3-N (μg/L)	NO_2-N (μg/L)	DON (μgN/L)	O-PO_4 (μg/L)	DOC ($mgCL^{-1}$)
Upstream	361.48	11.60	226.83	2.19	120.86	8.78	6.07

Downstream	1512.00	26.02	1151.54	1.90	332.54	212.41	5.32

Significance of Water Chemistry Data

These data indicate that the addition of the treated wastewater effluent into the main branch of the Cahaba River introduces a significant amount of nutrients, primarily as N and P. Total N increases by an order of magnitude, while PO_4 concentrations increase by two orders of magnitude. It has not yet been determined if these nutrient additions are sufficient to alter the structure of the functional microbial communities residing at the two sampling sites.

Molecular Data

Various genes (described in the research methodology section) were used to examine the potential functional microbial communities at the two sites. The following table indicates the number of sequences that have currently been obtained for each of the genes selected. Sequencing and data analysis are on-going. A phylogenetic tree generated using parsimony in PAUP* for recovered ammonia oxidizer 16S rRNA genes is shown below (Figure 1).

Functional gene	Upstream (pristine)	Downstream (impacted)	Total
nifH	0	6	6*
Ammonia oxidizer 16S rRNA gene	15	17	32
Nitrobacter 16S rRNA gene	13	14	27
nirS	7	11	18
nosZ	NA	NA	74^

* = additional clones are currently being sequenced

^ = these sequences have not yet been aligned

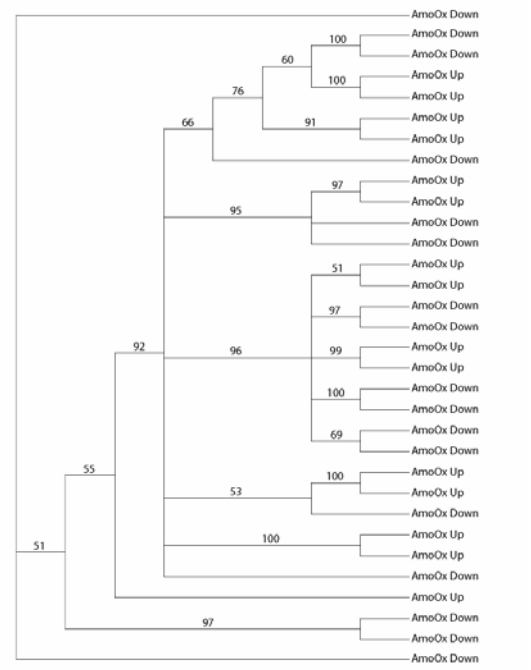


Figure 1. Strict consensus tree prepared in PAUP* using ammonia oxidizer partial 16S rRNA gene sequences. Bootstrap values from 1000 iterations that are greater than 50% are shown.

Significance of Molecular Data

This information will allow us to determine if the functional microbial communities involved in N-cycling are altered by the addition of nutrients from the wastewater effluent. Changes in these communities could serve as an early indicator of watershed water quality degradation.

Development and Characterization of a New Class of High-Capacity Ion Exchangers and and Environmentally Benign Process for Removal of Perchlorate in Water

Basic Information

Title:	Development and Characterization of a New Class of High-Capacity Ion Exchangers and and Environmentally Benign Process for Removal of Perchlorate in Water
Project Number:	2004AL25B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	3rd
Research Category:	Not Applicable
Focus Category:	Management and Planning, Surface Water, Groundwater
Descriptors:	
Principal Investigators:	Dongye Zhao, Willie F. Harper, Aliecia R. McClain

Publication

1. Xiong, Z., Zhao D., and W. Harper (2005) "Sorption and Desorption of Perchlorate With Conventional and Non-conventional Ion Exchangers" Water Research. (to be submitted)
2. An, B., Z. Xiong, Z. FU, Donge Zhao, (2005) "preparation and Application of a New Class of Polymeric Ligand Exchangers for Selective Separation of Trace Contaminants" Separation Science and Technology, (to be submitted)
3. Dimick, P., D. Zhao, A. Kney, J. Tavakoli (2005) Regeneration of a Perchlorate Loaded Polymeric Ligand Exchanger, DOW 3N-Cu" 2005 Spring National Meeting Proceedings, April 10-14, Atlanta, GA.
4. Xiong, Z. and D. Zhao "Removal of Perchlorate From Drinking Water Using a New Class of Ion Exchangers" 2004 Alabama Water Resources Conference, Environmental Institute, Auburn University, AL

PROJECT SYNOPSIS

TITLE: DEVELOPMENT AND CHARACTERIZATION OF A NEW CLASS OF HIGH-CAPACITY ION EXCHANGERS AND AN ENVIRONMENTALLY BENIGN PROCESS FOR REMOVAL OF PERCHLORATE IN WATER

Don Zhao, Principal Investigator and Project Director
Assistant Professor
Department of Civil Engineering, 334-844 6277

Willie Harper, Co-Principal Investigator
Assistant Professor
Department of Civil Engineering

Aliecia McClain, Co-Principal Investigator
Assistant Professor
Department of Textile Engineering

a) Problem statement and research objectives

In the recent years, perchlorate has been widely detected at dangerous levels in drinking water in at least 22 states including Alabama. Drinking water for more than 20 million Americans is contaminated with this toxic legacy of the Cold War. The chemical has been demonstrated to pose a variety of serious health risks relating to thyroid function, especially in newborns, children, and pregnant women. It can cause both physical and mental retardation and has been linked to thyroid cancer. Based on long-term epidemiological data, the draft assessment proposed a reference dose (RfD) of 0.00003 mg/kg/day. Translated to a drinking water equivalent level (DWEL), EPA recommended a provisionary a maximum contaminant level (MCL) of 1 ppb (part per billion) in drinking water. While a final MCL is under deliberation, eight states have established various action levels for perchlorate in drinking water ranging from 1 ppb to 14 ppb. California, where at least 7 millions of people are affected, has adopted a 4 ppb action level. Given the extremely high mobility and persistency of perchlorate, there is an urgent need for developing cost effective and environmentally friendly processes to remove perchlorate from drinking water and to safeguard the health of affected Alabama citizens.

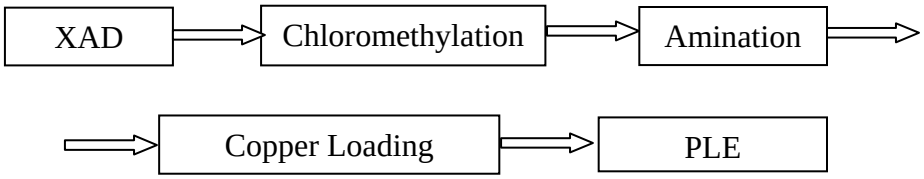
This research aims to develop an environmentally benign, cost-effective process for effective removal and complete destruction of perchlorate in drinking water from affected Alabama sources. A new class of novel sorbents, referred to as polymeric ligand exchangers or PLE's will be prepared, characterized and compared with other sorbents. The specific research **objectives** are to:

1) Develop a new class of ion exchangers that can treat perchlorate and compare them with commercially available adsorbents;
2) Develop a novel regenerative, and environmentally benign fixed-bed process based on the new materials; and
3) Explore new strategies to completely destroy perchlorate in water.

b) Research Methodology

The proposed research was carried out by executing the following tasks:

Task 1: Preparation of PLEs. A number of new polymeric ligand exchangers (PLE's) were synthesized through functionalizing commercially available polystyrene polymer adsorbents, XAD resins (XAD7HP, XAD16, and XAD1180) in accord with the following general scheme:



For comparison, an earlier PLE, DOW 3N-Cu, was used as a benchmark sorbent. In addition, two strong base anion (SBA) exchangers (IRA 958 and IRA 900), two modified SBA resins (Purolite 520 and Purolite 530), a fiber resin, and two weak base anion (WBA) exchangers (DOWEX22 and Diaion®WA21J) were also studied for comparison.

Task 2: Batch equilibrium and kinetic tests. This task includes a series of equilibrium and kinetic experiments. The equilibrium tests are designed to test and compare the equilibrium sorption capacity of PLEs and commercial resins for perchlorate removal. Sorption isotherms were constructed for PLEs and other resins in binary and multiple component systems. Perchlorate/co-solute binary ion exchange separation factors were calculated for each resin and then compared. Effects of solution pH, ionic strength, and concentration of competing anions such as sulfate on sorption capacity will be investigated in details. The kinetic tests are geared to study the sorption rates of PLEs compared to commercial resins for practical applications. Batch kinetic tests were carried out. Diffusion models were then applied to interpret the experimental kinetics data. The intraparticle diffusion coefficients for various resins were determined by fitting the models to experimental data and then compared.

Task 3: Column tests. Fixed-bed column runs were carried out to test the dynamic breakthrough behaviors of various resins. Breakthrough curves for perchlorate, other common anions (SO_4^{2-}, NO_3^-, Cl^-, HCO_3^-), DOM and pH were measured using bench-scale column set-up.

Task 4. Regeneration. Regeneration tests are aimed to compare regeneration efficiencies of PLE's as compared to commercial resins. Perchlorate-saturated beds were regenerated in-situ using two regenerants 1) 4% (wt.) NaCl (brine) with 0~10 ethanol; and 2) brine plus various concentrations of NaOH with 0-30% ethanol. Subsequently, optimal conditions such as brine concentration, pH, hydrodynamic conditions, and solvent need were determined.

Task 5. **Ultimate destruction of perchlorate.** We tested the feasibility of destroying perchlorate in water or in the spent regenerant brine using biotic and abiotic methods. The biodegradation of perchlorate was carried out using microorganisms isolated from marine sediments; whereas the abiotic degradation of perchlorate was achieved using a newly synthesized nanoscale zero-valent iron particles.

c) Principal findings and significance

The major findings are summarized as follows:

(1) Three new PLEs were synthesized with varying matrix properties and hydrophobicity;
(2) The PLE's offer perchlorate sorption capacity comparable to that for standard SBA resins, but PLE's can be regenerated more efficiently at higher pH.
(3) Resins based on polystyrene matrix offer higher affinity and capacity for perchlorate than resins based on polyacrylic matrix. However, regeneration of the resins based on polyacrylic matrix is much more efficient.
(4) Although sorption of perchlorate is enhanced by hydrophobic interactions, the perchlorate uptake follows ion-exchange stoichiometry. The concurrent ion-pairing, Lewis acid-base interaction and hydrophobic interaction between PLE's and perchlorate are the underlying mechanism for perchlorate uptake.
(5) Despite completely different functionalities, the regenerability of PLE's and SBA resins is comparable at pH below 9.
(6) Fibrous ion-exchanger (Smopex 103) turns out to be a promising choice for perchlorate removal. It showed good perchlorate uptake capacity (117.78 mg/g), much better sorption kinetics than any other sorbents, and efficient regeneration. Over 85% its ion-exchange capacity was recovered using 38 bed volumes of a brine solution (12% NaCl at pH ~7.0)
(7) The regeneration efficiency of exhausted ion-exchangers can be improved by adding organics like methanol or ethanol into the regenerant and/or increasing the eluant pH.

These findings are instrumental for designers and decision makers to select the best sorbent for removal of perchlorate from contaminated waters.

The Evaluation of an Approach to Estimate Regional Scale Surface Moisture as an Indicator of Drought for Alabama Using NASA's MODIS Data

Basic Information

Title:	The Evaluation of an Approach to Estimate Regional Scale Surface Moisture as an Indicator of Drought for Alabama Using NASA's MODIS Data
Project Number:	2004AL26B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	3rd
Research Category:	Not Applicable
Focus Category:	Hydrology, Climatological Processes, None
Descriptors:	
Principal Investigators:	Luke J. Marzen, Jean-Marie Paul Wersinger

Publication

1. Marzen, Luke J., A. B. Kanaan, and N. Sills Estimating Surface Moisture Conditions in the Southeast With MODIS NDVI and LST. 2004 Proceedings of the Southeastern Division of the Association of American Geographers Conference, Biloxi, MS.

THE EVALUATION OF AN APPROACH TO ESTIMATE REGIONAL SCALE SURFACE MOISTURE AS AN INDICATOR OF DROUGHT FOR ALABAMA USING NASA'S MODIS DATA

by

Luke J. Marzen, Ph.D.
Principal Investigator
Assistant Professor
Department of Geology and Geography
108 Tichenor Hall
Auburn University, AL 36849
Tel: 334-844-3462

J-M Wersinger, Ph.D.
Principal Investigator
Associate Professor
Department of Physics
208 Allison
Auburn University
Auburn, AL 36849
Tel: 334-844-4223

A. Identification and Statement of the major regional water problem

It is estimated that on an annual basis drought conditions occur on average in 12% of the contiguous US and cost the nation $6-8 billion US dollars (Wilhite and Svodoba, 2000). In the state of Alabama drought has caused serious problems for farming communities for the past several years. These conditions place farming communities in difficult financial situations which also substantially affects other economic sectors within the state. The drought of 2000 is estimated to have cost the state over 360 million dollars of revenue. Reliable and up to date information related to surface moisture conditions could be used to forecast crop yields, assess distressed areas for allocation of disaster relief funds, and could help resource managers and government officials plan ahead for difficult financial times.

Conventional measures of estimating drought (i.e. Palmer Drought Severity Index, Crop moisture Index, or Standard Precipitation Index) are calculated from weather station data and thus are limited to relatively few point observations. Remote sensing can provide observations where few previously existed with point data (Legates, 2000). In the past, AVHRR data has been widely used to assess surface conditions of vegetation related to drought at the continental scale with success (Cihlar 1997). Less research using remote sensing to evaluate moisture conditions has been conducted at the regional scale. However these studies indicate that the relationship between the normalized difference vegetation index (NDVI) and land surface temperature (LST) as measured by AVHRR may provide a means to effectively assess moisture conditions at the regional scale (Nemani 1993, Kondoh, A., and Y. Oyomada. 2000). NASA's MODIS data products are processed to correct for errors that users of AVHRR data commonly dealt with. Changes in the ranges of the NIR and Red bands enhance the sensitivity of MODIS vegetation indices and thus offer improved opportunities over AVHRR. The improved vegetation index products, taken along with the validated LST product (shown to be accurate within 1 degree K as opposed to 2-3 degrees K with AVHRR data), suggest that a drought index developed with NDVI and LST MODIS data, may provide an effective indicator of drought conditions that can be calculated more rapidly and with more observations than those indicators derived from ground based data.

The overall goal of this project is to evaluate methods to use remotely sensed data to estimate surface moisture conditions as an indication of drought. This information will ideally provide improved forecasting and prediction of drought conditions and will be useful to resource managers in the state of Alabama. The following objectives and tasks will be completed to meet the overall goal:

1. Investigate the use of NASA's MODIS data to exploit the relationship between NDVI and LST in an effort to develop an effective indicator of regional scale drought conditions.
2. Determine parameters that define drought index thresholds based on measurements from weather station data during known drought periods in the growing seasons of 2000 and 2001. The established thresholds will be used to produce maps of current drought conditions.
3. Share drought index products with user communities on the Alabama From Space website for independent validation research. Alabama From Space (evolved into AlabamaView with membership to the USGS supported AmericaView program; www.alabamaview.org) based at Auburn University is under construction and will ultimately be designed to share image data files of environmental surface characteristics

with the public in Alabama. Ideally the maps will be available using an interactive web-based GIS.

4. Provide undergraduate and graduate level training in the use of remote sensing and GIS for hydroclimatologic and remote sensing research.

B. Research methodology

For this study, MOD11 (land surface temperatures and emissivity) and MOD13 (vegetation indices) data products were used to produce ratio images of WSVI ([NDVI/LST]). WSVI values were compared to conventional ground based drought index values at the climate division level. In addition since we collected NDVI and LST data to produce WSVI we also compared these data to the ground based indices. The Crop Moisture Index (CMI) and Palmer Drought Severity Index (PDSI) were collected for climate divisions for Alabama and surrounding states from the Southeast Climate Division Center over a three year period (2000-2003). Of the two indices CMI is more sensitive to short-term changes in surface moisture conditions and PDSI is more sensitive to long-term changes.

Pearson's Product correlation was used to compare WSVI, NDVI, and LST to CMI. The MODIS data products for NDVI are provided in a 16 day composite and therefore we matched this as closely as possible to a two week average of CMI for 45 climate divisions in 6 states in the Southeast (AL, GA, FL, NC, SC and VA).

C. Principal Findings

Our results are listed in Table 1 and indicate that Land Surface Temperature (LST) as gathered in the thermal bands from emitted surface energy provided the best match with CMI. The analysis indicates that a moderate negative relationship exists between satellite and ground observations of surface moisture conditions suggesting that as dryer conditions occur CMI decreases and LST increases. This analysis suggests that as vegetation dries out on the surface less evapotransporation occurs and temperatures tend to increase. When taking NDVI into consideration the results are not as strong. In all cases LST has a stronger relationship with CMI than NDVI or WSVI (NDVI/LST). On average throughout the 3 year study period analyzed LST has an r value averaging -.60 as compared to a 0.1 for NDVI and a 0.3 for for WSVI. Although a more intensive study is required to validate our results, this pilot study suggests that NDVI or WSVI are not as reliable of drought indicators when compared to the MOD11 LST product. This is a significant finding as NDVI has been the primary indicator of drought conditions used in the remote sensing community for over two decades. A recent publication that focused on drought research featured two articles using NDVI as the sole method of investigating drought conditions (Boken et. al. 2005) even though there is no validation of the results with ground based data.

Table 1. Pearson's Product Correlations for Remotely sensed variables with CMI

Duration	LST-CMI	NDVI-CMI	WSVI-CMI
April-May 2000	-0.73	0.305	0.53
June-July 2000	-0.69	0.035	0.04
Oct-00	-0.44	-0.110	-0.2

April-May 2001	-0.57	0.340	0.66
Oct-01	-0.41	-0.162	0.36
April-May 2002	-0.83	0.720	0.776
June-July 2002	-0.74	-0.560	-0.502
Oct-02	-0.66	0.259	0.77
April-May 2003	-0.44	0.085	0.45
June-July 2003	-0.57	-0.009	0.02
Oct-03	-0.55	0.228	0.43

The work on this project also played a role in securing additional funds to post the LST and NDVI data throughout the growing season on the AlabamaView website (www.alabamaview.org) and to conduct ongoing research for goal # 2 above.

Information Transfer Program

Researchers are required to present their research results at the Annual Alabama Water Resources Conference and Symposium held each year in September. Along with an oral presentation from the researchers, their graduate students are encouraged to present posters of their contributions to the projects.

The Institute co-sponsors an on campus seminar series that allows the researchers and/or their graduate students to present their research to other members of Auburn University's faculty and staff. We also co-sponsor the Black Belt Environmental Science and Arts Network program that increases environmental awareness for middle school students in the black belt region of Alabama.

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	4	0	0	0	4
Masters	3	0	0	0	3
Ph.D.	2	0	0	0	2
Post-Doc.	0	0	0	0	0
Total	9	0	0	0	9

Notable Awards and Achievements

The research performed in the "Evaluation of an Approach to Estimate Regional Scale Surface Moisture as an Indicator of Drought for Alabama Using NASA’s MODIS Data" played a major role in securing additional funds to post the LST and NDVI data throughout the growing season on the AlabamaView website and to conduct ongoing research to determine parameters that define drought index thresholds based on measurements from weather station data during known drought periods in the growing seasons.

The results from the project "Development and Characterization of a New Class of High-Capacity Ion Exchangers and an Environmentally Benign Process for Removal of Perchlorate in Water" are instrumental for designers and decision makers to select the best sorbent for removal of perchlorate from contaminated waters.

Publications from Prior Projects

None