

**Alabama Water Resources Research Institute
Annual Technical Report
FY 2017**

Introduction

The Alabama Water Resources Research Institute (AL WRC) was created in 1964 by the Alabama Legislature. In 2007, the AL WRC was combined with the newly created Auburn University Water Resources Center (AU WRC) and in 2008 it was designated as part of the Auburn University Center of Excellence for Watershed Management. In 2013, the AU WRC and the AL WRC were re-organized and funded under the auspices of Auburn University's Alabama Agricultural Experiment Station (AAES) and the Alabama Cooperative Extension System (ACES). The mission of the AU WRC is to facilitate successful collaboration among Auburn University faculty and staff on multidisciplinary water-related research, outreach, and teaching; and to facilitate the active involvement of private citizens in the stewardship of water resources.

The AL WRC is one of 54 water resources institutes nationwide authorized by the federal Water Resources Research Act and retains membership in the National Institutes for Water Resources (NIWR). The AL WRC serves the state of Alabama at large in administering the funding provided under the Water Resources Research Act that is administered by the US Geological Survey. The NIWR program provides funding via two mechanisms: (1) Annual Base Grants (104b) and (2) Nationally Competitive Grants (104g) to the center.

All 50 states annually receive 104b grants to support research, education, and outreach activities to address state water issues. To address state water issues, WRC provides funding through a competitive process (modeled after nationally competitive grant programs from federal agencies) to researchers from all Alabama universities. WRC is responsible for issuing the RFP, receiving proposals, convening a review panel to select projects worthy of funding, and managing grants. This includes all activities associated with pre- and post-award management.

The 104g grant program is a nationally competitive grants program facilitated through the AWRRI program and WRC. Researchers from Alabama universities submit proposals to WRC/AWRRI, which are then forwarded to NIWR for review. If a proposal is funded by NIWR, WRC/AWRRI manages all post-award activities associated with the funded project.

The AU WRC/AWRRI consists of interdisciplinary teams of research, teaching, and Extension/outreach faculty and staff who address all types of water related issues in Alabama, the Southeast, and around the globe. The research activities are funded through the AL WRC, the AAES, and a wide variety of extramural sources. The Extension and outreach activities are carried out through the ACES, extramural sources and through three longstanding AU WRC programs, Alabama Water Watch (AWW), 4-H AWW, and Global Water Watch (GWW).

AWW is a statewide citizen volunteer, water quality monitoring program that was developed at Auburn University. AWW promotes community-based watershed stewardship by training and supporting volunteer monitoring of Alabama's streams, rivers, lakes and coastal waters. AWW has a successful history exceeding twenty-five years. The AWW Program became part of the AU WRC in 2013. The 4-H AWW Program, included in the AWW Program, is a statewide youth watershed education and volunteer water quality monitoring program created through a partnership between AWW and Alabama 4-H, the youth development program of ACES. Qualified volunteers and educators lead students in water data collection and watershed stewardship activities that promote environmental literacy and science education.

GWW is a worldwide network of citizen groups developed by Auburn University, promoting community-based, science based watershed stewardship. GWW is committed to spreading environmental literacy, and monitoring of streams, rivers, lakes and coastal waters to achieve improvements in water quality, water policy and public health. The GWW Program has a successful history of more than twenty years and

became part of the AU WRC in 2013.

WRC is also the lead in hosting the annual Alabama Water Resources Conference (AWRC) in Orange Beach, AL. This conference is the main water conference for the state. WRC has been hosting this conference for more than 30 years. WRC staff is engaged in all aspects of hosting this conference.

The AU WRC and AL WRC are led by the Center's Director, Dr. Puneet Srivastava. Dr. Srivastava has a 50% administrative and 50% research appointment, and manages a rigorous research program in addition to the aforementioned three programs within the AU WRC.

Impact/outcome relative to center/institute mission

Impact of Research Program

1. Apalachicola-Chattahoochee-Flint (ACF) River Basin Drought Early Warning System (DEWS). Our extensive climate/drought research and outreach efforts have allowed us to become a leader in drought/climate research and outreach in the Southeast. Last year saw us emerging as the main institution to lead the National Integrated Drought Information System (NIDIS) effort in developing DEWS for the Southeast. 2. Alabama Public Television created an hour-long documentary called Spotlight on Agriculture that featured many of the WRC research and outreach programs. 3. Funding received by the Center were highlighted by a number of news channels including WSFA. 4. AU WRC conducted research received a Superior Paper Award from the Soil and Water Division of the Transactions of the American Society of Agricultural and Biological Engineers (ASABE) and Applied Engineering in Agriculture. 5. Research conducted by a WRC affiliated student received 1st Place Boyd-Scott Research Paper Award at the Annual ASABE International Meeting in Spokane, WA. 6. Research conducted by a WRC affiliated student also received 1st Place Paper Award from the Association of Agricultural, Food and Biological Engineers of Indian Origin (AABFEIO) at the Annual ASABE International Meeting in Spokane, WA.

Impact of Extension, Outreach, and 4-H Programs

AWW conducted 101 training sessions with a total of 642 certifications awarded; about 50% were conducted by or with a volunteer trainer. Thirty-one water chemistry workshops (258 people), 17 bacteriological workshops (156 people), four Stream Biomonitoring (57 people), four Exploring Our Living Streams workshops (56 people), 42 recertification sessions (111 people), and three Training-of-Trainer sessions were completed in 2017 (see www.alabamawaterwatch.org/about-us/reports). Seventy groups (304 active monitors) collected and submitted water quality data from all ten major river basins in AL in 2017. Eleven new groups started water monitoring activities with AWW in 2017. A total of 3,236 water data records (2,459 water chemistry and 777 bacteriological) collected in 2017 were submitted by volunteers to the AWW office. The estimated value of these water data records to the state was \$584,236.45 (calculated based on cost analysis conducted during the USDA/CSREES-funded study, A Transferable Model of Stakeholder Partnerships for Addressing Nutrient Dynamics in Southeastern Watersheds (Deutsch et al 2007), modified with cost adjustments to 2017 values.) In addition, the volunteer time of monitors, trainers, and workshop participants was worth more than \$110,000 (Calculated at 7 hours per workshop and \$22.28/hour for volunteer trainer time for AL, from www.independentsector.org/resource/the-value-of-volunteer-time).

AWW released a new app for iOS and Android devices that allows active monitors to submit water data and view watershed maps, monitoring location, and water quality data directly from the field. In addition, monitors can submit new site coordinates using smartphone geolocation services. The AWW App will make data entry easier and more accessible to volunteer monitors.

There were more than 5,400 subscribers to the AWW email list through which the AWWareness Newsletter, blog and other important AWW watershed stewardship activities and success stories are publicized. The AWW website, www.alabamawaterwatch.org, experienced 58,999 page views (over 3,000/month), was viewed by 50 of 50 states, viewed by 134 countries worldwide by 14,391 unique users, average visit of 2.7 minutes.

In addition, AWW was able to increase awareness of Alabama's aquatic biodiversity and abundance of water resources via the distribution of the America's Amazon Infographic, designed and printed by AWW. In a visually appealing way, the America's Amazon infographic highlights water and biodiversity related facts about Alabama, notably that Alabama is the state with the highest aquatic biodiversity. In addition, the graphic presents the concern that 19% of all fish species in the state are at risk. The intent of the infographic is to help Alabamians appreciate water resources, to become aware of threats to water quality and aquatic species, and furthermore to take action to protect these resources. Viewers are encouraged to visit the AWW website to get involved as volunteer water monitors. By collaborating with organizations and agencies throughout Alabama, AWW distributed over 100 posters of the infographic in the following locations: the 12 major Alabama Welcome Centers (AL Department of Conservation and AL Bureau of Tourism), 12 AL Department of Conservation and Natural Resources Offices, 67 Soil and Water Conservation District Offices, DeSoto State Park Nature Center, Alabama Museum of Natural History, and Dauphin Island Sea Lab.

AU WRC Drought Early Warning Webinars provided more than 330 stakeholders up-to-date drought condition and forecast information on a monthly to aid in drought preparedness and provided webinar summaries to a wider network of stakeholders throughout the Southeast. A number of emails were received from stakeholders commending our effort and describing how they use the information in making decisions related to their water management.

Global Water Watch (GWW) GWW assists in promoting, fostering and backstopping community-based, science-based watershed stewardship, in other US states and countries; through the development of long-term citizen monitoring of surface waters. In addition to helping identify pollution hazards in water, the citizen-generated data is used to determine the condition and trends of water quality and quantity for the improvement of both public and watershed health. GWW has certified about 1,300 citizen monitors who have submitted, to an AU-based online database, more than 10,000 water quality and quantity data records from about 500 sites on 200 waterbodies. In 2017, GWW training sessions were held in Bolivia and Seattle; and intensive training and monitoring activities were conducted in Mexico as part of a large, 5-yr project funded by the World Bank. GWW Mexico has spread to half of the 31 states in Mexico as of 2017. GWW is also active in Argentina, Kenya, and Peru. GWW-Mexico has become the model to follow for citizen science and environmental monitoring, as scores of individuals are now conducting six types of water monitoring.

The 4-H Alabama Water Watch Program (4-H AWW) is the statewide youth water quality monitoring program created through a partnership between Alabama Water Watch and Alabama 4-H, the youth development program of the Alabama Cooperative Extension System (ACES). 4-H AWW increases environmental literacy by building capacity in volunteer trainers and educators to provide youth with an increased awareness and understanding of watershed issues and tools that cultivate the critical thinking skills students need to identify and solve problems related to water quality. In 2017, more than 8,400 youth were reached through 4-H AWW activities which was a 300% increase from 2016; and 66 youth were certified as 4-H AWW water quality monitors.

The 4-H AWW Program completed the two-year project, "Increasing Environmental Literacy and Watershed Stewardship through Youth-Focused Citizen Science" funded by an EPA Environmental Education Local Grant. The project outputs and outcomes exceeded what the project proposed to accomplish. For example, five workshops were proposed, but a total of eight were conducted. As a result, 116 educators were trained to use the 4-H AWW Curriculum. It was projected that 4-H AWW educators would reach up to 1,500 youth

during the project period; however, the actual youth involvement surpassed 11,000. Actual outputs for youth participation exceeded the projected outcomes by more than 700%. In addition, more than 60 water monitoring kits were made available to 4-H AWW educators throughout the state as opposed to the 30 proposed by the project. In part this was made possible by the growing partnership with the EPA Gulf of Mexico Office who provided approximately \$3,500 worth of kits and materials. A total of 34 counties now have materials and trained educators. More than 30 employees of the AL Cooperative Extension System were trained through the project.

Student evaluation data shows that participation in 4-H AWW activities increases motivation to protect Alabama's water resources. After participating with 4-H AWW, about 95% reported that they would help take care of streams, rivers, lakes, the ocean, and other water resources. In addition, over 95% of 4-H AWW student participants evaluated reported that following their participation in the program they believe citizens including students could collect scientific information about water quality, as opposed to the only 64% who agreed in pre-test responses.

Awards to center/institute affiliated faculty/staff

1. Srivastava, P. Superior Paper Award, Soil and Water Division, Transactions of the ASABE and Applied Engineering in Agriculture
2. Srivastava, P. Gary Brown ePortfolio Faculty Cohort Award, Auburn University
3. Srivastava, P. Director's Grantsmanship Award. Awarded by the Dean of College of Agriculture and Director of Alabama Agricultural Experiment Station, Auburn University
4. Deutsch, B. Environmental Education Association of Alabama (EEAA) Jeffrey Hughes Lifetime Achievement Award, EEAA Annual Conference, Solon Dixon Center, Andalusia, AL.
5. Reutebuch, E. Project Team Award for participation with the Farm and Consumer Environmental Safety and Security Working Group led by C. Bratcher, Awarded by the Dean of College of Agriculture and Director of Alabama Agricultural Experiment Station, Auburn University.

Research Program Introduction

Research Program Introduction The essential ingredient for determining proper policies and practices is factual information. Often such information must be obtained by means of scientific research. The Alabama Water Resources Institute (AL WRRI) conducts a program that stimulates, sponsors, and provides funding for research, investigation, and experimentation in the fields of water and of resources as they affect water, and encourages the training of scientists in the fields related to water.

Objectives of the AU WRC and AL WRRI are: 1. To plan, conduct and otherwise arrange for competent research that fosters (a) the entry of new research scientists into the water resources fields, (b) the training and education of future water scientists, engineers and technicians, (c) the preliminary exploration of new ideas that address water problems or expand understanding of water and water-related phenomena, and (d) the dissemination of research results to water managers and the public. 2. To identify major research needs and develop for Alabama and the Southeastern Region short- and long-term research priorities. 3. To encourage research applying to other environmental resources closely associated with water. 4. To maintain close consultation and collaboration with governmental agencies, public groups, and cooperate closely with other colleges and universities in the state that have demonstrated capabilities for research, information dissemination, and graduate training in order to develop a statewide program designed to resolve state and regional water and related land problems.

Environmentally-Friendly Alternatives to Bulkheads for Resilient and Healthy Shorelines: Evaluation and Implementation of Two Living Shoreline Designs

Basic Information

Title:	Environmentally-Friendly Alternatives to Bulkheads for Resilient and Healthy Shorelines: Evaluation and Implementation of Two Living Shoreline Designs
Project Number:	2016AL188S
USGS Grant Number:	
Sponsoring Agency:	Army Corps of Engineers
Start Date:	6/1/2016
End Date:	5/31/2019
Funding Source:	104S
Congressional District:	
Research Category:	Not Applicable
Focus Categories:	None, None, None
Descriptors:	None
Principal Investigators:	

Publications

There are no publications.

ANNUAL TECHNICAL REPORT SYNOPSIS

- A. PROJECT TITLE: Environmentally-friendly alternatives to bulkheads for resilient and healthy shorelines: evaluation and implementation of two living shoreline designs
- B. PRIMARY PI(s): Name(s), Title(s) & Academic Rank(s) Dr. Just Cebrian, Professor of Marine Science, University of South Alabama; Senior Marine Scientist, Dauphin Island Sea Lab
- C. OTHER PI(s): Name(s), Title(s) & Academic Rank(s)
- D. START DATE: November 2015
- E. END DATE: August 2018
- F. PROJECT OVERVIEW/SUMMARY: Provide a brief narrative overview or summary of the project.

This project is a collaborative effort between private landowners and researchers at the Dauphin Island Sea Lab to determine the effectiveness of two living shoreline designs created for the purpose of coastal stabilization. The first method will involve attaching gabion cages to a bulkhead and creating a sloping marsh seaward of the bulkhead. The second design is a constructed marsh on an eroded shoreline, which is meant for properties where a bulkhead is absent. Both of these types of shorelines will be compared with each other, as well as with no action situations, in order to determine cost-effectiveness and benefits from ecosystem services.

The proposed project will consist of building four living shorelines, and it will take place in 4 stages: pre-construction measurements, construction phase 1, post-construction measurements, construction phase 2. The project will follow a Before After Control Impact (BACI) design. Of the shorelines that are created, two will be marshes created over a bulkhead and two will be marshes created on natural, sandy shorelines. The experiment features a block design in order to compare among and between sites. Both shoreline approaches will have two randomly selected segments of each block planted at 50% and 100% densities along with a control (planted at 0% density). Shoreline success will be determined by measuring plant cover, shoreline stabilization, sediment accrual, and nekton abundance. Plant counts will be conducted for plant cover. Elevation transects using a Real Time Kinematic (RTK) rover will be conducted to measure shoreline stabilization and elevation. Marked stakes will be used to determine sediment accrual or erosion, and Breder traps deployed at low tide and a beam plankton trawl will measure nekton abundance.

- G. PROJECT OBJECTIVE(s): Briefly explain the project objectives.

The main objective of this project is to help implement the USACE Living Shorelines General Permit ALGP-10 with recommendations of cost-effective marsh construction designs to promote adoption of the permit. Specific objectives include analyzing the cost and effectiveness of various versions of two marsh construction designs in stabilizing the shoreline in comparison with bulkheads and eroding sediment slopes and quantifying additional benefits of the

constructed marshes such as enhanced habitat for commercial fish species and reduced erosion. This project also aims to create relationships with homeowners, show them the negative effects of bulkheads, and give them alternatives to protect their shoreline and neighboring shorelines. This study will create a new direction for researchers and stakeholders who wish to limit anthropogenic impacts in a world that is already armored. If bulkheads can be made less detrimental to the surrounding habitats, there may be substantial changes in an current environment that is surrounded by walls.

H. METHODOLOGIES: Briefly explain the research methodology used.

Pre-Construction

Plant Counts will not be applicable for Black needlerush (*Juncus roemerianus*) pre-construction, as it will not have been planted yet. However, there is submerged aquatic vegetation present at some of the project sites, so transects will be conducted to measure SAV. Two transects, located at the 0.3m and 0.9m marks in the plot, will be walked out to 3.6m at the sandy shoreline sites. Abundance percentages will be taken every 0.9m using a 0.3m by 0.3m quadrat separated into 16 segments. The same procedure will be conducted at the bulkhead sites, but distance walked will be 5.5m instead of 3.6m.

RTK transects will be taken at the same location as the seagrass transects with elevation points taken continuously once every second. The transects for the sandy shoreline will start 0.6m above each plot and will be walked out to 3.6m beyond the plot. The RTK transects for the bulkheads will start 1.5m above the plots and extend 5.5m beyond the plot.

Marked pvc pipes will be placed in each plot to determine sediment erosion or accrual. These pipes are 1.5 m long and will be hammered 60 cm into the ground. The pipes will have holes drilled 5cm apart from the 50 cm mark to 70 cm mark, so that the top two drilled holes are above ground, the middle hole will be aligned with the sediment, and the bottom two holes are below the sediment. This method will be used to associate the length of exposed pvc with erosion or accretion. In the 50% planted plots, there will be two stakes placed in a segment where Black needlerush will be planted. Two pvc pipes will be placed in segments that are to remain unplanted. There will be two pipes placed in two segments in the 100% planted plots and two pipes placed in two segments in the control plots. These stakes are to be kept within the same horizontal tiers, so that they can be compared before and after construction. After six months of pre-construction measurements have passed, we can determine if any accrual or erosion has occurred. The marked pvc pipes can only be applied to the sandy shorelines during the pre-construction phase and are not applicable to the bulkheads.

Nekton abundance will be conducted with Breder traps and a beam plankton trawl. The Breder traps are only applicable for the sandy shorelines. They have to be placed and anchored on the ground and experience tidal fluxes of being submerged and exposed. The traps are boxes made of plexiglass with wings that face the experimental plots. They are set at peak low tides with two traps placed in front of each plot. As the tide rises, the traps become submerged, and fish and crustaceans can enter the traps. As the tide goes back out, nekton become trapped in the boxes. After one full tidal cycle, the traps are checked, and any nekton present is identified

and recorded. (Fulling et al. 1999). The beam plankton trawl (BPT) will be used at both the sandy shorelines and the bulkheads. This trawl will be walked out to 3.6 beyond the plots at the sandy shorelines and 5.5 beyond the plots at the bulkheads. The trawl is then pulled up to the plot, and any nekton caught is identified and recorded (Guest et al. 2003).

Post-construction

The metrics recorded post-construction are meant to mirror the ones conducted pre-construction. However, plant counts will be included in this phase since the Black needlerush will have been planted. In the 50% plots and control plots of the sandy shoreline, interior percentages using a 1-foot by 1-foot quadrat will be measured. Peripheral counts will also be recorded, which accounts for the new shoots of Black needlerush that may appear along the edges of the plots (Sparks et al. 2013). Peripheral counts will be the only plant counts conducted in the 100% plots. In the bulkhead sites, peripheral counts will not be recorded at all, as the plants are contained in the gabions. However, percentages will still be recorded in the 50% and control plots. Seagrass counts will be conducted again exactly as they were in the pre-construction measurements.

Monthly RTK transects will also be conducted exactly as they were in the pre-construction phase. After construction marked pvc pipes will be placed in the same squares they were previously located in at the sandy shoreline sites. After the six months of post-construction measurements have passed, the stakes will be observed to determine if accrual or erosion has occurred. Since the gabion cages will have been built, the pvc pipes can also now be applied to the bulkhead sites. It will be placed in the same manner as the sandy sites and a core will be taken after the six months have passed.

Nekton abundance with Breder traps and the BPT in the post-construction phase will occur in the same manner that they did in the pre-construction phase. Again, Breder traps will only be applicable for sandy sites, and the BPT will be used at both sandy and bulkhead sites.

Following the completion of construction and sampling, we will be able to analyze the data for any observable differences of habitat loss or creation, shoreline loss or gain, sediment erosion or accrual, and increases or decreases in plant density. We will also be able to conduct our cost effectiveness investigation following the data analysis of the ecosystem services.

I. PRINCIPAL FINDINGS/RESULTS: Explain the results of findings of this research project.

In progress

J. NOTABLE AWARDS AND ACHIEVEMENTS. List any awards or recognitions for this research

K. PUBLICATIONS GENERATED:

Number of Research Publications generated from this research project:	
Publication Category	Number
Articles in Refereed Journals	0
Book Chapters	0

Theses and Dissertations	In progress
Water Resources Institute Reports	0
Articles in Conference Proceedings	0
Other Publications	0

PROVIDE A CITATION FOR EACH PUBLICATION USING THE FOLLOWING FORMATS:

1. Articles in Refereed Scientific Journals Citation

Author (first author; last name, first name; all others; fist name, last name), Year, Title, Name of Journal, Volume(Number), Page Numbers.

2. Book Chapter Citation

Author (first author; last name, first name; all others: first name, last name), Year, Title of chapter, "in" Name(s) of Editor "ed.", Title of Book, City, State, Publisher, Page Numbers.

3. Dissertations Citation

Author (last name, first name), Year, Title, "MS (Ph.D.) Dissertation," Department, College, University, City, State, Number of Pages.

4. Water Resources Research Institute Reports Citation

Author (first author; last name, first name; all others: first name, last name), Year, Title, Name of WRRRI, University, City, State, Number of Pages.

5. Conference Proceedings Citation

Author (first author; last name, first name; all others: first name, last name), Year, Title of Presentation, "in" Title of Proceedings, Publisher, City, State, Page Numbers.

6. Other Publications Citation

Author (first author; last name, first name; all others: first name, last name), Year, Title, other information sufficient to locate publications, Page Numbers (if in publication) or Number of Pages (if monograph).

L. PRESENTATIONS MADE:

Presenter(s) (last name, first name; all others presentation authors: first name, last name), Year, Title, other information sufficient to identify the venue in which the presentation was made.

Amato, Jamie; Just, Cebrian, Joshua, Goff, 2016, Environmentally-friendly alternatives to bulkheads for resilient and healthy shorelines: evaluation and implementation of two living shoreline designs. Bays and Bayous Symposium, Biloxi, Mississippi.

Amato, Jamie; Just, Cebrian, Joshua, Goff, 2017, Environmentally-friendly alternatives to bulkheads for resilient and healthy shorelines: evaluation and implementation of two living shoreline designs. Gulf of Mexico Graduate Student Symposium, LUMCON, Cocodrie Louisiana.

Amato, Jamie; Just, Cebrian, Joshua, Goff, 2018, Environmentally-friendly alternatives to bulkheads for resilient and healthy shorelines: evaluation and implementation of two living shoreline designs. Benthic Ecology Meeting, Corpus Christi, Texas.

Amato, Jamie; Just, Cebrian, Joshua, Goff, 2018, Environmentally-friendly alternatives to bulkheads for resilient and healthy shorelines: evaluation and implementation of two living shoreline designs. Gulf of Mexico Graduate Student Symposium, Dauphin Island, Alabama.

M. STUDENTS SUPPORTED (Complete the following table)

Number of Students Supported, by Degree	
Type	Number of students funded through this research project:
Undergraduate	0
Masters	0
Ph.D.	1
Post Doc	0
Number of Theses and Dissertations Resulting from Student Support:	
Master's Theses	0
Ph.D. Dissertations	In progress

N. RESEARCH CATEGORIES: (In column 1 mark all that apply)

	Research Category
X	Biological Sciences
	Climate and Hydrological Processes
X	Engineering
	Ground Water Flow and Transport
	Social Sciences
	Water Quality
	Other: Explain

O. FOCUS CATEGORIES (mark all that apply with "X" in column 1):

	ACID DEPOSITION	ACD
	AGRICULTURE	AG
	CLIMATOLOGICAL PROCESSES	CP
	CONSERVATION	COV
	DROUGHT	DROU
X	ECOLOGY	ECL
	ECONOMICS	ECON
	EDUCATION	EDU
	FLOODS	FL
	GEOMORPHOLOGICAL PROCESSES	GEOMOR
	GEOCHEMICAL PROCESSES	GEOCHE
	GROUNDWATER	GW
	HYDROGEOCHEMISTRY	HYDGEO
X	HYDROLOGY	HYDROL
	INVASIVE SPECIES	INV
	IRRIGATION	IG
	LAW, INSTITUTIONS, & POLICY	LIP
X	MANAGEMENT & PLANNING	M&P
	METHODS	MET
	MODELS	MOD
	NITRATE CONTAMINATION	NC
	NONPOINT POLLUTION	NPP
	NUTRIENTS	NU
	RADIOACTIVE SUBSTANCES	RAD
	RECREATION	REC
	SEDIMENTS	SED
	SOLUTE TRANSPORT	ST
	SURFACE WATER	SW
	TOXIC SUBSTANCES	TS
	TREATMENT	TRT
	WASTEWATER	WW
	WATER QUALITY	WQL
	WATER QUANTITY	WQN
	WATER SUPPLY	WS
	WATER USE	WU

X	WETLANDS	WL
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- P. DESCRIPTORS: (Enter keywords of your choice, descriptive of the work)
Living shorelines, wetlands, bulkheads, erosion, ecosystem services, cost-effectiveness

Utilizing Biogeochemical Cycling Processes for the Remediation/Treatment of Persistent Perfluorinated Chemical (PFCs) in Soil and Groundwater

Basic Information

Title:	Utilizing Biogeochemical Cycling Processes for the Remediation/Treatment of Persistent Perfluorinated Chemical (PFCs) in Soil and Groundwater
Project Number:	2017AL184B
Start Date:	3/1/2017
End Date:	8/15/2018
Funding Source:	104B
Congressional District:	7th
Research Category:	Not Applicable
Focus Categories:	Geochemical Processes, Toxic Substances, Treatment
Descriptors:	None
Principal Investigators:	Geoffrey R. Tick

Publications

There are no publications.

TECHNICAL PROGRESS REPORT SYNOPSIS

Grant GR26069; Sponsor ID 17-WRC-362437-UAT-TICK (USGS 104(b) Program-2017)
No-Cost Extension: A00-643-001

A. PROJECT TITLE: Utilizing Biogeochemical Cycling Processes for the Remediation/Treatment of Persistent Perfluorinated Chemicals (PFCs) in Soil and Groundwater

B. PRIMARY PI(s): Geoffrey R. Tick, Ph.D., Associate Professor of Hydrogeology, Department of Geological Sciences, The University of Alabama, Tuscaloosa, 35487

C. OTHER PI(s): N/A

D. START DATE: August 2017, Funds Received August 2017 (delayed due to continuing resolution not being passed in March 2017)

E. END DATE: August 30, 2018 (no-cost extension)

F. PROJECT OVERVIEW/SUMMARY:

Perfluorinated chemicals (PFCs) such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), among other toxic compounds, have been recently discovered in groundwater and surface water resources (i.e. Tennessee River and Wheeler Reservoir) in northern (Decatur) Alabama ([Pillion, 2015; 2018](#)). There is currently little to no research on understanding the physical and biological processes that act to reduce, transform, and/or transport these toxic chemicals in the environment.

This research project focuses on understanding and quantifying the processes controlling the fate and transport of perfluorinated chemicals (PFCs) in soil and groundwater for the development of effective remediation/treatment strategies. Specifically, this work aims to assess both the physical (abiotic) and biological (microbial) processes that impact the fate and transport of PFCs in soil and groundwater systems. Physical (abiotic) processes will be quantified through bench-scale sediment characterization, batch-reactor, and column experiments to determine how geochemistry (carbon-content and mineral composition) impacts the transport of PFCs in these systems. To date, bioremediation studies attempting to isolate bacteria have had little to no success isolating a bacterial strain capable of biodegrading PFCs in aerobic conditions ([Yi et al., 2016; Tseng, 2012](#)). When considering anaerobic environmental conditions, there has been no published research to date ([Liu and Avendaño, 2013](#)). Anaerobic conditions would better replicate groundwater, wetland, and certain lacustrine conditions for applications to in-situ bioremediation methods. Therefore, a series of batch-reactor experiments will utilize PFC-contaminated soils (3M Site, Decatur, AL) and biosolids from waste-water treatment facilities (i.e. Dry Creek WWTP, Decatur, AL) to isolate anaerobes that most effectively biodegrade PFCs. In particular, this research will yield specific bacterial genomes (degraders) for PFC degradation, determine impacts on microbial diversity, define specific bacterial metabolic pathways, elucidate resulting metabolites and degradation products of interest, and provide insight into biogeochemical cycling (degradation) rates in the environment.

The second aspect of this research will utilize the results of the PFC fate and transport experiments, (i.e. adsorption coefficients, retardation factors, photochemical decomposition rates, viable anaerobe isolates, metabolites and degradation products, etc.) to develop two novel remediation (treatment) techniques based on 1) physical processes: enhanced activated persulfate oxidation, and 2) biological processes: enhanced bioremediation using conditioned PFC-degrading anaerobes. The combined results from the physical and biotic experiments will allow for direct comparison of the factors most responsible for controlling the transport and fate of these PFC compounds (PFOA and PFOS) in soil and groundwater, both in the absence and presence of microbiological degradation. Specifically the biotic experiments will allow for new genetic microbial strains to be discovered for utilization in enhanced-bioremediation and biotreatment applications. Understanding the fate and transport processes within these environments are critical for the development of predictive transport models, accurate risk assessments, prevention control measures, and effective remediation/treatment strategies.

G. PROJECT OBJECTIVES(s):

The objectives of this study are part of a comprehensive effort to **1)** characterize the physical mechanisms controlling PFC fate and transport in soil and groundwater; **2)** determine the primary biodegradation conditions and metabolic pathways of PFCs in soil, groundwater and aqueous systems; **3)** isolate viable bacteria strains from contaminated soils and biosolids for effective biodegradation purposes; **4)** build new conceptual models for anaerobic degradation pathways for PFCs; and **5)** use the physical fate/transport and microbiological results to develop in-situ and ex-situ physical- and biological- based remediation/treatment techniques for PFCs and in soil and groundwater. Outcomes from this research will be valuable for researchers and practitioners (water managers) alike for the development of predictive fate and transport models, accurate risk assessments, prevention control measures, and effective remediation/treatment strategies for such persistent and highly toxic emerging contaminants (PFCs) in the environment

H. METHODOLOGIES:

The methods outlined herein have been distilled down to provide a brief description of the methods conducted and still currently in progress.

1. Physical Fate and Transport Experiments

Soils collected from the 3M (PFC manufacturing/disposal) Site (Decatur, AL) and/or in close proximity (depending on access) were collected and thoroughly characterized for grain-size analysis, clay content, mineralogy, clay structure, and carbon content. The soil samples were sieved to remove the finest clay and silt particles. The sieved bulk soils will be or have been homogenized and amended to make 3 different soil-type with either different total-carbon fraction or different “expanding” (smectite- montmorillonite) clay ratios for fate/transport experiments. One set of soil samples will be sterilized (HgCl_2) and another set will be amended with growth substrate to try and yield PFC degrading microbial cultures for both abiotic and biotic experiments, respectively.

Batch Reactor Experiments

A series of batch reactor experiments were conducted and/or are currently in progress. PFOA and PFOS solutions of different concentrations (0.05, 0.1, 1, 10, 50 mg/L) will (or were) be added to the 1-L flasks to create a 300 mL soil (slurry). This 1:10 solid-to-liquid ratio was conducted for non-amended site soil and amended soil batch fate/transport experiments are being prepared to understand retention and partitioning process of PFOA and PFOS as a function of

soil properties and intercalation within the clay structures of the soil (Matthieu et al., 2013). The sorption batch reactor experiments were split into six treatment groups: (1) NANOpure water, (2) PFOA-saturated (9500 mg L⁻¹) solution with NANOpure. (3) PFOS-saturated (370 mg L⁻¹) solution with NANOpure water, (4) artificial groundwater (9 mg L⁻¹ Ca(NO₃)₂, 85 mg L⁻¹ CaCl₂, 124 mg L⁻¹ MgSO₄, 171 mg L⁻¹ NaHCO₃ and 20 mg L⁻¹ NaCl), (5) PFOA-saturated artificial groundwater, (6) PFOS-saturated artificial groundwater. The PFC-saturated NANOpure solutions (Groups 1-3) were performed with both 70-mesh and 200-mesh sediments. The PFC-saturated artificial groundwater solutions (Groups 4-6) were performed with only the 200-mesh sediments. All treatment groups were performed in duplicate and compared with the untreated sediment controls. These methods will be (or were) applied for the 5 different PFOA and PFOS concentrations for the 3 different amended soil systems (high to low carbon and/or clay content). Each 1-L flask-reactor (slurry) will be capped and placed on a shaker table (constantly agitated) over the 2-day (48 hour, i.e. short-term) sampling period to allow equilibrium partitioning (i.e. adsorption) to be achieved (Radke et al., 2009). Additional long-term experiments will evaluate 9-month PFC-soil contact-time effects on PFOA/PFOS intercalation and retention processes. A series of leaching experiments were performed for 48 h using PFC-saturated (PFOS/PFOA) NANOpure water solutions with only the 70-mesh size sediments. These experiments were conducted to investigate PFC intercalation processes under leaching (dilution) rather than sorption (loading) conditions. For these leaching studies sediment from the sorption batch experiment contaminated with PFCs and 15 mL NANOpure water were sealed in a borosilicate vial for 48 h. All batch reactor experiments were placed on shaker table at 150 rpm for a consistent agitation for the duration of the batch experiments to prevent sediment stratification.

For all sorption and leaching intercalation experiments, the solid-phase dominated slurry remaining was vortexed briefly before poured into a beaker to dry. The dried sediment was placed on a bulk powder mount for analysis. Oriented clay smears were made by adding 20 g sediment (70-mesh, 200-mesh) to 350 mL of NANOpure water. Bulk powder mounts and oriented clay smear mounts were analyzed on a Bruker zs D8 Advanced X-Ray Diffractometer using 40kV and 40Ma at 2.4° 2- Θ per min Goniometer analysis occurred between 2.5-60° 2- Θ . Results gave a qualitative sample mineralogy from 2- Θ peak intensities of *d*-spacing values and relative peak counts and intensities (Table 1). XRD patterns were standardized to the quartz peak (2- Θ = 26.703; *d*-spacing = 3.339 Å) for comparison of *d*-spacing results between treatment groups. The 200-mesh sediment was viewed under a Scanning Electron Microscope (SEM) to gain a qualitative understanding of the surface texture of the sediment. Sediment was sprinkled on a tape and either carbon- or gold-coated for SEM imaging. Grains photographed were of the clay minerals present in the sediment (e.g., Figure 1).

Two additional controls for PFOA and PFOS solution will be tested for loss of PFOA or PFOS due to volatilization, photochemical decomposition, or other potential mass-loss processes during the course of the batch experiments. PFOA and PFOS concentrations will be analyzed using high-performance liquid chromatography (HPLC), housed in Dr. Tick's Lab. Tandem solid-phase extraction (SPE) high performance liquid chromatography (UV detector) (HPLC-UV) will be employed to quantify the target PFOA and PFOS concentrations or sent to New Mexico State University (Dr. Carroll's Lab) for analysis (methods described in Salome, 2015; Salome and Tick, 2018). PFC-Soil intercalation, adsorption parameters, adsorption partition coefficients, retardation factors, and adsorption rate can be determine from these batch results by developing appropriate adsorption isotherm models for PFOA and PFOS.

Another set of batch reactor experiments were conducted to evaluate PFC partitioning between nonaqueous phase liquids (NAPL). The presence of NAPL at mixed waste disposal sites and at fire-training facilities (NAPL is the ; or fire source) has the potential to retain PFCs (PFOA/PFOS) within the subsurface as sources, leading to long-term slow release to groundwater (Guelfo and Higgins, 2013; SERDP-ESTCP, 2017). Specifically, these experiments tested various aqueous concentrations of PFOA in the presence of pure phase NAPL. Two-phase (PFOA aqueous-NAPL) batch systems were prepared for 8 different PFOA concentrations (0.01, 0.1, 1, 10, 50, 100, 250, and 500 mg/L) independently within 3 different bulk-NAPLs including n-hexane (HEX), n-decane (DEC), and n-hexadecane (HEXDEC). Thus, 24 different batch experiments were conducted, each done in triplicate (72 total). The batch experiments were created in 20-mL headspace vials (Thermo Scientific, Waltham, MA). Each experiment was created with 10-mL of PFOA solution at the respective aqueous concentration and 10-mL of the respective NAPL (HEX, DEC, or HEXDEC). Due to the fact that the NAPL mixtures were predominantly LNAPL, the PFOA solution was placed in the batch reactor vial first and the respective NAPL mixture was then carefully placed on top via a slow displacement from a glass syringe, so as not to cause any disturbance or mixing between the two immiscible fluids (PFC and NAPL). The vials were then sealed with crimp top caps (with silicone septa) with no headspace (no volatilization losses). Each batch system was left to sit for seven days to ensure equilibrium partition between PFOA and NAPL was maintained. A 3-mL sample was collected from the PFOA aqueous solution in the batch experiment, diluted if necessary, and transferred to a 2-mL direct inject vial where it was capped (no headspace) and sent to a collaborator's laboratory for analysis (New Mexico State University, Dr. Carroll's Lab) via liquid chromatography tandem mass spectrometry (LC/MS/MS). Such quantification provides information about how much PFOA (mass) exchanged or was retained by the particular NAPL (HEX, DEC, HEXDEC), an important process to know for assessing the fate and transport of PFCs in groundwater when mixed sources (i.e. NAPL) are present (disposal site or fire-training facility site) at a contamination site.

Column Flow Experiments

A series of column flow experiments are in progress to evaluate effects of flow on the transport and retention of PFOA and PFOS through saturated soil conditions. Stainless steel columns (7-cm length x 2.2-cm diameter; Alltech Co.) will be packed with the 3 different soil types (high to low clay or carbon content) and saturated using a synthetic groundwater solution (0.1 N CaCl₂). Constant concentrations (100 mg/L) of PFOA and PFOS doped with a conservative (nonreactive) tracer (bromide) will be used as the input solution to be injected into the soil-packed column systems. A constant input (100 mg/L) of PFOA or PFOS (PFBA doped) will be injected at a constant flow rate of 0.4 mL/min (pore velocity ~10 cm/hr) through the column. Once effluent concentrations reach the initial input concentration the input solution will be switched to "clean" water (synthetic groundwater devoid of PFOA or PFOS). Effluent samples will be collected over time and analyzed using the same HPLC analytical methods discussed previously. These results will generate breakthrough curves that can be used in combination with reaction models to determine transport parameters such as adsorption rates, retardation factors, and Peclet transport numbers (ratio of advection to dispersion).

2. Microbiological PFC Degradation Experiments

Microbiological and Bacteria Cultures for PFC Degradation

The aim is to isolate and grow native appropriate bacteria cultures from bulk soil PFC-contaminated regions and disposal sites at the 3M site (Decatur, AL) and/or biosolid sludge

waste from wastewater treatment facilities in Decatur, AL (i.e. Dry Creek WWTP). Bulk soil samples were collected from a site adjacent to the 3M facility and Tennessee River, areas known to have PFC contamination (up to 10 years exposure). Having viable degraders depends on natural selection and time for bacteria populations to mutate and evolve to utilize such compound for energy and cell growth. These soils were well characterized for mineralogy and grain size distribution from previously obtained samples. The primary steps for the series of microbiological (bacteria) characterization and culture isolation experiments: (1) sediment microcosm slurries, (2) test tube cultures, (3) agar plate cultures, and (4) isolation cultures. Soil samples will be used to make an anaerobic sediment slurry with an anoxic N₂ atmosphere. 2-mL of sediment inoculate will be added to a 28-mL of artificial groundwater media (0.225 g/L K₂HPO₄, 0.225 g/L KH₂PO₄, 0.46 g/L NaCl, 0.225 g/L (NH₄)SO₄, 0.117 g/L MgSO₄·H₂O, 0.06 g/L CaCl₂·2H₂O). Killed microcosm controls will be used to verify that no contamination occurred during study. These killed microcosms will be autoclaved at 120 °C for 50 minutes for heat sterilization. The sediment slurries will be incubated at 27 °C in a temperature-regulated shaker (agitated), set at a constant rpm. The slurries will be shaken occasionally to prevent stratification and settling that might result in the development of small bacterial colonies. Activity levels of the microcosms will be analyzed with UV-Vis spectrophotometry. Access to anaerobic chamber and the long-term stimulation required for degrader culturing may prove to be challenging as the success of culturing PFC-degrader has been limited to date.

3. Remediation / Treatment of PFCs in Soil and Groundwater

Two primary remediation approaches are to be conducted: 1) physical-based in-situ chemical oxidation (ISCO) using iron activated persulfate; and 2) Bioremediation which is dependent on whether viable PFC-degrading cultures can be isolated and grown in the initial experiments. The ISCO experiments focus on two methods one in which iron filings are used (macro particles) for use in permeable reactive barriers for PCF plume treatment and nanoscale zero-valent iron (NZVI) solution injections for treating plume sources. The bioremediation studies are proposed to force anaerobic conditions to enhance PFC degradation.

Activated Persulfate Oxidation (Physical-Based) – Batch Reactor Experiments

The degradation of PFOA and PFOS by iron-filings-activated persulfate and by nanoparticle iron will be measured in batch reactors. A solution of 10 mM Na₂S₂O₈ and 200 µg/L PFOA and PFOS will be mixed 1:1 (v:v) in a glass flask. Iron filings mixed and nanoparticle iron (10 mM as solution) will be mixed with 3M sediments (high to low carbon or clay content) and added to the mixture to yield a solid-liquid ratio of 1:10 (w/w). PFOA and PFOS samples will be collected and centrifuged for 1 min to separate iron filing particles or nanoparticles, and the supernatant will be transferred to a glass tube, cooled to ~0°C in an ice-water bath, and immediately analyzed for concentrations of PFOA or PFOS, persulfate, sulfate, ferrous ion, total iron, and pH. A control experiment of PFOA and PFOS solution with no oxidant or iron amendment will be conducted to test for loss of PFOA / PFOS due to volatilization, photochemical decomposition, or other potential mass-loss processes during the course of the batch experiments.

Activated Persulfate Oxidation (Physical-Based) – Column Experiments

Column flow experiments will be conducted to evaluate transport and degradation of PFOA and PFOS via persulfate-activated iron flushing. Stainless steel columns will be packed with homogenous mixtures of 3M sediments (high to low carbon or clay content) and iron filings and nanoparticle iron (10 mM as solution). Column will then be saturated with a synthetic groundwater solution (0.1 N CaCl₂). Two cases will be evaluated whereby the injection of a

solution of mixed 10 mM persulfate and 200 µg/L PFOA or PFOS into the column (*Case-1*: iron filings mixed 3 M soil; *Case-2*: nano-iron solution mixed 3M soil) at a constant flow rate of 0.4 mL/min (pore velocity ~10 cm/hr). After 7-9 pore volumes of injection, the influent will be switched to water. Effluent samples will be collected in glass tubes emplaced in an ice-water bath to quench the reaction, and weighed. The samples will then immediately analyzed for concentrations of PFOA or PFOS, persulfate, sulfate, ferrous iron, total iron, and pH, as described previously. The concentrations of PFOA and PFOS in the reservoir will be measured before, during, and after each experiment to monitor for potential loss.

Anaerobic Bioremediation (Biological-Based) – Batch Bioreactor Experiments

A sample of 3M soil (30-g) will be amended (inoculated) with the successfully cultured PFC-degrading (PFOA and PFOS) anaerobes in a N₂ anaerobic chamber (Dr. Sobecky's Lab – UA). As mentioned previously, appropriate nutrients amendments will be provided to maintain the growth of the PFC-degrading bacteria. The batch-reactor flasks containing the 3M-bacteria amended soil will then be spiked with 200 µg/L solutions of PFOA and PFOS to create a solid-liquid ratio mixture of 1:10 (w/w) (i.e. 3M-soil:PFC-solution). These flasks will be agitated on an anaerobic shaker table (Sobecky's Lab). Subsamples will collected for PFOA and PFOS over the course of the batch experiment and treated with a biological killer (i.e. HgCl₂) to stop any further biodegradation after sample collection. PFOA and PFOS will be analyzed using HPLC methods (Tick's or NMSU/Carroll Lab) and evaluated for loss due to microbial metabolism (degradation). Subsamples will also be evaluated for metabolites and degradation products via HPLC-mass spectrometry.

Anaerobic Bioremediation (Biological-Based) – Column Bioremediation Experiments

Columns will be packed with a homogenous mixture of homogenized 3M sediment (high carbon-content which represents the natural soil from the site) that has been amended (inoculated) with the successfully cultured PFC- (PFOA/PFOS)-degrading bacteria (anaerobes) in a N₂ anaerobic chamber (Dr. Sobecky's Lab – UA). Column will then be saturated with a synthetic groundwater solution containing appropriate nutrients to sustain microbial growth and survival. 200-µg/L solutions of PFOA or PFOS will then be injected through the 3M-bacteria amended sediment at a constant flow rate of 0.4 mL/min (pore velocity ~10 cm/hr). After 7-9 pore volumes of injection, the influent will be switched to water. PFOA and PFOS concentrations will be monitored from the flushing effluent at regular intervals throughout the entire experiment.

I. PRINCIPAL FINDINGS/RESULTS AND WORK IN PROGRESS

Physical Fate and Transport Experiments

Batch Reactor and Column Flow Experiments – Intercalation of PFCs (Retention Processes)

Soil and sediments collected adjacent to the 3M Site (Decatur, AL) and the Tennessee River were characterized using a variety of techniques including sieve (grain-size) analysis, carbon furnace combustion, X-ray diffraction (XRD), and scanning electron microprobe (SEM) to determine major mineralogical and carbon composition, silt/clay content, fraction of clay type, and overall grain-size distribution of the site soils ([Table 1A](#), [1B](#)).

Table 1A.

Sieve Mesh	Quartz(%)	Montmorillonite (%)	Illite (%)	Kaolinite (%)
-70	55.2 (±4.1)	11.8 (±0.29)	21.6 (±4.2)	11.3 (±0.45)
-200	63.4 (±3.4)	9.48 (±0.39)	15.8 (±1.8)	11.4 (±1.2)

Table 1B.

Sieve Mesh	Montmorillonite (%)	Illite (%)	Kaolinite (%)
-70	46.8	25.6	27.6
-200	45.7	24.4	29.8

Table 1. (A) Bulk powder mount and (B) clay smear mineralogy of clay-rich sediment via analysis of first order mineral peak intensity. Comparison of mineralogy for the 70-mesh and 200-mesh from normalization of minerals identified in the no treatment sediment data. Clay smear mineralogy normalized after exclusion of quartz to determine differences in clay mineral composition.

PFOA and PFOS fate/transport, specifically retention, processes via contaminant intercalation into clay structure was examined (Greenberg et al., 2018; Greenberg et al., 2017). A series of batch reactor experiments were conducted to determine the impacts of PFC-contamination on the *d*-spacing of the clays present in the sediment as a function of compound chemistry, sediment geochemistry, aqueous geochemistry, and sediment grain size under both sorption and leaching condition and variations in contact time (48 h vs. 9 month). Also, each system was tested using both “ion-free” water (NANOpure) and an artificial groundwater mimicking the groundwater chemistry of the region. The retention of PFCs via intercalation (PFOA and PFOS diffusing or “trapped” within clay interlayers) was evaluated using XRD analysis. The methods are not provided in detail but the sediments are prepared using standard techniques to generate bulk-powder (sediment) mounts and clay smears for analysis on the XRD. Shifts in XRD patterns allow for the determination of PFC intercalation into the clay interlayers. XRD patterns were standardized to the quartz peak ($2-\Theta = 26.703$; d -spacing = 3.339 Å) for comparison of *d*-spacing results between treatment groups. In addition, the 200-mesh sediment was viewed under a Scanning Electron Microscope (SEM) to gain a qualitative understanding of the surface texture of the sediment. Sediment was sprinkled on a tape and either carbon- or gold-coated for SEM imaging. Grains photographed were of the clay minerals present in the sediment (Figure 1).

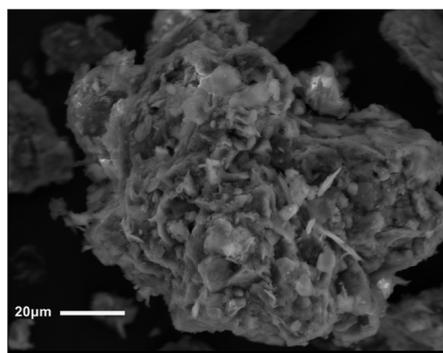
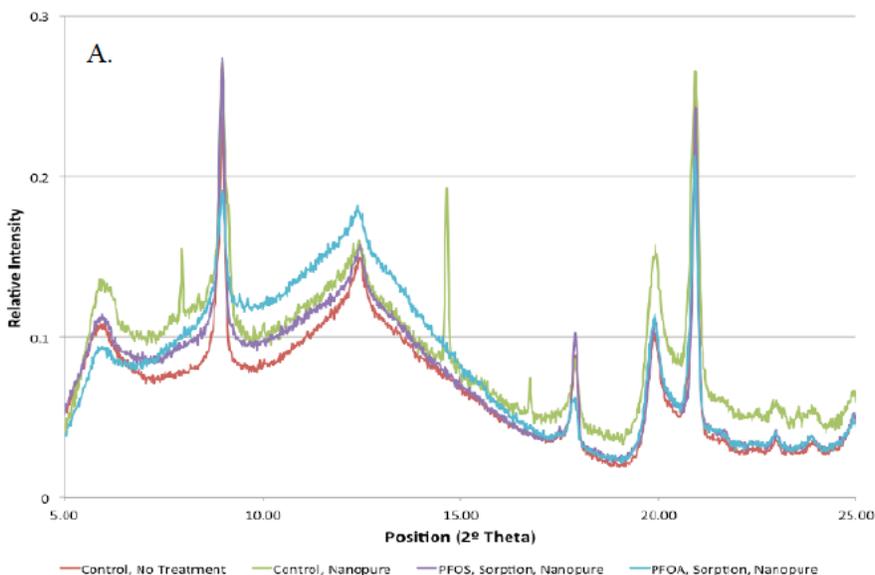


Figure 1. Scanning Electron Microscope image of a carbon coated clay mineral, showing fibrous texture.

Overall, *d*-spacing changes were not dramatically observed in montmorillonite, illite, and kaolinite clay minerals using XRD analysis of 70-mesh and 200-mesh sediment bulk powder mounts. Therefore, no significant peak shifts resulted due to any treatments (dry sediment vs. NANOpure treatment vs. artificial groundwater treatment), solution chemistry (NANOpure versus artificial groundwater solution base), compound (PFOS vs. PFOA), sediment grain size (70-mesh vs. 200-mesh), sorption vs. leaching processes, and exposure duration (48 h vs. 9 month) (Figures 2 and 3). However, subtle first-order peak montmorillonite shifts (1.3-2%) were observed for the long-term (9 month contact) experiments compared to the short-term (48 h) experiments for the finer 200-mesh sediment fraction (Figure 4). This finding suggests that some PFOS and PFOA or parts of the molecule may in fact associate into the *d*-spacing interlayer of the montmorillonite clay structure. Such an effect would potentially lead to greater retention of PFCs and delay transport and/or provide a source of PFC slow release to groundwater over time. However, further analysis is underway to determine whether these shifts are statistically significant.



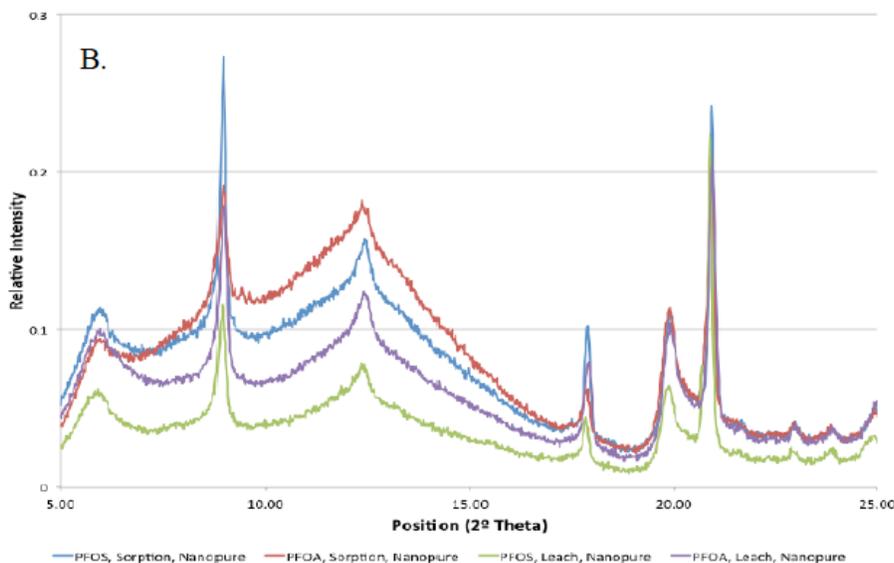


Figure 2. XRD patterns of 70-mesh clay-rich sediment bulk powder mounts. Comparison of relative intensity to maximum intensity peak (quartz, not shown) at 5-25 2° Theta for (A.) PFOS (purple) and PFOA (blue) 48 h sorption batch experiments versus controls of no treatment (red) or NANOpure water (green) treatment, and (B.) PFOS (blue) and PFOA (red) 48 h sorption experiments versus PFOS (green) and PFOA (purple) 48 h leaching experiments.

Unlike the no to subtle peak shifts observed due to PFC treatment, there was a notable change in the XRD pattern between the $2-\Theta$ positions that corresponded to the first order peaks of montmorillonite, illite, and kaolinite (Figure 4). Peaks at these locations were less distinct from background counts (relative intensity between first order peaks was higher). Other than XRD instrument adjustments between the initial 48 h batch experiments and the 9 month batch experiments, this behavior suggests that there could be differential intercalation for these longer term (9 month) contact experiments (Figure 4). Meaning, some of the clay minerals had changes in the d -spacing, and this d -spacing change was not consistent nor of the same displacement. Mineral surface texture (Figure 1) showed heterogeneity that would support differential rates of intercalation. This would create the effect of more “background noise” between mineral first peaks observed at 9 months. Such mineralogical changes in clay structure could also be induced by observed changes in pH, potentially contributing to variation in PFC intercalation (described in following section).

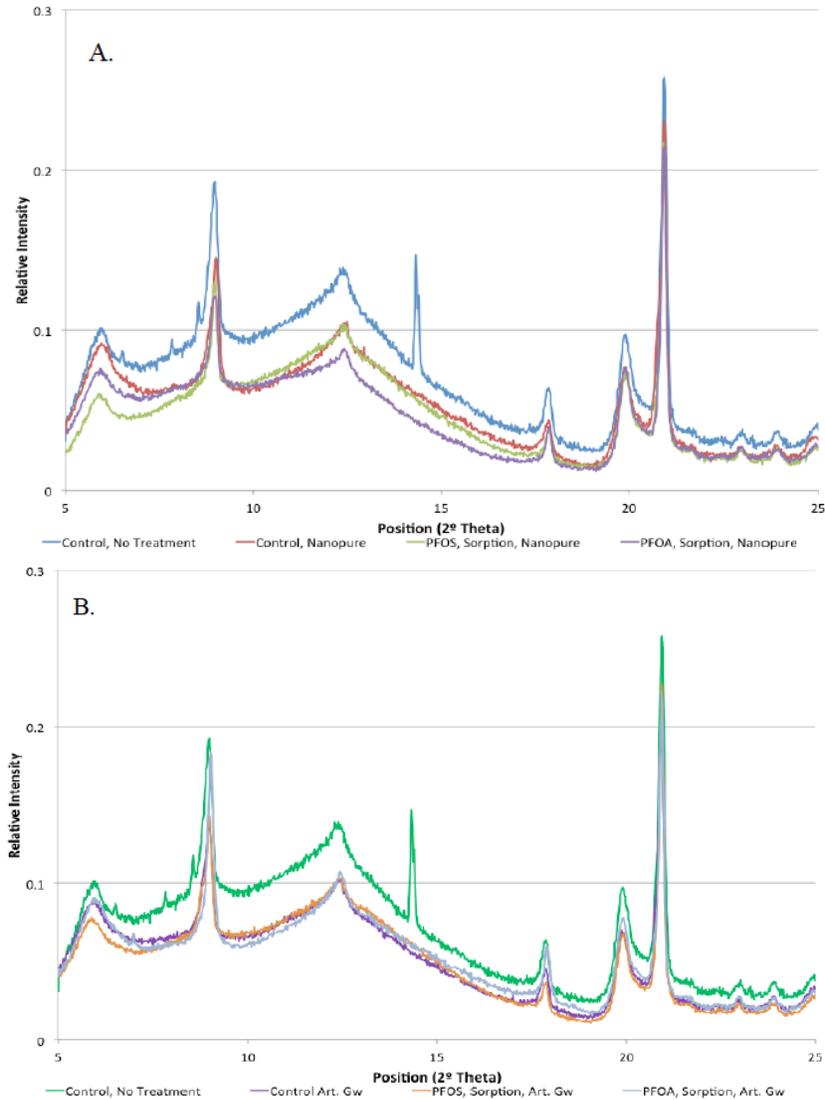


Figure 3. XRD patterns of 200-mesh clay-rich sediment bulk powder mounts. Comparison of relative intensity to maximum intensity peak (quartz, not shown) at 5-25 2° Theta for (A.) PFOS (green) and PFOA (purple) 48 h sorption batch experiments versus controls of no treatment (blue) or NANOpure water (red) treatment, and (B.) PFOS (orange) and PFOA (lavender) 48 h sorption experiments in artificial groundwater (GW) solution base versus controls of no (green) and artificial GW (purple) treatment.

Batch experiments were not buffered for pH consistency between the PFOS experiments, PFOA experiments and control experiments. This would affect the mineral surface charge. PFOS solutions with a NANOpure or artificial groundwater base had a pH 6-6.5. However, the PFOA solutions with a NANOpure or artificial groundwater base exhibited pH ranges between 2 and 3, which is consistent with the montmorillonite point of zero charge (PZC) (Krauskopf and Bird, 1995). Kaolinite would have a positive charge as the pH is below the PZC (Krauskopf and Bird, 1995). Kriaa et al. (2009) found the PZC of illite had a pH range of 7.5-9. Although the surface charge changed for montmorillonite between the controls, PFOS and PFOA treatment groups, the charge of illite remained consistently negative. Although changes in the mineral surface charge may affect the extent of sorption to the mineral surface and therefore the aqueous

concentrations of the batch experiments, this was not found to affect the extent of intercalation in a significant way. Although, as mentioned prior, noticeable shifts and XRD patterns were noticed, primarily for the finer mesh (200-mesh) sediments fraction treated with PFOA. The observed reduction of pH under such circumstances may alter or impact the sediment mineralogy and or dissolution of minerals thereby imparting potential differences in intercalation capabilities under such conditions. These observable affects, mentioned above, may in part be attributed to changes in the clay chemistry via pH changes.

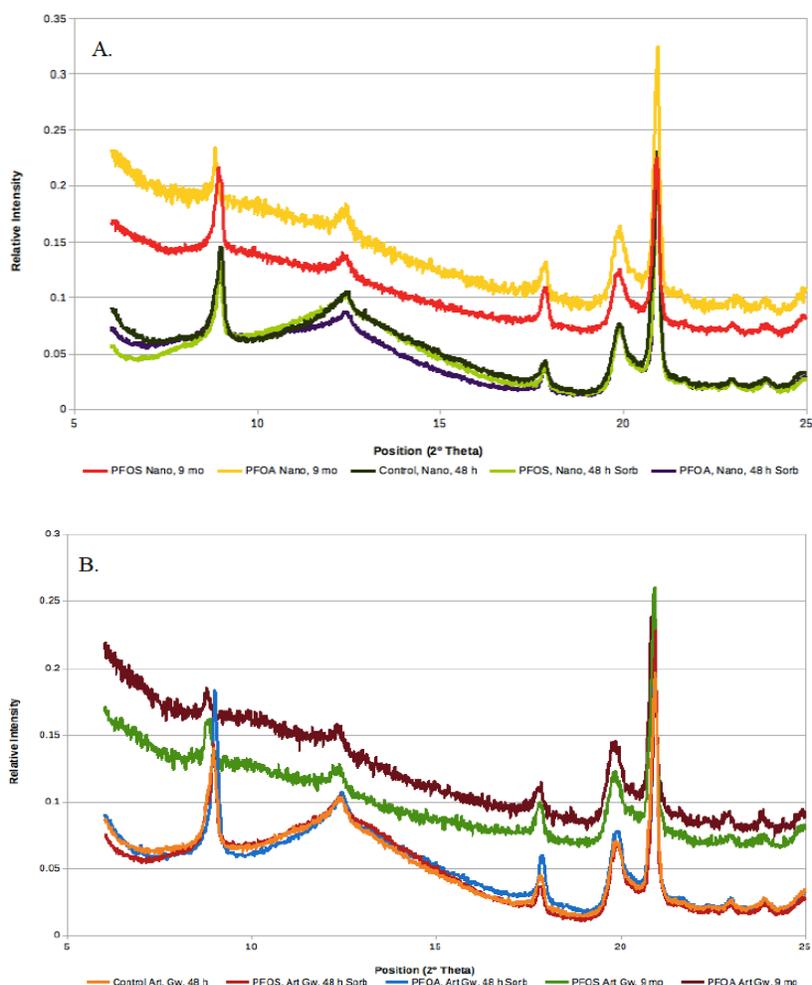


Figure 4. XRD patterns of 200-mesh clay-rich sediment bulk powder mounts. Comparison of relative intensity to maximum intensity peak (quartz, not shown) at 5-25 2° Theta for (A) PFOS (red) and PFOA (yellow) 9 month sorption batch experiments compared with 48 h NANOpure-only treatment control (black), 48 h sorption experiments with PFOS (green) and PFOA (purple) NANOpure treatment, and (B) PFOS (green) and PFOA (brown) 9 month sorption experiments in artificial groundwater (GW) solution base versus controls of 48 h artificial GW (orange) treatment, 48 h sorption experiments with PFOS (red) and PFOA (blue) artificial (GW) treatment.

Size exclusion of PFOS/PFOA from intercalation into the clay layers and/or unsatisfactory charge distribution within the clay interlayer and the PFC molecule itself is likely responsible for the lack of any significant PFOS/PFOA intercalation and via lack of *d*-spacing changes after treatment. Under such conditions, it would be expected that these PFCs (PFOS and PFOA) would exist in the aqueous phase, exhibit limited retention moving with groundwater or

water flow, and have relatively high bioavailability factors and exposure pathways to biological systems.

Batch Reactor and Column Flow Experiments – PFCs in NAPL (Retention Processes)

The mass transfer processes of PFC (PFOS/PFOA) to NAPL (HEX, DEC, HEXDEC) were investigated and quantified via PFC-NAPL batch reactor experiments (*described in Methods*) (Abbott, 2018; Abbott et al., 2017). Currently, PFOA experiments have been conducted but PFOS experiments are in progress and expected to be finished toward the end of August 2018. The results of the analytical analyses were recently received (May 2018) from NMSU (Dr. Carroll's Analytical Lab). Thus, the data of the PFOA-NAPL batch-reactor experiments represent only preliminary results and a portion of the total experiments conducted. However, the data generated provides an indication of how PFOA may react (partition) to various NAPL sources (i.e. within the field), contributing to retention processes and slow release for long-term PFC plume evolution. Preliminary results were generated from PFOA partitioning in both hexane (HEX) and hexadecane (HEXDEC) for an aqueous PFOA concentration range. The PFOA exchange (partitioning) was calculated for in terms of PFOA concentration in the aqueous phase versus PFOA concentration in the NAPL phase (HEX or HEXDEC) after equilibrium conditions were attained (7 days). The plotted relationship can be observed and the slope of the trend (linear fit) generally represents the magnitude of retention or partitioning between PFOA and the NAPL (NAPL-water partitioning coefficient, K_{NW}). Two selected plots (Figures 5 and 6) of the preliminary data show average PFOA-NAPL concentrations for the triplicate experiments (values) conducted.

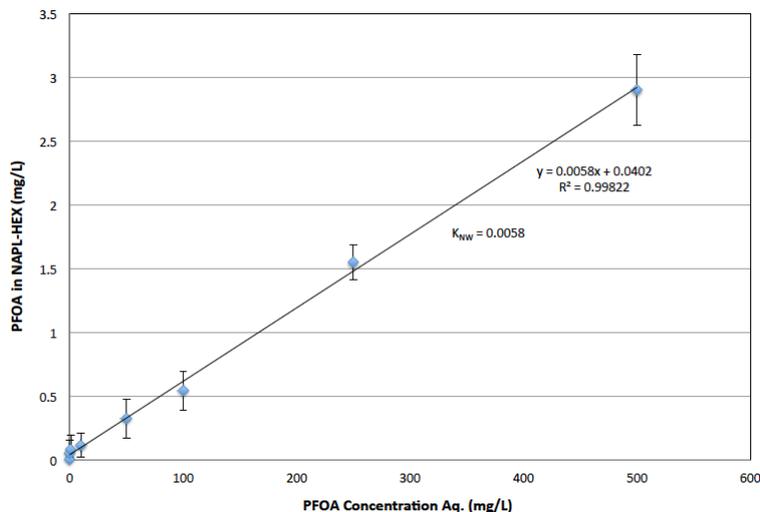


Figure 5. PFOA-NAPL partitioning equilibrium batch-reactor experiments over a range of aqueous PFOA concentrations in contact with hexane (HEX) NAPL, with a K_{NW} value of ~ 0.0058 . Error bars represent 95% confidence intervals about average values from triplicate experiments.

Figure 5 shows the PFOA partitioning behavior via the PFOA-HEX batch experiments over the range of PFOA aqueous phase concentrations tested. This preliminary data show a good linear fit ($R = 0.998$) over the range of concentrations and relatively small error via measurement or experimental variation. The PFOA-HEX partitioning (NAPL-water partitioning) coefficient is about 0.0058, demonstrating that there is some exchange and partitioning of PFOA within or at the surface of the HEX NAPL. It is likely that the PFOA primarily distributes at the NAPL-water boundary, based on surfactant-type distribution and that reported in other sources (Brusseau,

2018; Guelfo and Higgins, 2013). However, this is only speculated and not confirmed via these experiments. Further interfacial studies would be needed to quantify such PFOA distribution.

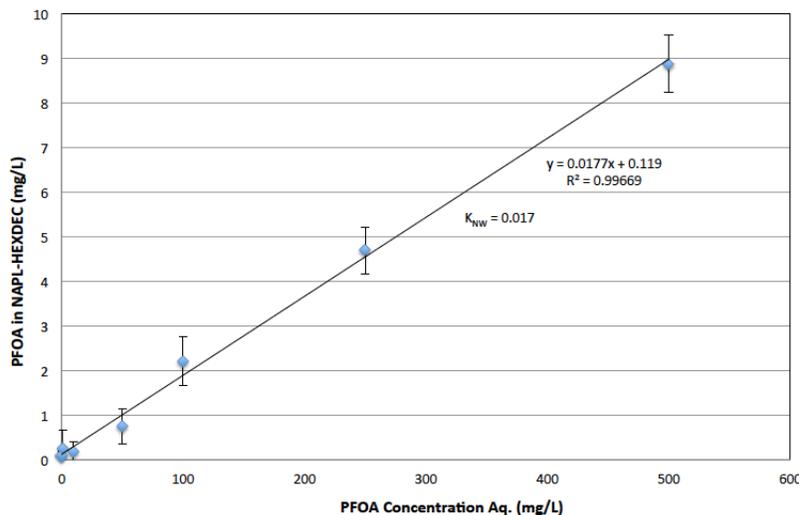


Figure 6. PFOA-NAPL partitioning equilibrium batch-reactor experiments over a range of aqueous PFOA concentrations in contact with hexadecane (HEXDEC) NAPL, with a K_{NW} value of ~ 0.0177 . Error bars represent 95% confidence intervals about average values from triplicate experiments.

Figure 6 shows the PFOA partitioning behavior via the PFOA-HEXDEC batch experiments over the range of PFOA aqueous phase concentrations tested. This preliminary data show a good linear fit ($R = 0.996$) over the range of concentrations and relatively small error via measurement or experimental variation. The PFOA-HEXDEC partitioning (NAPL-water partitioning) coefficient is about 0.0177, demonstrating that there is some exchange and partitioning of PFOA within or at the surface of the HEXDEC NAPL. It is likely that the PFOA primarily distributes at the NAPL-water boundary, based on surfactant-type distribution and that reported in other sources (as mentioned previously). Further interfacial studies would be needed to quantify such PFOA distribution within the NAPL.

In general, by comparing the two plots generated (PFOA-HEX and PFOA-HEXDEC), it can be observed that PFOA partitioned to a greater extent within the hexadecane NAPL systems than the hexane NAPL systems (K_{NW} of 0.0177 vs. 0.0058, respectively). This would suggest that longer-chained hydrocarbons (NAPL, at least for these simple straight chains alkanes, HEX vs. HEXDEC) would tend to retain the PFOA greater, leading to potentially longer release times, greater concentration tailing, and lower concentration groundwater plumes. Although, the plume concentrations may be lower under such scenarios for PFOA (or PFC) within longer chained alkanes, the amount of PFA associated with the NAPL-phase would be greater and serve as a potentially longer-term source of PFOA contamination to groundwater. Conversely, the lower plume concentrations may be more amenable to natural attenuation processes (via dilution, dispersion, physical degradation, and biodegradation).

Again, these data represent preliminary data that was recently generated as the analytical results were just received (May 2018). A wealth of batch data still requires further analysis (PFOA-HEX, PFOA-DEC, PFOA HEXDEC), including the PFOA-decane (DEC) (NAPL) batch experiments (not presented here), which will aid in understanding the partitioning and retention

of PFC (PFOA) in various NAPL derivatives and/or bulk-NAPL analogs at real world sites. Results from such experiments can provide value for developing better risk assessments and remediation designs for PFOA (PFCs) in the presence of NAPL at contamination sites.

WORK IN PROGRESS

Physical Fate and Transport Experiments

Soil Site Characterization

Soils and sediments were collected near the 3M Site (Decatur, Alabama) and from Tuscaloosa, Alabama to represent conditions with various fractions and types of organic carbon content and of clay (expanding and non-expanding clays). Detailed characterization of site soils have taken place and are described in the Results section herein. Such characterization included conducting sieve analyses (grain-size distribution), carbon content, clay type fraction and content, XRD analysis to assess intercalation processes, and SEM to determine clay textures (Table 1, Figures 2-4). However, more soil characterization is underway to determine PFC distribution in site soils (3M site area) and to prepare synthetic mixtures with either variation in organic carbon or clay content (high to low contents as described in *Methods and Proposal*) for a series of PFC (PFOA and PFOS) adsorption-desorption, PFC biodegradation/bioremediation, and PFC (PFOS/PFOA) in-situ activated persulfate remediation experiments.

Batch and Column Experiments – Adsorption/Desorption

The site soils prepared and synthetically amended with organic carbon and/or specific clay content is currently being used to conduct batch reactor and column adsorption/desorption experiments (*as described in Proposal*). Soils are to be amended with different PFOS and PFOA concentrations in 48-h equilibrium batch experiments. The results of this work will generate PFOA/PFOS adsorption and desorption rate coefficients as well and PFC distribution coefficients for each soil batch systems as a function of high to low carbon or clay content. Similarly, a set of column experiments are in progress, whereby column systems are packed with the site soils synthetically amended with organic carbon and/or specific clay content (i.e. high to low known fractions/content). PFOA and PFOS constant concentrations (100 mg/L), doped with conservative tracer (bromide-100 mg/L), are to be input into the column and PFC (and bromide) effluent concentrations are analyzed over time (describes adsorption/retention). Once maximum PFC (and bromide) concentrations bromide) are attained the systems are then flushed with “clean” synthetic groundwater solution and effluent PFC and bromide concentrations are analyzed over time (describes desorption/release). These will result generate breakthrough curves which can be used in combination with reaction models to determine transport parameters such as adsorption rates, retardation factors, and Peclet transport numbers (ratio of advection to dispersion).

Microbiological and Bacteria Cultures for PFC Degradation

The proposed microbiological experiments have been challenging to develop, as culturing bacteria from site soils has proven to be extremely difficult if not impossible under the time-frames available and under constraints of access and repair of the available anaerobic (N₂) chamber (Dr. Sobecky’s Lab). The most current literature to date (NGWA, 2017; SERDP-ESTCP, 2017) suggest that several months to years may be required to condition microbiological communities (i.e. bacteria or fungi) to degrade PFC compounds and/or their derivatives. In our initial experiments, we have not observed any PFC degradation, even over the longer-term 9-month intercalation studies. However, a biofilm was observed with our most recent long-term (9-month) intercalation experiments (as of April 2018) (with the exception of the PFOA-spiked

artificial groundwater batch experiment), which suggests that biological activity (anaerobic conditions) is capable under the relatively high PFOA/PFOS concentrations used. Attempts to determine the particular strain of bacteria/fungi are underway, and whether this strain can degrade the PFC (PFOA/PFOS) in these systems. Under the challenges faced with the biological-based experiments, this may be a promising observation/result that we are currently investigating in more detail.

Soil and Biosolid Collection and Characterization

To date we have been unsuccessful at isolating and culturing PFC degraders. We continue to characterize site soils for anaerobic chamber experiments. Access to a working anaerobic chamber has limited our ability to culture anaerobes in an anoxic (N₂) environment. We plan to continue these efforts as soon as the anaerobic chamber is available for use. We are looking into alternative experiments that can give us an indirect assessment of biodegradation potential via geochemistry and biodegradation indicators within the selected site soils. We are currently working on ways to progress these experiments directly and/or provide indirect means to assess biodegradation potential of PFCs in soil and groundwater. Under such challenges with the bio-related experiments/characterizations, we have moved our current focus on the physical in-situ iron-activated persulfate-oxidation remediation experiments which do not rely on the number of challenges/constraints and variables associated with biological growth and PFC persistence (i.e. lack of degradation potential). However, a biofilm was observed with our most recent long-term (9-month) intercalation experiments (as of April 2018) (with the exception of the PFOA-spiked artificial groundwater batch experiment), which suggests that biological activity (anaerobic conditions) is capable under the relatively high PFOA/PFOS concentrations used. Attempts to determine the particular strain of bacteria/fungi are underway, and whether this strain can degrade the PFC (PFOA/PFOS) in these systems. Under the challenges faced with the biological-based experiments, this may be a promising observation/result that we are currently investigating in more detail.

Microbial (bacteria) Characterization and Growth Experiments

Similar to the conditions described in the previous sections, we have been unsuccessful at isolating and culturing PFC degraders. Access to a working anaerobic chamber has limited our ability to culture anaerobes in an anoxic (N₂) environment. We plan to continue these efforts as soon as the anaerobic chamber is available for use. We are looking into alternative experiments that can give us an indirect assessment of biodegradation potential via geochemistry and biodegradation indicators within the selected site soils. We are currently working on ways to progress these experiments directly and/or provide indirect means to assess biodegradation potential of PFCs in soil and groundwater. As mentioned above, however, a biofilm was observed with our most recent long-term (9-month) intercalation experiments (as of April 2018) and we are simultaneously attempting to determine the particular strain of bacteria/fungi, and whether this strain can degrade the PFC (PFOA/PFOS) in our systems.

Microcosm Culture and Isolates – PFC Degradation

As mentioned above, we have been unsuccessful at isolating and culturing PFC degraders. Access to a working anaerobic chamber has limited our ability to culture anaerobes in an anoxic (N₂) environment. We are currently working on ways to progress these experiments with access to a working anaerobic chamber (culturing and isolating anaerobes) directly and/or provide indirect means to assess biodegradation potential of PFCs in soil and groundwater. As mentioned above, however, a biofilm was observed with our most recent long-term (9-month) intercalation experiments (as of April 2018) and we are simultaneously attempting to determine

the particular strain of bacteria/fungi, and whether this strain can degrade the PFC (PFOA/PFOS) in our systems.

PFOA / PFOS Degradation Pathways, Metabolites and Degradation Products

As mentioned above, we have been unsuccessful at isolating and culturing PFC degraders. Access a working anaerobic chamber has limited our ability to culture anaerobes in an anoxic (N₂) environment. We are currently working on ways to progress these experiments with gained access to a working anaerobic chamber (culturing and isolating anaerobes) directly and/or provide indirect means to assess biodegradation potential of PFCs in soil and groundwater. As mentioned above, however, a biofilm was observed with our most recent long-term (9-month) intercalation experiments (as of April 2018) and we are simultaneously attempting to determine the particular strain of bacteria/fungi, and whether this strain can degrade the PFC (PFOA/PFOS) in our systems.

Remediation / Treatment of PFCs in Soil and Groundwater

In light of some challenges with the biological-based degradation experiments due to challenges of microbiological growth, isolation, and culturing in the laboratory, we have focused current efforts (spring/summer 2018) on the physical adsorption-desorption and in-situ iron-activated persulfate oxidation remediation experiments as described herein. A combined permeable reactive barrier (PRB) with persulfate and persulfate/nanoparticle-iron injection solutions has the potential to treat large volumes of soil and groundwater contaminated by PFCs (Lee et al., 2012; USEPA, 2006). Activated persulfate, as the primary oxidant for our application, is selected based on the advantages of persulfate over other regularly used oxidants such as H₂O₂ and permanganate (Zhong et al., 2015). Zero-valent iron (particles or nano-iron solutions) has been shown to activate persulfate through release of Fe²⁺ which then yield sulfate and hydroxyl radicals (long-term quantities) for contaminant (PFC) degradation (Lee et al., 2012).

Physical Activated-Iron Persulfate Oxidation Experiments

Batch Reactor and Column Experiments

The degradation of PFOA and PFOS by iron-filings-activated persulfate and by nanoparticle iron will be measured in batch reactors. For batch experiments (spring/summer 2018), a solution of 10 mM Na₂S₂O₈ and 200 µg/L PFOA and PFOS will be mixed 1:1 (v:v) in a glass flask. Iron filings mixed and nanoparticle iron (10 mM as solution) are being mixed with 3M sediments (*A*-high carbon or clay content; *B*-mid carbon or clay content; and *C*-lowest carbon or clay content) and added to the mixture to yield a solid-liquid ratio of 1:10 (w/w). The flask will be sealed with parafilm and placed on a rotary shaker table at approximately 200 rpm at a room temperature of 25±1°C for 1-hr. 2-mL subsamples will be collected for PFOA and PFOS over the course of the batch experiment in glass vials, and placed in an ice-water bath to quench further reaction. PFOA or PFOS, persulfate, sulfate, ferrous ion, total iron, and pH will be analyzed immediately after the batch duration. A control experiment of PFOA and PFOS solution with no oxidant or iron amendment will be conducted to test for loss of PFOA / PFOS due to volatilization, photochemical decomposition, or other potential mass-loss processes during the course of the batch experiments. PFOA and PFOS will be analyzed using HPLC methods at the NMSU analytical facility in Dr. Carroll's laboratory (collaborator).

Column flow experiments (spring/summer 2018) will be conducted to evaluate transport and degradation of PFOA and PFOS via persulfate-activated iron flushing. Stainless steel columns will be packed with homogenous mixtures of 3M sediments (high to low carbon and/or clay content) and iron filings and nanoparticle iron (10 mM as solution). Columns will then be

saturated with a synthetic groundwater solution (0.1 N CaCl₂). Two cases will be evaluated whereby the injection of a solution of mixed 10 mM persulfate and 200 µg/L PFOA or PFOS into the column (*Case-1*: iron filings mixed 3 M soil; *Case-2*: nano-iron solution mixed 3M soil) at a constant flow rate of 0.4 mL/min (pore velocity ~10 cm/hr). After 7-9 pore volumes of injection, the influent will be switched to water. Effluent samples will be collected in glass tubes emplaced in an ice-water bath to quench the reaction, and weighed. The samples will then immediately analyzed for concentrations of PFOA or PFOS, persulfate, sulfate, ferrous iron, total iron, and pH, as described previously.

Anaerobic Bioremediation (Biological-Based) Experiments

A series of batch and column experiments utilizing cultured bacteria (microbes) from the initial-phase microbiological experiments will be conducted in similar methodology as the physical persulfate experiments described above. This proposed work is slated to begin once the initial challenges with isolation and culturing of PFC degrading bacteria are solved. Outcomes are dependent on the initial characterization steps described previously under the *Microbiological and Bacteria Cultures for PFC Degradation* sections.

Batch Bioreactor Experiments

The batch experiments will be performed using same methods as described previously in *Methods and/or Proposal*. A 30-g sample of 3M soil (high to low carbon or clay content) will be amended (inoculated) with the successfully cultured PFC-degrading (PFOA and PFOS) anaerobes in a N₂ anaerobic chamber (Dr. Sobecky's Lab – UA). As mentioned previously, appropriate nutrients amendments will be provided under constant temperature (25±1°C) to maintain the growth of the PFC-degrading bacteria. The batch-reactor flasks containing the 3M-bacteria amended soil will then be spiked with 200 µg/L solutions of PFOA and PFOS to create a solid-liquid ratio mixture of 1:10 (w/w) (i.e. 3M-soil:PFC-solution). These flasks will be agitated on an anaerobic shaker table (Sobecky's Lab). Subsamples will collected for PFOA and PFOS over the course of the batch experiment and treated with a biological killer (i.e. HgCl₂) to stop any further biodegradation and PFOA and PFOS will be analyzed using HPLC methods (Dr. Carroll's Analytical Laboratory). To date we have been unsuccessful at isolating and culturing PFC degraders. We continue to characterize site soils for anaerobic chamber experiments. Access a working anaerobic chamber has limited our ability to culture anaerobes in an anoxic (N₂) environment. We plan to continue these efforts as soon as the anaerobic chamber is available for use. We plan to initiate this experiment this summer (2018) but the results are on dependent on the initial characterization steps described previously under the *Microbiological and Bacteria Cultures for PFC Degradation* sections.

Column Flow Bioremediation Experiments

Columns will be packed with a homogenous mixture of homogenized 3M sediment (high carbon-content only which represents the natural soil from the site) that has been amended (inoculated) with the successfully cultured PFC- (PFOA/PFOS)-degrading bacteria (anaerobes) in a N₂ anaerobic chamber (Dr. Sobecky's Lab – UA). Columns will then be saturated with a synthetic groundwater solution containing appropriate nutrients (see *Methods or Proposal*) to sustain microbial growth and survival. 200-µg/L solutions of PFOA or PFOS will then be injected through the 3M-bacteria amended sediment at a constant flow rate of 0.4 mL/min (pore velocity ~10 cm/hr). After 7-9 pore volumes of injection, the influent will be switched to water. PFOA and PFOS concentrations will be monitored from the flushing effluent at regular intervals throughout the entire experiment. Effluent samples will be collected in glass tubes and treated with a biological killer (i.e. HgCl₂) to stop any further biodegradation and PFOA and PFOS will

be analyzed using HPLC methods (Dr. Carroll's Analytical Laboratory). To date we have been unsuccessful at isolating and culturing PFC degraders. We continue to characterize site soils for anaerobic chamber experiments. Access a working anaerobic chamber has limited our ability to culture anaerobes in an anoxic (N₂) environment. We plan to continue these efforts as soon as the anaerobic chamber is available for use. We plan to initiate this experiment this summer (2018) but the results are on dependent on the initial characterization steps described previously under the *Microbiological and Bacteria Cultures for PFC Degradation* sections.

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- Greenberg, R.R., Tick, G.R., Donahoe, R.J., Carroll, K.C., and Zhang, Y., 2018. Intercalation of perfluoroalkyl substances in clay-rich sediments, *Chemosphere* (In preparation to be submitted).
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J. NOTABLE AWARDS AND ACHIEVEMENTS

N/A

K. PUBLICATIONS GENERATED/SUBMITTED/IN-PREPARATION

Number of Research Publications generated from this research project:	
Publication Category	Number
Articles in Refereed Journals (to be published)	4 (to be)
Book Chapters	0
Theses and Dissertations	1 (some work)
Water Resources Institute Reports	0
Articles in Conference Proceedings (abstracts)	6 (abstracts)
Other Publications	0

PROVIDE A CITATION FOR EACH PUBLICATION USING THE FOLLOWING FORMATS:

1. Articles in Refereed Scientific Journals Citation (to be submitted summer 2018/fall 2018)

- Greenberg, R.R., G.R., Tick; R.J., Donahoe; K.C., Carroll; Y. Zhang, 2018, Intercalation of perfluoroalkyl substances in clay-rich sediments, *Chemosphere*, (almost ready to be submitted summer 2018).
- Greenberg, R.R., G.R., Tick; K.C., Carroll; Y. Zhang, 2018, Effects of Clay and Organic Content on Per- and Polyfluoroalkyl Substances (PFAS) Adsorption-Desorption Behavior in Groundwater: Laboratory-scale Investigations, *Journal of Contaminant Hydrology*, , (in preparation to be submitted fall 2018).
- Greenberg, R.R., G.R., Tick; K.C., Carroll, 2018, In-situ Iron Activated Persulfate Oxidation of Per- and Polyfluoroalkyl Substances (PFAS) in Soils of Varying Organic Carbon and Clay Content, *Environmental Science and Technology*, (in preparation to be submitted fall 2018).
- Abbott, J.B., G.R., Tick; R.R., Greenberg, K.C., Carroll, 2017, Quantifying Mass Transfer Processes in Groundwater as a Function of Molecular Structure Variation for Multicomponent NAPL Sources, *Journal of Contaminant Hydrology*, (In preparation to be submitted summer 2018).

2. Book Chapter Citation

N/A

3. Dissertations/Thesis Citation

- Abbott, Joe Booth III, 2018, Quantifying Mass Transfer Processes in Groundwater as a Function of Molecular Structure Variation for Multicomponent NAPL Sources. M.S. Thesis, Department of Geological Sciences, University of Alabama, Tuscaloosa, p.1-76. (defended April, 2018 – graduate in August 2018). Some of the work was funded by AWRRI award (PFCs work, partially related).

4. Water Resources Research Institute Reports Citation

N/A

5. Conference Proceedings Citation

- Greenberg, Rebecca R.; G.R. Tick, 2018, Physicochemical Processes Affecting the Fate and Transport of Perfluoroalkyl Substances in Clay-rich Sediments and Groundwater in the Proceedings of the Emerging Contaminants in the Aquatic Environment Conference 2018, June 5-6, 2018, Champaign, IL; Illinois Sustainable Technology Center Illinois-Indiana Sea Grant, Funding provided in part by University of Illinois Extension National Science Foundation Illinois Hazardous Waste Research Fund (Presentation).
- Greenberg, R.R. and G.R., Tick, 2018, A Laboratory-based Study on Intercalation of Perfluoroalkyl Substances in Clay-rich Sediments, Proceedings in the Water Policy Summit, Community Resiliency: Summit to Sea Conference, National Water Center, Tuscaloosa, AL, March 27-29, 2018, (Presentation).
- Greenberg, R.R., G.R., Tick; J.A., Abbott, J.A., K.C., Carroll, 2017, Mass Transfer Behavior of Perfluorinated Chemicals in Saturated Clay-rich Soils: A Laboratory-based Study on Fate

- and Transport in Groundwater and Sediments, in Proceedings as an *Abstract* (#295735) *H11F-1266*, presented at 2017 Fall Meeting, AGU, New Orleans, LA, 11-15 Dec. (Presentation).
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- Greenberg, R.R. and G.R., Tick, 2017, Intercalation of Perfluoroalkyl Substances in Clay-rich Sediments 9th Annual Graduate Research Symposium of the Department of Educational Studies in Psychology, Research Methodology, and Counseling, March 31, 2017, University of Alabama (Presentation).

6. Other Publications Citation

N/A

L. PRESENTATIONS MADE:

- Greenberg, Rebecca R.; G.R. Tick, 2018, Physicochemical Processes Affecting the Fate and Transport of Perfluoroalkyl Substances in Clay-rich Sediments and Groundwater in the Proceedings of the Emerging Contaminants in the Aquatic Environment Conference 2018, June 5-6, 2018, Champaign, IL; Illinois Sustainable Technology Center Illinois-Indiana Sea Grant, Funding provided in part by University of Illinois Extension National Science Foundation Illinois Hazardous Waste Research Fund (Presentation).
- Greenberg, R.R. and G.R., Tick, 2018, A Laboratory-based Study on Intercalation of Perfluoroalkyl Substances in Clay-rich Sediments, Proceedings in the Water Policy Summit, Community Resiliency: Summit to Sea Conference, National Water Center, Tuscaloosa, AL, March 27-29, 2018, (Presentation).
- Greenberg, R.R., G.R., Tick; J.A., Abbott, J.A., K.C., Carroll, 2017, Mass Transfer Behavior of Perfluorinated Chemicals in Saturated Clay-rich Soils: A Laboratory-based Study on Fate and Transport in Groundwater and Sediments, in Proceedings as an *Abstract* (#295735) *H11F-1266*, presented at 2017 Fall Meeting, AGU, New Orleans, LA, 11-15 Dec. (Presentation).
- Abbott, J.B., G.R., Tick, R.R., Greenberg, R.R., K.C., Carroll, 2017, Quantifying Mass Transfer Processes in Groundwater as a Function of Molecular Structure Variation for Multicomponent NAPL Sources, in Proceeding as an *Abstract* (#235147) *H11F-1245*, presented at 2017 Fall Meeting, AGU, New Orleans, LA, 11-15 Dec. (Presentation).
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University of Illinois Extension National Science Foundation Illinois Hazardous Waste Research Fund (Presentation).

Greenberg, R.R. and G.R., Tick, 2017, Intercalation of Perfluoroalkyl Substances in Clay-rich Sediments 9th Annual Graduate Research Symposium of the Department of Educational Studies in Psychology, Research Methodology, and Counseling, March 31, 2017, University of Alabama (Presentation).

M. STUDENTS SUPPORTED (Complete the following table)

Number of Students Supported, by Degree	
Type	Number of students funded through this research project:
Undergraduate	2 (partially – some hrs)
Masters	1 partially (Joe Boone Abbott)
Ph.D.	1 entirely (Rebecca Greenberg)
Post Doc	0
Number of Theses and Dissertations Resulting from Student Support:	
Master’s Theses	1 (partially)
Ph.D. Dissertations	1 entirely

N. RESEARCH CATEGORIES: (In column 1 mark all that apply)

	Research Category
x	Biological Sciences (intended biodegradation)
	Climate and Hydrological Processes
	Engineering
x	Ground Water Flow and Transport
	Social Sciences
x	Water Quality
	Other: Explain

O. FOCUS CATEGORIES (mark all that apply with “X” in column 1):

	ACID DEPOSITION	ACD
	AGRICULTURE	AG
	CLIMATOLOGICAL PROCESSES	CP
	CONSERVATION	COV
	DROUGHT	DROU
	ECOLOGY	ECL
	ECONOMICS	ECON
	EDUCATION	EDU
	FLOODS	FL
	GEOMORPHOLOGICAL PROCESSES	GEOMOR
X	GEOCHEMICAL PROCESSES	GEOCHE
X	GROUNDWATER	GW
X	HYDROGEOCHEMISTRY	HYDGEO
X	HYDROLOGY	HYDROL
	INVASIVE SPECIES	INV
	IRRIGATION	IG
	LAW, INSTITUTIONS, & POLICY	LIP
	MANAGEMENT & PLANNING	M&P
	METHODS	MET
	MODELS	MOD
	NITRATE CONTAMINATION	NC
	NONPOINT POLLUTION	NPP
	NUTRIENTS	NU
	RADIOACTIVE SUBSTANCES	RAD
	RECREATION	REC
X	SEDIMENTS	SED
X	SOLUTE TRANSPORT	ST
X	SURFACE WATER	SW
X	TOXIC SUBSTANCES	TS
X	TREATMENT	TRT
X	WASTEWATER	WW
X	WATER QUALITY	WQL
	WATER QUANTITY	WQN

	WATER SUPPLY	WS
	WATER USE	WU
	WETLANDS	WL

P. DESCRIPTORS: (Enter keywords of your choice, descriptive of the work)

Perfluorinated Chemicals (PFCs); Per- and Polyfluoroalkyl Substances (PFAS); Groundwater Contamination; Intercalation; Retention Processes; Contaminant Fate and Transport; Adsorption-Desorption Processes; PFAS/PFCs Characterization; Mass-Transfer Processes; Biodegradation; Water Treatment; In-situ Chemical Oxidation; Iron-Activated Persulfate Oxidation Treatment; Soil and Groundwater Remediation; Emerging Contaminants.

Enhancing Seasonal Hydrological Forecasts in the Alabama-Coosa-Tallapoosa (ACT) River Basin using the North American Multi-Model Ensemble

Basic Information

Title:	Enhancing Seasonal Hydrological Forecasts in the Alabama-Coosa-Tallapoosa (ACT) River Basin using the North American Multi-Model Ensemble
Project Number:	2017AL185B
Start Date:	3/1/2017
End Date:	2/28/2018
Funding Source:	104B
Congressional District:	AL003
Research Category:	Not Applicable
Focus Categories:	Water Quantity, Surface Water, Climatological Processes
Descriptors:	None
Principal Investigators:	Di Tian

Publications

There are no publications.

ANNUAL TECHNICAL REPORT SYNOPSIS

The Terms and Conditions of the grants awarded under the Water Resources Research Act state that each institute shall prepare an Annual Program Report summarizing its activities during the reporting period under its base grant, and National Competitive Grant Program awards. The reporting period is March 1, through February 28. All Annual Reports must be submitted by 5:00 PM, Eastern Daylight Time, June 1, and must be submitted electronically. In order to do this we need your assistance by providing the following information about your current or recent WRRRI-funded research project to me by May 25, 2016:

- A. PROJECT TITLE: Enhancing Seasonal Hydrological Forecasts in the Alabama-Coosa-Tallapoosa (ACT) River Basin using the North American Multi-Model Ensemble
- B. PRIMARY PI(s): Di Tian, Assistant Professor
- C. OTHER PI(s): Latif Kalin, Professor; Alan L. Peebles, Reservoir Manager
- D. START DATE: 03/01/2017
- E. END DATE: 02/28/2018
- F. PROJECT OVERVIEW/SUMMARY: The overall goal of this project is to develop improved hydrological forecasts for basin-scale water resources planning and management.
- G. PROJECT OBJECTIVE(s): Since streamflow and evaporation are two of the most important factors for water and reservoir management, specific objectives of this proposed research are to: (1) Develop climate-informed seasonal reservoir inflow forecasts using machine-learning techniques in the ACT river basin, and (2) generate daily evaporation forecasts using multi-model ensemble medium-range weather forecasts.
- H. METHODOLOGIES: This study employs hybrid methods combining statistical-dynamic models to develop hydrologic forecasting, which involves large climate and hydrologic data manipulation, analysis, and modeling using weather and climate model forecasts and advanced statistical techniques. Specifically, we compared three machine-learning techniques, including random forest, extreme learning machine, and gradient boosted regression tree for seasonal reservoir inflow forecasts using climate forecasts and observations. We produced multi-model reference evapotranspiration forecasts using numerical weather predictions and assessed its probabilistic and deterministic forecast performance retrospectively over the past decades.
- I. PRINCIPAL FINDINGS/RESULTS: For the reservoir inflow forecasts, the results showed that seasonal climate forecasts play an important role in reservoir inflow forecasts. Without predictors' screening, extreme learning machine methods showed the best forecasting performance, followed by random forest, and gradient boosted regression tree. Using selected number of predictors identified by the random forest technique, the forecasting performance improved dramatically with the random forest model showing the best forecasting performance. For the evaporation forecasts, the results showed that the European Center for Medium-range Weather Forecast model provided the best forecasts, followed by the UK Meteorology Office model, and US National Center for Environmental Prediction model. The multi-model ensemble forecasts performed slightly better than the single model forecast. A simple bias correction procedure considerably improved evaporation forecast performance. The

radiation forecast errors had the strongest impact on evaporation forecasts. The forecast methods, models, and products developed in this project can be employed by water managers and relevant users to improve their management practices.

J. NOTABLE AWARDS AND ACHIEVEMENTS.

K. PUBLICATIONS GENERATED:

Number of Research Publications generated from this research project:	
Publication Category	Number
Articles in Refereed Journals	2
Book Chapters	
Theses and Dissertations	
Water Resources Institute Reports	
Articles in Conference Proceedings	
Other Publications	

PROVIDE A CITATION FOR EACH PUBLICATION USING THE FOLLOWING FORMATS:

1. Articles in Refereed Scientific Journals Citation

Medina, H., D. Tian, P. Srivastava, A. Pelosi, G. B. Chirico. In press. Medium-range reference evapotranspiration forecasts for the contiguous United States based on multi-model numerical weather predictions. *Journal of Hydrology*. <https://doi.org/10.1016/j.jhydrol.2018.05.029>

Tian, D., M. Valipour, X. He, Y. Duan, and P. Srivastava. In preparation. Developing Climate-informed Reservoir Inflow Forecasts Using Machine Learning Techniques. *Journal of Hydrometeorology*.

2. Book Chapter Citation

3. Dissertations Citation

4. Water Resources Research Institute Reports Citation

5. Conference Proceedings Citation

6. Other Publications Citation

L. PRESENTATIONS MADE:

Medina, H. and D. Tian. Comparison of multiple statistical post-processing methods for TIGGE-based reference evapotranspiration forecasts. AGU Fall Meeting, 11–15 December 2017, New Orleans, LA

Medina, H. and D. Tian. Medium-range forecasting of reference evapotranspiration in the continental US using numerical weather predictions. 2017 Alabama Water Resources Conference and Symposium, September 6-8, 2017. Orange Beach, Alabama

Medina, H. and D. Tian. Forecasting medium-range reference evapotranspiration for the continental U.S. using the TIGGE multi-model ensembles. This is Research: Student Symposium. April 13, 2017. Auburn, AL.

Duan, Y. and D. Tian. Enhancing Lake Inflow Forecasts in the Alabama-Coosa-Tallapoosa (ACT) River Basin using the North American Multi-Model Ensemble. This is Research: Student Symposium. April 13, 2017. Auburn, AL.

Medina, H. and D. Tian. Probabilistic Forecasts of Daily Reference Evapotranspiration for the Continental U.S. Based on Numerical Weather Predictions. 2017 ASA-CSSA-SSSA Annual Meeting, October 22-25, 2017. Tampa, Florida

Duan, Y., H. Medina, and D. Tian. Developing Reservoir Seasonal Inflow Forecasts based on Dynamic Climate Forecasts and Large-Scale Climate Information. 98th AMS Annual Meeting, 7–11 January 2018, Austin, TX

Tian, D., H. Medina, Y. Duan, and T. Schillerberg. A data-driven framework of agroclimate monitoring and forecasting for decision making. Big Data Driven Agriculture Workshop: Advances, Challenges, and Opportunities, 25–28 February 2018, Arlington, VA

M. STUDENTS SUPPORTED (Complete the following table)

Number of Students Supported, by Degree	
Type	Number of students funded through this research project:
Undergraduate	
Masters	1
Ph.D.	1
Post Doc	
Number of Theses and Dissertations Resulting from Student Support:	
Master's Theses	1 ongoing
Ph.D. Dissertations	1 ongoing

N. RESEARCH CATEGORIES: (In column 1 mark all that apply)

	Research Category
	Biological Sciences
X	Climate and Hydrological Processes
X	Engineering
	Ground Water Flow and Transport
	Social Sciences
	Water Quality
	Other: Explain

O. FOCUS CATEGORIES (mark all that apply with "X" in column 1):

	ACID DEPOSITION	ACD
X	AGRICULTURE	AG
X	CLIMATOLOGICAL PROCESSES	CP
	CONSERVATION	COV
X	DROUGHT	DROU
	ECOLOGY	ECL
	ECONOMICS	ECON
	EDUCATION	EDU
	FLOODS	FL
	GEOMORPHOLOGICAL PROCESSES	GEOMOR
	GEOCHEMICAL PROCESSES	GEOCHE
	GROUNDWATER	GW
	HYDROGEOCHEMISTRY	HYDGEO
X	HYDROLOGY	HYDROL
	INVASIVE SPECIES	INV
	IRRIGATION	IG
	LAW, INSTITUTIONS, & POLICY	LIP
X	MANAGEMENT & PLANNING	M&P
X	METHODS	MET
X	MODELS	MOD
	NITRATE CONTAMINATION	NC
	NONPOINT POLLUTION	NPP
	NUTRIENTS	NU
	RADIOACTIVE SUBSTANCES	RAD
	RECREATION	REC
	SEDIMENTS	SED
	SOLUTE TRANSPORT	ST
X	SURFACE WATER	SW
	TOXIC SUBSTANCES	TS
	TREATMENT	TRT
	WASTEWATER	WW
	WATER QUALITY	WQL
X	WATER QUANTITY	WQN
X	WATER SUPPLY	WS

	WATER USE	WU
	WETLANDS	WL

P. DESCRIPTORS: Drought, Evaporation, Instream Flow, Rainfall, Weather Forecasting

SIGNIFICANCE OF THE COASTAL SEDIMENTS AS A SOURCE/SINK OF NUTRIENTS TO COASTAL WATERS IN THE MOBILE BAY

Basic Information

Title:	SIGNIFICANCE OF THE COASTAL SEDIMENTS AS A SOURCE/SINK OF NUTRIENTS TO COASTAL WATERS IN THE MOBILE BAY
Project Number:	2017AL186B
Start Date:	3/1/2017
End Date:	8/15/2018
Funding Source:	104B
Congressional District:	AL007
Research Category:	Not Applicable
Focus Categories:	Groundwater, Hydrogeochemistry, Sediments
Descriptors:	None
Principal Investigators:	Natasha T Dimova

Publications

There are no publications.

ANNUAL TECHNICAL REPORT SYNOPSIS

- A. PROJECT TITLE: Significance of the coastal sediments as a source/sink of nutrients to coastal waters in the Mobile Bay (MB)**
- B. PRIMARY PI(s): Natasha T. Dimova, Ph.D., Assistant Professor**
- C. OTHER PI(s): Prabhakar Clement, Ph.D., Professor, Director of the Center for Water Quality Research, University of Alabama**
- D. START DATE: January 2017**
- E. END DATE: December 2017 (no-cost extension to August 31st, 2018)**

F. PROJECT OVERVIEW/SUMMARY:

Large-scale mortalities of fish and shellfish, locally known as “*Jubilees*”, have been observed along the eastern shore of Mobile Bay, Alabama for at least 150 years. During these events, moribund fish and blue crabs are forced by the lack of oxygen to approach the beach. In addition to this local phenomenon, an excess of nutrients (more often measured as nitrogen, N-) in coastal waters has been held responsible for persistent harmful algae blooms (HABs) both in Mobile Bay and adjacent coastal sites. An assumed obvious source of the elevated levels of N- in coastal waters that triggers the HABs and Jubilees is the Mobile-Tensaw River System. However, recent studies have indicated indirectly that *submarine groundwater discharge* (SGD) might play an important role in the occurrences of these events.

With this research, we investigate the origin of the different components of SGD-derived nutrient fluxes to MB and compare it to a previously identified hot spot of SGD in the southeast (SE) part of the Bay. This location is also identified as one of the sites where *Jubilees* occur more frequently.

G. PROJECT OBJECTIVE(s):

Three primary research questions arise from the preliminary data collected that will be answered by the proposed study:

- 1) What is the source of nitrogen of the total SGD-N loadings in Mobile Bay? Is it the result of anthropogenic land contamination (e.g., fertilizers, livestock manure, and sewage leakages) or naturally produced in-situ in the coastal sediments?
- 2) What is the significance of the coastal sediments as a source (or sink) of nitrogen to in the nutrient budget of Mobile Bay (i.e. determining the in-situ production or loss of nitrogen)?
- 3) How do the complex interactions and dynamics of the groundwater-saltwater wedge impact this in-situ production or sink of nitrogen?

H. METHODOLOGIES:

To answer these research questions, we are applying a three-component mass-balance model, which can be summarized with the following equations:

$$F_{total} = F_{river} + F_{gw} \quad (1)$$

$$F_{gw} = F_{in-situ\ produced} + F_{gw\ entrained} \quad (2)$$

$$F_{in-situ\ produced} = F_{total} - F_{gw\ entrained} \quad (3)$$

Where: F_{total} is the total nutrient fluxes to MB composed on river-derived (F_{river}) and groundwater-derived (F_{gw}) components. The F_{gw} component itself can be delineated into in-situ produced fluxes ($F_{in-situ}$), i.e. nutrient produced via geochemical transformations in the adjacent to MB coastal sediments, and F_{gw} entrained, land-born nutrients that were transported to the MB shoreline via advective gw flux.

To solve for these fluxes, we are applying two complimentary approaches, a lab-based flow-cell approach (Clement's contribution) and a field-based (Dimova's contribution). Both PIs have made progress on the tasks as described below.

Lab approach: Clemen's Lab will run experiments with clean sand to mimic the N-transport in the subterranean estuary in MB. This will give us values for F_{gw} entrained. Note: this is work in progress. Clemet's Lab is setting up the sand box at UA and running blank tets at the moment.

Field approach: Dimova's Lab has preliminary data (collected in fall 2017 and spring 2018) for the remaining of the fluxes (F_{gw} and F_{total}) in this three-equation system. We are planning one more large sampling campaign in July 2018.

The unknown flux ($F_{in-situ}$) produced in the coastal sediment will be determined by the difference of the field and lab results (eq. 3).

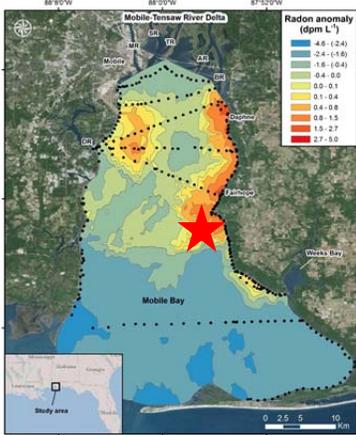
I. PRINCIPAL FINDINGS/RESULTS:

Results presented here are only from field investigation. This first phase of our research focuses on the importance of nitrogen fluxes and origin of N-loading to the Bay.

All field work was carried at the NE side of Mobile Bay which was identified as a "hot spot" of SGD from our previous work. Results from field work carried during fall 2017 and spring 2018 indicates that the sediments maybe a considerable player in the N-fluxes to MB.

1.) SGD fluxes summer 2017 (at SE SGD hot spot)

Spatial SGD distribution

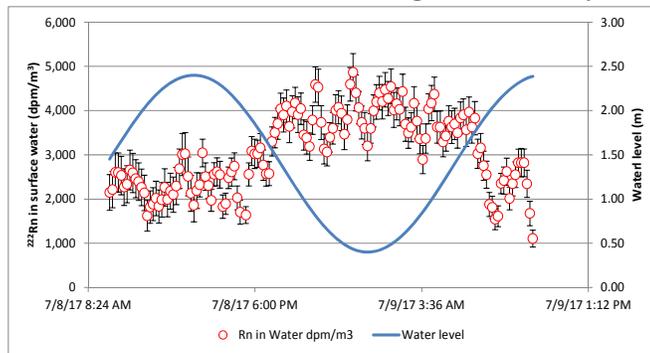


From previous work (2013-2017) we have identified that the east shoreline of Mobile Bay receives significantly larger SGD compared to the rest of the Bay. This is the reason that for this project we focused our research at one of these SGD hot spot locations.

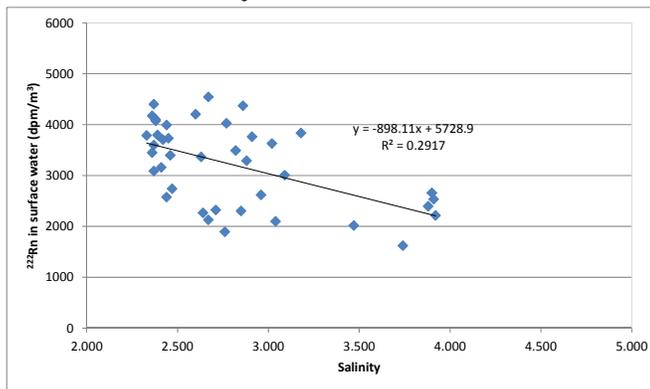
Temporal variations of SGD on SE hot spot (indicated by the red star sign on the map)

During a fieldwork in July-August of 2017 we deployed continuous radon system to determine the SGD fluxes at one of the previously identified “SGD hot spots in the SE shore of the Bay. The variation of radon in water concentration (dpm/m³) versus the water high (m) at the SE “SGD hot spot” location is shown in the following plot:

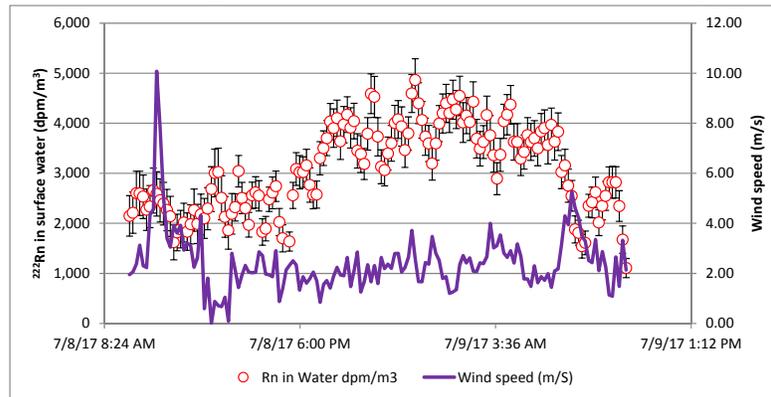
Radon 24-hour time-series in MB water during a full tide cycle



Radon in MB water versus salinity



Radon 24-hour and wind speed time-series in MB water during a full tide cycle



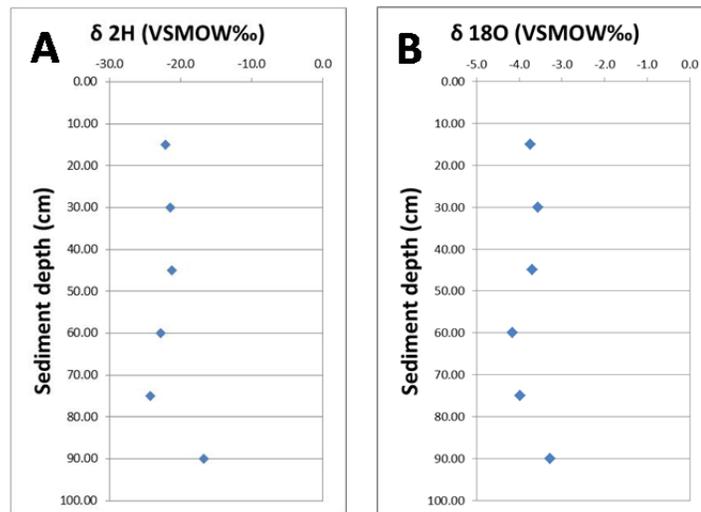
Preliminary conclusions about SGD dynamics and driving forces based on 2017 time-series at SE SGD hot spot:

1. Radon concentration and thus groundwater fluxes to MB are controlled by tidal variation, i.e. **tidal pumping** is considered the main mechanism of short-term discharge.
2. Atmospheric losses (**wind speed above 5.5-6.0 m/s**) also have effect on the radon inventories.
3. The composition of SGD is brackish with only about one third of it fresh. This is in agreement with the tidal pumping mechanism. Most of the discharge water is **re-circulated SGD**.
4. Using a mass-balance for radon and using a radon **groundwater end-member** (determined from previous sampling) **of 47,000 dpm/m³**, we calculated that the average SGD fluxes during this particular tide cycle vary between 0 and 310cm/day with **an average SGD 27 cm/day**.

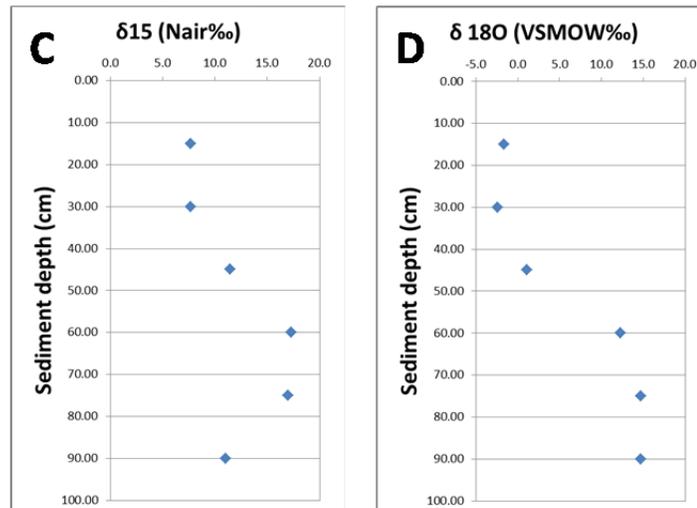
2.) Pore water chemistry

We installed a multi-point sampling piezometer at the NE side of Mobile Bay at the tidal zone and collected pore water for a full set of nutrients (N- speciation and PO_4). Water stable isotopes (^{18}O and ^2H) along with ^{15}N and ^{18}O in NO_3 were measured to identify water sources and potential effects of geochemical microbial transformation. Water samples were also collected and filtered for microbial DNA analyses which will facilitate identification of N-transformation in the subterranean estuary. The DNA samples were sent to the Department of Biogeochemistry and Geology, Leibniz Center for Tropical Marine Ecology, ZMT in Germany and we expect to find about the results this summer (August-September 2018). Below we present the nutrient pore water results.

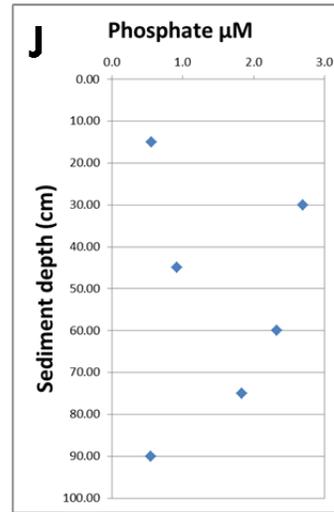
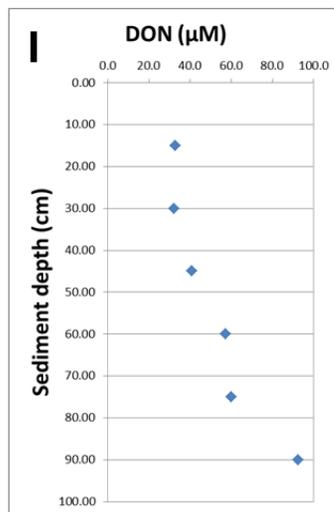
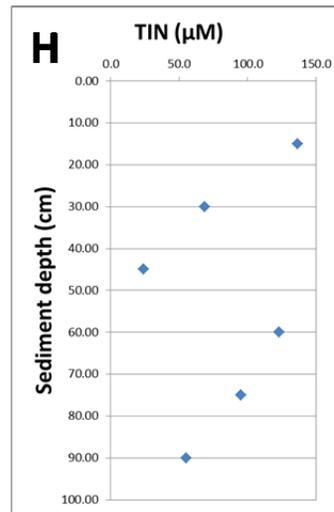
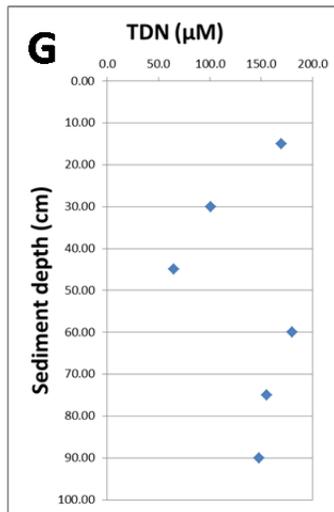
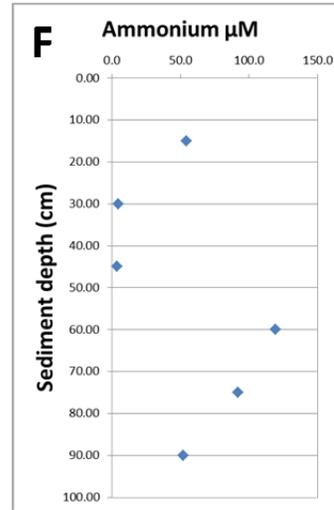
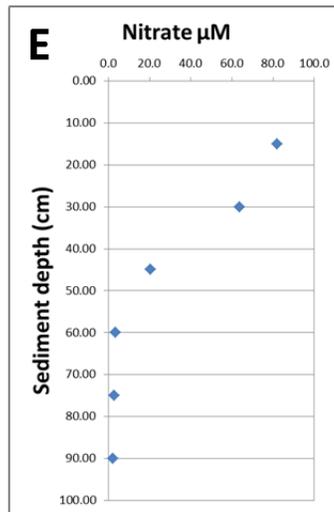
Water ^2H and ^{18}O stable isotopes in pore water



Nitrate ^{15}N and ^{18}O stable isotopes in pore water



Nutrient (N- and P-) concentrations in pore water



3.) Nitrogen fluxes to Mobile Bay (N-fluxes at the SE SGD hot spot are highlighted in red)

Average N-fluxes				
	Nitrate (μM)	Nitrite (μM)	Ammonium (μM)	DON (μM)
SE	9.1	0.4	128.1	96.8
NE	19.2	0.1	7.0	26.3
W	5.3	0.2	3.5	24.9
($\mu\text{m m}^{-3}$)	9107	442	128,146	96,788
	19,183	148	7,047	26,341
	5,324	157	3,451	24,944
Total SGD-derived N-loading	33,613	748	138,644	148,072
M-T River derived N-loading	8.4	0.3	5.1	31.0
($\mu\text{m m}^{-3}$)	8,393	265	5,110	30,996

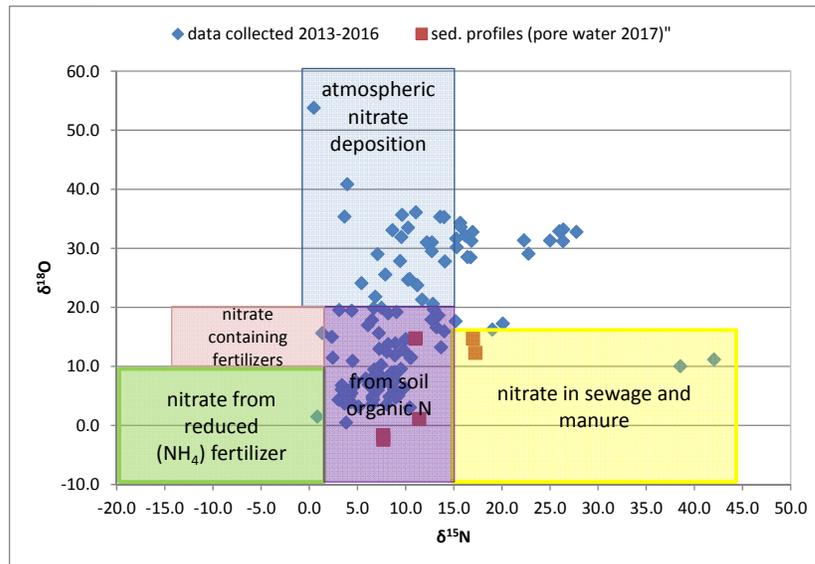
4.) Percent contribution of N-speciation derived by SGD (data compiled with previous years) for the whole Bay

	DRY ($\text{m}^3 \text{d}^{-1}$)	WET ($\text{m}^3 \text{d}^{-1}$)	Unc. DRY	Unc. WET
Nitrate ($\mu\text{M d}^{-1}$)	14%	2%	6%	1%
Nitrite ($\mu\text{M d}^{-1}$)	10%	1%	4%	1%
Ammonium ($\mu\text{M d}^{-1}$)	51%	12%	22%	5%
DON ($\mu\text{M d}^{-1}$)	16%	2%	7%	1%
TOTAL N-loading	22%	3%	9%	1%

5.) Percent contribution of N-speciation derived by SGD (data compiled with previous years) for the SE hot spot (this study)

	DRY (m ³ d ⁻¹)	WET (m ³ d ⁻¹)	Unc. DRY	Unc. WET
Nitrate (μM d ⁻¹)	69%	33%	30%	14%
Nitrite (μM d ⁻¹)	77%	43%	33%	19%
Ammonium (μM d ⁻¹)	98%	92%	42%	40
DON (μM d ⁻¹)	86%	59%	37%	25%

6.) Nitrate sources in pore water revealed by stable isotopes (¹⁵N and ¹⁸O) in nitrate (NO₃). Red symbols represent data from pore water collected during this study (summer 2017)



Preliminary conclusions about N-loadings to Mobile Bay and at the examined SE SGD hot spot;

- 1.) Although previous studies have shown that volumewise the SGD water contribution to the Bay is insignificant (0.2-2.5%), the SGD-nitrogen loading to MB are up to 22%.**
- 2.) SGD-derived nitrogen fluxes are specifically very important at the areas of higher discharge. At the SE location we found that SGD delivers up to 86% of the DON during the dry season and almost all (98%) of the ammonium.**
- 3.) Stable isotopes in nitrate indicate that the sources of nitrogen delivered by SGD are generated in the coastal sediments, i.e. it's natural; our data does not indicate contaminations delivered from land (i.e. fertilizers and/or sewage).**

J. NOTABLE AWARDS AND ACHIEVEMENTS

K. PUBLICATIONS GENERATED:

Number of Research Publications generated from this research project:	
Publication Category	Number
Articles in Refereed Journals	0 (2 in prep)
Book Chapters	0
Theses and Dissertations	1 (projected defense fall 2018)
Water Resources Institute Reports	0 (only this report)
Articles in Conference Proceedings	0
Other Publications	0

PROVIDE A CITATION FOR EACH PUBLICATION USING THE FOLLOWING FORMATS:

1. Articles in Refereed Scientific Journals Citation

None, but have two papers in preparation:

1. Montiel, D and N. Dimova. *Effects of small-scale hydrogeological heterogeneity on submarine groundwater discharge (SGD) dynamics in river dominated estuaries: example of Mobile Bay, Alabama*. In preparation for *Estuaries and Coasts* (IF 2.182); to be submitted May 2018.
2. Montiel, D and N. Dimova. *The importance of groundwater-delivered N-fluxes to Mobile Bay, Alabama*. In preparation for *Geochimica et Cosmochimica Acta* (IF 4.609) to be submitted **August 2018**.

2. Book Chapter Citation

None, but one Ph.D. dissertation by Daniel Montiel, student funded by this project on the research topic is projected to be defended by the end of fall 2018.

Dissertation topic: *Comparing magnitude and mechanisms of SGD and associated nutrient fluxes in two contrasting coastal aquifer systems: Mobile Bay (AL) and Maro Cerrogordo (Spain)*.

3. Dissertations Citation (n/a)

4. Water Resources Research Institute Reports Citation (n/a)

5. Conference Proceedings Citation (n/a)

6. Other Publications Citation (n/a)

L. PRESENTATIONS MADE (since August 2017)

Presenter(s) (last name, first name; all others presentation authors: first name, last name), Year, Title, other information sufficient to identify the venue in which the presentation was made.

1. Dimova, N.T. *Examining the groundwater-derived nitrogen fluxes to Mobile Bay, Alabama* (invited talk at the Department of Geology and Geological Engineering, University of Mississippi, April 23rd, 2018)

2. Montiel, D. and Dimova, N. *Effects of small-scale hydrogeological heterogeneity on submarine groundwater discharge (SGD) dynamics in river dominated estuaries: example of Mobile Bay, Alabama.* Oral presentation at the 2017 AGU Fall Meeting, December 11-15, New Orleans, LA, USA.

4. Dimova et al. *Examining the role of SGD on the nitrogen budget of the fourth largest estuary in the USA, Mobile Bay, Alabama, (poster).* December 11-15, 2017 AGU Fall Meeting, New Orleans, LA, USA.

5. Dimova, N. and Montiel, D. *The importance of groundwater-delivered N-fluxes to Mobile Bay, Alabama.* oral presentation at 2017 Goldschmidt Conference, August 13-17, Paris, France.

M. STUDENTS SUPPORTED)

Number of Students Supported, by Degree	
Type	Number of students funded through this research project:
Undergraduate	2
Masters	0
Ph.D.	1
Post Doc	0
Number of Theses and Dissertations Resulting from Student Support:	
Master's Theses	0

N. RESEARCH CATEGORIES:

	Research Category
	Biological Sciences
	Climate and Hydrological Processes
	Engineering
X	Ground Water Flow and Transport
	Social Sciences
	Water Quality
	Other: Explain

O. FOCUS CATEGORIES (mark all that apply with “X” in column 1):

	ACID DEPOSITION	ACD
	AGRICULTURE	AG
	CLIMATOLOGICAL PROCESSES	CP
	CONSERVATION	COV
	DROUGHT	DROU
	ECOLOGY	ECL
	ECONOMICS	ECON
	EDUCATION	EDU
	FLOODS	FL
	GEOMORPHOLOGICAL PROCESSES	GEOMOR
X	GEOCHEMICAL PROCESSES	GEOCHE
X	GROUNDWATER	GW
X	HYDROGEOCHEMISTRY	HYDGEO
	HYDROLOGY	HYDROL
	INVASIVE SPECIES	INV
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	MANAGEMENT & PLANNING	M&P
	METHODS	MET
	MODELS	MOD

X	NITRATE CONTAMINATION	NC
X	NONPOINT POLLUTION	NPP
X	NUTRIENTS	NU
	RADIOACTIVE SUBSTANCES	RAD
	RECREATION	REC
X	SEDIMENTS	SED
	SOLUTE TRANSPORT	ST
	SURFACE WATER	SW
	TOXIC SUBSTANCES	TS
	TREATMENT	TRT
	WASTEWATER	WW
X	WATER QUALITY	WQL
	WATER QUANTITY	WQN
	WATER SUPPLY	WS
	WATER USE	WU
	WETLANDS	WL

P. DESCRIPTORS: (n/a)

Information Transfer Program Introduction

None.

USGS Summer Intern Program

None.

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

Notable Awards and Achievements