Water Resources Research Institute of the University of North Carolina Annual Technical Report FY 2006

Introduction

During the Fiscal Year 2006 reporting period, the Water Resources Research Institute of The University of North Carolina supported research from 6 universities for 33 related projects. Research priorities, as directed by the WRRI (Water Resources Research Institute) Advisory Committee included the following: Water availability: water use, water allocation, and water supply security; Drinking water quality: contaminant screening, disinfection by-products, simultaneous compliance with drinking water standards, drinking water vs. groundwater standards, county well programs; Nutrient and water quality: chlorophyll a standard, nutrient trading, nutrient balance standards; Urbanization impacts on water quality: erosion and sediment control, low impact development, stormwater management; Agricultural impacts on water quality: agronomic rates for nutrients, best management practices, trout farms; Ecosystem function: riparian buffers, ecological impacts of landscape changes, ecosystem restoration, aquatic weed control, green space protection; Waste management: reverse osmosis plants, septic systems, and power plant by-products; Water quality monitoring: laboratory data analysis, mercury. The research projects reported herein provide relevant data within the WRRI priority constraints.

The information transfer program continued to focus on disseminating results of sponsored research and providing information on emerging water issues, regulations, and problems. Results of research are disseminated by publication of technical completion reports, summaries in the WRRI newsletter, publication of summaries on the WRRI website, and presentations by investigators at WRRI seminars and the Annual Conference. WRRI continues to be a sponsor of continuing education credits by the NC Board of Examiners of Engineers and Surveyors and the NC Board of Landscape Architects. This allows WRRI to offer Professional Development Hours (PDHs) and contact hours for attendance at WRRI seminars, the Annual Conference, and other workshops WRRI sponsors.

Research Program

The Water Resources Research Institute of The University of North Carolina is responsible for fostering and developing a research training and information dissemination program responsive to the water problems of the State and region. To develop its programs, the Institute maintains an aggressive effort to interact and communicate with federal, state, and local water managers. The close contact with water managers is a basis for determining the ever-changing water research priorities.

Priority water research needs for the FY 2006 program were developed in close consultation with the Institutes' Advisory Committee. Following their annual meeting, a statement of priority research needs was developed. The proposal solicitation, as in the past, is sent to all presidents and relevant department heads of senior colleges and universities in North Carolina as well as historically black colleges, to apprise them of the opportunity to submit proposals. The call for proposals is also sent to an email distribution list of approximately 180 university faculty across North Carolina. The proposals received are sent to the Technical Committee and to external peer reviewers to determine the relevancy, need for the proposed research and relative strength and weaknesses. The Technical Committee meets to review all comments made by reviewers and make recommendations regarding proposal funding. Factors considered in the review of proposals are: (1) scientific quality of the proposed work; (2) need for the results of the research in North Carolina and the region; (3) the probability that useful results can be obtained in one-year; (4) the potential for the continued support from other funding sources; (5) the cost of the proposed work; (6) opportunities for application in teaching.

Use of Indicators to Distinguish Between Point and Non-Point Sources of Chemical Contamination in North Carolina Streams

Basic Information

Title:	Use of Indicators to Distinguish Between Point and Non-Point Sources of Chemical Contamination in North Carolina Streams		
Project Number:	2005NC44B		
Start Date:	3/1/2006		
End Date:	2/28/2007		
Funding Source:	104B		
Congressional District:	4		
Research Category:	Water Quality		
Focus Category:	Agriculture, Non Point Pollution, Acid Deposition		
Descriptors:	chemical monitoring, endocrine active substances, organic compounds, wastewater treatment		
Principal Investigators:	Howard Weinberg		

Publication

<u>Title</u>

Use of Indicators to Distinguish Between Point and Non-Point Sources of Chemical Contamination in North Carolina Streams

Project Summary

Effluent discharged into receiving streams from wastewater treatment plants has to meet National Pollutant Discharge Elimination System permit levels on a variety of parameters that are designed to protect the stream's ecology and aquatic life from deleterious effects and to ensure that the natural flora and fauna can remediate the residual chemicals and micro-organisms prior to subsequent usage. As new chemicals are constantly being introduced into the domestic and industrial market, it is inevitable that they will be found in the raw waters entering these treatment plants. When their presence in receiving streams is undesirable, research studies are implemented to evaluate alternate approaches to control their levels in plant effluents. No equivalent gesture is guaranteed for the same fate of these chemicals originating from nonpoint sources. Consequently, downstream reservoirs and lakes are likely to be sinks for many of these compounds from a variety of unregulated sources. The management of nonpoint source contamination wasn't designed to account for the presence of chemicals with far different properties to those mimicking natural compounds and the presence of pharmaceutically and endocrine active chemicals with biological functions in environmental waters is testament to the ineffectiveness of current contaminant control. Drugs used for human and animal therapy and endocrine-disrupting compounds are introduced into agricultural systems via land application of recycled wastewater and accumulated biosolids as well as through direct usage of pesticides. The widespread domestic use of many of these compounds also ensures that they will be present in septic systems and in landfills. Leakage and runoff from any of these systems will contribute significant loading into receiving waters and contribute to impairment. It is unknown what percentage of accumulations of these compounds derive from point and non-point sources but from extrapolation of what is known about nonpoint pollution from regulated compounds, the contribution from the nonpoint sources is likely to be very significant.

Until now, it has been a major challenge to provide an effective strategy that would permit identification of non-point sources of chemical pollution as distinct from point sources. This proposal will investigate the use of chemical profiling that distinguishes between point and non-point sources of pollution and develop an approach for characterizing the contributions of surrogate measures of chemical contamination in the form of antibiotics and endocrine disrupting hormones and pesticides from land application runoff and on-site wastewater treatment seepage. The results of this study will provide an indication of the relative contributions to overall pollution from chemicals originating in both point and non-point sources and a strategy that can be applied to survey impaired streams for these chemicals.

Methodology

During the first 6 months of this project we have reviewed the literature to assist in making reasoned judgments about the identity of chemicals that will serve as indicators to distinguish between point and nonpoint sources of surface water contamination. For conventional wastewater treatment plants that use chlorine for final disinfection we are targeting tlie nonvolatile haloacetic acids that we have detected in the effluents of several plants across North Carolina practicing effective nitrification. We have adapted standard methods for these analyses usually deployed for levels in excess of I pg/L in finished drinking waters so that we can monitor their fate downstream of the point of discharge at levels as low as 20ng/L. Chlorinated haloacetic acids (HAAS) are proposed as an indicator of wastewater treatment plant effluent in surface waters with the hypothesis that they will be created as the wastewater is chlorinated before discharge and will not be 1.en10ved during dechlorination. It is also hypothesized that H.4.4~ will

not be created in septic system treatment since. in normal household use, there will be insufficient dose to create them.

Wastewater treatment plant (WWTP) effluent samples have been collected from Morgan Creek and sampled were collected upstream of the effluent discharge. approximately 10 feet below the discharge point, and at approximately **0.5** miles downstream of the discharge point. This wastewater treatment plant is chlorinated with sodium hypochlorite, which is delivered usually in a 15% solution. The dose rate varies daily, but an average dose rate is 2.5 mg/L. Upstream samples contained no measurable HAAs and there are no documented upstream wastewater plant discharges. Samples at both points in the receiving creek after discharge from the Orange Water and Sewer Authority WWTP do contain measurable levels of both dichloroacetic acid (Cl_2AA) and trichloroacetic acid (Cl_3AA) . The levels are somewhat lower than would be expected with the chlorine dose and contact time employed. This is likely due to incomplete nitrification of the effluent prior to chlorination and measurable levels of ammonia that would have been converted to chloramines and, therefore, unavailable for the formation of high levels of HAAs. Nevertheless, in order to use HAAs as a tracer of chlorinated wastewater it became apparent that the analytical method will have to be evolved to target lower concentrations. Method development for this is almost complete and involves either solid phase extraction of acidified 200mL filtered aqueous samples into 1mL extracts or the blowing down to 200µL of liquid-liquid solvent extracts prior to dcrivatization. The target quantitation limit is 20ng/L and we are currently able to reproduce measurements at 50ng/L spiked into the upstream Creek samples. We are currently studying the occurrence fate and transport of HAAs discharged from the City of Burlington South plant that practices both nitrification and chlorination.

Septic effluent sample collection locations were established with the assistance of Mr. Steven Berkowitz of NC DENR. Samples were collected during state inspections of systems with sand filters. At the time of sample collection, the systems were in operation and samples were collected as effluent trickled into the ranks. Samples were also collected from a failed septic system after digging up the drainage trench with a backhoe. Visibly there **was** effluent on the ground surface and flowing straight from the trench. Additional samples were collected from a septic system associated with an office building with the design created by Integrated Water Systems Inc. with who we have established collaboration on this project. A schematic showing the various unit processes employed with this system and the sample points from which samples were collected is shown in Figure 1.

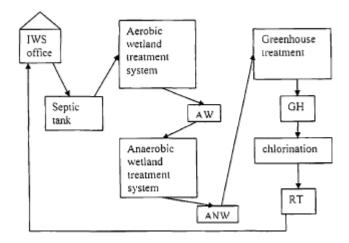


Figure 1. Integrated Water Systems Office (Chatham County) Septic System Design (AW, ANW, GH, RT are the sampling locations)

Flow was turned on and samples were collected starting six minutes later as effluent began to move through the system. Samples were collected from the septic tank (ST), after aerobic wetland treatment (AW), after anaerobic wetland treatment (ANW), after greenhouse treatment (GH), and from the chlorinated reuse tank (RT). ST and RT were collected by dipping the sampling cup into liquid collected at bottom of tank. AW, ANW, and GH samples were collected by filling the sampling cup from the flow and pouring this into 40mL vials with preservation agent. The sampling cup was rinsed with laboratory-grade water (LGW) between sampling locations. The effluent in the greenhouse tank (GH) is exposed to chlorination fumes from the reuse tank. Free chlorine measurements were collected onsite with a HACH colorimeter using each sample as its own blank. Levels were determined at ST, AW, ANW, GH, and RT as 0, 0.09, 0.03, 0.16, and 2.2 mg/L respectively. Haloacetic acid concentrations were below detection in the samples collected before exposure lo chlorine (i.e. AW, ANW, and GH) but were at concentrations above the highest calibration curve level of 50 pg/L in the samples collected from the reuse tank. However, the samples collected prior to chlorination would be more typical of domestic use of septic systems and the non-detectable HAAs were consistent with the non-detects in the other septic systems sampled. We can conclude, therefore, that haloacetic acids are unlikely to be found in septic systems.

Tracers for septic systems are also being evaluated. Triclosan and caffeine are the chemicals chosen for this study based on a review of previous research reports that includes occurrence data for these chemicals in a variety of conventional wastewater treatment plant effluents. Methods have been adapted for the analysis of these chemicals in the aqueous phases of septic system waste down to concentrations of 20ng/L The systems sampled for HAAs described above were also analyzed for both caffeine and triclosan. Levels up to 1µg/L of caffeine were detected in the samples collected from the drainage ditch and we are currently evaluating the transport of this tracer as h e septage moves through the topsoil towards a nearby receiving stream.

Principle Findings

This study has been looking at two major sources of nonpoint contamination of surface waters; failed septic systems and land application of biosolids. Caffeine and triclosan were proposed as indicators of nonpoint sources of pollution originating from failed septic systems due to their elevated levels in septic tanks compared to effluents from wastewater treatment plants (WWTPs). Caffeine from WWTP effluents (n-29) ranged below detection (BD) to 1.2μ g/L. Both analyses were detected in pooled sewage around failed systems (n=3) at average concentrations of 2.3μ g/L caffeine and 1.6μ g/L triclosan. Caffeine was detected downstream of a failed septic system during a rain event an average of 270ng/L. The results indicate that these compounds survive in septage that has surfaced and have the possibility to flow overland to streams.

The combination of aerobic and anaerobic degradation processes used in advanced treatment with septic tanks reduce the high concentrations in the septic tank (average caffeine (n-7): $26\mu g/L$ and triclosan (n-7): $1.5\mu g/L$) to an average of 70ng/L for both compounds after treatment. Advanced treatment systems using these processes are effective at removing these indicator compounds and these results can be extrapolated to suggested that a functioning septic system would also effectively remove them.

The potential for biosolids to pollute surface water, particularly with endocrine disrupting chemicals has been demonstrated in this research. The biosolids assessed in this study were from two separate wastewater treatment plants, one of a large city (Plant B) and the other of a small town (Plant A). Surprisingly, the

concentrations of nonylphenols and triclosan due to were less in the larger city. Upon review of different methods of treatment at the wastewater plants, it seemed possible that the Plant B biosolids had lower concentrations of nonylphenols and triclosan due to the shorter solids retention time (SRT) and a more aerated process for conditioning the biosolids. This suggested that wastewater treatment plants with a shorter SRT would accumulate less contaminants, although this could cause greater concentrations in the wastewater effluent. The aeration of the biosolids that occurs during limekiln treatment may also assist in the degradation of nonylphenols, which is mainly by aerobic organisms. There is also concern that these contaminants will cycle from a domestic waste stream back into drinking water through contamination of the source water used to produce drinking water. This further promotes the need to remove these contaminants from biosolids as an action to prevent their contamination in surface water. Triclosan may be degraded through photolysis and nonylphenols through microbial degradation, which could be incorporated into the processes for drinking water treatment.

Significance

The potential for biosolids to pollute surface water, particularly with endocrine disrupting chemicals has been demonstrated in this research. The biosolids assessed in this study were from two separate wastewater treatment plants, one of a large city (Plant B) and the other of a small town (Plant A). Surprisingly, the concentrations of nonylphenols and triclosan due to were less in the larger city. Upon review of different methods of treatment at the wastewater plants, it seemed possible that the Plant B biosolids had lower concentrations of nonylphenols and triclosan due to the shorter solids retention time (SRT) and a more aerated process for conditioning the biosolids. This suggested that wastewater treatment plants with a shorter SRT would accumulate less contaminants, although this could cause greater concentrations in the wastewater effluent. The aeration of the biosolids that occurs during limekiln treatment may also assist in the degradation of nonylphenols, which is mainly by aerobic organisms. There is also concern that these contaminants will cycle from a domestic waste stream back into drinking water through contamination of the source water used to produce drinking water. This further promotes the need to remove these contaminants from biosolids as an action to prevent their contamination in surface water. Triclosan may be degraded through photolysis and nonylphenols through microbial degradation, which could be incorporated into the processes for drinking water treatment.

References

Bester, K. Water Research, 2003.37: p. 3891-3896.

Buerge, 1.J.P. et al. Environmental Science and Technology, 2003. 37: p. 691-700.

Heberer, T. et al. Water Science and Technology, 2002.46(3): p. 81-88.

Kolpin, D.W., et al., Environmental Science and Technology, 2002.36(6): p. 1202-1211.

Morrall, D., et al. Chemosphere, 2004. 54: p. 653-660.

Parveen, S., et al. Applied and Environmental Microbiology, 1997,63(7): p 2607-2612.

Sabaliunas, D.W. et al. Water Research, 2003.37: p. 3 145-3 154.

Seiler, R.L.Z. et al. Ground Water, 1999.37(3): p. 405-410.

Singer, H.M. et al. Environmental Science and Technology, 2002.36: p. 4998-5004.

Wiggins, B.A., et al. Applied and Environmental Microbiology, 1999, 65(8): p. 3483-3486.

Wilson, J., Caffeine Content of Popular Drinks. 1999.

Wren, A., *Occurence and fate of endocrine disruptors in onsite wastewater systems.* 2001, Colorado School of Mines: Golden. p. 1- 12.

Endocrine and Reproductive Effects of the Pharmaceutical Fluoxetine on Native Freshwater Mussels: Proximity to Measured Environmental Concentrations

Basic Information

Title:	Endocrine and Reproductive Effects of the Pharmaceutical Fluoxetine on Native Freshwater Mussels: Proximity to Measured Environmental Concentrations	
Project Number:	2006NC61B	
Start Date:	3/1/2006	
End Date:	8/31/2007	
Funding Source:	104B	
Congressional District:	2	
Research Category:	Water Quality	
Focus Category:	Toxic Substances, Water Quality, Surface Water	
Descriptors:	Unionid Mussel, endocrine disruptor, pharmaceutical, toxic substances, pollutants	
Principal Investigators:	W. Gregory Cope, Robert B Bringolf, Rebecca M Heltsley, Damian Shea	

Publication

- Bringolf, R. B., R. M. Heltsley, C. Eads, T. J. Newton, S. Fraley, D. Shea, and W. G. Cope. 2007. Effects of fluoxetine on freshwater mussel reproduction: relation to environmental occurrence. Annual Meeting of the Water Resources Research Institute of North Carolina, Raleigh, NC, March 27-28, 2007
- Bringolf, R. B., R. M. Heltsley, C. Eads, T. J. Newton, S. Fraley, D. Shea, and W. G. Cope. 2007. Environmental occurrence of fluoxetine and its effects on freshwater mussel reproduction. 5th Biennial Symposium of the Freshwater Mollusk Conservation Society, Little Rock, AR, March 12-15, 2007.
- 3. Heltsley, R. M., W. G. Cope, R. B. Bringolf, C. B. Eads, and D. Shea. 2006. Environmental concentrations of prozac induce spawning in freshwater mussels. 27th Annual Meeting of the Society of Environmental Toxicology and Chemistry, Montreal, Canada, November 5-9, 2006.
- 4. Heltsley, R. M., W. G. Cope, R. B. Bringolf, C. B. Eads, and D. Shea. 2006. Prozac elicits spawning in native freshwater mussels. 232nd Annual Meeting of the American Chemical Society, San Francisco, CA, September 10-14, 2006.

Title

Endocrine And Reproductive Effects Of The Pharmaceutical Fluoxetine On Native Freshwater Mussels: Proximity To Measured Environmental Concentrations

Project Summary

Recent research by Johnson et al. (2005), Kolpin et al. (2002; 2004) and others have measured concentrations of pharmaceuticals and personal care products (PPCPs) in surface waters that have the potential to adversely impact human and ecological health. The ubiquitous detection of these compounds in the environment has revealed an emerging class of contaminants that has largely been unrecognized or ignored in the past (Sanderson et al. 2004). Although some of these compounds are not as persistent as the traditionally studied priority pollutants (e.g., polychlorinated biphenyls and organochlorine pesticides), the continuous release of these PPCPs and other polar compounds into our rivers and streams presents similar exposure conditions as that of a persistent organic pollutant (Johnson et al. 2005). Studies have indicated that many of these compounds enter the environment completely un-metabolized or as a mixture of metabolites (Daughton and Ternes 1999). Therefore, compounds that were manufactured with the intent of being bioactive enter surface waters and may be responsible for not only acute toxicity but also chronic abnormalities and endocrine disruption in aquatic organisms (Colborn et al. 1993; Desbrow et al. 1998; Routledge et al. 1998).

Native freshwater mussels (family Unionidae) may unfortunately be among the groups of aquatic organisms adversely affected by persistent, low-level exposure to PCPPs and other endocrine disrupting compounds (EDCs) in our surface waters. Unionid mussels are filter and deposit feeding, long-lived (30-100 yr) benthic organisms that live burrowed in sediments of streams and rivers. They are one of the most rapidly declining faunal groups in North America. About 67% of the nearly 300 freshwater mussel species found in North America are considered vulnerable to extinction or already extinct (Bogan 1993; Williams et al. 1993). The decline of mussel populations in North America has occurred steadily since the mid 1800s and has been attributed to pollution, construction of dams and impoundments, sedimentation, navigation, and habitat degradation (Fuller 1974; Bogan 1993; Neves 1997; Brim Box and Mossa 1999; Vaughn and Taylor 1999). The surface waters of North Carolina have historically supported 56 species of unionid mussels (Bogan 2002). Today, 82% of these species are listed as endangered, threatened, or of special concern by the U.S. Fish and Wildlife Service and the State of North Carolina (Code of Federal Regulations 1993; NC Wildlife Resources Commission 2002) or are already extinct. Many of the same human-mediated and environmental stressors responsible for the declines of freshwater mussels throughout North America have also contributed to the declines in North Carolina. Principally, the stressors associated with human development and urbanization in almost all of the State's 17 river basins has hastened these declines over the past 20 to 50 years.

The primary focus of this project has been to generate a robust set of toxicological information on the sub-lethal endocrine and reproductive effects of fluoxetine on adults (both male and female) of the eastern elliptio (*Elliptio complanata*) mussel in laboratory tests. The intended pharmacologic action of fluoxetine in human therapy as an anti-depressant is to act as a selective serotonin reuptake inhibitor (SSRI) and increase serotonin levels at nerve synapses. Serotonin (5-hydroxytrypamine; 5-HT), an important neurotransmitter in vertebrate and

invertebrate systems, has been used to artificially induce spawning in freshwater bivalves for aquaculture purposes (Cunha and Machado 2001) and has been investigated as a potential chemical control mechanism (i.e., disruptor of reproduction) for exotic bivalve species like the zebra mussel (*Dreissena polymorpha*; Fong et al. 1994, Ram et al. 1992; 1996). Prior to this work funded by WRRI in the 2005-2006 cycle, there was limited evidence that fluoxetine and other SSRIs may exert reproductive effects on bivalves (Cunha and Machado 2001) similar to serotonin (Gibbons and Castagna 1984), making environmental exposures from this class of pharmaceuticals to native freshwater mussels and other aquatic biota through discharge of pharmacologically active compound in treated wastewater to surface waters an imminent concern. The specific objectives of this project were to:

- 1. Conduct a 96-hour laboratory toxicity test with gravid female eastern elliptio mussels and a range of concentrations of fluoxetine, serotonin (used as a positive control), and methiothepin (an inhibitor of serotonin pathways) to assess effects on reproductive endpoints such as time to parturition (or spontaneous abortion) of mussel larvae (glochidia) and viability of released glochidia.
- 2. Conduct a 96-hour laboratory toxicity test with ripe male eastern elliptio mussels and a range of concentrations of fluoxetine, serotonin (used as a positive control), and methiothepin (an inhibitor of serotonin pathways) to assess effects on reproductive endpoints such as time to spawning (or premature release of sperm) and viability of released sperm.
- 3. Quantify exposure concentrations of fluoxetine in the test chambers during the 96-h toxicity tests by analyzing samples of water and the novel passive sampling device simultaneously deployed in the test chambers with the mussels.
- 4. Quantify concentrations of fluoxetine accumulated in novel passive sampling devices deployed at sites in Crabtree Creek of the Neuse River Basin immediately downstream of the City of Cary Wastewater Treatment Plant effluent discharge.
- 5. Compare the results of the mussel toxicity tests with fluoxetine to any available toxicity data for standard aquatic test organisms such as *Ceriodaphnia dubia* and rainbow trout to assess relative risk of exposure.
- 6. Compare the results of the mussel toxicity tests with fluoxetine to measured environmental concentrations from the Neuse River Basin in this study, to the peer-reviewed literature, or to predicted environmental concentrations, if they exist, to assess relative risk of adverse effects of fluoxetine.
- 7. Conduct a 96-hour laboratory toxicity test with gravid female *Lampsilis* spp. mussels and a low range of concentrations of fluoxetine, and serotonin (used as a positive control) to assess the reproductive behavioral effects on mantle flap (fish lure) display, time used, and relative action (e.g., beats per minute)

Methods, Procedures, and Facilities

Adult eastern elliptio mussels were collected from several relatively uncontaminated, rural forested streams in the central Piedmont of North Carolina. The mussels were transported (methods in Cope et al. 2003) to the Aquatic Toxicology Laboratory at North Carolina State University, where they were maintained in reconstituted hard water (ASTM 1993) at 18-20°C for at least 24 h prior to beginning any experiments to ensure that spawning or release of glochidia is not a result of handling or transport stress. For testing, mussels that had not released gametes or

glochidia were placed in 3.75-L glass aquaria containing 2 L of reconstituted hard water and aerated with compressed air to ensure dissolved oxygen concentrations greater than 60% of saturation at all times (ASTM 1993). The mussels were exposed to five fluoxetine treatments (0, 0.3, 3.0, 30, 300, or 3000 μ g/L), with 3 replicates per treatment and 3 mussels per replicate in static renewal tests for 96 h. In addition, a serotonin treatment was included as a positive control and another treatment included mussels that had been briefly exposed to a serotonin inhibitor, methiothepin (Fong et al. 1994), and then exposed to serotonin or fluoxetine to demonstrate that fluoxetine is acting as an SSRI in *E. complanata*. All mussels were monitored continuously for the first 6 h for release of gametes (available literature indicates that serotonin and SSRI action is relatively rapid), then at 24 h intervals over the remaining exposure duration. Relevant endpoints quantified during the exposure included time to release of sperm or glochidia (larvae); in the case of parturition (females), glochidia were examined for viability and recorded as either immature or mature and a likewise assessment of sperm viability from males. Water quality conditions (dissolved oxygen, temperature, conductivity, hardness, and alkalinity) were measured with standard methods (ASTM 1993) in samples taken from the test chambers at time 0, 24, 48, 72, and 96 h of the test. A 100% renewal of fluoxetine concentrations was done at 24 h intervals on replicates of a treatment in which mussels had not released to ensure target test concentrations were maintained. Water samples were taken from each test chamber at the time mussels were initially placed in fluoxetine treatments and again at the time of first release for analysis of fluoxetine concentrations by liquid chromatography/mass spectroscopy (LC-MS), with methods already developed by R.M. Heltsley (in our laboratory) and modified from Brooks et al. (2003a).

The novel PSDs were deployed in triplicate at four sites in Crabtree Creek of the Neuse River Basin immediately downstream of the City of Cary Wastewater Treatment Plant effluent discharge. The PSDs were retrieved approximately 30 d after deployment, transported to the Analytical Toxicology Laboratory at NCSU, extracted, and analyzed for fluoxetine and a suite of other polar and non-polar contaminants by LC/MS and/or gas chromatography/mass spectroscopy methods.

For the behavioral test, adult female Lampsilis fasciola were collected from a relatively uncontaminated, rural forested portion of the Little Tennessee River in the mountain region of North Carolina. The mussels were transported (methods in Cope et al. 2003) to the Aquatic Toxicology Laboratory at North Carolina State University, where they were maintained in reconstituted hard water (ASTM 1993) at 18-20°C for at least 48 h prior to beginning any experiments to ensure that spawning or release of glochidia was not a result of handling or transport stress and that the gravid females were displaying their mantle flaps as normal behavior. For testing, mussels that had not released glochidia and were displaying normally were placed into 3.75-L glass aquaria containing 2 L of reconstituted hard water and aerated with compressed air to ensure dissolved oxygen concentrations greater than 60% of saturation at all times (ASTM 1993). The mussels were exposed to five fluoxetine treatments (0, 0.3, 3.0, 30, 300, or 3000 µg/L), with 3 replicates per treatment and 5 mussels per replicate in static renewal tests for 96 h. In addition, a serotonin treatment was included as a positive control. All mussels were monitored continuously for the first 6 h for release of gametes and the occurrence, frequency and duration of mantle flap display, and then at selected hourly intervals over the remaining exposure duration. Relevant endpoints quantified during the exposure included time to release of glochidia (larvae); in the case of parturition, glochidia were examined for viability and recorded as either immature or mature. The occurrence, frequency, and duration of mantle flap display were categorized as follows: shell closed, shell gaped-no mantle exposed, shell

gaped-mantle extended, shell gaped-mantle extended with fish lure out, and shell gaped-mantle extended with fish lure out and beating (if lure was out, the number of beats/min was quantified). Water quality conditions (dissolved oxygen, temperature, conductivity, hardness, and alkalinity) were measured with standard methods (ASTM 1993) in samples taken from the test chambers at time 0, 24, 48, 72, and 96 h of the test. A 100% renewal of fluoxetine concentrations was done at 24 h intervals on replicates of a treatment in which mussels had not released to ensure target test concentrations were maintained. Water samples were taken from each test chamber at the time mussels were initially placed in fluoxetine treatments and again at the time of first release of behavioral effect for analysis of fluoxetine concentrations by liquid chromatography/mass spectroscopy (LC-MS).

Principal Findings and Significance

Toxicity tests with gravid female adult eastern elliptio (*Elliptio complanata*) mussels and a range of fluoxetine concentrations were completed. These tests evaluated the potential for fluoxetine to cause pre-mature release (spontaneous parturition) of glochidia and the viability of the glochidia that were released. We found that fluoxetine does indeed cause the pre-mature release of non-viable and viable larvae (glochidia) in native freshwater mussels in < 48 h of exposure (Fig. 1). The major threshold concentration for significant effects appears to be between 150 and 223 μ g/L, a concentration range greater than those measured in environmental samples.

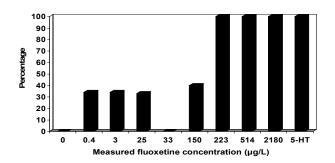


Fig. 1. Percentage of gravid female mussels pre-maturely releasing glochidia with 48 h of fluoxetine exposure in two laboratory tests.

Therefore, our study has confirmed that fluoxetine (and possibly other SSRIs) may exert reproductive effects on bivalves similar to serotonin (5-HT, the positive control in our tests), making environmental exposures from this class of pharmaceuticals to native freshwater mussels and other aquatic biota through discharge of pharmacologically active compound in treated wastewater to surface waters an imminent concern. We have also successfully completed the behavioral test of mantle flap display and have found that fluoxetine alters display behavior at the highest concentration tested. The analytical chemistry results of PSDs deployed in Crabtree Creek are forthcoming.

The ecological effects of an ill-timed release of larval mussels or gametes caused by environmental fluoxetine exposure could be potentially devastating to localized mussel

populations. Likewise, the inability of a female mussel to attract her obligate fish host through reduced or non-existent mantle flap (fish lure) display behavior such that she would not be able to successfully infest a fish with glochidia could also result in total reproductive failure and devastate local mussel populations. Because the mode of action of fluoxetine is to alter behavior through neuroendrocrine pathways, this scenario is biologically plausible and warrants further investigation.

References

- ASTM (American Society for Testing and Materials). 1993. Standard guide for conducting acute toxicity tests with fishes, macroinvertebrates, and amphibians. E 729-88a, American Society for Testing and Materials, Philadelphia, PA, pp 102-121.
- Augspurger, T. P., A. E. Keller, M. C. Black, W. G. Cope, and F. J. Dwyer. 2003. Water quality guidance for protection of freshwater mussels (Unionidae) from ammonia exposure. *Environmental Toxicology and Chemistry* 22:2569-2575.
- Bogan, A. E. 1993. Freshwater bivalve extinctions (Mollusca: Unionoida): a search for causes. *American Zoologist* 33:599-609.
- Bogan, A. E. 2002. A Workbook and Key to the Freshwater Mussels of North Carolina. NC Museum of Natural Sciences, Raleigh, NC.
- Brim Box, J. and Mossa, J. 1999. Sediment, land use, and freshwater mussels: prospects and problems. *Journal of the North American Benthological Society*, 18:99-117.
- Brooks, B. W., Foran, C. M., Richards, S. M., Weston, J., Turner, P. K., Stanley, J. K., Solomon, K. R., Slattery, M., and La Point, T. W. 2003a. Aquatic ecotoxicology of fluoxetine. *Toxicology Letters* 142:169-183.
- Brooks, B. W., Turner, P. K., Stanley, J. K., Weston, J., Glidewell, E. A., Foran, C. M., Slattery, M., La Point, T. W., and Huggett, D. B. 2003b. Waterborne and sediment toxicity of fluoxetine to select organisms. *Chemosphere* 52:135-142.
- Code of Federal Regulations. 1993. Part 17--Endangered and threatened wildlife and plants, Section 17.11, Endangered and threatened wildlife, U.S. Government Printing Office, 50, 108-110.
- Colborn, T., vom Saal, F. S., and Soto, A. M. 1993. Developmental effects of endocrinedisrupting chemicals in wildlife and humans. *Environmental Health Perspectives* 101:378-384.
- Cope, W. G., M. C. Hove, D. L. Waller, D. J. Hornbach, M. R. Bartsch, L. A. Cunningham, H. L. Dunn and A. R. Kapuscinski. 2003. Evaluation of relocation of unionid mussels to *in situ* refugia. *Journal of Molluscan Studies*, 69:27-34.
- Cunha, E. M. and Machado, J. 2001. Parturition in *Anodonta cygnea* induced by selective serotonin reuptake inhibitors (SSRIs). *Canadian Journal of Zoology* 79:95-100.
- Daughton, C. G. and Ternes, T. A. 1999. Pharmaceuticals and personal care products in the environment: agents of subtle change? *Environmental Health Perspectives* 107:907-938.
- Desbrow, C., Routledge, E. J., Brighty, G. C., Sumpter, J. P., and Waldock, M. 1998. Identification of estrogenic chemicals in STW effluent. 1. Chemical fractionation and in vitro biological screening. *Environmental Science and Technology* 32:1549-1558.
- Fong, P. P., Duncan, J., and Ram, J. L. 1994. Inhibition and sex specific induction of spawning by sertonergic ligands in the zebra mussel *Dreissena polymorpha* (Pallas). *Experientia* 50:506-509.

- Foran, C. M., Weston, J., Slattery, M., Brooks, B. W., and Huggett, D. B. 2004. Reproductive assessment of Japanese medaka (*Oryzias latipes*) following a four-week fluoxetine (SSRI) exposure. *Archives of Environmental Contamination and Toxicology* 46:511-517.
- Fuller, S. L. H. 1974. Clams and mussels (Mollusca: Bivalvia). In: Pollution Ecology of Freshwater Invertebrates, (C. W. Hart, Jr. and S. L. H. Fuller, eds), 215-273. Academic Press, New York.
- Gibbons, M. C. and M. Castagna. 1984. Serotonin as an inducer of spawning in six bivalve species. *Aquaculture* 40:189-191.
- Goudreau, S. E., Neves, R. J. and Sheehan, R. J. 1993. Effects of wastewater treatment plant effluents on freshwater mollusks in the upper Clinch River, Virginia, USA. *Hydrobiologia*, 252: 211-230.
- Henry, T. B., Kwon, J-W., Armbrust, K. L., and Black, M. C. 2004. Acute and chronic toxicity of five selective serotonin reuptake inhibitors in *Ceriodaphnia dubia*. *Environmental Toxicology and Chemistry* 23:2229-2233.
- Johnson, D. J., Sanderson, H., Brain, R. A., Wilson, C. J., Bestari, K. T., and Solomon, K. R. 2005. Exposure assessment and microcosm fate of selected selective serotonin reuptake inhibitors. *Regulatory Toxicology and Pharmacology* 42:313-323.
- Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zaugg, S. D., Barber, L. B., and Buxton, H. T. 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. *Environmental Science and Technology* 36:1202-1211.
- Kolpin, D. W., Skopec, M., Meyer, M. T., Furlong, E. T., and Zaugg, S. D. 2004. Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions. *Science of the Total Environment* 328:119-130.
- Levine, J. F., A. E. Bogan, K. H. Pollock, H. A. Devine, L. L. Gustafson, C. B. Eads, P. P. Russel, and E. F. Anderson. 2003. Distribution of freshwater mussel populations in relationship to crossing structures. Final completion report to the NC Department of Transportation, NC State University, College of Veterinary Medicine, Raleigh, NC.
- McMahon, R. F. and A. E. Bogan. 2001. Mollusca: Bivalvia. In: J. H. Thorpe & A. P. Covich, editors. *Ecology and classification of North American freshwater invertebrates*. New York: Academic Press. pp. 331-429.
- NC Wildlife Resources Commission. 2002. List of State Threatened and Endangered Mussel Species web resource: http://216.27.49.98/fs_index_07_conservation.htm.
- Neves, R. J. 1997. A national strategy for the conservation of native freshwater mussels. In: *Conservation and management of freshwater mussels II: initiatives for the future*, (K. S. Cummings, A. C. Buchanan, C. A. Mayer & T. J. Naimo, eds), 1-10. Proceedings of a UMRCC Symposium, 16-18 October 1995, St. Louis, Missouri. Upper Mississippi River Conservation Committee, Rock Island, Illinois.
- Ram, J. L., Fong, P., Croll, R. P., Nichols, S. J., and Wall, D. 1992. The zebra mussel (*Dreissena polymorpha*), a new pest in North America: reproductive mechanisms as possible targets of control strategies. *Invertebrate Reproduction and Development* 22:77-86.
- Ram, J. L., Fong, P. P., and Garton, D. W. 1996. Physiological aspects of zebra mussel reproduction: maturation, spawning, and fertilization. *American Zoologist* 36:326-338.

- Routledge, E. J., Sheahan, D., Desbrow, C., Brighty, G. C., Waldock, M., and Sumpter, J. P. 1998. Identification of estrogenic chemicals in STW effluent. 2. In vitro responses in trout and roach. *Environmental Science and Technology* 32:1559-1565.
- Sanderson, H.Y., Johnson, D. J., Reitsma, T., Brain, R. A., Wilson, C. J., and Solomon, K. R. 2004. Ranking and prioritization of environmental risks of pharmaceuticals in surface waters. *Regulatory Toxicology and Pharmacology* 39:158-183.
- Vaughn, C. C. and Taylor, C. M. 1999. Impoundments and the decline of freshwater mussels: a case study of an extinction gradient. *Conservation Biology* 13:912-920.
- Williams, J. D., Warren, Jr., M. L., Cummings, K. S., Harris, J. L. and Neves, R. J. 1993. Conservation status of freshwater mussels of the United States and Canada. *Fisheries* 18:6-22.

Restoring Biogeochemical Functions in Degraded Urban Stream Ecosystems

Basic Information

Title:	Restoring Biogeochemical Functions in Degraded Urban Stream Ecosystems
Project Number:	2006NC63B
Start Date:	3/1/2006
End Date:	5/31/2007
Funding Source:	104B
Congressional District:	4
Research Category:	Biological Sciences
Focus Category:	Nutrients, Water Quality, Ecology
Descriptors:	biogeochemistry, denitrification, hydrologic connectivity nitrogen, organic matter, restoration, urban streams
Principal Investigators:	Emily S Bernhardt

Publication

- 1. Bernhardt,E.S., 2006. Ecological Systems and Renaturalization Success, Montana River Center Symposium: Assessing Stream Restoration Success: Developing Sustainable Ecological and Physical Systems.
- 2. Bernhardt,E.S., 2006, Evaluating Restoration Effectiveness Lessons from a National Synthesis, 2006 North Carolina Stream Restoration Institute Conference.

Title

Restoring biogeochemical functions in degraded urban stream ecosystems

Project Summary

High levels of nitrogen are loaded to increasingly degraded streams: Humans have roughly doubled the annual supply of nitrogen (N) to the planet. This has numerous detrimental impacts, including increased fluxes of nitrogen in rivers, leading to excessive nitrogen concentrations, harmful algal blooms, and regional hypoxia in many coastal waters and estuaries (Green, Vorosmarty et al. 2004). The streams that receive these increasingly high nitrogen inputs have a tremendous capacity to transform reactive N (available to plants and microbes) back into inert atmospheric N_2 through biological uptake and denitrification within river sediments (Peterson, Wollheim et al. 2001; Bernhardt, Likens et al. 2003; Bernhardt, Likens et al. 2005). Recent global modeling estimates have suggested that at least half of the nitrogen entering river systems appears to be lost to denitrification on its way to the sea (Galloway, Dentener et al. 2004). The smallest streams are the most effective at nitrogen removal (Alexander, Smith et al. 2000; Seitzinger, Styles et al. 2002), yet many of our smallest streams are poorly protected by current environmental regulations and are heavily impacted by pollution and channelization. Currently, over 130,000 km of U.S. streams are impaired by urbanization (USEPA 2003). This estimate will certainly increase over the next 30 years, as virtually all of the world's population growth is expected to occur in urban areas, with over 60% of the world's population in urban areas by 2030 (UNPD 2003). Urbanization and suburbanization of watersheds results in a series of predictable changes in streams, leading to radically altered channel forms (wide, shallow, straight channels with little depth or velocity variation) and hydrology (high peak flows, reduced base flows, and discontinuity between channel and subsurface sediments (Paul and Meyer 2001). Because urbanization simultaneously increases the loading of sediments and nutrients while simplifying the stream channel, urban rivers are effectively changed from functioning ecosystems to gutters. A number of recent papers demonstrate that urban streams have very reduced capacities for nutrient uptake and retention (Grimm, Crenshaw et al. In Press; Groffman and Dorsey In Press; Groffman, Law et al. In Press; Meyer, Paul et al. In Press), yet to date this work been primarily descriptive rather than mechanistic.

Investments in river restoration attempt to reduce N export: Concern over the impacts that land use changes may have on the ability of river systems to provide the ecological and social services upon which human life depends has resulted in the initiation of major investments in urban river restoration (Bernhardt, Palmer et al. 2005). More than one third of all river restoration projects in the U.S. are implemented to "manage and improve water quality", yet these projects are rarely evaluated to determine if this goal is achieved (Bernhardt, Palmer et al. 2005). In urban areas, multi-million dollar projects are aimed at "renaturalizing" these simplified channels back (hopefully) into functioning ecosystems (supporting of diverse fauna and capable of retaining sediments and nutrients) (Bernhardt and Palmer In review).

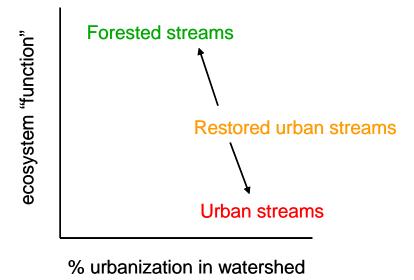
A growing body of research demonstrates the important effect stream ecosystems have in altering the form, timing and magnitude of watershed nitrogen (N) losses. Most of this research has been conducted in minimally impacted watersheds. Streams in heavily urbanized watersheds may be functionally disconnected from upland soils, with a high proportion of precipitation routed over pavements and through storm drains directly into channels. Receiving streams, in turn, will become little more than gutters routing stormwaters towards the sea. Urban streams thus represent the worst case scenario, integrating a large number of simultaneous watershed insults. Several very recent studies suggest that these streams have very reduced capacities to transform and retain N. These same studies also demonstrate that N transformation and retention is closely tied to organic matter (OM) dynamics. For the last year we have examined differences between 12 focal stream reaches in the Raleigh-Durham metropolitan area, comparing streams from forested watersheds (n=4) with those in urban watersheds (n=8) in reaches that are degraded (n=4) or

recently restored (n=4). We have found that stream restoration efforts do not appear to be restoring habitat or flow heterogeneity. The urbanized streams in our survey tend to have slower flows, more homogeneous substrate, and greater channel incision than their forested counterparts and indeed restored stream reaches are virtually identical to urban streams, with the exception of having reduced channel incision. Our efforts to document differences in ecosystem function across these twelve streams have proven less sensitive. Urbanization tends to shift stream ecosystems towards increasingly productive systems, with higher nutrients, slower flow and higher light levels stimulating algal growth. Restoration projects tend to eliminate riparian trees, thus the major effect of restoration on ecosystem function is warmer, more well lit streams that have higher algal production and higher nutrient uptake than their urban counterparts.

Methodology

We predicted that streams in urban watersheds would have simplified habitat structure and be impaired in ecosystem function relative to their minimally impacted counterparts in predominantly forested watersheds (Figure 1). We also predicted that restoration efforts would lead to stream ecosystems that fell out intermediate in both structural and functional attributes relative to forested and urban watershed streams.

Figure 1: Hypothetical predictions for the effects of urbanization and restoration on stream ecosystem function

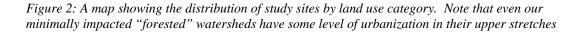


We examined these predictions through detailed comparison of 12 stream reaches distributed between 3 categories: forested watersheds (4 streams draining watersheds that were minimally impacted by urban development); urban degraded streams (4 streams draining heavily urbanized watersheds without any channel restoration); and urban restored (4 streams draining heavily urbanized watersheds that have undergone some form of natural channel design river restoration within the last eight years). For this set of 12 streams we made the following set of predictions in our original proposal (Table 1). In each case, we

predicted that these factors would differ between the forested and the urban stream reaches, and hypothesized that successful restoration would lead to measurements that were intermediate to the urban and forested endpoints.

Table 1 . Response Variables	Develope	Developed relative to		
	unde	undeveloped		
	Mean	Variance		
Hydrologic				
Storm pulse amplitude	>	na		
Transient storage	<	na		
Hydraulic connectivity	<	<		
Geomorphic				
Channel Incision	>	<		
Water depth	<	<		
Channel width	>	<		
Biogeochemical				
Benthic Organic Matter (BOM)	<	<		
Community Respiration (CR)	<	<		
Denitrification potential (DEA)	<	<		
Microbial biomass	<	<		
DIN uptake velocities	<	<		
Nitrification	>	<		

We set up a comparative study of streams from 12 watersheds within the Raleigh-Durham metropolitan area (see Figure 2). Four streams were in predominantly forested watersheds (<10% impervious cover) with our study reaches at least a kilometer downstream of any impervious cover (impacts in headwaters) (Table 1). Eight "urban" streams drained watersheds ranging from 11-40% impervious cover (Table 1). Four of our study reaches within these urban streams had been restored within the last decade and were recommended as the "best case scenarios" for restoration by staff of the NC EEP and the NC Stream Restoration Institute. In each stream we located an intensive study reach that was representative of local conditions and which allowed at least one hour of water travel time during summer baseflow. In the restored streams we chose reaches at the downstream end of the restored segments, operating on the assumption that these segments would benefit from both local and upstream effects of the restoration project. Our goal in this study was not to examine the average restoration project, but instead to examine the potential for restoration to achieve habitat improvement or ecosystem functional benefits, thus we chose the projects and the reaches that we expected would maximize restoration benefits.



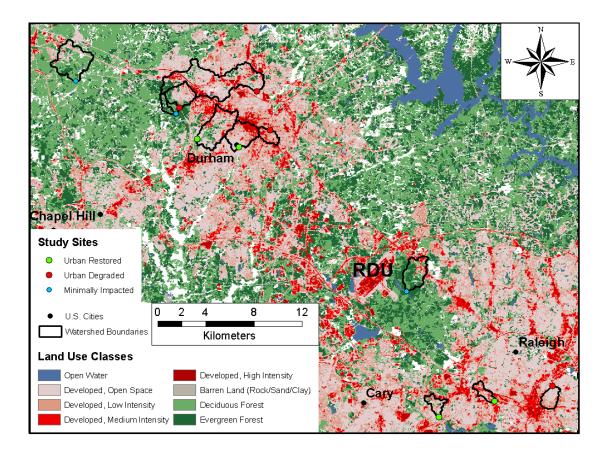


Table 2: Watershed Characteristics					
Block	Status	Site Name	Watershed Size (km ²)	% Developed	% Impervious
	Forested	Stony Creek	6.9	24.4	3.4
Α	Restored	Forest Hills	4.4	99.5	32.4
	Urban	Northgate Park	7.6	88.7	20.8
	Forested	Potts Branch	4.2	27.4	9.9
В	Restored	Abbott Creek	1.7	84.5	17.8
	Urban	Cemetary Creek	2.2	98	19.1
	Forested	Mud Creek Tributary	0.9	4.4	0.5
С	Restored	Rocky Branch	1.5	99.2	34.8
	Urban	Goose Creek	1.7	100	39.4
D	Forested	Mud Creek Reach 4	4.1	58.6	9.5
	Restored	Sandy Creek	6.7	76.9	16.8
	Urban	Mud Creek Reach 1	3.5	66.9	11

This research program will focus on measuring A) stream metabolism and inorganic nitrogen uptake in a series of degraded and restored urban streams as well as several reference streams (n=4 of each) and relating these vital ecosystem functions to two key structural attributes of stream channels; B) hydraulic connectivity between the stream channel and its riparian zone and between surface water and hyporheic groundwater; and C) organic matter retention and storage. We request funding for the initial year of research, but anticipate pursuing renewal funding from WRRI and additional funds from other sources (e.g., NSF, EPA, NC EEP) to continue this research for at least three years.

Functional Measures: Metabolism and Nitrogen Uptake

Metabolism: Ecosystem metabolism is an expression of all heterotrophic and autotrophic activity in the stream and thus would be expected to be influenced by any change in shading, allochthonous input, thermal regime, or nutrient concentrations due to urbanization or stream restoration. Restoration efforts should slow streamflow and increase transient storage of surface water and exchange with hyporheic and shallow groundwater reservoirs. The resulting increase in water-sediment contact time and depositional habitats should lead to higher net ecosystem metabolism rates. Although metabolism rates may not be linearly affected by urbanization, ecosystem metabolism has been shown to control ammonium uptake in both relatively pristine (Hall and Tank 2003) and urban streams (Meyer, Paul et al. *In Press*).

Methods: Gross primary production (GPP), community respiration (CR), and net ecosystem metabolism (NEM=GPP-CR) will be estimated using the two-station method described by (Marzolf, Mulholland et al. 1994). This method uses oxygen probes at the top and bottom of a reach to measure oxygen change over the reach, and a propane and conservative tracer release to estimate transit time and oxygen exchange rate. We will also measure redox potential and respiration, using respiration chambers and redox probes, to determine the status of heterotrophic metabolism in riparian soils and hyporheic sediments.

Expected Results: Little structure and frequent disturbance due to flashy floods may limit the algal population in the urban streams, limiting GPP, and these effects may not be mitigated in the restored streams. CR is associated with stable, organic substrate, such as leaf packs, so we expect CR to be correlated with in-stream benthic organic matter. Naturally occurring stream complexity in the reference streams, and increased structure in the restored streams, will lead to larger transient storage zone volume, which could increase NEM.

Nitrogen Uptake

Whole-stream uptake: We will use standard methods(Newbold 1981; Bernhardt, Hall et al. 2002) to measure the rate at which inorganic nitrogen is removed from the water column. Briefly, we will perform back to back co-injections of NaNO₃ then NH₄Cl with a hydrologic tracer (NaBr then NaCl). We will examine the downstream change in the concentration of the nutrient relative to the inert tracer. We will use the slope of the decline for each release to estimate, NH₄, NO₃ and total nitrogen uptake rates and whole-stream nitrification.

Riparian and Hyporheic Denitrification Rates: Denitrification is the only process by which nitrogen can be permanently removed from the stream channel and is thus the critical biogeochemical function that we would like to promote within restored stream reaches. We will measure denitrification potential by incubating stream and riparian sediment samples from each reach (**Groffman**, **Holland** et al. 1999). We will compare rates between streams to determine whether urbanization and/or restoration affects denitrification rates. We will also examine the relationship between BOM and denitrification potential for individual cores. In one representative stream within each category, we will supplement these estimates by measuring *in situ* denitrification rates in riparian and hyporheic sediments using ¹⁵N single-well push-pull tests (Addy, Kellogg et al. 2002). Briefly, groundwater is extracted from a riparian or hyporheic well, supplemented with ¹⁵NO₃ along with hydrologic (NaBr) and gas (propane) tracers, and returned to the well. Samples are removed from the well 1, 3 and 8 hours following the injection and analyzed for NO₃, N₂O, Br, propane and δ^{15} N of NO₃ and N₂O. This technique provides a direct measure of biological uptake of labeled NO₃-N, as well as production rates of N₂O through denitrification.

Structural Measures: Hydraulic connectivity and organic matter storage

Stream Hydrographs: We have continuously monitored stream height in all streams by installing a pair of datalogging Hobo[©] pressure transducers at the upstream end of each reach *[these were purchased with funds from the NC EEP Monitoring and Research program]*. We are still working to develop rigorous flow rating curves for each reach by calculating changes in instantaneous flow throughout at least one storm event in each stream (more rigorous rating curves will be developed through time, but are beyond the scope of this one year study). The stream height data will be used to calculate daily, seasonal, and annual flow statistics (e.g., flood frequency and magnitude, and "flashiness").

Hydraulic connectivity: We consider hydraulic connectivity to be maximum in streams with: 1) less incised channels; 2) more variable water table depths (in riparian zone) and vertical hydraulic gradients (in channel); and 3) movement of solutes between riparian, hyporheic and surface water.

1) *Channel Incision*: We worked within the existing monitoring framework of the NC Ecosystem Enhancement Program (NC EEP) to assess channel incision by measuring bankfull channel shape and dimension at 5 transects in each study stream(Pizzuto, Hession et al. 2000). We also determined channel slope, grain-size distributions, channel sinuosity and created detailed habitat maps for each reach. These physical measurements are made annually by NC EEP for each of the restored streams in our survey. Thus we utilized many of the same approaches for the other 8 streams. 2) Movement of Solutes Between Channel and Subsurface: At each study site we conducted solute tracer releases once in summer 2006 and again in winter 2007, and continuously record solute breakthrough curves in the water column (to estimate water residence time and physical water storage) (Jones and Mulholland 2000).

Organic Matter: Organic matter (OM) in streams serves many functions, but it is especially important as a carbon source for the ecosystem. As a food source for macroinvertebrates, it serves as the base of the food web. As a food and substrate source for bacteria, algae, and fungi, it supports the ecosystem function of water quality improvement which these organisms provide. In particular, fine benthic organic matter (FBOM) in streams has been shown to be a highly correlated with nitrogen removal. In urban systems, OM levels are very low due to both reduced inputs from the riparian zone and reduced retention in the stream(Paul and Meyer 2001). Because organic matter is a cornerstone of several ecosystem functions which stream restoration targets, it could serve as a proxy for those functions in post-construction monitoring.

The first step in understanding OM dynamics in urban streams is to quantify the existing levels. In summer 2006, we sampled 10 transects for each study reach. All coarse benthic organic matter (CBOM) was first removed from 1-m long transect across the full width of the streambed at each transect. After surface CBOM was removed, a core sampler was inserted into the stream bed to measure FBOM, by mixing sediments to 10cm depth within the sampler, recording the volume within the core and removing a subsample. Each sample was weighed in the field and subsamples were returned to the lab. We characterized each sample for % wood and % leaves. All samples or subsamples were subsequently dried and ashed. This allows us to estimate both total dry mass and total ash-free dry mass for the stream bed CBOM and FBOM.

Principle Findings

With the help (and additional financial support of \sim \$21K) of the NC Ecosystem Enhancement Program we identified 6 urban streams included in their existing program, four previously restored projects and 2 soon to be restored degraded urban streams. These 6 streams, along with 4 reference streams in Umstead Park and the Duke Forest and 2 additional urban streams (one in Raleigh and one in Durham) make up our set of 12 intensive field sites. Within the project period we have: (1) monitored water chemistry once monthly at all 12 streams; (2) developed GIS watershed analyses of land use for the watershed draining to each study reach; (3) performed nutrient injection experiments, measured whole ecosystem metabolism, and modeled transient storage in each reach using low level experimental enrichments of nutrients and hydrologic tracers (each of these measurements were made for each stream in June 2006 and February 2007); (4) conducted a detailed survey of stream and riparian morphology; (5) installed continuously recording water level sensors to develop hydrographs for each site and (6) intensively sampled benthic organic matter at all 12 sites.

Our comparison of these 12 stream reaches was motivated by a desire to understand: (1) how urbanization changes both the structure (habitat heterogeneity, hydrologic connectivity, riparian characteristics) and function (metabolism, nutrient uptake) of stream ecosystems; and (2) the extent to which interventionist restoration approaches that use natural channel design to re-engineer degraded channels can move degraded urban ecosystems back towards "reference" conditions.

We are still in the midst of working up the entire dataset, and expect to submit at least two manuscripts arising from this work in fall 2007. One manuscript will focus on the structural and hydrologic changes in stream channels associated with urbanization and will report our findings that stream restoration efforts do not appear to be "restoring" habitat or flow heterogeneity. The urbanized streams in our survey tend to have slower flows, more homogeneous substrate, and greater channel incision. Restored streams are virtually identical to urban streams, with the exception of channel incision, likely reflecting the focus by

restoration practitioners on channel geometry rather than habitat quality. A second manuscript will report our findings on nitrogen processing and metabolism across this urbanization gradient. Urbanization tends to shift streams towards increasingly productive systems, with higher nutrients, slower flow and higher light levels stimulating algal growth. Restoration projects tend to eliminate riparian trees, thus <u>the</u> major effect of restoration on ecosystem function is warmer, more well lit streams that have higher algal production and higher nutrient uptake than their urban counterparts.

Related work in these same stream reaches by PhD student Christy Violin has found that macroinvertebrate community composition is quite different between the urban and forested streams (with many more sensitive taxa found in the reference streams), but that macroinvertebrate communities in the restored stream reaches are not different from their urban degraded stream counterparts. We have found that simple measures of habitat heterogeneity are the best predictors of macroinvertebrate community composition, and suggest the lack of attention to creating fine scale habitat diversity in restored streams may limit their success.

Our study to date has found that:

1) Streams in urban catchments have:

Flashier hydrographs

- More highly incised stream channels
- Higher loads of both nitrate and total nitrogen (as well as Cl⁻ and SO₄⁻)
- Simplified flow and substrate defined habitats
- Less variable distributions of organic material
- Very low occurrences of sensitive macroinvertebrate taxa

 Restored streams differ from their urban degraded counterparts by Having less incised stream channels Having higher summer uptake efficiencies for NO₃⁻

Having reduced canopy cover relative to unrestored urban streams targeted for restoration

3) Restored streams are indistinguishable from their urban degraded counterparts in

- Having little variation of bed and flow habitat types
- Having low variation in depth and velocity
- Having nitrogen concentrations that are higher than reference watershed streams

Having identical macroinvertebrate community composition

These findings suggest that restoration efforts are failing to ameliorate many of the insults to urban stream ecosystems. We recommend that increasing attention be paid to reestablishing fine-scale variation in habitat heterogeneity (introducing a variety of substrate sizes and varying depths within restored stream reaches) in order to better mimic less impacted streams. We caution that all urban restoration efforts are unlikely to succeed without addressing the primary cause of channel degradation, the flash hydrographs associated with high watershed impervious cover. Restoration of channels without accompanying stormwater management efforts are unlikely to be successful at reaching the goals of "reestablishing ecosystem function".

Significance

These findings suggest that restoration efforts are failing to ameliorate many of the insults to urban stream ecosystems. We recommend that increasing attention be paid to reestablishing fine-scale variation in habitat heterogeneity (introducing a variety of substrate sizes and varying depths within restored stream reaches) in order to better mimic less impacted streams. We caution that all urban restoration efforts are

unlikely to succeed without addressing the primary cause of channel degradation, the flash hydrographs associated with high watershed impervious cover. Restoration of channels without accompanying stormwater management efforts are unlikely to be successful at reaching the goals of "reestablishing ecosystem function".

Urbanization tends to shift stream ecosystems towards increasingly productive systems, with higher nutrients, slower flow and higher light levels stimulating algal growth. Restoration projects tend to eliminate riparian trees, thus <u>the</u> major effect of restoration on ecosystem function is warmer, more well lit streams that have higher algal production and higher nutrient uptake than their urban counterparts.

References

Addy, K., D. Q. Kellogg, et al. (2002). "In situ push-pull method to determine ground water denitrification in riparian zones." Journal of Environmental Quality 31(3): 1017-1024.

Alexander, R. B., R. A. Smith, et al. (2000). "Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico." Nature 403(6771): 758-761.

Baker, M. A., C. N. Dahm, et al. (1999). "Acetate retention and metabolism in the hyporheic zone of a mountain stream." Limnology and Oceanography 44(6): 1530-1539.

Bernhardt, E. and M. Palmer (In review). "Restoring streams in an urbanizing world." Freshwater Biology.

Bernhardt, E. S., R. O. Hall, et al. (2002). "Whole-system estimates of nitrification and nitrate uptake in streams of the Hubbard Brook Experimental Forest." Ecosystems 5(5): 419-430.

Bernhardt, E. S. and G. E. Likens (2002). "Dissolved organic carbon enrichment alters nitrogen dynamics in a forest stream." Ecology 83(6): 1689-1700.

Bernhardt, E. S., G. E. Likens, et al. (2003). "In-stream uptake dampens effect of major forest disturbance on watershed nitrogen export." Proceedings of the National Academy of Science 100(18): 10304-10308.

Bernhardt, E. S., M. A. Palmer, et al. (2005). "Restoration of U.S. rivers - a national synthesis." Science 308.

Bilby, R. E. (1981). "Role of organic debris dams in regulating the export of dissolved and particulate matter from a forested watershed." Ecology 62(5): 1234-1243.

Galloway, J. N., F. J. Dentener, et al. (2004). "Nitrogen cycles: past, present, and future." Biogeochemistry 70: 153-226.

Green, P. A., C. J. Vorosmarty, et al. (2004). "Pre-industrial and contemporary fluxes of nitrogen through rivers: a global assessment based on typology." Biogeochemistry 68(1): 71-105.

Grimm, N. B., C. L. Crenshaw, et al. (In Press). "Nutrient retention and transformation in urban streams." Journal of the North American Benthological Society.

Groffman, P. M. and A. M. Dorsey (In Press). "Nitrogen processing within geomorphic structures in urban streams." Journal of the North American Benthological Society.

Groffman, P. M., E. Holland, et al. (1999). Denitrification. Standard Soil Methods for Long Term Ecological Research. G. P. Robertson, C. S. Bledsoe, D. C. Coleman and P. Sollins. New York., Oxford University Press: 272-288.

Groffman, P. M., N. L. Law, et al. (In Press). "Nitrogen fluxes and retention in urban watershed ecosystems." Ecosystems.

Hall, R. O. and J. L. Tank (2003). "Ecosystem metabolism controls nitrogen uptake in streams in Grand Teton National Park, Wyoming." Limnology and Oceanography 48(3): 1120-1128.

Jones, J. B. and P. J. Mulholland (2000). Streams and Ground Waters. San Diego, CA, Academic Press.

Marzolf, E. R., P. J. Mulholland, et al. (1994). "Improvements to the Diurnal Upstream-Downstream Dissolved-Oxygen Change Technique for Determining Whole-Stream Metabolism in Small Streams." Canadian Journal of Fisheries and Aquatic Sciences 51(7): 1591-1599.

Meyer, J. L., M. J. Paul, et al. (In Press). "Ecosystem function in urban streams." Journal of the North American Benthological Society.

Newbold, J. D., J.W. Elwood, R.V. O'Neill and W. VanWinkle (1981). "Measuring nutrient spiraling in streams." Candian Journal of Fisheries and Aquatic Science 38: 860-863.

Paul, M. J. and J. L. Meyer (2001). "Streams in the urban landscape." Annual Review of Ecology and Systematics 32: 333-365.

Peterson, B. J., W. M. Wollheim, et al. (2001). "Control of nitrogen export from watersheds by headwater streams." Science 292(5514): 86-90.

Pizzuto, J. E., W. C. Hession, et al. (2000). "Comparing gravel-bed rivers in paired urban and rural catchments of southeastern Pennsylvania." Geology 28(79-82).

Seitzinger, S. P., R. V. Styles, et al. (2002). "Nitrogen retention in rivers: model development and application to watersheds in the northeastern USA." Biogeochemistry 57(1): 199-237.

Strauss, E. A. and G. A. Lamberti (2000). "Regulation of nitrification in aquatic sediments by organic carbon." Limnology and Oceanography 45(8): 1854-1859.

UNPD (2003). United Nations Population Division, World Population Prospects: the 2002 Revision, Highlights (online database). ESA/P/WP.180, revised 26 February 2003. http://esa.un.org/upp/World Urbanization Prospects: The 2001 Revision.

USEPA (2003). Ambient water quality criteria for dissolved oxygen, water clarity, and chlorophyll a for the Chesapeake Bay and its tidal tributaries. Annapolis, MD, United States Environmental Protection Agency, Region III Chesapeake Bay Program Office.

Webster, J. R., P. J. Mulholland, et al. (2003). "Factors affecting ammonium uptake in streams - an interbiome perspective." Freshwater Biology 48(8): 1329-1352.

Improved Water Management Strategies for the Neuse basin Utilizing Climate-Information based Probabilistic Streamflow Forecasts

Basic Information

Title:	Improved Water Management Strategies for the Neuse basin Utilizing Climate-Information based Probabilistic Streamflow Forecasts
Project Number:	2006NC65B
Start Date:	3/1/2006
End Date:	8/31/2007
Funding Source:	104B
Congressional District:	2
Research Category:	Climate and Hydrologic Processes
Focus Category:	Water Quantity, Floods, Drought
Descriptors:	hydroclimatology, hydrological forecasting, watershed management, risk analysis, climate, decision models, flood control, multi-objective planning, optimization, reservoir modeling, systems analysis
Principal Investigators:	Sankarasubramanian Arumugam

Publication

- 1. Sankarasubramanian, A., N. Deveneni, and S. Ghosh, 2006, Multi-model Ensembling of Probabilistic Streamflow Forecasts: Role of Predictor State, Space in Skill Evaluation, Institute of Statistics Mimeo Series 2595,NC State University.
- 2. Arumugam, S., N. Devineni, and S. Ghosh, December 11-15, 2006. Multi-model Ensembling based on Predictor State Space: Seasonal Streamflow Forecasts and Causal Relations, American Geophysical Union Conference, San Francisco.

Title

Improved Water Management Strategies for the Neuse basin utilizing Climate-Information based Probabilistic Streamflow Forecasts

Project Summary

A strategy to improve water allocation in the Neuse basin is proposed by developing a seamless integration climate-information based streamflow forecasts into water systems planning (3 months to 6 months) and operation. The proposed research will develop long-lead probabilistic streamflow forecasts in the Neuse basin contingent on both local land-surface and exogenous climatic conditions. Retrospective streamflow forecasts will be combined with a reservoir management model to understand the utility of streamflow forecasts in operating the Falls Dam. With the decadal variability in the tropical Atlantic Sea Surface Temperature (above-normal conditions) resulting in more hurricanes, it is imperative to develop a prognostic approach for water management in the Neuse basin given the basin accounts for 22% of state's population. Such an approach based on climate information could help water managers to prepare well in advance to reduce the impacts resulting from hydroclimatic extremes.

Benefits/Information from this project will support other ongoing activities in the Neuse including Neuse river basin planning program (supported by DENR), National Water Quality Assessment Program (supported by USGS) and NC Drought Monitoring (supported by Division of water resources, DENR) in coordination with the state's climate office. Analyses from this research will also promote identification of alternate river basin management plans during critical drought conditions including conjunctive use, instream flow maintenance and estuaries management. Informative web portal will de developed that summarizes the hydroclimatic predictability of the Neuse basin as well as updates of streamflow potential for the seasons ahead. Potential implications and its relevance to several ongoing researches in the Neuse basin will include quantitative representation of uncertainty in streamflows to support TMDL process, development of seasonal water management plans considering conjunctive use for the coastal zone and prediction outlooks for floods and droughts. We envisage that this effort for Neuse basin will motivate other basins in NC to incorporate to follow a prognostic, climate-information driven approach towards water management.

Methodology

Probabilistic Streamflow Forecasts Development: First, an assessment of different AGCMs' ability to predict both winter (January-March) and summer (June-September) precipitation over the Neuse basin will be investigated. This will be analyzed online at IRI data library (http://iridl.ldeo.columbia.edu/). Based on that, the best AGCM will be selected for developing the streamflow forecasting model. Three different approaches can be adopted when developing climate-information based streamflow forecasts: (a) Couple AGCM outputs with a Regional Spectral Model (RSM) whose outputs are combined with a large-scale watershed model16(b) Statistically downscale AGCM precipitation to streamflow at a particular point of interest18,19 (c) Develop a low dimensional statistical model that predicts the streamflow based on dominant climate predictors that influence the streamflow/rainfall potential over the basin17. Given only one year for this study, we will pursue approaches (b) and (c) to develop climate-information based streamflow forecasts. Coupling of AGCM with RSM and a watershed model will be pursued as future research activities. To pursue approach (b), we will develop different statistical downscaling methodologies to predict streamflow based on the selected AGCM's precipitation grids18,19. To develop a low-dimensional statistical model, detailed diagnostic analyses will be first carried out to identify the dominant predictors that influence the streamflow potential of the Neuse basin. The study will exploit the NC state climatological office's database

(http://www.nc-climate.ncsu.edu/cronos/) and various other databases including climate Diagnostic Center (http://www.cdc.noaa.gov/PublicData/) to perform diagnostic analyses for predictor identification. We will employ state-of-the-art multivariate techniques including independent component analyses (ICA)20 to develop predictors that are independent to each other. Once the predictor set is developed, we will develop retrospective probabilistic streamflow forecasts for the Falls Lake using different statistical approaches including parametric and nonparametric regression techniques. Figure 6 shows an example of a probabilistic streamflow forecasts developed for a reservoir system in Ceara, North East Brazil.

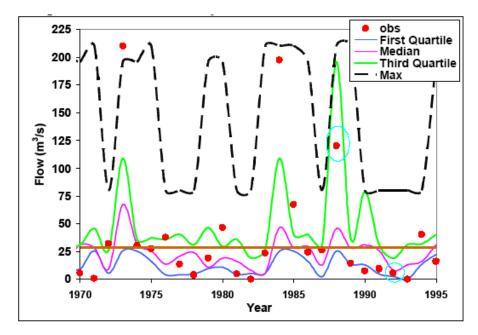


Figure 6: Retrospective, Leave one-out cross-validated 7-months ahead streamflow forecast ensembles for the Oros reservoir, Ceara, NE brazil17. The correlation between the observed streamflow and the predicted median streamflow is 0.7 over the period 1949-1996. Predictors employed for this purpose include Nino3.4 and Atlantic Dipole17. Note the ensembles shift according to the nature of flows for the two circled years in comparison to the long-term average (solid brown line). More than 60% of the mass is above the long-term average for the above normal inflow year in 1988, whereas in a below normal year in 1992, more than 80% of the mass is below the long-term average.

Reservoir Analyses: To develop a customized reservoir management model for the Falls Lake, the study will employ MORAPS, which has been tested on many basins for climate forecasts application. Figure 7 shows a snapshot of MORAPS for representing a multi-reservoir system in the Greater Horn of Africa14. MORAPS incorporates novel features with the ability to run both retrospective analyses and to perform adaptive analyses of reservoir systems for real-time decision-making. Downscaled streamflow forecasts based on AGCM precipitation can also be used as an input to the model. MORAPS also incorporates a novel contract structure11,15 with an ability to perform the analyses under both optimization and simulation modes. Using retrospective streamflow forecasts developed from the study, we will employ MORAPS to identify optimal operating policies for the Falls Dam for reducing downstream flood damages as well as meeting both water quality and water quantity targets.

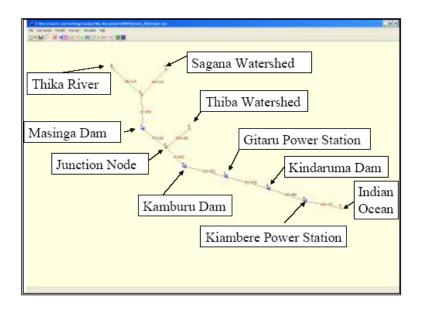


Figure 7: A snap shot of the Tana River 7-Forks Reservoir Management Model in the Greater Horn of Africa shown within MORAPS (Authors: Sankarasubramanian Arumugam, PI of this proposal and Upmanu Lall; copyrighted to IRI, Columbia University).

Dissemination: An important goal of this research is to develop a prognostic approach to improvise water management in the Neuse basin, which can help local/state water managers prepare well in advance for mitigation of the impacts resulting from hydroclimatic extremes. In this regard, we would like to invite NC DENR (Division of Water Resources), USACE (Wilmington District) and NC Drought Monitoring Council as external advisory board. In collaboration with them, we plan to perform the retrospective analyses of Falls Lake management contingent on probabilistic streamflow forecasts. A web portal will also be developed as part of the project that will update the long-lead streamflow forecasts for the Neuse basin on a monthly basis. We envisage that this effort for Neuse basin will motivate other basins in NC to incorporate to follow a prognostic, climate-information driven approach towards water management.

Relevance to Other Neuse Basin Initiative and Scope for Future Research

Given the diversity of hydrologic and geographic settings as well as water management issues related to the ongoing developments in the basin, Neuse has been a target basin towards monitoring, understanding and modeling of hydrological processes from both national and state agencies. Neuse which is located in the Albemarle-Pamlico drainage basin has been identified as one of the 20 selected basins for National Water Quality Assessment Program from the USGS33. Consortium of Universities for the Advancement of Hydrologic Science (CUAHSI), a collection of Universities for advancing hydrologic science, has identified Neuse as a target basin for setting up hydrologic observatory34. NC state DENR has developed a detailed water management plans to protect water quality and quantity issues in the basin given 22% of state's population live in the Neuse basin35,36,37. Several non-profit organizations, NC Water Resources Research Institute and Neuse River Foundation support many basin wide initiatives38,39,40. Research findings from this proposal will support the above programs in quantifying the uncertainty related seasonal streamflow potential as well as in providing prediction outlooks on floods and droughts. Findings from this research will also support future research initiatives of the PI that includes understanding the linkages between climate variability and ground water availability,

utility of climate forecasts in reservoir/lake water quality management to guide the TMDL process and in understanding the importance of policy instruments in forecast applications in water management.

Principle Findings

Three specific objectives are encompassed in the proposed study: (a) Development of a climateinformation based streamflow forecasting model (b) Perform retrospective analyses on the utility of climate forecasts in improving Falls Lake operation (c) Dissemination of results from the analyses with various state agencies that coordinate water-related activities in the Neuse basin.

Objective 1: Development of a climate-information based streamflow forecasting model

Substantial progress on streamflow forecasting model development has been made:

- Two low dimensional (one regression and another resampling) streamflow forecasting models were developed, one for January-March and another one for July-September, using sea surface temperature conditions in tropical Pacific, tropical Atlantic and NC Coast. Both models have been verified and validated.
- Based on the comments on one of the reviewer in the proposal, we developed multi-model ensembles of streamflow forecasts for predicting the summer flows, July-September and it has been found to improve single model forecasts. This work has been published as a report in the Institute of Statistics, Mimeo Series (<u>http://www.stat.ncsu.edu/library/mimeo.html</u>). A paper on the new methodology on multimodel forecasts is also under revision in Water Resources Research.
- The multimodel combination methodology was also extended to combine various General Circulation Models (GCMs) so that multimodel precipitation forecasts could be used for downscaling to Falls Lake. Three different GCMs, ECHAM4.5, CCmV6, and COLA, were combined for the entire US. The multimodel precipitation forecasts are much better than the single model forecasts as shown below using Rank Probability Skill Score. This is another paper in preparation for submission to the Journal of Climate.

Objective 2: Perform retrospective analyses on the utility of climate forecasts in improving Falls Lake operation

Progress on this objective is summarized as follows:

- A Falls Lake Management Model has been developed and verified in modeling releases for the period July-August-September.
- The model has been tested with multi-model forecasts developed from the earlier objective and the importance of multimodel forecasts in improving reservoir management has been analyzed.
- Performance of the model using forecasts was analyzed to support the following decision analyses: (a) Restrictions if the forecasts suggests dry year (b) Having additional storage beyond 251.5 msl during wet summer years (c) Probability of meeting the target storage at 251.5 msl by the end of summer.

Objective 3: Dissemination of results from the analyses to various state agencies that coordinate waterrelated activities in the Neuse basin.

• Reasonable progress has been made and a project website has been developed with a content management system http://www.ce.ncsu.edu/research/hydroclimatology/.

- We issued a forecast for the summer of 2006 and it was reasonably on target (observed streamflow 331 cfs and predicted streamflow 346 cfs).
- We are currently trying to schedule a meeting with NCDENR to share the findings from this study.

Significance

Benefits/Information from this project will support other ongoing activities in the Neuse including Neuse river basin planning program (supported by DENR), National Water Quality Assessment Program (supported by USGS) and NC Drought Monitoring (supported by Division of water resources, DENR) in coordination with the state's climate office. Analyses from this research will also promote identification of alternate river basin management plans during critical drought conditions including conjunctive use, instream flow maintenance and estuaries management. Informative web portal will de developed that summarizes the hydroclimatic predictability of the Neuse basin as well as updates of streamflow potential for the seasons ahead. Potential implications and its relevance to several ongoing researches in the Neuse basin will include quantitative representation of uncertainty in streamflows to support TMDL process, development of seasonal water management plans considering conjunctive use for the coastal zone and prediction outlooks for floods and droughts. We envisage that this effort for Neuse basin will motivate other basins in NC to incorporate to follow a prognostic, climate-information driven approach towards water management.

References

1. Weaver, C.J., The Drought of 1998–2002 in North Carolina—Precipitation and Hydrologic Conditions, USGS Scientific Investigations Report, 2005.

2. Yonts, W., North Carolina Department of Environment and Natural Resources, written column, April 1, 2004.

3. Hayes, M.J., Svoboda, M.D., Knutson, C.L., and Wilhite, D.A., Estimating the economic impacts of drought [abs.]: Proceedings of the 84th annual meeting of the American Meteorological Society, January 10–16, 2004, Seattle, Washington.

4. U.S. Army corps of engineers annual flood damage reduction report to congress for fiscal year 2003; http://www.usace.army.mil/inet/functions/cw/cecwe/ flood2003/

5. Fread, D.L., R.C. Shedd, G.F. Smith, R. Farnsworth, C. Hoffeditz, L.A. Wenzel, S.M. Wiele, J.A. Smith, and G.N. Day., Modernization in the National Weather Service River and Flood Program. American Meteorological Society, *Weather and Forecasting*, Vol. 10, No.3.Boston, Massachusetts, 1995.

6. Stallings, E.A. and L.A. Wenzel., Organization of the River and Flood Program in the National Weather Service. American Meteorological Society, *Weather and Forecasting*, Vol.10, No. 3. Boston, Massachusetts, 1995

7. National Hydrologic Warning Council, Use and benefits of the National Weather Service river and flood forecasts. EASPE, Inc., 33 pp,2002.

8. Hamlet, A.H., D. Huppert and D.P. Lettenmaier, 2002, Economic value of long-lead streamflow forecasts for Columbia River hydropower, *J. Water Resour. Planning and Management* 128, 91-101,2002.

9. Ward, M.N., A. Sankarasubramanian, J. Hansen, M. Indeje, and C. Mutter, To what extent can climate information contribute to solving problems, Clivar Exchanges, 9(2), 5-8, 2004. 10. Maurer EP, Lettenmaier DP., Potential effects of long-lead hydrologic predictability on

Missouri River main-stem reservoirs, Journal of Climate, 17 (1): 174-186, 2004

11. Sankarasubramanian, A., Lall, U. and Sharma, A., Dynamic Water Allocation Framework for multiple uses II: Performance under Climate Information based Reservoir Inflow Forecasts (To be submitted to *Journal of Climate*).

12. Roswintiarti, O., D.S.Niyogi, and S.Raman., Teleconnections between the tropical Pacific sea surface temperature anamolies and North Carolina precipitation anamoloies during El Nino events, Geophysical Research Letters, 25, 4201-42, 1998.

13. Jamie R. Rhome, Dev dutta S. Niyogi, and Sethu Raman, Mesoscale analysis of severe weather and ENSO interactions in North Carolina., *Geophysical Research Letters*, Vol. 27, pp 2269-2272, 2000.

14. International Research Institute for Climate Prediction, Regional Climate Prediction and Risk Reduction in the Greater Horn of Africa, Final Report to USAID, 2005.

15. Sankarasubramanian, A. and Lall, U., Dynamic water allocation framework for multiple uses: Utility of climate forecasts towards short-term water management, International conference "Climate Change: A challenge or a threat for water management", September 27-29 2004. Amsterdam.

16. Wood, A.W., Kumar, A. and Lettenmaier, D.P., A retrospective assessment of National Centers for Environmental Prediction climate model-based ensemble hydrologic forecasting in the western United States, Journal of Geophysical Research-Atmospheres 110 (D4): Art. No. D04105,2005.

17. Souza, F.A., and Lall, U., Seasonal to interannual ensemble streamflow forecasts for Ceara, Brazil: Applications of a multivariate, semiparametric algorithm, Water Resources Research, 39 (11): Art. No. 1307, 2003.

18. Landman, W.A., S.J.Mason, P.D.Tyson, and W.J.Tennant, Statistical downscaling of GCM simulations to streamflow, Journal of Hydrology 252 (1-4): 221-236 OCT 31 2001.

19. Arumugam, S. and Lall, U., Operational Streamflow Forecasts Development Using GCM Predicted Precipitation Fields, Proceedings of AGU Fall conference, San Francisco, 2004.

20. Hyvärinen, A., J. Karhunen, and E. Oja, Independent Component Analyses, John Willey and Sons, 2001.

21. Lettenmaier, D.P. and E.Wood., Hydrolgoic Forecasting, Hand book of Hydrology, edited by V.Maidment, McGraw-Hill Publisheres, 1993.

 Shaake, J., and Larson, L., Ensemble Streamflow Prediction (ESP): Progress and Research needs, Special Symposium on Hydrology, Am.Meteorol., Soc., Boston, Mass, J19-J24, 1998.
Trenberth, K. E., C. J. Guillemot, Physical Processes involved in the 1988 Drought and 1993

Floods in North America. Journal of Climate, 9, 6, 1288–1298, 1996.

24. Cayan, D. R., K. T. Redmond, and L. G. Riddle, ENSO and Hydrologic Extremes in the Western United States. *J. Climate*, 12, 2881-2893, 1999.

25. Dettinger, M.D. and H.F. Diaz, Global characteristics of stream flow seasonality and variability, Journal of Hydrometeorology, 1 (4): 289-310, 2000.

26. Guetter, A. K., and K. P. Georgakakos, 1996: Are the El Nin^o and La Nin^a predictors of the Iowa River seasonal flow? *J. Appl. Meteor.*, **35**, 690–705.

27. Piechota, T. C., and J. A. Dracup, 1996: Drought and regional hydrologic variation in the United States: Associations with the El Nin^o-Southern Oscillation. *Water Resour. Res.*, **32**, 1359–1374.

28. Piechota, T.C., F.H.S.Chiew, J.A.Dracup and T.A.McMahon, Development of exceedance probability streamflow forecast, Journal of Hydrologic Engineering, 6 (1), 20-28, 2001.

29. Yao, H. and A. Georgakakos, Assessment of Folsom Lake response to historical and potential future climate scenarios, 2- reservoir management, J. Hydrology, 249, 176-196, 2001.

30. Hamlet, A.H., D. Huppert and D.P. Lettenmaier, 2002, Economic value of long-lead streamflow forecasts for Columbia River hydropower, *J. Water Resour. Planning and Management* 128, 91-101.

31. Georgakakos, A.P., H.M.Yao, M.G.Mullusky, and K.P.Georgakakos, Impacts of climate variability on the operational forecast and management of the upper Des Moines River basin, Water Resources Research, 34 (4), 799-821, 1998.

32. Arumugam, S., A. Sharma., and U.Lall., Water Allocation for multiple use based on probabilistic reservoir inflow forecasts, Proceedings, IAHS, Soppore, 2003.

- 33. http://nc.water.usgs.gov/albe/background.html
- 34. http://www.cuahsi.org/publications/reports.html
- 35. http://www.ncwater.org/basins/Neuse/
- 36. http://h2o.enr.state.nc.us/basinwide/
- 37. http://www.eenorthcarolina.org/
- 38. http://www2.ncsu.edu/ncsu/CIL/WRRI/neuse.html
- 39. http://www.neuseriver.org/
- 40. http://www.epa.gov/owow/watershed/index2.htm

Information Transfer Program

In addition to activities related to specific research projects, WRRI maintains a strong information transfer program by cooperating with various state agencies, municipalities, and professional organizations to sponsor workshops and other events and by seeking grants for relevant activities. During the current fiscal year, WRRI continued to be designated by the N.C. Board of Examiners for Engineers and Surveyors as an Approved Sponsor of Continuing Professional Competency activity for Professional Engineers and Surveyors licensed by the State of North Carolina. In addition, WRRI is an approved sponsor for the N.C. Board of Landscape Architects to offer contact hours. This allows WRRI to offer Professional Development Hours to engineers and surveyors for attending our water resources research seminars, our Annual Conference, and other workshops we sponsor.

The WRRI Information Transfer Program includes the WRRI Annual Conference, which the institute has done since 1998. The 9th Annual Conference was held on April 4-5, 2006 and was titled North Carolina Water Resources: Preparedness for Natural and Manmade Disaster, held in at the NCSU McKimmon Center in Raleigh, NC. It is the state's premier water research conference. Many questions about North Carolina's water resources will be addressed through research presented by university and corporate researchers, students, local, state, and federal government agency representatives, and environmental professionals. The Institute's goal is to provide a forum for attendees to become informed and educated on the most current research addressing water resource issues in North Carolina, as well as network and discuss water-related issues with other attendees.

The WRRI Information Transfer Program includes workshops supported by the NC Department of Environment and Natural Resources (DENR), Land Quality Section along with the NC Sedimentation Control Commission (SCC). Workshops held during this period include: (1) Three Spring Erosion and Sediment Control Planning and Design Workshop, 3/14-15/2006, Greenville, NC; 4/19-20/2006, Charlotte, NC; and 2/22-23/2007, Raleigh, NC; (2) Two Fall Planning and Design Erosion and Sedimentation Control Workshops, 9/19-20/2006, New Bern, NC; and 10/29-30/2006, Hickory, NC; and (3) Erosion and Sedimentation Control Local Programs Training Workshop, 1/30-31/2007, Winston-Salem, NC.

Another way WRRI provides Information Transfer is through the North Carolina Water Resources Association (NCWRA) Luncheon and Forums: (1) September 11, 2006: North Carolina Nutrient Criteria and the Reservoir Protection Act, Michelle Woolfolk, NC Division of Water Quality, and Melissa Kenney, Ph.D. Candidate, Water Quality Modeling & Decision Analysis, Duke University (2) December 4, 2006: Future Conditions Floodplain Mapping, Danny Bowden, Stormwater Program Manager, and Ben Brown, Stormwater Engineering Supervisor, City of Raleigh Stormwater Management Division (3) February 5, 2007: Stormwater BMPs: Taking Ownership, David Phlegar, Water Quality Supervisor City of Greensboro Stormwater Management Division Joseph R. Pearce, PE, CPESC, CFM, Division Manager Durham County Stormwater and Erosion Control Division

WRRI maintains six electronic mail lists (listservs): (1) Water Research list - 180 subscribers inform water researchers from NC universities about calls for papers, grants, upcoming conferences, student internships, etc.; (2) WRRI-News list - 740 subscribers - informs researchers, local governments, municipalities, interest groups etc. about calls for papers, grants, upcoming conferences and events, etc.; (3) NCWRA-info list - 270 subscribers - provides information of the North Carolina Water Resources Association sponsored events; (4) Sediments list - 215 subscribers - sent out SEDIMENTS newsletter and

information on erosion and sediment control regulations and educational workshops/seminars; (5) Urban Water Consortium (UWC) for Urban Water Consortium member communications; (6) and UWC-Stormwater Group list for the UWC Stormwater Group communications.

WRRI maintains its own website (http://www.ncsu.edu/wrri). The website provides on-line access to the WRRI-News, the WRRI technical report summaries, water research seminars, and information on WRRI-sponsored workshops, conferences, and seminars. During this fiscal year, WRRI has scanned its old research reports and made them into searchable pdf files. These reports will be made available on the WRRI web site later in 2007.

WRRI administers the NC Urban Water Consortium (UWC) and meets with its members quarterly. The consortium was established in 1985 by the Institute, in cooperation with several of North Carolina's larger cities to provide a program of research and development and technology transfer on water problems that urban areas share. Through this partnership, WRRI and the State of North Carolina help individual facilities and regions solve problems related to local environmental or regulatory circumstances. Participants support the program through annual dues and enhancement funds and guide the program through representation on an advisory board, selection of research topics, participation in design of requests for proposals, and review of proposals. Currently there are 11 member cities/special districts in North Carolina that met on the following dates: March 28, 2006, Greensboro, NC; June 13, 2006, Carrboro, NC; September 29, 2006, Greenville, NC; and December 5, 2006, Durham, NC.

In 1998, several members of the NC UWC partnership formed a special group to sponsor research and technology transfer on issues related to urban stormwater and management. The Urban Water Consortium (UWC) Stormwater Group is administered by WRRI. Participants support the program through annual dues and enhancement funds. They guide the program through representation on an advisory board, selection of research topics, participation in the design of requests for proposals and review of proposals. Currently there are eight members that met on the following dates: March 16, 2006, High Point, NC; June 15, 2006, Greensboro, NC; September 21, 2006, Raleigh, NC; and December 7, 2006, Charlotte, NC.

WRRI Research Seminar Series

Basic Information

Title:	WRRI Research Seminar Series		
Project Number:	2006NC101B		
Start Date:	3/1/2006		
End Date:	2/28/2007		
Funding Source:	104B		
Congressional District:	2		
Research Category:	Not Applicable		
Focus Category:	None, None, None		
Descriptors:			
Principal Investigators:	David Moreau, Kelly A Porter		

Publication

Spring 2006 Water Resources Research Seminar Series

Dr. Bill Hunt NC State University "Stormwater Best Management Practice Performance Evaluations" Tuesday, March 7, 2006, 3:00 pm 1132 Jordan Hall, NC State University

Dr. Brad Lamphere Dr. Jim Gilliam NC State University "Stream Fish as Bioindicators of Water Quality: Assessing Threshold Responses to Urbanization and Correlations with Invertebrate Indices" Wednesday, March 22, 2006, 3:00 pm 1132 Jordan Hall, NC State University

Dr. Rory Maguire NC State University "Validating the Phosphorus Loss Assessment Tool for the Organic Soils of North Carolina" Tuesday, April 18, 2006, 3:00 pm 1132 Jordan Hall, NC State University

Dr. Kenneth H. Reckhow Duke University "A Predictive Approach to Nutrient Criteria Development" Wednesday, April 26, 2006, 3:00 pm 1132 Jordan Hall, NC State University

The WRRI Institute NEWS

Basic Information

Title:	The WRRI Institute NEWS			
Project Number:	2006NC102B			
Start Date:	3/1/2006			
End Date:	2/28/2007			
Funding Source:	104B			
Congressional District:	2			
Research Category:	Not Applicable			
Focus Category:	None, None, None			
Descriptors:				
Principal Investigators:	Kelly A Porter			

Publication

Published the *WRRI News* two times during the reporting period. The WRRI News is an 8-page newsletter that covers a wide range of water-related topics from current federal and state legislation and regulatory activities to new research findings, waterrelated workshops and conferences, and reviews of water-related publications. The WRRI News is sent to nearly 4,300 federal and state agencies, university personnel, multi-county planning regions, city and local officials, environmental groups, consultants, businesses and individuals.

New WRRI Research Reports

Basic Information

Title:	New WRRI Research Reports			
Project Number:	2006NC104B			
Start Date:	3/1/2006			
End Date:	2/28/2007			
Funding Source:	104B			
Congressional District:	2			
Research Category:	Not Applicable			
Focus Category:	None, None, None			
Descriptors:				
Principal Investigators:	David Moreau			

Publication

New WRRI Research Reports – During the year, the Institute published the following reports for distribution to users throughout the state and nation. A number of the reports are in the formatting stage and have not been assigned a number.

WRRI-355 – Pilot Project on Groundwater Dating in Confined Aquifers of the North Carolina Coastal Plain, by D. Genereux & C. Kennedy, NC State University.

WRRI-356 – Method Development for the Occurrence of Residual Antibiotics in Drinking Water, by H. Weinberg, University of North Carolina at Chapel Hill.

WRRI-357 – Effectiveness of Three "Best Management Practices" for Reducing Nonpoint Source Pollution from Piedmont Tobacco Fields, by C. Franklin, NC State University.

WRRI-358 – Improving Dewatering of Wastewater Biosolids using Innovative Approaches, by F. de los Reyes, NC State University.

WRRI-359 – Trophic Basis for Restoration of Fish Fauna in Restored Urban Streams, by A. Hershey, University of North Carolina at Greensboro.

WRRI-360 - The Cost Effectiveness of Standard Alternative Sediment and Turbidity Control Systems on Construction Sites in North Carolina, by A. Wossink, H. Mitasova & R. McLaughlin, NC State University.

WRRI-TBD Role of Sediment Process in Regulating Water Quality of the Cape Fear River, P.V. Sundareshwar and C. Richardson, Duke University

WRRI-TBD Mechanistic Evaluation of the Combined Action of Environmentally-Relevant Chemical Mixtures on Endocrine signaling in Crustaceans, G. LeBlanc, NC State University

WRRI-TBD Effects of Riparian Buffers on Removal of Nutrients and Sediment in Urban Streams, A. Hershey, University of North Carolina at Greensboro

WRRI-TBD Evaluation of Ecological Function in Restored Urban Streams, A. Hershey, University of North Carolina at Greensboro

WRRI-TBD Surface Water/Ground Water Interactions Along the Tar River, M. O'Driscoll, East Carolina University

WRRI-TBD Arsenic and Heavy Metal Leaching Potential From Turkey Litter Stockpiled on Bare Soil, S. Shah, NC State University

WRRI-TBD Determining BMP Inspection and Maintenance Costs for Structural BMP's in North Carolina, W. Hunt, NC State University

WRRI-TBD Impact of Hurricane Floyd on Sediment Deposition, Erosion, and Benthic Nutrient Fluxes in Pamlico Sound, NC, L. Benninger, University of North Carolina at Chapel Hill

WRRI-TBD Sediment Resuspension in the Pamlico and Neuse River Estuaries- An Additional Source of Nutrients and Contaminants, R. Corbett, East Carolina University

WRRI-TBD Harmful Algal Species from Wilson Bay, New River, NC Composition Nutrient Bioassay and HPLC Pigment, C. Tomas, University of North Carolina at Wilmington

WRRI-TBD Bioanalytical Analysis of Natural Estrogens at Concentrated Animal Feed Operations Affecting NC River Waters, S. Kullman, Duke University

WRRI-TBD Estimated Compliance with the Proposed Stage 2 Disinfection Byproducts Rule for Eleven Water Utilities in NC, P. Singer and N. Han, University of North Carolina at Chapel Hill

WRRI-TBD Control of Haloacetic Acid Formation in NC Drinking Water, P. Singer and J. Shi, University of North Carolina at Chapel Hill

WRRI-TBD Monitoring Study of the Performance of Stormwater Best Management Practices in the City of Charlotte, W. Hunt, NC State University

WRRI-TBD Is There a Relationship Between Phosphorous and Fecal Microbes in Aquatic Sediments, L. Cahoon, University of North Carolina at Wilmington

WRRI-TBD Urban Sediment Source Tracing and Delivery Rations: A Mineral Magnetic Assessment, D. Royall, University of North Carolina at Greensboro

WRRI-TBD The Effacy of Starter Fertilizer Phosphorous for Corn and Cotton Production on Soils Testing Very High for Phosphorous, D. Osmond, NC State University

WRRI-TBD Estuarine Sediment Beds as a Reservoir for Human Pathogens: Monitoring Transport of Population of Enterocci and Vibrio sp. In the Neuse River Estuary, R. Noble and S. Fries, University of North Carolina at Chapel Hill

JA-TBD Drought Tolerance Versus Drought Avoidance: A Comparison of Plant Water Relations in Herbaceous Wetland Plants Subjected to Water Withdrawal and Repletion, B. Touchette, Elon University

JA-TBD An Equilibrium Approach to Integrating Regional Surface Water Treatment and Limited Groundwater Pumping Capacity, G. Characklis and B. Kirsch, University of North Carolina at Chapel Hill JA-TBD Quantifying Mosquito Presence at Stormwater Treatment Wetlands and Innovative Wet Ponds, W. Hunt, NC State University

WRRI Annual Conference

Basic Information

Title:	WRRI Annual Conference			
Project Number:	2006NC105B			
Start Date:	4/4/2006			
End Date:	4/5/2006			
Funding Source:	104B			
Congressional District:	2			
Research Category:	Not Applicable			
Focus Category:	None, None, None			
Descriptors:				
Principal Investigators:	David Moreau			

Publication

Convened the Annual Conference: North Carolina Water Resources: Preparedness for Natural and Manmade Disaster. Dr. David Moreau, Ph.D., Chair, Dept of City & Regional Planning, delivered plenary addresses. Investigators from universities, agencies, industry, and consulting firms presented results of work on topics ranging from erosion and sedimentation control technologies to air borne water pollutants. Some 230 people participated in the conference. Participants had 36 technical presentations in 9 concurrent sessions from which to choose, as well as 20 technical posters to view. Abstracts were made available on the WRRI website.

Student Support

Student Support							
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total		
Undergraduate	6	0	1	0	7		
Masters	5	0	1	0	6		
Ph.D.	0	0	0	0	0		
Post-Doc.	1	0	0	0	1		
Total	12	0	2	0	14		

Notable Awards and Achievements

The results of Dr. Gregory Cope's research on "Endocrine and Reproductive Effects of the Pharmaceutical Fluoxetine on Native Freshwater Mussels: Proximity to Measured Environmental Concentrations" were featured in a Press Release stemming from our presentation of this information at the 232nd Annual Meeting of the American Chemical Society held September 10-14, 2006 in San Francisco, CA. As such, this research garnered national and international attention, being picked up by thousands of media outlets worldwide (as can be evidenced by a Google search on the terms prozac and mussels).

Publications from Prior Projects

- 2005NC47B ("Characterization of Surface Water/Ground Water Interactions along the Tar River using Ground Penetrating Radar") - Other Publications - Johnson, P.K., 2007. Surface water/groundwater interactions along a Coastal Plain river system, MS Thesis (in review)Dept. of Geological Sciences, East Carolina University, Greenville, NC.
- 2005NC47B ("Characterization of Surface Water/Ground Water Interactions along the Tar River using Ground Penetrating Radar") - Other Publications - O'Driscoll, M.A., Mallinson, D.J., and Johnson, P.K. 2007. River-groundwater interactions along an asymmetrical coastal plain river system. American Water Resources Association, 2006 Annual Conference, Baltimore, MD.
- 2005NC47B ("Characterization of Surface Water/Ground Water Interactions along the Tar River using Ground Penetrating Radar") - Other Publications - Johnson, P.K., O'Driscoll, M.A. and Mallinson, D.J. 2006. Using ground penetrating radar in river channel and floodplain settings: implications for surface water/groundwater interactions, American Water Resources Association, 2006 Annual Conference, Baltimore, MD.
- 4. 2005NC47B ("Characterization of Surface Water/Ground Water Interactions along the Tar River using Ground Penetrating Radar") - Conference Proceedings - Johnson, P.K., O'Driscoll, M.A., and Mallinson, D.J. 2006. Characterization of surface water/ground water interactions along the Tar River, NC using ground penetrating radar. Geologic Society of America Abstracts with Programs Vol 38, No. 3.
- 5. 2004NC36B ("Is There a Relationship Between Phosphorus and Fecal Microbes in Aquatic

Sediments?") - Other Publications - Harrington, R.N. and Cahoon, L.B. 2007. Fecal Indicator Baceria in the water and sediments of local boat ramps, pp. 68-80 in Mallin, M.A., Cahoon, L.B., Alphin, T.D., Posey, M.H., Rosov, B.A., Parsons, D.C., Harrington, R.N. and Merritt, J.R., Environmental Quality of Wilmington and New Hanover County Watersheds 2005-2006, CMS Report, 07-01.

 2004NC36B ("Is There a Relationship Between Phosphorus and Fecal Microbes in Aquatic Sediments?") - Articles in Refereed Scientific Journals - Mallin,M.A., Cahoon, L.B., Toothman, B.R., Parsons, D.C., McIver, M.R., Ortwine, M.L., Harrington, R.N., 2007. Impacts of a Raw Sewage Spill on Water and Sediment Quality in an Urbanized Estuary. Marine Pollution Bulletin 54:81-88.