South Carolina Water Resources Research Institute
Annual Technical Report
FY 2007

Introduction

The South Carolina Water Resources Center uses its operating funds to carry out its mission as a liaison between the US Geological Survey, the university community and the water resources constituencies of those institutions. This is accomplished by serving as a water resources information outlet through our web site, by serving as a research facilitator through our annual grants competition and by operating as a catalyst for research and educational projects and programs across South Carolina. The Water Center also serves as a conduit for information necessary in the resource management decision-making arena as well as the water policy arena of the state.

While continuing to be involved with numerous water issues across the state including membership on an ad hoc statewide committee identifying policy issues related to primary water concerns and analyzing population growth impacts on water resources, the Water Center is collaborating with multidisciplinary teams investigating natural system/social system interactions. Foremost among these projects has been involvement with South Carolina Sea Grant's LU-CES program, which is studying the impacts of changing land use patterns on coastal watersheds. The LU-CES program is continuing for two additional years and Sea Grant has asked the Water Center to continue as a partner. In the upcoming months the Water Center will work with teams of modelers from various institutions to determine how physical, ecological, economic and spatial models can best be utilized for management of natural systems. The SCWRC secured funding for a project through SC Sea Grant and the "Development of a Conceptual Model for an Integrated Coastal Demographic-Economic-Environmental Prediction and Forecasting Initiative" (CIDEEP) program to provide coastal economic modeling through the Strom Thurmond Institute REDYN program as well as additional land cover change modeling in collaboration with Towson University's Geography Department.

The Water Center has worked closely on human population growth management issues in the Saluda/Reedy watershed. The SCWRC completed work on the Upstate South Carolina urban growth prediction model. The results of the model have already been presented to numerous city and county councils as well as chamber's of commerce. Numerous civic leaders have commented on the importance of the model in regard to both managing growth and development and protecting natural resources, especially receiving waters. Congessman Inglis has asked the SCWRC to propose a water budget analysis for the Upstate based upon the results of the urban growth model.

SCWRC has recently funded studies to: 1) build a statewide biomarker approach to investigate pollution effects on fish in wadeable streams of South Carolina; and 2) build a statewide sediment and water quality approach to characterize pollution in wadeable streams of South Carolina. In addition, resources have been supplied to undertake a statewide assessment of water rates charged by water providers in order to determine more efficient pricing structures.

Recent meetings with key individuals from the South Carolina Department of Natural Resources, the South Carolina Department of Health and Environmental Control and South Carolina Sea Grant have produced a working group that will fund and undertake a multi-disciplinary research program for assessing management strategies along the South Carolina coast. As an outcome of those meetings, the SCWRC has initiated work as a committee member of the SCDHEC-Ocean and Coastal Resource Management (OCRM) Shoreline Change Advisory Committee. That committee work will result in a report made to SCDHEC-OCRM with recommendations and potential input into a new Beachfront Management Act for South Carolina. In addition, the SCWRC confirmed funding for a proposal to SCDHEC-OCRM on determining the state of the knowledge of shoreline retreat policies for coastal South Carolina.

Finally, the SCWRC hired a Policy Education Coordinator for the DNR funded Reedy River Education Program. This individual has been meeting with stakeholders within the watershed to assess the effectiveness

of various local, state and federal policies in regard to water quality and quantity issues. The SCWRC also initiated negotiations with DNR on two potential projects regarding access to the Reedy River and the potential to implement cap and trade programs for water use.

Research Program Introduction

The SCWRC research program has included the following for 2007:

Secured funding for a project through SC Sea Grant and the CIDEEP – LUCES II program to provide coastal economic modeling through the STI REDYN program. $62,326 Initiated work as a committee member of the SCDHEC-OCRM Shoreline Change Advisory Committee. Completed work on the Upstate South Carolina urban growth prediction model. The results of the model have already been presented to numerous city and county councils as well as chamber's of commerce. Numerous civic leaders have commented on the importance of the model. Congessman Inglis has asked the SCWRC to propose a water budget analysis for the Upstate based upon the results of the urban growth model. Confirmed funding for proposal to SCDHEC-OCRM on determining the state of the knowledge of shoreline retreat policies for coastal South Carolina. $70,000 Hired Policy Education Coordinator for the DNR funded Reedy River Education Program. Initiated negotiations with DNR on two potential projects regarding access to the Reedy and Cap and Trade programs. Initiated project to begin decoding data and designing analysis for water use study for residential water customers in SC and GA

Projects specifically funded by the SCWRC through USGS include:

Title: A Statewide Biomarker Approach to Investigate Pollution Effects on Fish in Wadeable Streams of South Carolina (Phase 2). Principal Investigators: Peter van den Hurk, Ph.D. Assistant Professor, and Stephen J. Klaine, Ph.D., Professor. Department of Biology, Clemson University, Marc C. Scott, Ph.D., SCDNR Budget: $30,952

Title: A Statewide Sediment and Water Quality Approach to Characterize Pollution in Wadeable Streams of South Carolina (Phase 2). Principal investigators: Elizabeth R. Carroway, Associate Professor. School of the Environment, Clemson University, Stephen J. Klaine, Ph.D., Professor. Department of Biology, Clemson University, Marc C. Scott, Ph.D., SCDNR, Budget: $30,000

A Statewide Biomarker Approach to Investigate Pollution Effects on Sunfish (Lepomis sp.) in Wadeable Streams of South Carolina

Basic Information

Title:	A Statewide Biomarker Approach to Investigate Pollution Effects on Sunfish (Lepomis sp.) in Wadeable Streams of South Carolina
Project Number:	2007SC49B
Start Date:	3/1/2007
End Date:	2/29/2008
Funding Source:	104B
Congressional District:	Third
Research Category:	Not Applicable
Focus Category:	Water Quality, Toxic Substances, Surface Water
Descriptors:	Conservation, Environmental Risk Assessment, Biomarkers, Fish Toxicology, Point Sources, Non-point Sources
Principal Investigators:	Peter Van Den Hurk, Stephen Klaine, Marc C. Scott

Publication

1. Keaton, Molly, 2007, A Statewide Biomarker Approach to Estimate Contaminant Effects in the Wadeable Streams of South Carolina, MS Thesis, Graduate Program in Environmental Toxicology, Department of Biological Sciences, College of Agriculture, Forestry & LIfe Sciences, Clemson University, Clemson, SC, 115 p.

Progress Report

July 2008

A Statewide Biomarker Approach to Investigate Pollution Effects on Sunfish (*Lepomis* sp.) in Wadeable Streams of South Carolina.

Peter van den Hurk[1], Andrew Sayer[1], Stephen J. Klaine[1], Marc C. Scott[2]

Sponsored by:

SOUTH CAROLINA WATER RESOURCES CENTER

SOUTH CAROLINA COMPETITIVE GRANTS PROGRAM

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Executive summary

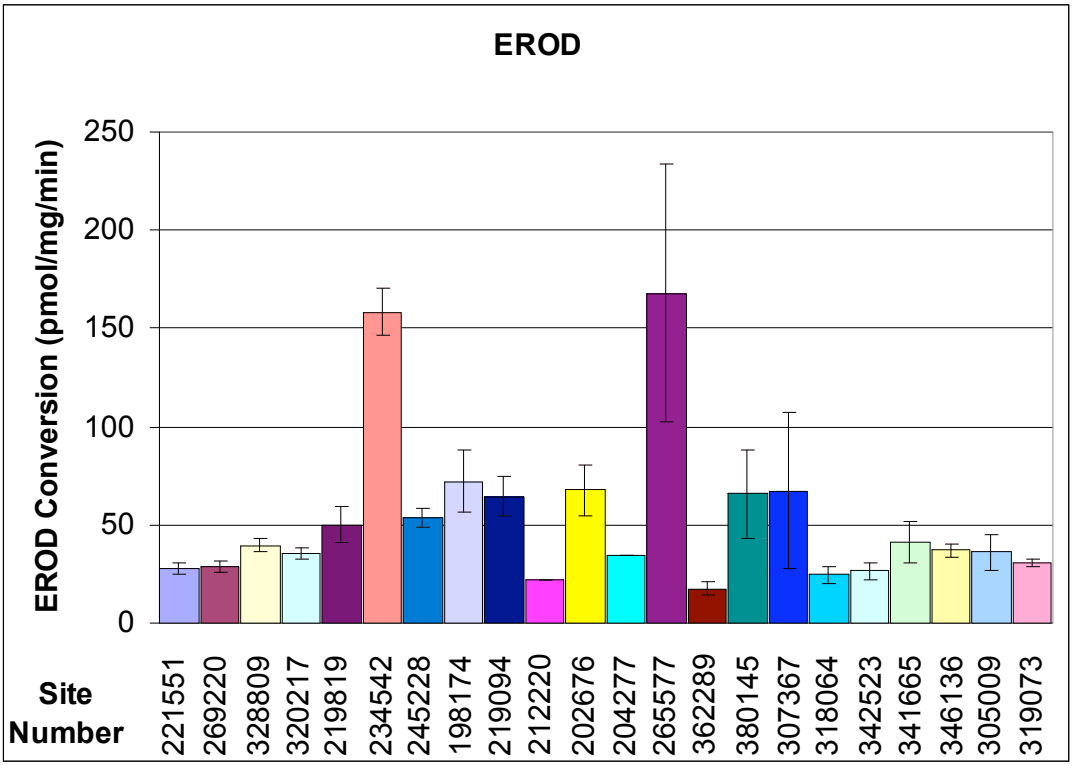
The numbers of freshwater species in South Carolina have been under pressure for many years. However, the threats that these organisms face from point and non-point source pollution is largely unknown. In May 2006 the South Carolina Department of Natural Resources (SCDNR) began a five year survey to establish the species richness and abundance of fish species in the wadeable streams of South Carolina. In addition to the fish population parameters, one of the goals of this study is to use molecular biomarkers of contaminant exposure to assess the health of fish populations in South Carolina's freshwater streams. Another objective of the project is to correlate the biomarker responses with fish population parameters and with land use data from the sampled watersheds.

During the second year of the study, different sunfish species (*Lepomis* sp.) were collected from May through September 2007 at 22 randomly selected sites in the Mid-Atlantic Coastal Plain watersheds in South Carolina. Somatic indices, including hepatosomatic index (HSI), spleen somatic index (SSI), gonadosomatic index (GSI) were measured to determine the overall physiological condition of the fish. Cytochrome p4501A (CYP1A) induction (as measured by the EROD assay) and bile fluorescence based on 2-ring, 4-ring and 5-ringed compounds were measured to estimate exposure to polycyclic aromatic hydrocarbons (PAHs). Glutathione S-transferase (GST) was measured to estimate oxidative stress, and the estrogen receptor binding assay was used on bile samples to measure exposure to endocrine disrupting compounds.

The first results showed that there was a variety of responses among the sample sites investigated. The EROD assay demonstrated that there were at least two sites where fish had been exposed to CYP1A inducing compounds. For one site, this induction coincided with increased bile fluorescence, indicating that PAHs were present at the site, and were able to trigger a biomarker response. At the other sites, the bile did not have an increased fluorescence, which excludes PAHs as inducing agents. Other CYP1A inducers were probably present at this site, or the CYP1A induction is a demonstration of a previous, temporary PAH exposure. Several sites showed increased bile fluorescence in some individuals, but this exposure did not yet lead to CYP1A induction. GST activity was induced in a large number of sites. It is unclear if there was actually exposure to compounds that can be responsible for this induction, or if there was suppression of GST activity at the sites that had lower activity than average.

The somatic indices showed a varied response picture. Previous investigations have suggested that an increased spleen weight may be related to increased parasite loadings. At this point we can not draw a conclusion about this because spleen or liver histology is not available. The gonado-somatic index also showed a diverse pattern, but results from the previous year suggest that this is related to time in the season that the fish were collected.

In conclusion we can say that most sites in the sample area were close to pristine, with very few sites that were under anthropogenic influence. In further analysis of the data we will compare these biomarker and fish health parameters with land use parameters and water chemistry data.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EROD Conversion (pmol/mg/min)
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219819
234542
245228
198174
219094
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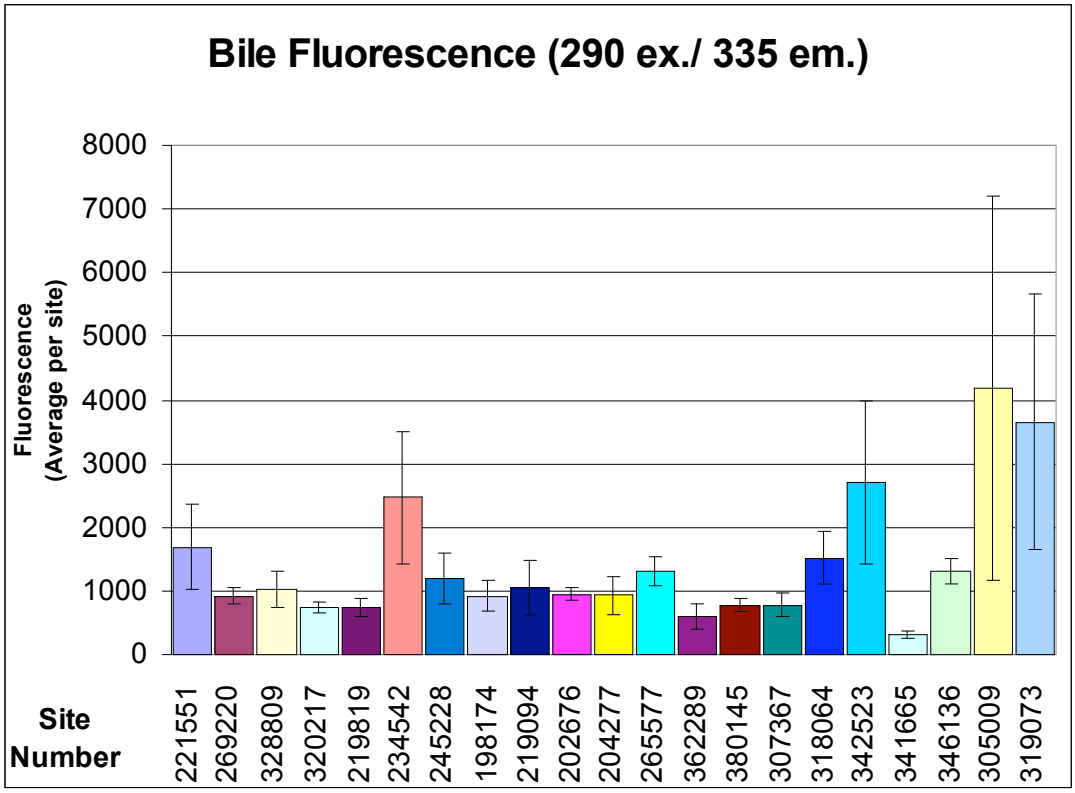
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Fluorescence (Average per site)
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5000
4000
3000
2000
1000
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320217
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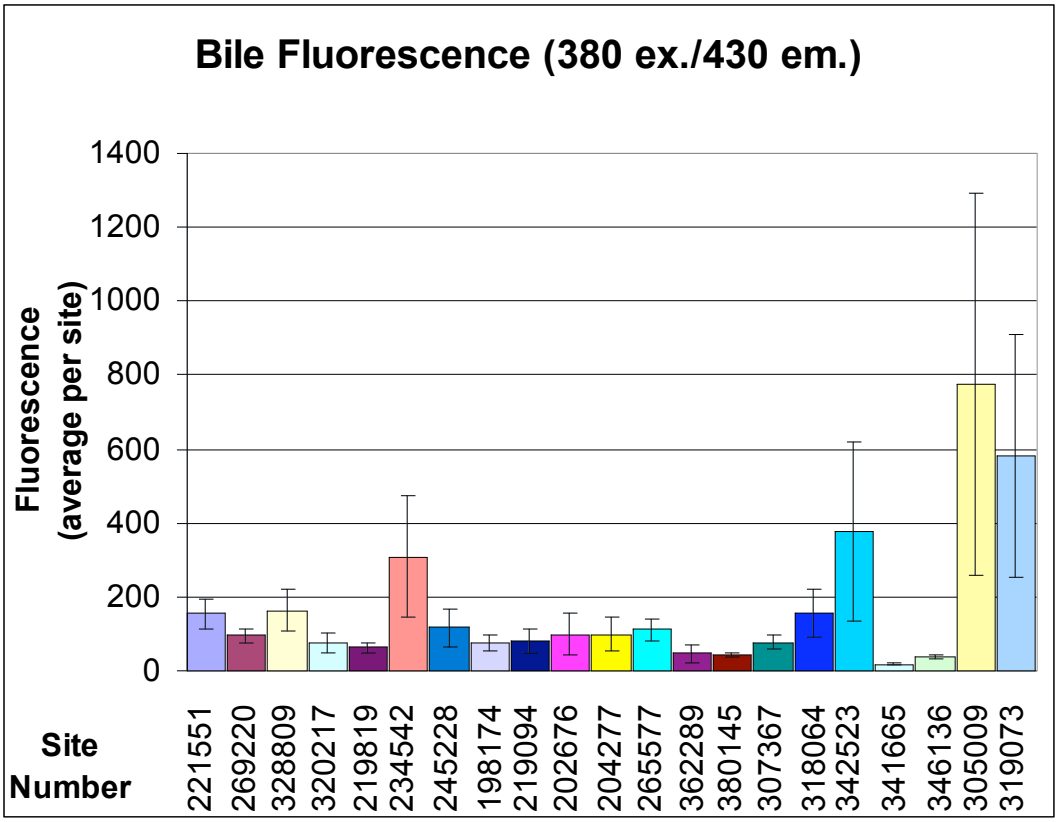
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Fluorescence (average per site)
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400
200
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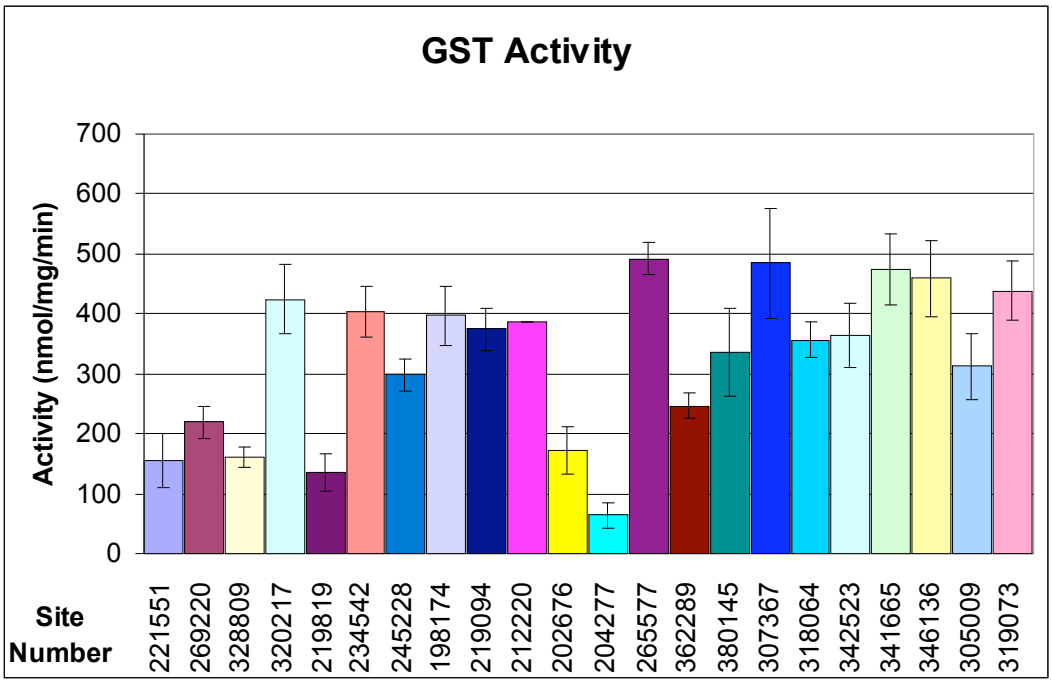
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Activity (nmol/mg/min)
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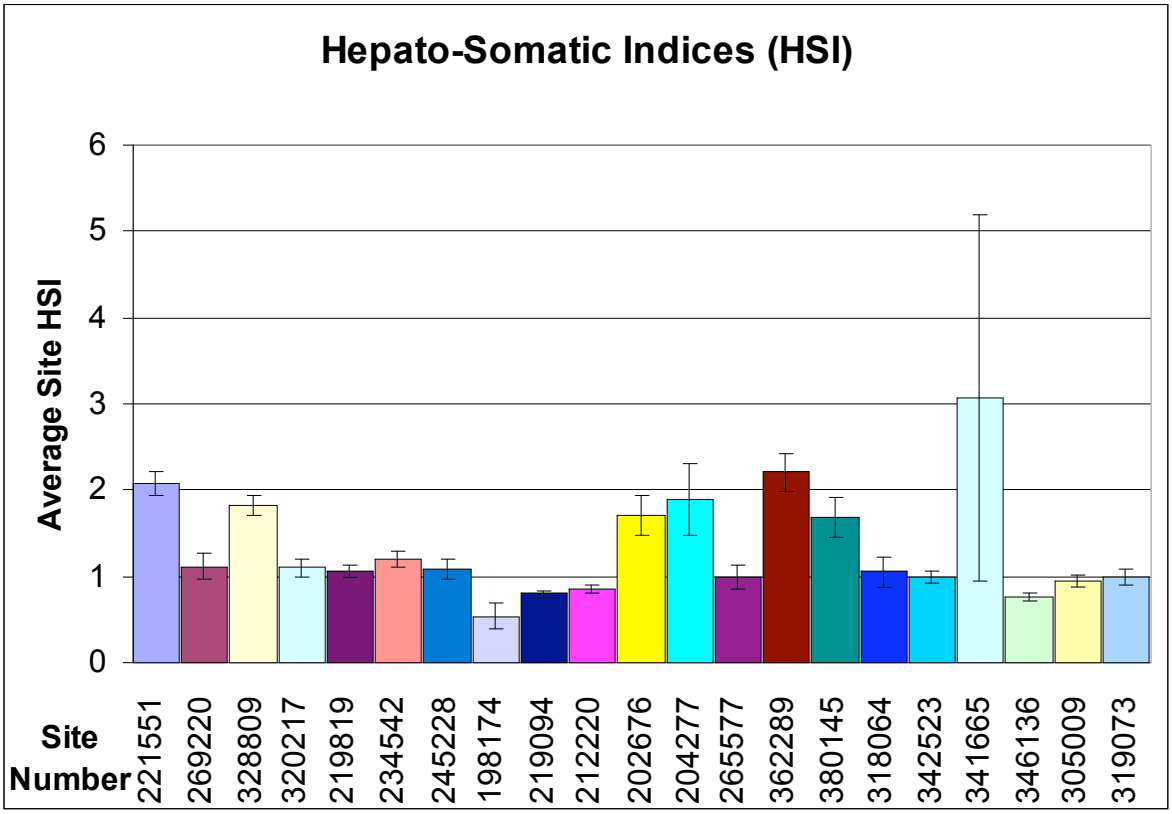
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4
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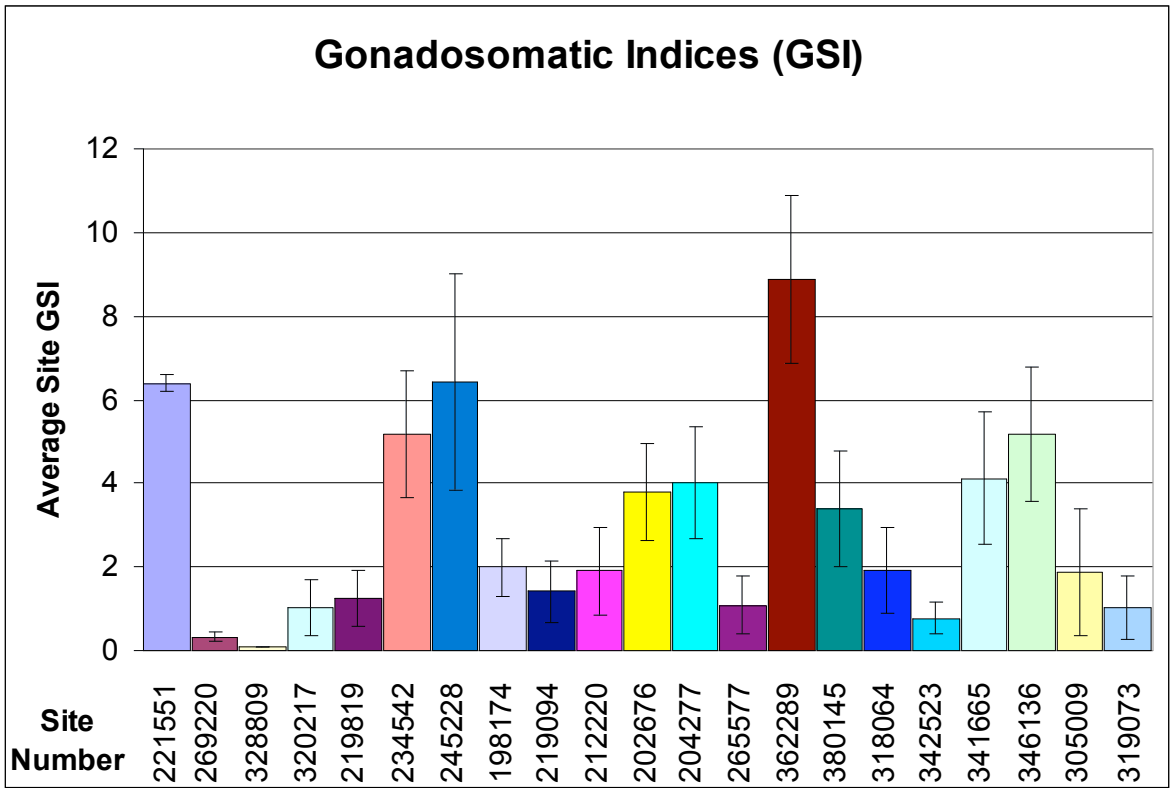
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8
10
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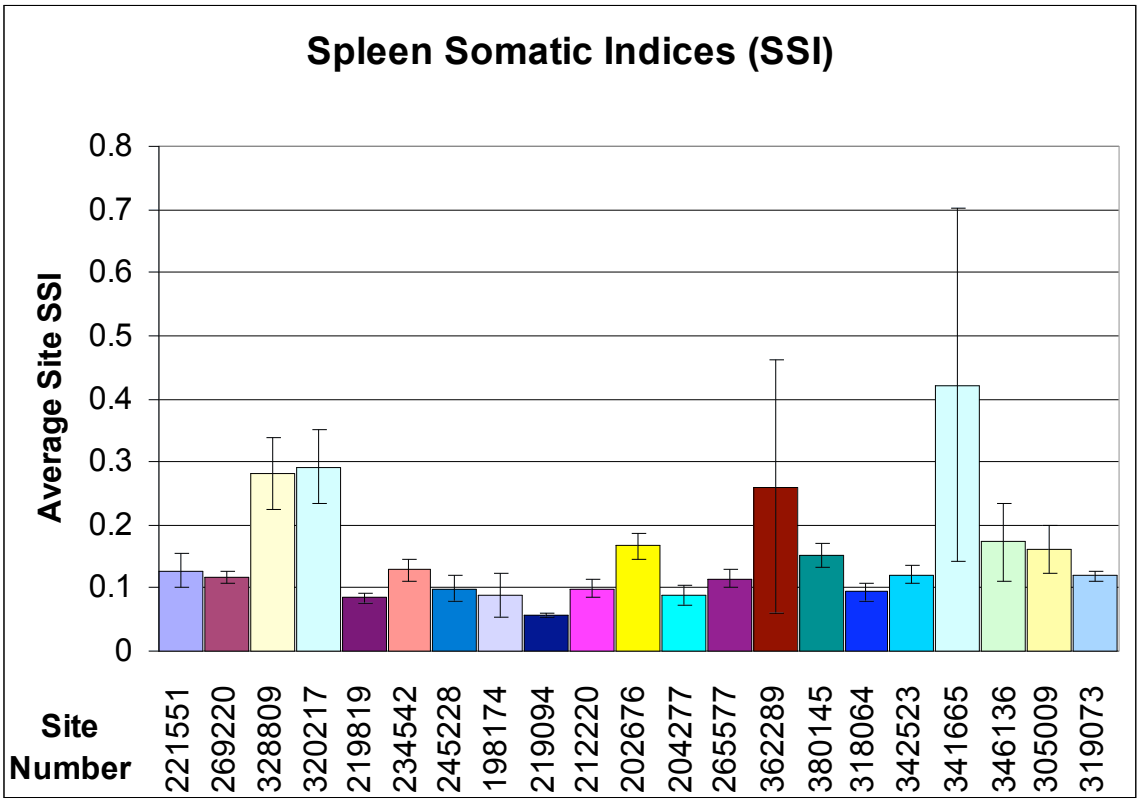
Spleen Somatic Indices (SSI)
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0.3
0.2
0.1
0
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198174
219094
212220
202676
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265577
362289
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318064
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319073

A Statewide Sediment and Water Quality Approach to Characterize Pollution in Wadeable Streams of South Carolina (Phase 2).

Basic Information

Title:	A Statewide Sediment and Water Quality Approach to Characterize Pollution in Wadeable Streams of South Carolina (Phase 2).
Project Number:	2007SC50B
Start Date:	3/1/2007
End Date:	2/29/2008
Funding Source:	104B
Congressional District:	Third
Research Category:	Not Applicable
Focus Category:	Water Quality, Sediments, Surface Water
Descriptors:	None
Principal Investigators:	Elizabeth R. Carraway, Stephen Klaine, Marc C. Scott

Publication

1. McNaughton, Christina, 2007, The Influence of Mercury-Dissolved Organic Matter (DOM) Complexation on Toxicity in Natural Waters, "Ph.D. Dissertation," Environmental Toxicology, Department of Biological Sciences, College of Agriculture, Forestry & LIfe Sciences, Clemson University, Clemson, SC, 225 p.
2. Jones, Alan, Elizabeth, Carraway, Steve, Klaine, 2007, A Statewide Sediment and Water Quality Approach to Characterize Pollution in Wadeable Streams of South Carolina, Poster presented at the SETAC (Society of Environmental Toxicology and Chemistry) North America 28th Annual Meeting, Milwaukee, WI, November 11-15, 2007.

Report for the South Carolina Water Resources Center, Clemson University

A Statewide Sediment and Water Quality Approach to Characterize Pollution in Wadeable Streams of South Carolina

prepared by Elizabeth R. Carraway and Alan J. Jones

Project information

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ABSTRACT

The South Carolina Department of Natural Resources (SCDNR) began in 2006 a statewide effort to "conduct an assessment of wadeable streams to gather appropriate data that will allow SCDNR to design effective and efficient management strategies to protect, conserve, and restore the aquatic resources of the State." In collaboration with SCDNR and other Clemson University researchers, water and sediment samples have been collected from 98 sites in 2006 and 2007. These samples have been analyzed for 19 metals using ICP-MS and ICP-AES. Six metals (chromium, copper, lead, nickel, silver and zinc) were found to exceed USEPA values for Constant Contaminant Concentration (CCC) and Contaminant Maximum Concentration (CMC), however, only copper (39 sites) and lead (30 sites) were found in excess at a large number of sites. Literature reported threshold effects concentrations (TEC) and probable effects concentrations (PEC) for arsenic, cadmium, chromium, copper, lead, nickel, and zinc were used to assess potential risk of sediment ecotoxicity. TEC levels were exceeded for all of the metals at two to eight sites each, with the notable exception of lead which exceed the TEC at all sites except two. No sites exceeded a PEC. Correlation of metal concentrations with land use show most significant concentrations for dissolved nutrient metals (potassium, magnesium) and a few trace metals (notably chromium, nickel, and lead) with agriculture in a 100m strip around the streams as well as with forests in that strip. Correlations with full watershed land use are fewer and weaker. Sediment silver concentrations were also found to correlate with land development activities. Initial results from Principal Components Analysis (PCA) for the entire data set indicate a relationship of dissolved nutrient metals with development and forest land uses in the full watersheds.

INTRODUCTION

Freshwater species worldwide face accelerated extinction rates relative to most other wildlife taxa. The southeastern US in particular has been suffering long-term declines in native species of fish and aquatic invertebrates. The Comprehensive Wildlife Conservation Plan (CWCP) submitted to the US Fish and Wildlife Service by the SC Department of Natural Resources (SCDNR) in 2006 describes priority species of concern, including over 125 species of fish, herpetofauna, mussels, crayfish, and snails that are directly dependent on aquatic systems. Common threats to these species are linked to point and non-point source pollution. Water coursing through freshwater streams integrates effects in the entire drainage area, with consequences of land use ending up in rivers, reservoirs, and coastal systems.

SCDNR, aided by funding from US Fish and Wildlife, began in 2006 a multi-year characterization of fish populations in three hundred wadeable streams across the State. These small watersheds are characteristic of larger "ecobasins" or designations of unique combinations of river basin drainage and ecoregion. Fish and invertebrate samples support characterization of population densities and aquatic community structure and development of indices of ecosystem health. SCDNR personnel and Clemson University researchers have been collaborating to maximize the value of this multi-year endeavor by adding characterization of chemical pollution and fish biomarker responses at the sampling sites.

The characterization of metal and organic chemical pollutants in water and sediment samples has been the focus of this project, funded by the South Carolina Water Resources Center. Results for metals (except mercury) in samples collected in 2006 and 2007 are presented in this report. For organic pollutants in water and for mercury in water and sediments, the following summary is given. The results obtained for the laboratory "tracer" organic compound have been good.

Meclofenamic acid was added to each water sample just before processing (extraction, derivatization, instrumental analysis) in the laboratory. This compound is similar to compounds of interest, but degrades rapidly under normal environmental conditions. Thus, it is expected to be present below detection limits and, when spiked into samples, to test analyst technique and instrument performance. The derivatized meclofenamic acid is observed in GC/MS chromatograms at the concentrations expected, indicating good recovery and detection. Quantitation of 17α-ethynylestradiol, 4-nonylphenol, caffeine, triclosan, atrazine, pyrene, benzo(a)pyrene, phenanthrene, and anthracene in water samples has showed results generally below detection limits except at one site where caffeine was found. Samples from several sites show responses similar to mixtures derived from diesel fuels or biological activity (e.g., fatty acids). Measurements of dissolved mercury have been below detection limits (15 ppt) but sediment-associated mercury levels are detectable.

MATERIALS AND METHODS

Site Selection. The generation of sampling sites at random locations in wadeable streams was conducted by SCDNR. A Geographical Information Systems (GIS) method was used to delineate stream locations with watershed areas less than 150 km^2. Potential sites were scouted by SCDNR to determine sampling suitability and to make changes necessary to avoid obstructions and excessively wide or deep stream sites.

Sampling Methods. For all sampling and analysis techniques a series of quality control blanks, spiked blanks, replicates and spiked samples were measured. All sample bottles were acid-washed and rinsed twice with 18mΩ•cm water. Total metals samples were collected (2007 only) in pre-cleaned, acid washed 250 ml brown high-density polyethylene bottles (Nalgene); 3 ml of trace metal grade nitric acid was added (Mallinckrodt Chemicals). Dissolved metals samples

were filtered onsite with 47 mm Supor filters (Pall Life Sciences) into pre-cleaned, acid washed 250 ml brown high-density polyethylene bottles. The homemade filtering device consists of a pressurizable garden sprayer fitted with a 47 mm inline polystyrene filter holder (Fisher Scientific) with polyethylene tubing. The apparatus was cleaned between each sample with DI water and rinsed twice with new site water. It was acid washed after each sampling trip (roughly 5 to 6 samples). Mercury samples were collected in the same manner, but with 125 ml brown borosilicate glass bottles with a PTFE lined cap. Sediments were collected as "scoop" samples in 50 ml conical vials and acidified. All samples were stored in the dark on ice for no more than 72 hours before returning to the lab.

Sample Preparation and Analysis. Filtered aqueous samples did not require further treatment. Total aqueous metals samples were digested using US Environmental Protection Agency (USEPA) Method 3015a (Microwave Assisted Acid Digestion of Aqueous Samples and Extracts). A 45 ml sample aliquot was acidified with 4 ml trace metal grade nitric acid and 1 ml trace metal grade hydrochloric acid. The mixture was transferred to a microwave digestion vessel (Milestone and CEM models were used), heated to 170 ºC ± 5 ºC in ~10 minutes, and held at 170 ºC ± 5 ºC for 10 minutes. Cooled samples were transferred to 50 ml HDPE vials for storage at 4 ºC until analysis. Digestion vessels were cleaned with the same acids and temperature program between each run.

Sediment metals were digested using USEPA Method 3051a (Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils). Approximately 0.5 g dried (at 60ºC) sample was combined with 9 ml trace metal grade nitric acid and 3 ml trace metal grade hydrochloric acid, transferred to a digestion vessel, heated to 175ºC ± 5ºC, and held at that temperature 5 minutes. Cooled samples were transferred to a 50 ml volumetric flask, diluted to 50.00 ml, and

transferred to a 50 ml HDPE conical vial. Samples were centrifuged 20 minutes at 500 G, decanted, and analyzed. Vessels were cleaned with the same acids and digestion program.

Filtered and digested samples were analyzed using ICP-MS and ICP-AES. The Laboratory for Environmental Analysis at the University of Georgia (http://www.uga.edu/lea/) performed ICP-MS analysis for the following ten metals: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), selenium (Se), silver (Ag), thallium (Tl), and zinc (Zn). The Agricultural Services Laboratory at Clemson University (http://www.clemson.edu/agsrvlb) performed ICP-AES analysis for the following twelve elements: aluminum (Al), boron (B), calcium (Ca), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), phosphorus (P), potassium (K), sodium (Na), sulfur (S), and zinc (Zn). Thus the samples were analyzed for nineteen metals plus sulfur. The analysis of copper and zinc by both laboratories is an added quality control.

Land Use Comparisons and Statistical Analysis. Land use data provided by SCDNR were correlated with metals concentrations using linear regression. Principle Components Analysis was also performed.

RESULTS AND DISCUSSION

Figure 1 part A indicates major rivers in SC and part B major ecobasins and ecoregions. Upstate to low country lines show river basins and their overlap with ecoregion classes (e.g., pink plains, brown piedmonts) delineate ecobasins. The points indicate sampling sites (successful and unsuccessful, dry attempts); ecobasin abbreviations are explained in Table 1. The table also indicates the number of sites from which samples (water and sediment) were obtained in each ecobasin. Appendix A contains site abbreviations used in this report and sampling dates.

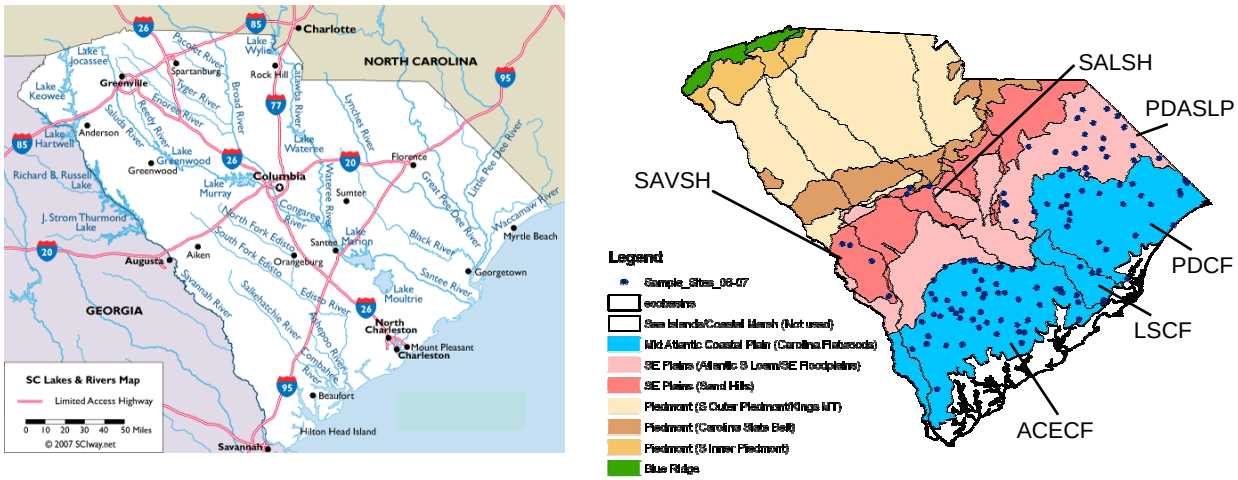

Figure 1. SC rivers, ecoregions, ecobasins, and 2006-2007 sampling sites
A. Major SC lakes and rivers (www.sciway.net/maps/south-carolina-lakes-rivers.html) B. 2006-2007 sampling sites (including dry sites), ecobasins, and ecoregions.

Table 1. Ecobasin abbreviations, descriptions, and samples obtained

Ecobasin abbreviation	*River basin*	*Ecoregion*	*# Samples (2006-2007)*
ACECF	ACE (Ashepoo, Combahee, Edisto)	Coastal Flatwoods (or coastal plain)	40
LSCF	Lower Santee	Coastal Flatwoods	5
PDASLP	Pee Dee	Atlantic Southern Loam Plains	22
PDCF	Pee Dee	Coastal Flatwoods	24
SALSH	Saluda (in Upper Santee)	Sand Hills	3
SAVSH	Savannah	Sand Hills	4

Aqueous Metals Results

Dissolved metal concentrations varied widely. In order to identify sites with higher potential for ecotoxic effects, results were compared to USEPA values for Constant Contaminant Concentration (CCC) and Contaminant Maximum Concentration (CMC). The CCC and CMC are used as chronic and acute toxicity threshold values, respectively. The values were calculated using the water hardness at each site (from measured calcium and magnesium concentrations), but adjustments for natural organic matter (NOM) have not made. It should be noted that the USEPA has not published CCCs and CMCs for all metals analyzed. In total, 98 sites were sampled for 19 metals over spring, summer, and fall seasons in 2006 and 2007. The following discussion emphasizes sites for which metal concentrations exceeded CCC and CMC values.

Six metals (chromium, copper, lead, nickel, silver and zinc) were found to occur at concentrations exceeding CMC or CCC thresholds, however, only copper and lead were found in excess at a large number of sites. The remaining metals were below threshold values or there were no published values. Cadmium was found at a high concentration at one site (PDA-NAS), but is excluded because it is an outlier (13.4 μg/L vs. an average of 0.3 μg/L at 68 sites with cadmium detected). Table 2 lists sites that were found to exceed CMC and CCC values with the corresponding measured metal concentrations (ICP-MS) and threshold levels. It is apparent the metal concentration required to meet a threshold varies significantly, reflecting the variability in water chemistry. Water hardness ranged from 10 to 200 mg/L, with an average value of ~50. The copper CCC was exceeded at a total of thirty-nine sites with twenty-eight of those also exceeding the CMC. There were thirty sites above the lead CCC, but none exceeded the CMC. Eight sites were found to have nickel concentrations above the CCC with one exceeding the CMC. The chromium CCC and zinc CMC values were found to be exceeded at two sites. For silver, only a CMC threshold has been established and it was exceeded at one site.

There were several sites with multiple metals at concentrations above threshold values. At site ACE-NIC, chromium, copper, lead, and nickel were above the threshold concentrations with copper and nickel above CMC levels. Sites ACE-BLA2, ACE-GMC, PDC-CTS, PDC-TLR, PDA-NAS, and SAV-SAN each had three metals at or above threshold concentrations, and several other sites had two metals exceeding threshold values. While several sites show exceedances of a single metal, the data do support instances of metals co-occurrence and that a stream might be suffering from multiple impacts. It should be noted that the threshold values are markers for potential impairment; parameters including alkalinity, pH, and metal-binding ligands (e.g., NOM) can have profound effects on the toxicity of metals to aquatic systems.

Table 2. Sites with aqueous metal concentrations exceeding CCC and CMC thresholds. Measured and threshold metal concentrations shown in µg/L or ppb.

Site	Measured	Threshold	Site	Measured	Threshold
Chromium (Cr) CCC			**Lead (Pb) CCC**		
ACE-GMC	151.00	108.50	ACE-BLA1	0.45	0.41
ACE-NIC	76.90	32.15	ACE-BLA2	4.31	2.70
Copper (Cu) CCC			ACE-BUC	0.72	0.26
ACE-BAB2	10.10	8.92	ACE-CCC1	1.72	1.13
ACE-BLA1	2.46	2.19	ACE-CLB	0.97	0.60
ACE-BLA2	13.90	9.63	ACE-HMB	2.95	0.77
ACE-CLB	3.21	2.96	ACE-JAB	0.50	0.28
ACE-GMC	15.50	13.47	ACE-MCC	0.52	0.29
ACE-SAN	2.12	1.95	ACE-NIC	2.71	0.84
LSC-LSW	3.94	3.34	ACE-SAN	0.78	0.35
PDA-TBS	5.09	4.60	ACE-SCC	0.74	0.29
PDA-TLP1	3.23	3.18	ACE-TDS	1.00	0.30
PDC-CAB	3.97	3.61	ACE-TRC	4.69	1.17
PDC-CTS	15.50	10.95	LSC-LSW	1.86	0.69
Copper (Cu) CMC			PDA-BKS	0.61	0.58
ACE-BUC	2.92	1.86	PDA-GUM	0.42	0.30
ACE-HMB	5.24	4.82	PDA-MUH	0.75	0.48
ACE-MCC	3.45	2.06	PDA-RCC1	0.73	0.43
ACE-NIC	14.00	5.16	PDA-TGR	2.31	0.69
ACE-TDS	3.39	2.08	PDA-TLP2	1.95	0.64
PDA-BKS	4.02	3.73	PDC-CAB	1.18	0.77
PDA-CAT	9.19	4.34	PDC-CAM	2.02	1.11
PDA-CSC	26.90	2.56	PDC-CTS	3.54	3.18
PDA-GUM	4.52	2.10	PDC-CYC	2.10	0.42
PDA-HOM	49.40	5.82	PDC-KSC1	1.84	0.82
PDA-MUD	4.35	2.81	PDC-NLR	9.79	0.56
PDA-MUH	4.55	3.19	PDC-SIM2	15.70	2.36
PDA-NAS	34.50	5.14	PDC-TLR	3.51	1.26
PDA-RCC1	9.23	2.88	SAL-DBB	0.69	0.62
PDA-TCT	4.23	3.32	SAV-SAN	0.32	0.18
PDA-TGR	14.00	4.33	**Nickel (Ni) CCC**		
PDA-TLP2	5.00	4.08	ACE-BAB2	228.00	50.47
PDA-TMC	4.63	2.25	ACE-BLA2	252.00	54.52
PDC-CYC	4.57	2.84	ACE-GMC	484.00	76.53
PDC-KSC1	6.28	5.09	PDA-NAS	84.20	21.59
PDC-NLR	5.47	3.64	PDC-CTS	156.00	62.07
PDC-TCB	7.76	6.52	PDC-KSC1	47.40	21.41
PDC-TKS	13.00	6.44	PDC-TLR	41.70	29.89
PDC-TLR	9.75	7.38	**Nickel (Ni) CMC**		
SAV-LHC	1.96	1.73	ACE-NIC	259.00	199.96
SAV-SAN	7.89	1.36	**Silver (Ag) CMC**		
SAV-TPS	14.50	4.28	ACE-CTC	1.14	0.84
SAV-UTR	1.87	1.86	**Zinc (Zn) CMC**		
			PDA-NAS	98.30	50.36
			SAV-SAN	24.30	15.49

Sediment Metals Results

At present there are no definite sediment quality criteria defined by any regulatory agency in the US. It was therefore necessary to rely on literature reported threshold effects concentrations (TEC) and probable effects concentrations (PEC), however TECs and PECs are not available for all of the trace metals of interest (selenium, silver and thallium). MacDonald et al. (2000) reported threshold effects concentrations for the remaining seven trace metals (arsenic, cadmium, chromium, copper, lead, nickel, and zinc). Threshold effects concentrations are defined as the theoretical concentration at which toxic effects could begin to be observed. A probable effects concentration is defined as the concentration at which one is likely to observe toxic effects. Background values were taken from NOAA Screening Quick Reference Tables (Buchman 1999). Table 3 below presents available background, TEC, and PEC levels.

Table 3. Background, TEC, and PEC values for sediment-associated metals. Concentrations in mg/kg.

Metal	Background	TEC	PEC
Arsenic (Ar)	1.1	9.79	33.0
Cadmium (Cd)	0.1-0.3	0.99	4.98
Chromium (Cr)	7-13	43.4	111
Copper (Cu)	10-25	31.6	149
Lead (Pb)	4-17	0.18	128
Nickel (Ni)	9.9	22.7	48.6
Selenium (Se)	0.29	*	*
Silver (Ag)	0.5	*	4.5
Zinc (Zn)	7-38	121	459

Each of the seven metals with reported TEC and PEC values was found at two or more sites at or above threshold effects concentrations, but no site exceeded a probable effects concentration. Table 4 lists sites found to exceed TECs and corresponding measured sediment concentrations. Lead exceeded the TEC at all sites except two. Arsenic and cadmium were found to exceed the TEC at two sites while there were three sites at which copper concentrations exceeded the TEC. The chromium TEC was exceeded at five sites, the nickel TEC at seven sites, and the zinc TEC at eight sites.

Table 4. Sites with sediment-associated metals exceeding TECs. Measured concentrations and TECs in mg/kg.					
Site	Measured	Site	Measured	Site	Measured
Arsenic (As), TEC=9.79		**Lead (Pb)**, TEC=0.18		**Zinc (Zn)**, TEC=121	
ACE-TGS	12.91	All except:		PDA-HHC2	324.95
PDC-PAL	9.88	ACE-CNB	ND*	PDA-MUD	135.54
Cadmium (Cd), TEC=0.99		ACE-CTC	ND	PDA-MUH	131.84
ACE-TGS	1.59	Data range all other sites:		PDA-RCC1	131.32
PDA-NAS	2.68		0.35-35.64	PDA-RCC2	167.05
Chromium (Cr), TEC=43.4		**Nickel (Ni)**, TEC=22.7		PDA-TCT	128.66
ACE-TGS	59.02	ACE-BAB1	24.61	PDA-TGR	139.00
PDC-CAB	60.13	ACE-SAW	25.98	SAL-LGB	135.78
PDC-NLR	685.43	ACE-TGS	25.60		
PDC-TLR	43.78	PDC-CAB	34.45		
PDC-WOB	1478.48	PDC-NLR	450.69		
Copper (Cu), TEC=31.6		PDC-TLR	30.14		
PDA-HHC2	61.12	PDC-WOB	1672.55		
PDA-RCC2	31.92				
PDC-WOB	63.65			*ND=Not detected.	

Site ACE-TGS exceeded the threshold effects concentrations of five metals: arsenic, cadmium, chromium, lead, and nickel. Four sites in the PDCF ecobasin exceeded TEC levels for three or four metals: PDC-WOB (chromium, copper, lead, nickel) and PDC-CAB, PDC-NLR, and PDC-TLR (chromium, lead, and nickel). Two sites in the PDASLP ecobasin (PDA-HHC2, PDA-RCC2) exceeded TEC levels for copper, lead, and zinc. Compared to the aqueous metal concentration results, fewer sites were found to exceed metal toxicity guidelines, with the notable exception of lead.

Correlations with Land Use

Each set of measured metal concentrations was analyzed to determine possible relationships with land use in the watersheds and in a strip defined as the area extending to 100m either side of the stream and upstream of the sampling site. This report may refer to this as buffer, buffer strip, or buffer land, but this term does not imply a riparian buffer. ARC-GIS and United States Geological Survey (USGS) National Land Cover Data (NLCD) were used to define land use percentages based on the Land Use Survey conducted in 1992 and 2001. Seventeen land use

categories ranging from open land and barren rock to evergreen forests were grouped into four broader categories (development, forest, wetland, and agriculture) to simplify data analysis and increase land use percentages per category to above 1 percent. Compared to sites accessed in 2006, the watersheds sampled in the 2007 season had significantly less development and were dominated by forest and agriculture. This mismatch, and possibly the much drier weather conditions in 2007, has complicated analysis of the combined data sets. Efforts to analyze the full data set continue, but at this point results are presented for each sampling year separately. Due to the variability associated with studies of this nature, correlations with an r^2 value greater than 0.10 and p value less than 0.05 were considered significant.

2006 Land Use Results

The 2006 land use parameters resulted in several correlations with agriculture, wetland, and forest land use coverage. Typically, positive correlations were observed with agriculture and wetland and negative correlations were observed with forest cover. Positive correlations with agricultural land use and negative correlations with forest cover are fairly easily understood, however, wetland correlations are more complex.

Buffer Land Use. The most significant single-metal correlations with land uses were observed in the buffer strip with dissolved metals. Correlations were observed with both nutrient metals (Mg and K) and trace metals. Positive correlations were observed with agricultural land use. Table 5 summarizes these correlations. Chromium is found at trace levels in many fertilizers and it is often used as a micronutrient in livestock operations. Phosphate fertilizers contain trace amounts of nickel and often metal parts of agricultural machinery are nickel-coated. Liu et al. (2007) found that the addition of phosphate and potassium fertilizers mobilized copper, chromium, and

nickel in soil. Correlations with lead may reflect long term agricultural uses of leaded fuel and lead arsenate as a pesticide.

Table 5. Correlation results with buffer strip agriculture (2006)

Metal	Land Use	r^2	p
K (aq)	Agriculture, strip	0.40	<0.001
Mg (aq)	Agriculture, strip	0.25	<0.01
Cr (aq)	Agriculture, strip	0.40	1.28×10^{-5}
Ni (aq)	Agriculture, strip	0.24	0.004
Pb (aq)	Agriculture, strip	0.22	0.005

Increasing forest cover in the buffer strip correlated with declining metal concentrations. Negative correlations with seven metals are summarized in Table 6. These trends are all consistent with forest cover preventing the mobilization of metals into aquatic systems.

Table 6. Correlation results with buffer strip forest (2006)

Metal	Land Use	r^2	p
K (aq)	Forest, strip	0.40	8.40×10^{-5}
Mg (aq)	Forest, strip	0.25	0.002
As (aq)	Forest, strip	0.23	0.003
Cr (aq)	Forest, strip	0.19	0.006
Ni (aq)	Forest, strip	0.28	0.001
Se (aq)	Forest, strip	0.24	0.01
Zn (aq)	Forest, strip	0.13	0.03

Buffer wetlands showed a significant positive correlation with selenium, as summarized in Table 7. In reducing environments such as wetlands, hydrogen sulfide (H_2S) and polysulfide ions (S_n^{2-}) may react with selenium to produce selenium-substituted polysulfide anions (S_nSe^{2-}). These selenium containing ions are much more soluble and mobile than the slightly soluble selenate and selenite species. Also, sulfur-containing organic matter may exchange sulfur with selenium (Weres, Jaouni, & Tsao, 1989).

Significant sediment metal correlations were found only for silver with development, also summarized in Table 7.

Table 7. Correlation results with selenium and silver (2006)

Metal	Land Use	r^2	p
Se (aq)	Wetland, strip	0.37	0.002
Ag (sed)	Development, strip	0.46	1.49×10^{-5}

Total Watershed Land Use. At each site the watershed is defined as the area upstream draining immediately into the stream. Significant correlations were observed with nutrient metals and trace metals, but were typically not as strong as correlations with the buffer strip land use. Table 8 summarizes these results.

Table 8. Correlation results with total watershed land use (2006)

Metal	**Land Use**	**r^2**	**p**
K (aq)	Agriculture	0.40	6.39×10^{-5}
Mg (aq)	Agriculture	0.35	2.46×10^{-5}
As (aq)	Agriculture	0.16	0.01
Cr (aq)	Agriculture	0.11	0.03
Ni (aq)	Agriculture	0.24	0.003
Se (aq)	Agriculture	0.14	0.04
K (aq)	Forest	0.28	0.001
Mg (aq)	Forest	0.24	0.003
Se (aq)	Wetland	0.17	0.03
Ag (sed)	Development	0.50	4.78×10^{-6}
Ag (sed)	Agriculture	0.15	0.015

Agricultural land uses in the watersheds showed the largest number and strongest correlations. As with buffer strip land use, nutrient metals tended to show the strongest relationships with agriculture whereas trace metal correlations are weaker. Forest cover in watersheds showed correlations only with the nutrient metals and as with buffer forest, these correlations were negative. Only selenium was found to have a dependence on wetlands in the watershed. As before, selenium showed a positive correlation with percent wetland. Sediment metals produced very few correlations with land use and again only with silver. However, there were two significant and positive correlations with agriculture and development.

2007 Land Use Results

The 2007 land use results produced no significant correlations with metal concentrations. This is due to the fact that there was very little variation in the land use parameters from site to site. As stated above development was significantly less than 2006 thus reducing the variability in the watersheds and making analysis difficult. Despite the relative lack of development in the

watersheds of sites sampled in 2007, variations in metal concentrations were observed, as evidenced by the occurrence of several ACE basin sites in Tables 2 and 4. Therefore, simply combining data sets from 2006 and 2007 did not strengthen correlations observed for 2006 data. These results may indicate that important effects are not captured appropriately in the land use data (e.g., historical effects or very recent effects) or that effects unrelated to land use are significant (e.g., ground water surface water exchange, atmospheric deposition). Continuing analyses will investigate these possibilities as well as analysis of the data by ecobasin in order to restrict comparisons to areas with more similar ecosystem characteristics and histories.

Principle Components Analysis

Principle Components Analysis (PCA) was used to elucidate possible interrelated components of the land use data set and to emphasize the key components or factors in correlations with metal concentration results. Principal components allows for a combination of independent variables, such as land use, resulting in dimensional reduction of the data set to 3 or 4 variables, and thus (ideally) simplifying analyses and interpretation of the data set. At this point, principal components has been performed only on the total data set (2006 and 2007) using total watershed land use data.

Three measures were used to determine the number of components retained: the eigenvalue-one criterion (retain principal components with an eigenvalue ≥ 1), the cumulative proportion of variance accounted for (retain if $\geq 70\%$), and individual proportion of variance accounted for (retain if $\geq 10\%$). In the application of PCA to all watershed land use data applicable to all sites sampled in 2006-2007, each of the four principal components (PC) described below met at least two of the three retention criteria, and each showed a significant proportion of cumulative percent of variance accounted for.

Table 9. Retention criteria for each PC			
PC	**Eigenvalue**	**Fraction of variance**	**Fraction of cumulative variance**
1	3.9498	0.3291	0.3291
2	2.5167	0.2094	0.5385
3	1.7023	0.1419	0.6804
4	1.2234	0.1020	0.7824

Table 10. Eigenvectors describing each PC				
	PC 1	**PC 2**	**PC 3**	**PC 4**
Dev. Open	0.451884	0.065520	-0.059683	0.006622
Dev. Low	0.486112	-0.081194	0.100233	0.038424
Dev. Med	0.466311	-0.139574	0.117779	0.047246
Dev. High	0.474886	-0.127341	0.108929	0.028153
Deciduous For.	0.028985	0.502625	0.318917	-0.016496
Evergreen For.	-0.212244	-0.218511	0.504598	-0.179261
Mixed For.	-0.080667	0.356415	0.346952	-0.043748
Woody Wet.	-0.225058	-0.416445	-0090426	0.110668
Herbaceous Wet.	-0.069875	-0.201202	0.185464	0.584728
Grassland	-0.099603	0.257221	0.121043	0.683307
Pasture	0.039440	0.440888	-0.027167	-0.333073
Cultivated Crops	-0.005314	0.232906	-0.652677	0.170668

It can be seen that PC1 to PC4 generally correspond to 1) development, 2) non-evergreen forests and pastures, 3) forests, and 4) wetlands and grasslands, respectively. Two significant correlations, one with PC1 and one with PC3, were found. Magnesium (aq) was shown to be positively related to PC1 (r^2=0.101, p=0.0015) while potassium (aq) was negatively related to PC3 (r^2=0.108, p=0.0009). These results show in part the power of PCA to reduce the number of components or effects considered. More significantly, the results confirm the small number of significant correlations obtainable for the full 2006-2007 data set. Thus the need for further analyses incorporating additional components (e.g., ground water influences) and ecobasin specific analysis is clear and such analyses are ongoing.

ACKNOWLEDGEMENTS

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Dr. Patrick Gerard, Clemson University, Dept. Applied Economics and Statistics, for assistance with PCA.

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Appendix A. Site Abbreviation Key and Sampling Dates

Site Abbreviation	Ecobasin	Name/Description of Stream	Date Sampled
ACE-BAB1	ACECF	Bachelor Branch	11-Jul-2007
ACE-BAB2	ACECF	Bachelor Branch	11-Jul-2007
ACE-BCB	ACECF	Baptist Church Branch	11-Sep-2007
ACE-BHR	ACECF	Bull Head Run	27-Jun-2007
ACE-BLA1	ACECF	Black Creek	21-Jun-2007
ACE-BLA2	ACECF	Black Creek	12-Sep-2007
ACE-BRB	ACECF	Bush Branch	20-Jun-2007
ACE-BUC	ACECF	Buckhead Creek	2-Aug-2007
ACE-CCC1	ACECF	Cow Castle Creek	11-Jul-2007
ACE-CCC2	ACECF	Cow Castle Creek	12-Jul-2007
ACE-CLB	ACECF	Colston Branch	1-Aug-2007
ACE-CNB	ACECF	Canady Branch/Broad Ax Branch	28-Jun-2007
ACE-CTC	ACECF	Cowtail Creek	31-Aug-2007
ACE-DBC	ACECF	Deep Bottom Creek	29-Aug-2007
ACE-FIS	ACECF	Fishburne Creek	23-Aug-2007
ACE-FSW	ACECF	Fullers Swamp Creek	20-Jul-2007
ACE-GMC	ACECF	Gantts Mill Creek	28-Jun-2007
ACE-HMB	ACECF	Halfmoon Branch	3-Aug-2007
ACE-IRE	ACECF	Ireland Creek	2-Aug-2007
ACE-JAB	ACECF	Jackson Branch	29-Aug-2007
ACE-JSC	ACECF	Jones Swamp Creek	2-Aug-2007
ACE-LWB	ACECF	Little Walnut Branch	12-Jul-2007
ACE-MCC	ACECF	Mechaw Creek	29-Jun-2007
ACE-MLC	ACECF	Mill Creek/Cane Gully Branch	28-Jun-2007
ACE-NIC	ACECF	Nicholson Creek	23-Aug-2007
ACE-PKS	ACECF	Polk Swamp	18-Jul-2007
ACE-SAN	ACECF	Sanders Branch	18-Jul-2007
ACE-SAV	ACECF	Savannah Creek	12-Sep-2007
ACE-SAW	ACECF	Sawmill Branch	30-Aug-2007
ACE-SCC	ACECF	Scotts Creek	19-Jul-2007
ACE-TDB	ACECF	tributary to Deep Branch	12-Sep-2007
ACE-TDS	ACECF	tributary to Drayton Swamp	21-Jun-2007
ACE-TGS	ACECF	tributary to Great Swamp	12-Sep-2007
ACE-TIM	ACECF	Timothy Creek	30-Aug-2007
ACE-TKB	ACECF	Tom and Kate Branch	24-Aug-2007
ACE-TLS	ACECF	tributary to Little Salkehatchie River	11-Sep-2007
ACE-TMS	ACECF	tributary to Middle Pen Swamp	22-Jun-2007
ACE-TRC	ACECF	tributary to Rantowles Creek/Drayton Swamp	19-Jul-2007
ACE-TUR	ACECF	Turkey Creek	21-Jun-2007
ACE-TWR	ACECF	tributary to Wando River	20-Jun-2007
LSC-LSW	LSCF	Little Swamp	23-Jun-2006
LSC-TCC	LSCF	tributary to Cedar Creek	22-Jun-2006
LSC-TLM	LSCF	tributary to Lake Marion	27-Jun-2007
LSC-TMC	LSCF	tributary to Mechaw Creek	21-Jun-2006
LSC-WTB	LSCF	Wee Tee Branch	22-Jun-2006
PDA-BKS	PDASLP	Back Swamp	28-Sep-2006
PDA-CAT	PDASLP	Catfish Canal	3-Aug-2006
PDA-CNB	PDASLP	Cane Branch	10-Aug-2006
PDA-CSC	PDASLP	Cane Savannah Creek	2-Aug-2006

PDA-GUM	PDASLP	Gum Swamp	17-Aug-2006
PDA-HHC1	PDASLP	High Hill Creek	9-Aug-2006
PDA-HHC2	PDASLP	High Hill Creek	18-Aug-2006
PDA-HOM	PDASLP	Home Branch	2-Aug-2006
PDA-MUD	PDASLP	Muddy Creek	16-Aug-2006
PDA-MUH	PDASLP	Mush Branch	23-Aug-2006
PDA-NAS	PDASLP	Nasty Branch	4-Aug-2006
PDA-RCC1	PDASLP	Rogers Creek Canal	8-Sep-2006
PDA-RCC2	PDASLP	Rogers Creek Canal	3-Aug-2006
PDA-TAB	PDASLP	tributary to Alligator Branch	10-Aug-2006
PDA-TBS	PDASLP	tributary to Bear Swamp	14-Sep-2006
PDA-TCT	PDASLP	tributary canal to Tobys Creek	17-Aug-2006
PDA-TGR	PDASLP	tributary to Gully Run	16-Aug-2006
PDA-TLP1	PDASLP	tributary to Little Pee Dee River	14-Sep-2006
PDA-TLP2	PDASLP	tributary to Little Pee Dee River	24-Aug-2006
PDA-TMB	PDASLP	tributary to Martins Branch	25-Aug-2006
PDA-TMC	PDASLP	tributary to Muddy Creek	7-Sep-2006
PDA-WOC	PDASLP	White Oak Creek	24-Aug-2006
PDC-BCR1	PDCF	Buck Creek	31-May-2007
PDC-BCR2	PDCF	Buck Creek	31-May-2007
PDC-CAB	PDCF	Canaan Branch	15-May-2007
PDC-CAM	PDCF	Camp Branch	4-May-2007
PDC-CTS	PDCF	Crab Tree Swamp	17-May-2007
PDC-CYC	PDCF	Cypress Creek	13-Jun-2007
PDC-DAM	PDCF	Big Dam Swamp	14-Jun-2007
PDC-DOB	PDCF	Dobson Branch	9-May-2007
PDC-HBR	PDCF	Horse Branch	2-May-2007
PDC-KSC1	PDCF	Kingstree Swamp Canal	10-May-2007
PDC-KSC2	PDCF	Kingstree Swamp Canal	22-Aug-2007
PDC-NLR	PDCF	Negro Lake Run	16-May-2007
PDC-PAL	PDCF	Palmetto Swamp	16-May-2007
PDC-SIM2	PDCF	Simpson Creek	1-Jun-2007
PDC-SIM2	PDCF	Simpson Creek	31-May-2007
PDC-SVC	PDCF	Savannah Creek	13-Jun-2007
PDC-TBS	PDCF	tributary to Big Swamp	3-May-2007
PDC-TCB	PDCF	Tearcoat Branch	30-May-2007
PDC-TKC	PDCF	tributary to Kingstree Swamp Canal	8-May-2007
PDC-TKS	PDCF	tributary to Kingstree Swamp Canal	8-May-2007
PDC-TLR	PDCF	tributary to Lynches River	3-May-2007
PDC-TRB	PDCF	Trestles Branch	2-May-2007
PDC-WIT	PDCF	Withers Swash	14-Jun-2007
PDC-WOB	PDCF	White Oak Bay	9-May-2007
SAL-DBB	SALSH	Double Branch	31-May-2006
SAL-LGB	SALSH	Long Branch	25-May-2006
SAL-TWC	SALSH	Twelvemile Creek	25-May-2006
SAV-LHC	SAVSH	Little Horse Creek	7-Jun-2006
SAV-SAN	SAVSH	Sand River	7-Jun-2006
SAV-TPS	SAVSH	tributary to Polk Swamp	14-Jun-2006
SAV-UTR	SAVSH	Upper Three Runs	8-Jun-2006

Information Transfer Program Introduction

None.

USGS Summer Intern Program

None.

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	0	0	0	0	0
Masters	3	0	0	0	3
Ph.D.	2	0	0	0	2
Post-Doc.	0	0	0	0	0
Total	5	0	0	0	5

Notable Awards and Achievements

University of Delaware Invited to UD and provided a workshop for faculty and administrators on urban growth modeling and potential affects of urban growth on receiving waters.

SUNY Albany Invited to SUNY and provided a workshop on sustainable growth, local policy and environmental protection for small municipalities.

SC Sea Grant Invited to three South Carolina coastal communities to provide information on coastal growth, potential environmental impacts from that growth and potential policy implications at the local, state and federal levels.

Mott Foundation Met with members of the Mott Foundation in Ann Arbor, Michigan to determine possible avenues of collaboration concerning aging dams in the Southeast and potential chemical contamination in impoundments.

U.S. Forest Service Invited to present information to a national USFS short course concerning urbanization and impacts to forests and other natural resources.

Clemson University Water Forum Co-hosted an educational forum for administrators, faculty and students in order to build a more cohesive network of water research on campus.

Leadership South Carolina Invited to address group on a broad range of natural resource and water issues facing South Carolina in the upcoming decades.

Catawba River Basin Commission Invited to address the Commission on work of the SCWRC and how the Center might assist the Commission as it works toward settling issues between SC and NC.

State Mapping Advisory Committee Invited to make a presentation at the annual meeting regarding using GIS and computer mapping technologies toward solving problems related to natural resource and water management.

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