Water Resources Research Institute of the University of North Carolina Annual Technical Report FY 2010

Introduction

During 2010-2011 (Fiscal Year 2010), the Water Resources Research Institute (WRRI) of The University of North Carolina System was 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.

Research priorities continue to be identified by the WRRI Advisory Committee, composed of representatives of several federal and state agencies, local governments, industries, and non-governmental environmental organizations (NGOs). A technical review committee is also convened on an annual basis to advise WRRI staff on the scientific merit of research proposals submitted for funding. Full-time faculty members from all North Carolina institutions of higher education are eligible to receive grants from WRRI.

The information transfer program continued to focus on disseminating results of sponsored research and providing information on emerging water issues, solutions, and regulations. 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 the WRRI Annual Conference and individual group meetings where appropriate. 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 the WRRI Annual Conference and other workshops and seminars that WRRI sponsors.

WRRI continues to adapt to changes in the landscape of its home institution, NC State University, by consolidating its operations and maximizing staff efficiencies and outputs (as described in the accomplishments section of this report). They continue to leverage funds from a variety of sources to expand the reach and impact of research and outreach activities, and grow their involvement in and support of water-related research and outreach across the state.

Research Program Introduction

During 2010-2011 (Fiscal Year 2010), WRRI continued its regular program of fostering research, training, and information transfer responsive to water issues of the state and region. Results from Institute-supported research efforts are expected to assist local, municipal, state, regional and federal agencies improve their decision-making in the management and stewardship of their water resources. To help it chart and sponsor a research program responsive to the water resource issues and opportunities in North Carolina, WRRI interacts closely with the N.C. Department of Environment and Natural Resources, other agencies, water and power utilities, and an array of research and outreach programs within the UNC system and at private higher educational institutions across North Carolina. A research advisory committee provides input, guidance, and review of the Institute's research priorities on an annual basis. This committee is composed of representatives of several federal and state agencies, local governments, industries, and non-governmental environmental organizations (NGOs).

The results of this process are shared with prospective investigators as part of WRRI's annual call-for-proposals. Proposals that address the annual priorities and meet peer review and other criteria receive preferential consideration for funding. Research priorities, as determined via the above process, are incorporated into our Section 104 Objectives on an annual basis. The proposal solicitation, as in the past, is sent to relevant contacts 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. Full-time faculty members from all North Carolina institutions of higher education are eligible to receive grants from WRRI.

The proposals received are sent to a Technical Committee and to external peer reviewers to determine the relevancy, need for the proposed research and relative strength and weaknesses. The Technical Committee convenes on an annual basis to to review all comments made by reviewers, advise WRRI staff on the scientific merit of research proposals, and make recommendations regarding proposal funding.

Efforts were made to refine, focus, and consolidate the list of FY10-11 research priorities compared to prior years based on in-depth discussions of the largest water research needs and priorities for the state of North Carolina. These priorities were included in the annual call for FY 2010-2011, and the projects resulting from this annual call will be funded from March 1, 2011 to February 28, 2012 and will be reported in the next USGS Annual Report. To view priorities related to the projects reported in the following pages, please refer to the 2009 USGS Annual Report for the research priorities that informed those projects.

The FY 2010-2011 research priorities are:

•feasibility of approaches for water conservation, efficiency, and reuse

•quantifying the economic value of water quality

•sources, transport, and fate of nutrients and sediments in surface waters, and assessment of approaches for improving the status of nutrient-sensitive waters

•defining and evaluating in-stream flow needs and aquatic ecosystem function

•groundwater, especially groundwater quality (nutrients, agricultural chemicals, metals, etc.), aquifer storage and recovery, and salt water intrusion

•understanding, quantifying, and managing risks and uncertainties in public water supplies, in the face of changing population, land use, climate, and regulations

•setting rates and financing capital improvements for water utilities, in the face of changing population, land use, climate, and regulations

•evaluation of methods for quantifying pollutant removal from stream restoration practices and projects

•defining the pros and cons of different stream restoration practices with regard to sediment, N, and P removal and restoration of aquatic habitat, and the appropriate pollutant removal credits for these practices

•defining and evaluating realistic management measures that can quantifiably mitigate the effects of impervious cover on aquatic life, in different urban settings and stormwater systems

•defining and evaluating realistic management practices that can quantifiably remove from stormwater both nutrients and pathogens/bacteria, and the relative pros and cons of these practices for different contaminants in different urban settings and stormwater systems

Protecting Receiving Waters: Removal of Biochemically Active Compounds from Wastewater by Ozonation and Activated Carbon Adsorption Processes

Basic Information

Title:	Protecting Receiving Waters: Removal of Biochemically Active Compounds from Wastewater by Ozonation and Activated Carbon Adsorption Processes
Project Number:	2009NC120B
Start Date:	3/1/2009
End Date:	12/31/2010
Funding Source:	104B
Congressional District:	02
Research Category:	Water Quality
Focus Category:	Treatment, Acid Deposition, Water Quality
Descriptors:	
Principal Investigators:	Detlef Knappe, Francis de los Reyes

Publications

There are no publications.

Protecting Receiving Waters: Removal of Biochemically Active Compounds from Wastewater by Ozonation and Activated Carbon Adsorption Processes

WRRI Project 70246

Progress Report
Submitted: May 18, 2011

Principal investigator and organization: Detlef Knappe, NC State University

Graduate and undergraduate research assistants: Leigh-Ann Bender, Qianru Deng, Ross Varin

Project objectives:

The **objectives** of this research are to

(1) measure oxidation kinetics of five model BACs during ozonation of NC wastewater and, with the aid of a mathematical model, predict ozone doses required to achieve BAC oxidation levels of 90 and 99% for wide range of BACs and

(2) identify suitable PAC types and effective PAC addition points in wastewater treatment plants and determine PAC doses that yield BAC removals of 90 and 99%.

Activities since the last progress report

The principal focus of activity during this reporting period was on experimental and modeling work related to objective 1 (measure oxidation kinetics of five model BACs during ozonation of NC wastewater and, with the aid of a mathematical model, predict ozone doses required to achieve BAC oxidation levels of 90 and 99% for wide range of BACs). The effectiveness of ozonation for BAC oxidation in the effluent from a North Carolina wastewater treatment plant (WWTP) practicing biological nutrient removal was assessed. In addition, the effectiveness of ozone in the wastewater matrix was compared to that in drinking water sources using typical preozonation conditions employed by North Carolina utilities.

Introduction

The presence of biochemically active compounds (BACs) such as endocrine disrupting chemicals and pharmaceuticals in water poses a potential threat to human and aquatic health. For example, EDCs can cause intersexuality in fish, and antimicrobial compounds may lead to an evolution of antibiotic-resistant bacteria. While it is unclear whether human health effects can be expected at the BAC concentrations commonly measured in drinking waters, the public is concerned about the presence of such compounds in their drinking water. Prior studies have shown that ozone effectively oxidizes many BACs in both drinking water and wastewater treatment (e.g. Westerhoff et al. 2005, Huber et al. 2005). In many instances, ozone targets functional groups that are responsible for the biochemical activity of a compound. As a result, ozonation products of antibiotics tend to lose their antimicrobial activity (e.g. Dodd et al. 2009). Similarly, ozone effectively destroys the estrogenic activity of both natural and synthetic estrogens (e.g. Huber et al. 2004, Kamiya et al. 2005). A recent study (Stalter et al. 2011) shows that ozonation lowers the overall endocrine activity and cytotoxicity of WWTP effluents.

Approach

The goal of the experimental approach was to determine the following parameters for each water: (1) the first-order rate constant (k) describing ozone decay in each water, (2) the instantaneous ozone demand of each water ($[O_3]_{0,fit}/[O_3]_{0,actual}$), and (3) the ratio of the hydroxyl radical concentration to the concentration of ozone (R_c) in each water.

To obtain k and ($[O_3]_{0,fit}/[O_3]_{0,actual}$, ozone decay was measured as a function of time in each water, and data were described by a first order decay model as follows:

$$ln\frac{[O_3]}{[O_3]_{0,fit}} = -kt \qquad \text{(eq. 1)}$$

Values of k and $[O_3]_{0,fit}$ were obtained by linear regression, and $[O_3]_{0,actual}$ was determined experimentally.

R_c values were determined from p-CBA data that were plotted as a function of ozone exposure (Elovitz and von Gunten 1999) and evaluated as follows:

$$ln\frac{[p\text{-}CBA]}{[p\text{-}CBA]_0} = -k_{OH,p\text{-}CBA} * R_c * \int [O_3]\, dt \qquad \text{(eq. 2)}$$

The ozone exposure ($\int [O_3]\, dt$) was calculated from the area under the ozone decay curve, and $k_{OH,p\text{-}CBA}$ is the second order rate constant describing the reaction between the hydroxyl radical and p-CBA ($k_{OH,p\text{-}CBA} = 3x10^{11}\ M^{-1}\ min^{-1}$).

The extent of BAC oxidation in a given water was predicted from:

$$\frac{[BAC]}{[BAC]_0} = e^{[\frac{([O_3]_{0,actual}}{k}\frac{[O_3]_{0,fit}}{[O_3]_{0,actual}})(k_{OH}R_c + k_{O_3})(e^{-kt}-1)]} \qquad \text{(eq. 3)}$$

where k_{OH} and k_{O3} are the second order rate constants describing the rate of BAC oxidation by the hydroxyl radical and by ozone, respectively. Values for k_{OH} and k_{O3} were compiled from the literature. The ultimate conversion, as time approaches infinity (or ozone has completely reacted away), is given by the expression:

$$\frac{[BAC]}{[BAC]_0} = e^{-[\frac{([O_3]_{0,actual}}{k}\frac{[O_3]_{0,fit}}{[O_3]_{0,actual}})(k_{OH}R_c + k_{O_3})]} \qquad \text{(eq. 4)}$$

Finally, percent parent compound removal was calculated with the expression:

$$\%\ Parent\ Compound\ Removal = \left(1 - \frac{[BAC]}{[BAC]_0}\right) \times 100 \qquad \text{(eq. 5)}$$

To distinguish between contributions of molecular ozone and hydroxyl radicals to the extent of BAC oxidation, the fraction of BAC removal due to reaction with the hydroxyl radical was determined from:

$$f_{OH^{\cdot}} = \frac{k_{OH}R_c}{k_{OH}R_c + k_{O_3}} \qquad \text{(eq. 6)}$$

The parent compound removal percentages attributable to hydroxyl radicals and due to ozone were calculated by multiplying percent parent compound removal (eq. 5) by f_{OH} for hydroxyl radicals and ($1-f_{OH}$) for ozone.

Materials and Methods

Pharmaceuticals

Five pharmaceuticals were selected for the experimental portion of this research: bezafibrate (BZF), diclofenac (DCF), ibuprofen (IBP), sulfamethoxazole (SMX), and trimethoprim (TMP). The selected compounds are commonly found in effluent-impacted water bodies. Table 1 summarizes physical-chemical characteristics of the selected pharmaceuticals, including the

octanol-water partition coefficient of the neutral form of each compound (logP) and the octanol-water partition coefficient at pH 7 (logD). The pK_a values illustrate that BZF, DCF, IBP, and SMX are predominantly present in their anionic form at neutral pH. For TMP, cationic and neutral forms coexist in almost equal proportions at neutral pH.

Table 1. Properties of selected pharmaceuticals

Chemical	Molecular Weight (g/mol)	pK_a		logP	logD (pH 7)
		Acid [0/-]	Base [+/0]		
BZF	361.82	3.3*		3.46	0.03
DCF	296.15	4.2+		4.06	1.28
IBP	206.28	4.9+		3.72	1.16
SMX	253.28	5.8*		0.89	-0.27
TMP	290.32		7.1+	0.79	0.38

* Predicted with Advanced Chemistry Development (ACD/Labs) Software v. 8.14 (as listed in SciFinder Scholar

\+ Experimentally determined values as listed in EPI Suite v. 4.0 database

Pharmaceutical stock solutions were prepared in ultrapure (DI) water (pH 7). All stock solutions were prepared at concentrations of ~10 mg/L, and stock solutions were filtered through a 0.22-µm PTFE membrane before use. The targeted initial pharmaceutical concentration was ~100 µg/L (<0.5 µM). This concentration is sufficiently low that the determined removal percentages are expected to match those obtained at concentrations more commonly encountered in drinking water sources and treatment plant effluents.

Water

The WWTP effluent was collected from the North Cary Reclamation Facility (Cary, NC). In addition, two drinking water sources were sampled: Cane Creek Reservoir water (Orange Water and Sewer Authority, Carrboro, NC) and Cape Fear River water (Wilmington, NC). Upon collection, water was stored in 55-gal stainless steel drums at 4°C. Water was filtered through 0.45-µm membranes prior to use. Dissolved organic carbon (DOC) concentrations of Cane Creek Reservoir, Cape Fear River, and Cary wastewater treatment plant effluent (WWTPE) were 4.6, 6.0, and 6.6 mg/L, respectively. Alkalinities of the two drinking water sources were between 25-30 mg/L as $CaCO_3$ and that of the WWTPE was 75 mg/L as $CaCO_3$.

Ozone Stock Solution

Ozone was generated by passing oxygen through an ozone generator (Pacific Ozone). The product gas from the ozone generator was bubbled through DI water in a glass flask that was placed in an ice bath. Typical ozone stock solution concentrations were 25-32 mg/L. The ozone stock solution concentration was measured prior to dosing each reactor. The volume of stock solution dosed into the reactor to obtain the desired initial concentration was adjusted accordingly. Ozone concentrations of the stock solution were measured with a spectrophotometer at a wavelength of 258 nm.

Ozone Decay Curves and p-CBA Oxidation Rates

Ozone decay curves and p-CBA oxidation rates were determined at two ozone doses that were based on the TOC of each water. The lower O_3 dose was in the range of 0.34-0.42 mg O_3/mg TOC while the higher dose O_3 was in the range of 0.67-0.76 mg O_3/mg TOC. Experiments were conducted in 20 mL amber glass EPA vials that were filled with the water of interest. Water in the reactors was spiked to an initial p-CBA concentration of 1 µM, and reactors were continuously mixed with PTFE coated magnetic stir bars. At predetermined times after the addition of ozone (5 sec, 10 sec, 20 sec, 30 sec, 1 min, 2 min, 4 min, 6 min, 8 min, 10 min, 20 min, and 30 min, or until the ozone concentration was non-detectable for two consecutive data points), ozone residuals in the reactors were quenched with 125 µL of 10 mM cinnamic acid. Cinnamic acid reacts quickly with the residual ozone to stoichiometrically form benzaldehyde (Dodd et al. 2006). For the t=0 samples, cinnamic acid was added to the vial prior to ozone dosing. Ozone residuals were determined from benzaldehyde concentrations (Dodd et al. 2006).

BAC Oxidation Tests

For each water and ozone concentration, the oxidative removal of the five pharmaceuticals shown in Table 1 was tested. Pharmaceuticals were dosed at a concentration of <0.5 µM. In parallel, a reactor without BACs but 125 µL of cinnamic acid was dosed in order to determine the initial ozone concentration. The reactors were mixed for the time that was sufficient for the ozone to completely dissipate, as determined from decay experiments.

Analytical methods

Concentrations of BACs, p-CBA, and benzaldehyde were determined by high performance liquid chromatography (Breeze, Waters). A RP-Amide C16 column (5 µm, 3.0 × 250 mm, Supelco, Sigma-Aldrich, St. Louis, MO) was used to separate analytes with isocratic methods. Table 2 summarizes the mobile phase compositions and detector wavelengths used for each analyte. Mobile phase compositions are given in % v/v acetonitrile (AcN) to % v/v 5 mM phosphate buffer (pH 2.2).

Table 2. Mobile Phases and Detector Wavelengths for HPLC Analyses

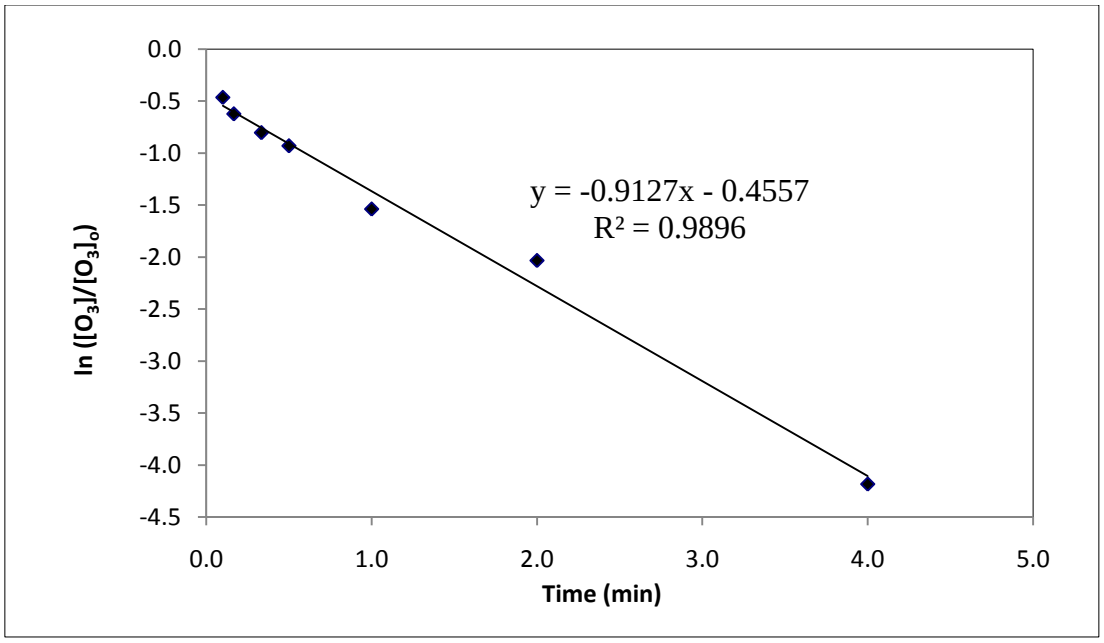
Compound	Mobile Phase (% AcN:% Buffer)	Detector Wavelength (nm)
BZF	50:50	240
DCF	50:50	282
IBP	50:50	222
SMX	25:75	266
TMP	10:90	238
Benzaldehyde	35:65	233
p-CBA	35:65	233

The mobile phase flow rate was 0.43 mL/min for all analyses. Prior to analysis, samples were filtered through a 0.22-µm PTFE membrane. Concentrations in bench-scale tests were sufficiently high that samples could be analyzed by direct injection, i.e. without sample preconcentration.

Results

Ozone Decay and p-CBA Oxidation Rates

Ozone decay and p-CBA oxidation data were used to determine k, instantaneous ozone demand, and R_c values for each water and ozone dose. Figure 1 summarizes representative data obtained with Cary WWTPE water and an ozone dose of 4.17 mg/L.



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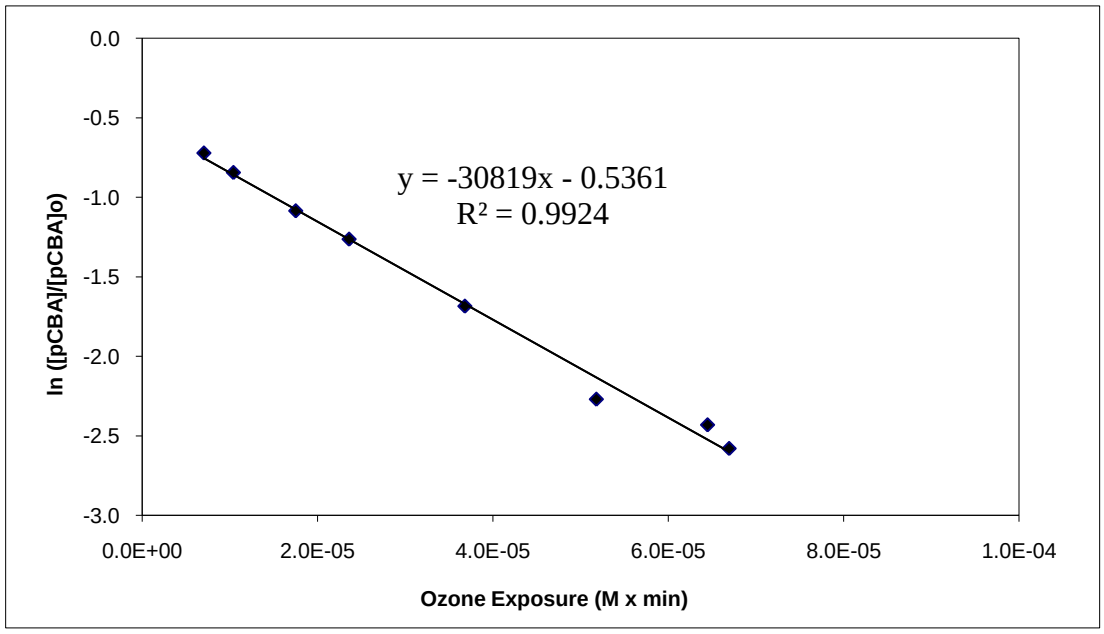


b)

Figure 1. Ozone decay data (a) and p-CBA oxidation data (b) in Cary WWTPE. Ozone dose: 4.17 mg/L.

Table 3 summarizes the rate constants describing ozone decay (k), ratios of fitted to measured initial ozone concentrations ($[O_3]_{0,fit}/[O_3]_{0,actual}$), and R_c values for each water and ozone dose.

Table 3. Ozone decay rate constants, ratios of fitted to measured initial ozone concentrations, and R_c values for three waters at two ozone doses.

Water	Ozone Dose (mg/L)	O_3:TOC	k (min^{-1})	$[O_3]_{0,fit}/[O_3]_{0,actual}$	R_c
Cary WWTP Effluent	2.18	0.34	4.990	0.321	4.55×10^{-7}
	4.17	0.67	0.913	0.634	1.02×10^{-7}
Cane Creek Reservoir	1.48	0.38	3.060	0.489	3.37×10^{-7}
	3.33	0.76	0.676	0.587	1.05×10^{-7}
Cape Fear River	2.48	0.42	7.820	0.522	9.34×10^{-7}
	4.74	0.75	0.804	0.540	1.19×10^{-7}

As shown in Table 3, both k and R_c values were higher at the lower ozone doses. The k values show that ozone decayed more rapidly at lower ozone concentrations. As a result, the hydroxyl radical concentration relative to the ozone concentration (R_c) was higher than that at higher ozone doses. For the three waters tested here, a strong linear trend between k and R_c was obtained ($r^2 = 0.97$, n = 6). It is also interesting to note that k and R_c values for the treated wastewater were similar to those for the Cane Creek Reservoir water. Although effluent organic matter in wastewater likely enhanced hydroxyl radical formation relative to the natural organic matter in surface water, the enhanced hydroxyl radical formation was likely counterbalanced by the higher alkalinity of the wastewater (~75 mg/L as $CaCO_3$ compared to ~25 mg/L as $CaCO_3$ in the surface water) because carbonate species act as hydroxyl radical scavengers.

Experimental BAC Removal

The removal of BZF, IBP, SMX, TMP, and DCF was determined experimentally at two ozone doses in each water. Table 4 summarizes the parent compound removals that were measured for each BAC.

Table 4. Experimentally determined percent parent compound removal for five model BACs. Ozone doses are $[O_3]_{0,actual}$

Water	Parent Compound Removal (%)									
	BZF		IBP		SMX		TMP		DCF	
	$[O_3]_o$ mg/L	%	$[O_3]_o$ mg/L	%	$[O_3]_o$ mg/L	%	$[O_3]_o$ mg/L	%	$[O_3]_o$ mg/L	%
Cary WWTP Effluent	2.00	70	2.09	70	2.21	> 99	1.76	> 99	1.94	> 99
	3.80	> 95	4.08	> 99	4.28	> 99	3.80	> 99	4.08	> 99
Cane Creek Reservoir	1.72	94.5	1.77	87	1.86	> 99	1.73	> 99	1.83	> 99
	3.68	> 95	4.06	> 99	3.86	> 99	3.68	> 99	4.06	> 99
Cape Fear River	2.03	94.5	2.14	92	2.39	> 99	2.28	> 99	2.50	> 99
	4.47	> 95	4.48	> 99	4.43	> 99	4.47	> 99	4.48	> 99

The results in Table 4 illustrate that essentially complete removal was obtained for SMX, TMP, and DCF at the lower O_3 doses (~0.3-0.4 mg O_3/mg TOC) and for all 5 compounds at the higher O_3 doses (0.6-0.9 mg O_3/mg TOC). BZF and IBP proved to be the most challenging to remove from WWTPE – at the lower O_3 dose, 70% parent compound removal was obtained for each compound (Table 4).

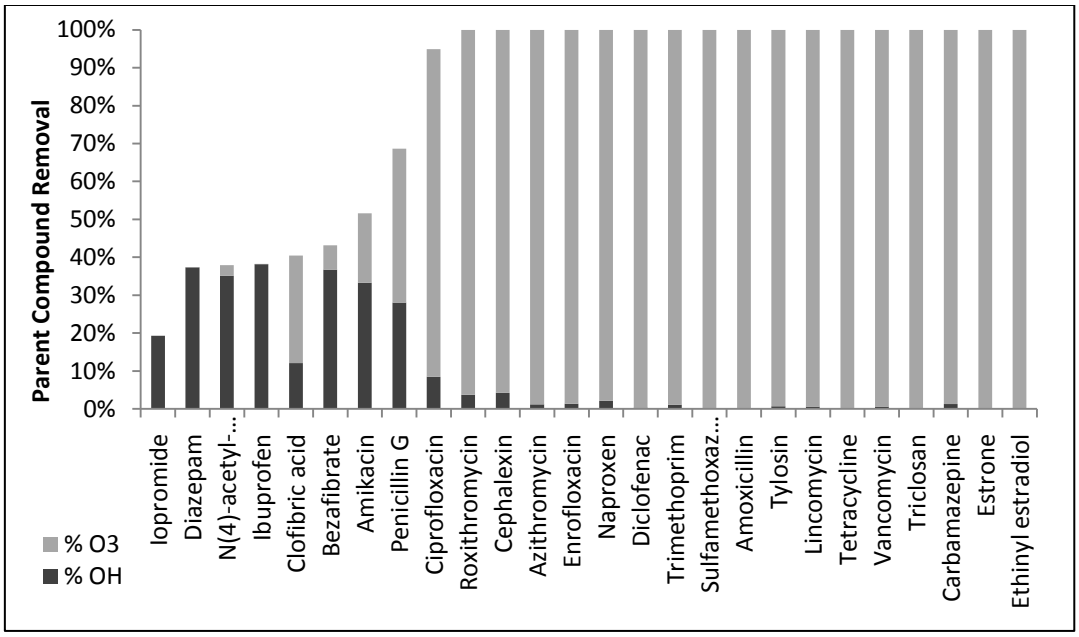
Parent Compound Removal Predictions

Using equation 4, the extent of BAC oxidation by ozone at ozone doses of ~0.35 mg O_3/mg TOC and ~0.7 mg O_3/mg TOC was predicted for 26 BACs in all three waters. Second order rate constants describing the oxidation rates by molecular ozone (k_{O3}) and by the hydroxyl radical (k_{OH}) were obtained from the literature (Table 5).

Table 5. Second order rate constants describing the oxidation of BACs by ozone and by hydroxyl radicals (from Huber et al. 2003, 2005; Dodd et al. 2006; Ikehata et al. 2006; Suarez et al. 2007)

Compound Name	Compound Class	k_{O3} (M^{-1} s^{-1})	k_{OH} (M^{-1} s^{-1})
Amoxicillin	β-lactam antibiotic	6×10^6 (pH 7)	3.93×10^9 (pH 5.5)
Penicillin G	β-lactam antibiotic	4.8×10^3 (pH 7)	7.3×10^9 (pH 7)
Cephalexin	β-lactam antibiotic	8.7×10^4 (pH 7)	8.5×10^9 (pH 7)
Azithromycin	Macrolide antibiotic	1.1×10^5 (pH 7)	2.9×10^9 (pH 7)
Roxithromycin	Macrolide antibiotic	6.3×10^4 (pH 7)	8.2×10^9 (pH 7)
Tylosin	Macrolide antibiotic	5.1×10^5 (pH 7)	5.4×10^9 (pH 7)
Sulfamethoxazole	Sulfonamide antibiotic	5.5×10^5 (pH 7)	5.5×10^9 (pH 7)
N(4)-Acetyl-sulfamethoxazole	Sulfonamide antibiotic metabolite	2.5×10^2 (pH 7)	6.8×10^9 (pH 7)
Ciprofloxacin	Fluoroquinolone antibiotic	1.9×10^4 (pH 7)	4.1×10^9 (pH 7)
Enrofloxacin	Fluoroquinolone antibiotic	1.5×10^5 (pH 7)	4.5×10^9 (pH 7)
Trimethoprim	Dihydrofolate reductase inhibitor antibiotic	2.7×10^5 (pH 7)	6.9×10^9 (pH 7)
Lincomycin	Lincosamide antibiotic	6.7×10^5 (pH 7)	8.5×10^9 (pH 7)
Tetracycline	Tetracycline antibiotic	1.9×10^6 (pH 7)	7.7×10^9 (pH 7)
Vancomycin	Glycopeptide antibiotic	6.1×10^5 (pH 7)	8.1×10^9 (pH 7)
Amikacin	Aminoglycoside antibiotic	1.8×10^3 (pH 7)	7.2×10^9 (pH 7)
Triclosan	Antimicrobial agent	3.8×10^7 (pH 7)	5.4×10^9 (pH 7)
Carbamazepine	Anticonvulsant	~ 3×10^5 (pH 7)	8.8×10^9 (pH 7)
Diazepam	Anti-anxiety agent	0.75 (pH 7)	7.2×10^9 (pH 7)
Diclofenac	Non-steroidal anti-inflammatory	~1×10^6 (pH 7)	7.5×10^9 (pH 7)
Naproxen	Non-steroidal anti-inflammatory	~2×10^5 (pH 7)	9.6×10^9 (pH 7)
Ibuprofen	Analgesic	9.6 (pH 7)	7.4×10^9 (pH 7)
Estrone	Natural estrogen	9.4×10^5 (pH 7)	2.6×10^{10}
17α-Ethinylestradiol	Synthetic estrogen contraceptive	~3×10^6 (pH 7)	~1×10^{10} (pH 7)
Bezafibrate	Lipid regulator	590 (pH 5-10)	7.4×10^9 (pH 7)
Clofibric acid	Lipid regulator metabolite	2550 (pH 6.5)	2.38×10^9
Iopromide	X-ray contrast medium	<0.8 (pH 5-10)	3.3×10^9 (pH 7)

For the 26 BACs, predicted parent compound removals in Cary WWPTP effluent are shown in Figure 2. For each compound, the fractional removals attributable to molecular ozone and the hydroxyl radical are indicated.



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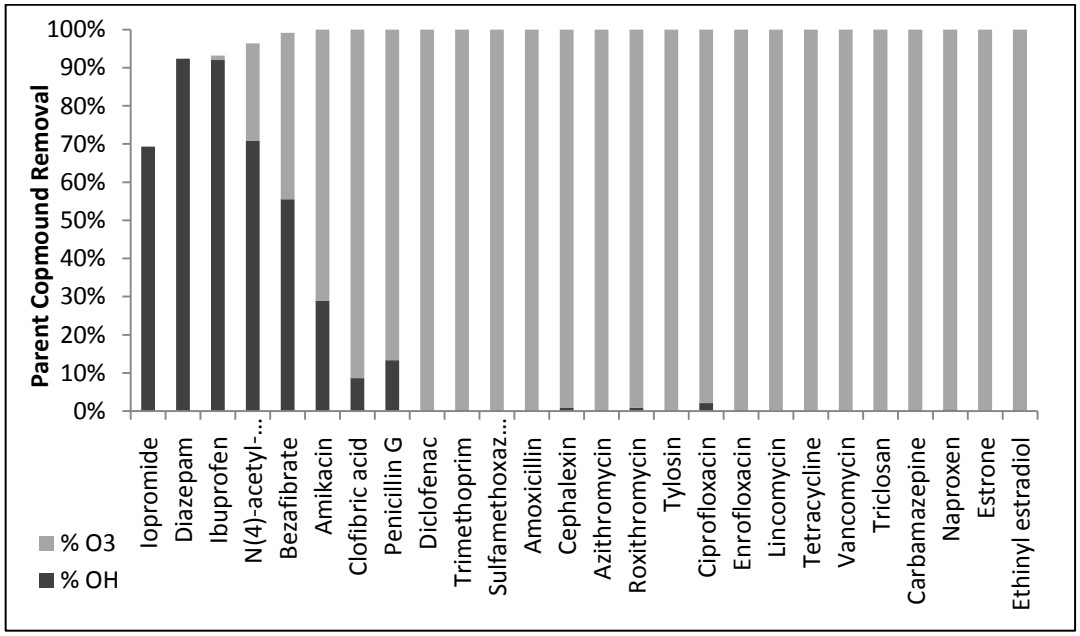

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Figure 2. Predicted parent compound removal percentages in Cary WWTPE water with (a) 2.25 mg/L ozone (0.34 mg O_3/mg TOC) and (b) 4.4 mg/L ozone (0.67 mg O_3/mg TOC)

At the lower ozone dose, essentially complete parent compound removal was predicted for 17 of the 26 compounds. At the higher ozone dose, >90% parent compound removal was predicted for all BACs except iopromide. For the majority of the BACs, oxidation by molecular ozone dominated overall parent compound removal (Figure 2), suggesting that their oxidative transformation is more effectively accomplished under conditions that favor long ozone half lives (high alkalinity, no H_2O_2 addition). These BACs were effectively oxidized by ozone, even

at the lower O_3 dose. For compounds with lower k_{O3} values (e.g., iopromide, diazepam, ibuprofen, N(4)-acetyl-sulfamethoxazole, bezafibrate), for which oxidation was governed by the hydroxyl radical, lower parent compound removals were predicted.

Validation of Model Predictions

Model predictions were compared with experimental results obtained for BZF, IBP, DCF, TMP, and SMX (Figure 3). The dashed error bars for the predicted removals represent the predicted range based on uncertainty in (1) the second order rate constants k_{O3} and k_{OH}, (2) the R_c values, and (3) the k values for ozone decay. Upper and lower bounds of the 95% confidence intervals of k, k_{O3}, k_{OH}, and R_c were used to determine the predicted range of parent compound removals. The error bars indicate that uncertainty in the predictions is substantial when BAC oxidation is incomplete (see BZF and IBP at lower ozone doses). For higher ozone doses, both predictions and experiments indicate essentially complete parent compound removal for all five BACs (Figure 3b, d, and f). At lower ozone doses, predicted and experimental removals compared well for DCF, TMP, and SMX (Figure 3a, c, e), the compounds for which oxidative transformation was essentially complete. For BZF and IBP, however, experimentally determined parent compound removals exceeded predicted removals at the lower O_3 doses. Model predictions were made assuming a constant R_c value throughout the entire ozone decay curve. It has been shown that the R_c value decreases in the period immediately following the addition of ozone (Buffle et al. 2006), and this phenomenon was not captured in the experimental and modeling approaches presented here. The negative y-axis intercept in Figure 1b illustrates that Rc values were higher during the initial period of ozone exposure, for which no data could be collected ($t < 5$ sec). As a result, the removal predictions for compounds for which oxidative removal is dominated by the hydroxyl radical, as is the case for IBP and BZF, were lower than those obtained in experiments.

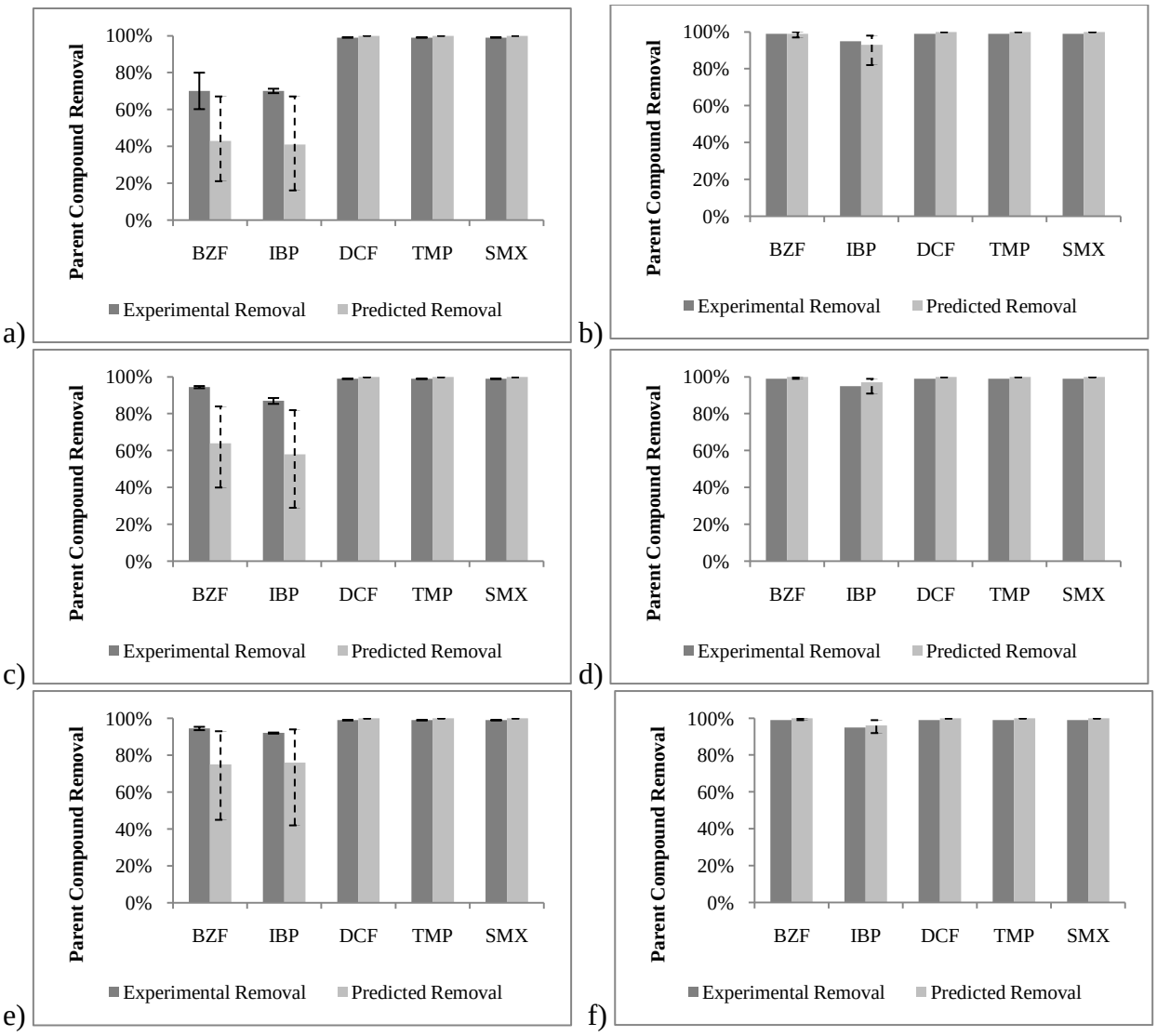

Figure 3. Comparisons of predicted and experimentally determine BAC removals from (a) WWTPE with 2.25 mg/L O_3, (b) WWTPE 4.4 mg/ L O_3, (c) Cane Creek with 1.75 mg/L O_3, (d) Cane Creek with 3.5 mg/ L O_3, (e) Cape Fear with 2.5 mg/L O_3, and (f) Cape Fear with 4.5 mg/L O_3,.

Ozone Dose Prediction for 99% Parent Compound Removal

Ozone doses required to achieve 99% parent compound removal were predicted for the four compounds that were most difficult to oxidize (iopromide, diazepam, ibuprofen, and N(4) acetyl-sulfamethoxazole, see Figure 2). For the predictions, values for k, $[O_3]_{0,fit}/[O_3]_{0,actual}$, and R_c were used that corresponded to the higher O_3 doses in Table 3. Table 6 illustrates that O_3 doses of ~1mg O_3/mg TOC will be sufficient to achieve 99% parent compound removal for all compounds except iopromide. Ozone doses in this range are not uncommon during preozonation of North Carolina surface waters. As a result, utilities employing this treatment practice can expect to effectively oxidize 25 of the 26 BACs evaluated in this study. To achieve 99% parent compound removal for iopromide, ozone doses >2 mg O_3/mg TOC would be required. Such doses are cost-prohibitive for the tested waters. In addition, byproduct formation (e.g. bromate) can become increasingly problematic as the O_3 dose is increased. One interesting result in Table

6 is that the effectiveness of ozone for BAC transformation is similar in the tested NC surface waters and in the WWTP effluent. This result suggests that the ozonation of WWTP effluents, an important source of BACs into the environment, can effectively remove BAC parent compounds at doses (costs) that closely match those required during the preozonation of surface waters with moderate levels of TOC.

Table 6. Predicted ozone doses for 99% parent compound removal in three waters

Water	Compound	O_3 Dose for 99% Parent Compound Removal (mg/L)
Cary WWTPE	Iopromide	15.7
	Diazepam	7.2
	Ibuprofen	6.9
	N(4) acetyl-SMX	5.6
Cane Creek Reservoir	Iopromide	12.2
	Diazepam	5.6
	Ibuprofen	5.4
	N(4) acetyl-SMX	4.4
Cape Fear River	Iopromide	13.9
	Diazepam	6.4
	Ibuprofen	6.2
	N(4) acetyl-SMX	5.2

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Seasonal Streamflow Forecasts for the Hydrologic Unit Code (HUC-8) Basins in North Carolina utilizing Multimodel Climate Forecasts

Basic Information

Title:	Seasonal Streamflow Forecasts for the Hydrologic Unit Code (HUC-8) Basins in North Carolina utilizing Multimodel Climate Forecasts
Project Number:	2009NC122B
Start Date:	3/1/2009
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	2
Research Category:	Climate and Hydrologic Processes
Focus Category:	Drought, Hydrology, Water Supply
Descriptors:	
Principal Investigators:	Sankarasubramanian Arumugam, Ryan Boyles

Publications

1. Singh, H., and A. Sankarasubramanian, Systematic uncertainty reduction in streamflow forecasts development: Importance of Input and Hydrologic Model Uncertainty, Water Resources Research, 2011 (to be submitted).
2. Singh, H., McNamara, A., Boyles, R. and S.Arumugam, Experimental Reservoir Inflow Forecast, NC Annual Water Conference, March 22-23, Raleigh, NC.
3. Almanaseer, N., Role of Climate Variability in Surface water-Groundwater interaction, NC state University, 2011
4. Almanaseer, N., A. Sankarasubramanian and J. Bales, Role of Climatic Variability in Influencing Interannual Groundwater Variability over Southeast US, Journal of Hydrologic Engineering, 2011, under revision.
5. Almanaseer, N., A. Sankarasubramanian and J. Bales, Developing seasonal groundwater forecasts using seasonal to interannual climate forecasts, Journal of Hydrologic Engineering, 2011, under preparation.
6. Almanaseer, N., and A. Sankarasubramanian, Climate, Streamflow and Groundwater Interaction over the Southeastern US, Proceedings of the EWRI- ASCE Conference, Providence, May 12-22, 2010.
7. Almanaseer, N., S. Arumugam and J. Bales, Role of Climate Variability in Modulating Surface Water and Groundwater Interaction over the Southeast United States, American Geophysical Union, Fall Conference, San Francisco, 2010.
8. Almanaseer, N., and A. Sankarasubramanian, Improving surface water and groundwater predictions using precipitation forecasts, Annual WRRI Conference, Raleigh, March 22-23, 2011.

Seasonal Streamflow Forecasts for the Hydrologic Unit Code (HUC-8) Basins in North Carolina utilizing Multimodel Climate Forecasts

Final Report

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Project No : 550367 and 550868

Project Report : March 01, 2010 – May 9, 2011

1.0 Introduction and Objectives

Despite the relative abundance of water in North Carolina (NC)(Moreau, 2006), increasing demand at major metropolitans make the local and regional water supply systems vulnerable to even moderate drought conditions(Weaver, 2005). For instance, in the Triangle Area in NC, the demand has grown by about 20%-62% from 1995-2000 resulting in three severe droughts/shortages (summers of 2002, 2005 and 2007) in the past five years. But, the reservoir systems in humid regions are typically designed as within-year storage systems with an intent to capture only the seasonal variability in streamflow, but do not carryover the deficit/surplus from year to year (e.g., reservoirs in the western US are over-year). Thus, the low storage (typically expressed as % of annual streamflow volume) and increasing urban demand necessitate the importance of utilizing climate-information based streamflow forecasts to develop strategies for water management. Unfortunately, the climate (precipitation and temperature) forecasts from General Circulation Models (GCMs) that are issued by the National Center for Environmental Prediction (NCEP) are typically available at large spatial scales (2.5°×2.5°) and also do not have streamflow forecasts. Though rainfall in NC have been shown to have significant predictability to various climatic signals such as El-Nino Southern Oscillation and Atlantic Dipole (Devineni et al., 2008; Roswintiarti et al., 1998), limited effort has been undertaken in developing seasonal streamflow forecasts (Rhome et al., 2000; Golembesky et al., 2009). In this study, we propose to downscale the large-scale climate forecasts issued by various national agencies and centers to develop seasonal streamflow forecasts to support various ongoing drought management activities in NC. Though we proposed to develop streamflow forecasts over the HUC, the project team realized that this first effort could focus on developing streamflow forecasts for four reservoir sites (Lake Jordan, Falls Lake, Kerr Scott, and Philpot) and for two USGS gaging stations in Catawba.

Three objectives are proposed under this project.

Objective 1: *Assemble precipitation forecasts from multiple General Circulation Models (GCMs) available from various research and national agencies and analyze their potential ability to predict seasonal streamflow variability in HUC-8 basins.*

Objective 2: *Statistically downscale the precipitation forecasts available from GCMs and RCMs and optimally combine them to develop seasonal streamflow forecasts for the HUC-8 basins.*

Objective 3: *Disseminate both retrospective and real-time streamflow forecasts developed for the winter and summer seasons through the NC CRONOS database.*

The findings under each of these objectives are summarized over the next three sections.

2.0 Multimodel Streamflow Forecasts Development (Objective 1)

Before developing multimodel streamflow forecasts, the study team focused on a fundamental research question: Given that we have climate forecasts from multiple climate models, which could be ingested with multiple watershed models, what is the best strategy to develop multimodel streamflow forecasts? *To answer this question, we consider the two possible strategies: (a) reduce the input uncertainty first by combining climate models and then use the multimodel climate predictions with multiple watershed models, which again could be combined to develop multimodel streamflow predictions (b) ingest the individual climate forecasts (without*

multimodel combination) with individual watershed models and then combine the streamflow predictions that arise from all possible combinations of climate and watershed models. To investigate this, we consider a synthetic streamflow and climate forecasting schemes, so that we will be able to compare all the performance of candidate strategies with the true flows.

2.1 Climate-Streamflow Generation Scheme

Climate Forecasts Generation: The generation model for developing synthetic climate forecasts follow the scheme suggested by Weigel *et al.* (2008). The skill of the forecasts is controlled by two parameters α and β, which denote the correlation between the forecasted precipitation and the true precipitation and the overconfidence of the forecasted precipitation respectively. We consider the observed winter (January-March) precipitation (P_t) at Tar River at Tarboro over the period 1951-1990 as the true precipitation with winter climatology represented by mean (μ_P) and standard deviation (σ_P).

$$\overline{P}_t = \overline{X}_t \cdot \sigma_P + \mu_P \qquad ...(1)$$

$$X_{t,m} = \alpha \cdot x_t + \varepsilon_{\beta,t} + \varepsilon_m \qquad ...(2)$$

$$\overline{X}_t = \sum_{m=1}^{M} X_{t,m} \qquad ...(3)$$

$$x_t = \frac{P_t - \mu_P}{\sigma_P} \qquad ...(4)$$

$$\varepsilon_\beta \sim N(0, \beta) \qquad ...(5)$$

$$\varepsilon_m \sim N(0, \sqrt{1-\alpha^2-\beta^2}) \qquad ...(6)$$

We assume the precipitation forecasts for each winter season, *t*, to constitute 100 ensembles (M=100) following Gaussian distribution. It is important to note that the noise term ε_β which denotes the overconfidence of the forecasts is fixed for a given year. The parameter β is used to control the relocate the conditional mean by generating the overconfidence with Gaussian noise term with zero mean and standard deviation β. The parameter α is used to control the average correlation between the observed precipitation and the precipitation ensembles. Since α is a correlation coefficient, its value should be less than or equal to one. By adjusting these two parameters the center and the spread of the precipitation ensembles can be controlled. The forecasted precipitation will equal the observed precipitation if $\alpha = 1$ and $\beta = 0$. By assuming different α and β, we generate climate forecasts having different skill for the Tarboro site.

Streamflow Models: Using the generated ensemble mean, we obtain the predicted streamflow using any of the three watershed models: (a) Simple linear model (b) Log-linear model and (c) Non-linear 'abcd' model. Suppose if we have two climate forecasts, then we can obtain a total of six streamflow predictions, which could be combined to develop a multimodel streamflow prediction for the site (Strategy 2). On the other hand, if one combines the precipitation forecasts first, then we will have only three streamflow predictions, which could be combined to develop one prediction (Strategy 1). In this study, we consider a total of three watershed models and two

sets of candidate forecasts for our analyses with the true streamflow being generated by one of the candidate models. To obtain the true flows, we fit the watershed model between observed flows and precipitation at the site and estimate the parameters (θ). These estimated parameters are used to generate 40 years of streamflows and the performance of the multimodel strategies are compared in predicting these true flows using mean square error. We evaluate these two strategies by comparing over 1000 sets of Mean Square Error (MSE) computed by generating 1000 sets of 40 years of flows. For this report, we present the results under just one watershed model (linear case) with three sets of climate forecasts. However, important findings from the study are summarized at the end of this section. A manuscript is currently under preparation for potential publication in water resources research.

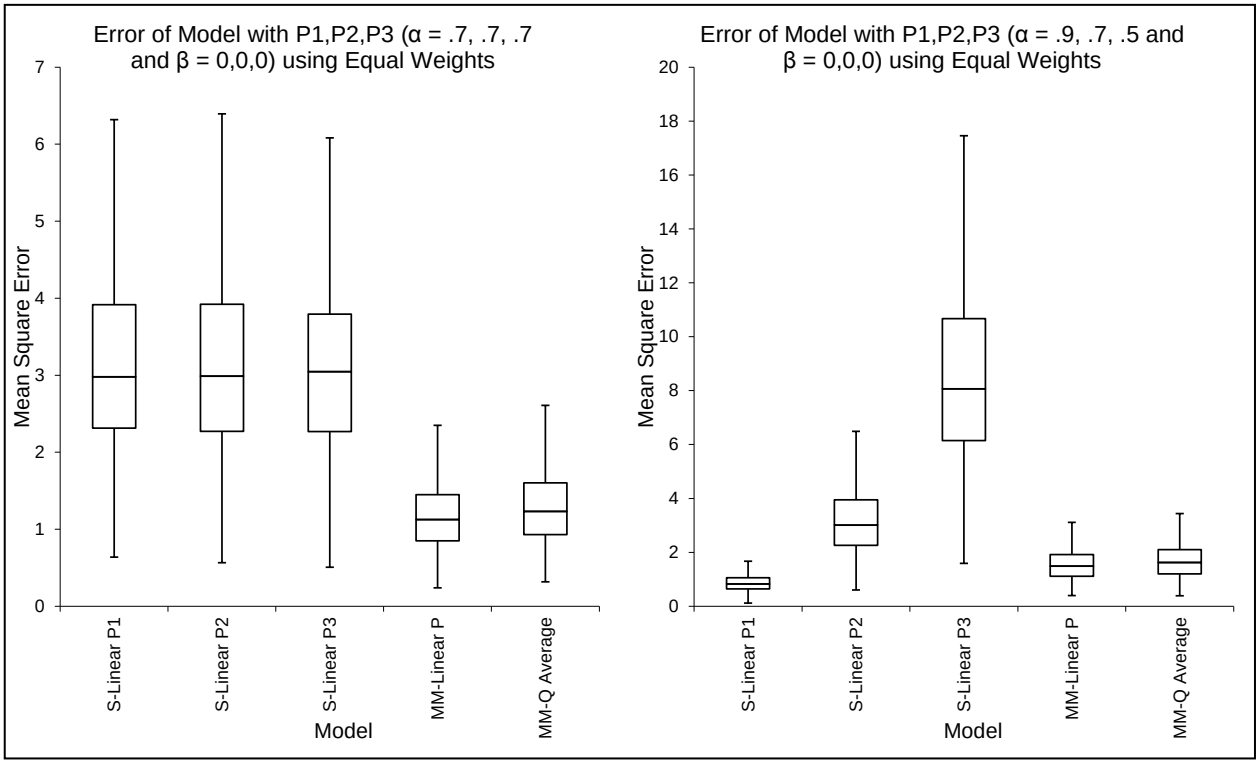

Figure 1: Box-plots of Mean Square error from fitting of 1000 sets of 40 years of synthetic streamflows generated from a linear model. Three climate forecasts are generated with all models having b =0, but with a = 0.7 for all the models (left) and having different a = 0.9, 0.7 and 0.5 (right). The performances of six predictions are summarized with single model (S). Two multimodel strategies (MM) are summarized next with the first strategy (MM-Linear P) – reducing input uncertainty first – followed by the second strategy (MM-Q Average) – combining the individual model predictions to develop multimodel predictions.

Analyses from Figure 1 clearly show that reducing input uncertainty first results in reduced MSE (MM-Linear P) compared to multimodel combinations developed from the combinations of individual model forecasts and watershed models (MM-Q Average). This is mainly because reduced uncertainty in the watershed model inputs results in better correspondence towards both model fitting and prediction. It is important to note the skill of the climate forecasts could be improved by reducing combining multiple models that primarily arise from reducing the overconfidence of the individual models. Further, single model performs better than the

multimodel in the second case, since the multimodel combination is performed with equal weights on the individual models. These limitations on multimodel combination could be overcome by combining models based on their optimal combination (Devineni et al., 2008).

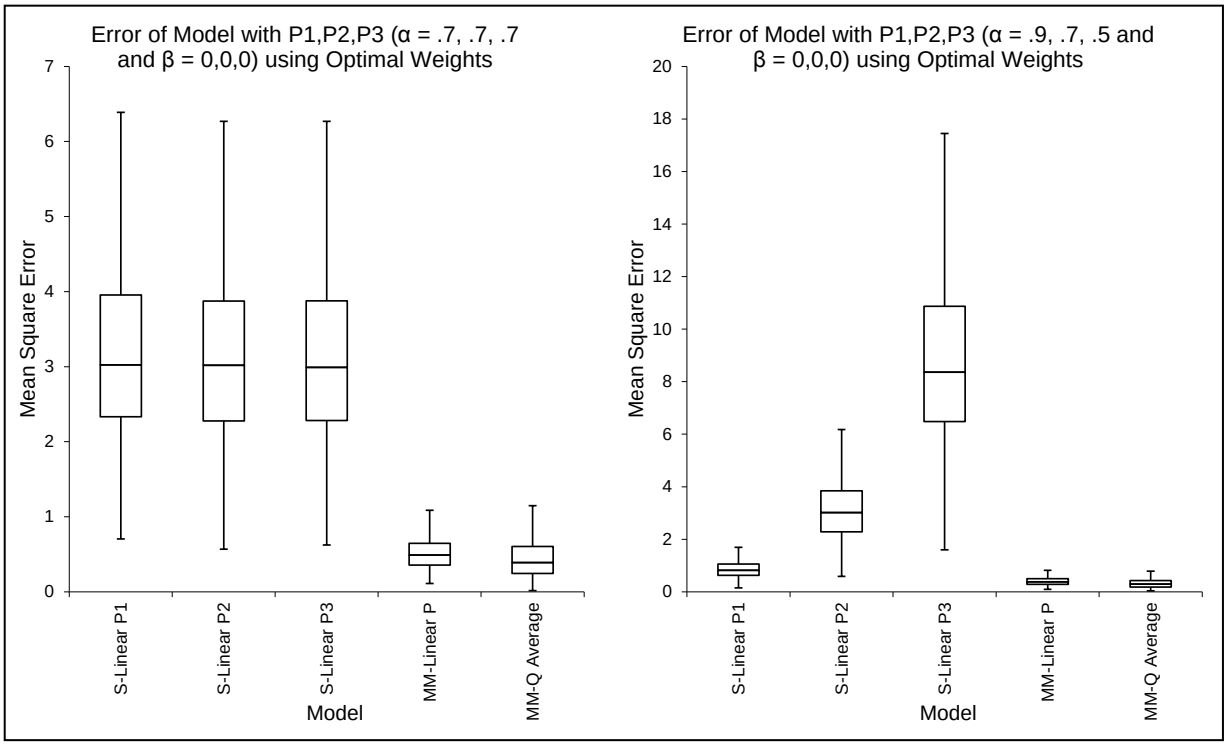

Figure 2: Same as Figure 1, but multimodel predictions are obtained based on optimal combinations of the individual models based on the algorithm of Devineni et al., (2008).

Figure 2 shows the similar analyses as Figure 1, but here the multimodel predictions are obtained based on optimal combinations. Under this case, the poorly (better) performing models during the calibration period are given lesser (higher) weights resulting in improved predictions. From Figure 2, when all the models have same skill, optimal combinations distribute the weights equally (box-plots on the left), whereas with models having different skills (box-plots on the right), we clearly see multimodel predictions (MM-Linear P and MM-Q average) have the lowest MSE compared to the individual models. Among the multimodels, though it is difficult to see, MM-Linear P performs better than the MM-Q Average. Thus, given the hydrologic model, we reach the following conclusions for developing multimodel predictions (Figures 1 and 2):

(a) Multimodel streamflow predictions perform better than the streamflow predictions obtained from individual models even if we employ the individual models having the true model form.
(b) Reducing the input certainty – precipitation and temperature forecasts – through multimodel combinations on climate outputs is more critical than developing multimodel combinations without reducing uncertainty.
(c) Multimodel predictions obtained through optimal combinations perform better than the streamflow predictions obtained from the best single model as well as over the multimodel predictions obtained based on equal weights approach.

Similar analysis was performed with multiple hydrologic models with multimodel combinations obtained based on equal and optimal combinations. The above conclusions are true even under the case with unknown hydrologic model form. Thus, to reduce the uncertainty in streamflow

predictions, it is important to first reduce the input uncertainty, which needs to be followed with reduction in hydrologic model uncertainty (Results under this case is not presented here). A manuscript based on these findings is under preparation to Water Resources Research: *Singh, H., and A. Sankarasubramanian, Systematic uncertainty reduction in streamflow forecasts development: Importance of Input and Hydrologic Model Uncertainty, Water Resources Research, 2011.*

3.0 Reservoir Inflow Forecasts Development over Target Basins in NC (Objective 2)

For this purpose, we have focused on developing inflow forecasts over four target basins and two USGS gauging stations because of their significance to water management and hydropower generation. The four reservoir sites are: Falls Lake, Lake Jordan, Kerr-Scott and Philpot Lake in Virginia. The two USGS gaging stations selected from the Catawba River system are South Fork Catawba River at Lowell, NC and Rocky Creek at Great Falls, SC.

2.1 Forecast Development Overview

Retrospective and real-time streamflow forecasts for the above six sites are currently available (http://www.nc-climate.ncsu.edu/inflowforecast) for the winter season over the period 1990 to till date. The approach we employ for developing streamflow forecasts is principal components regression, which is one of the commonly employed methodologies for statistical downscaling [Sankarasubramanian et al., 2008]. Given that the precipitation fields obtained from GCMs and SSTs are spatially correlated, application of Principal Components Analysis (PCA) rotates the original GCM fields into orthogonal components with the first mode representing the maximum variance of the original GCM fields. PCA, also known as empirical orthogonal function (EOF) analysis, on the predictors (GCM and SST fields) could also be performed by singular value decomposition on the spatial correlation matrix or covariance matrix of the predictors. Since PCA is scale dependent, loadings (eigenvectors or EOF patterns) obtained from the covariance matrix and the correlation matrix are different. Importance of each EOF pattern is quantified by the fraction of the variance the principal component represents with reference to the original predictor variance. In the case of PCA performed using correlation matrix approach, the sum of all eigenvalues is equal to the total number of elements in the data.

2.2 Dimension Reduction and Predictor Selection

For developing streamflow forecasts for various basins, we consider two candidate predictors for statistical downscaling: (a) Precipitation forecasts from ECHAM4.5 forced with constructed analogue SST forecasts over the Southeast US (23-40N; 92-73W) (b) observed monthly streamflow at the site. The grid points of precipitation forecasts that correlate well with the observed streamflow are identified based on Spearman rank correlation. These grid points of precipitation forecasts together with observed streamflow provide the predictor set for predicting streamflow for each basin. Since these predictors are correlated, it is better to employ principal components regression than multiple linear regression.

Principal Components Regression (PCR), otherwise known as Model Output Statistics (MOS) when employed with gridded predictors, primarily recalibrates large-scale GCM fields or

the principal components of the GCM fields to the observed smaller spatial scale hydroclimatic variable of interest using regression analyses. The predictand could be either streamflow (Q_t) or observed rainfall over a region. PCR not only relates large-scale climatic information to the smaller spatial scale variable of interest, but also eliminates systematic errors and biases in GCM fields by regressing with the predictand fields. Expressing PCR in equation (7):

$$\ln(Q_t) = \beta_0 + \sum_{k=1}^{K} \beta_k * PC_{k,t} + \varepsilon_t \qquad \ldots (7)$$

where Q_t denotes the seasonal streamflow in year't', PC_t^k denotes the 'k'th PCs from the retained 'K' PCs of precipitation forecasts and $\hat{\beta}$ s denote the regression coefficients whose estimates are obtained by minimizing the sum of squares of error. We consider the logarithm of the streamflow as predictand to eliminate the possibility of estimating negative flows. To select 'K' PCs from the predictor set (gridded precipitation forecasts and streamflow), we employ step-wise regression that maximize the correlation between the observed streamflow and predicted streamflow for the chosen validation scheme.

We present the model performance under two types of validation: Leave-one out cross-validation (L1CV) (displayed under Retrospective Forecasts) and Split-sample validation (displayed under Individual Year forecasts). L1CV is a rigorous model validation procedure in which the prediction for t' th year is obtained based on the PCR model developed using the predictand and predictor(s) available over the remaining 'n-1' years. In essence, L1CV develops 'n' PCR models to obtain seasonal streamflow conditioned on the PCs. Under split-sampling validation (SSV), a predictive model is developed using the Q_t and *PCs* over the calibration period (1957-1989) and the developed PCR model is employed for predicting the loadings over the validation period (1991- till date). We also obtain the conditional variance for each year (otherwise known as point forecast error in regression model) to develop ensembles of streamflow by assuming the flows follow lognormal distribution. The performance of the PCR model is summarized based on both deterministic and probabilistic verification measures, which are detailed next.

2.3 Forecast Verification Measures

Ensembles of streamflow forecasts developed under L1CV and SSV for each year are summarized using box-plots. The box-plot gives the various percentiles (to be selected by the user) of the forecasts obtained from the conditional mean and variance of the PCR model. The background of the box-plot also gives the streamflow corresponding to the chosen climatological probabilities. The forecast probability distribution table gives the probability of the forecasted flow occurring under different flow ranges that correspond to different climatological probabilities. For a reliable forecast, the number of times the observed flow exceeded the flow corresponding to a given climatological percentile (p) should be approximately equal to 'p' times the number of years of forecasts considered for verification. For instance, for flow corresponding to the below-normal category (33rd percentile of climatological probability), the observed flow should exceed 67% of the time the flow corresponding to the forecasted 33rd percentile.

The performance of the forecast is also summarized by comparing the conditional mean of the forecast with the observed flows using three different measures: (a) Correlation (b)

Relative root mean square error (R-RMSE) (c) Mean Square Skill Score (MSSS). The correlation is computed as Pearson correlation between the observed and the predicted flows (conditional mean, $\hat{Q}_t$) from the PCR. A good forecast is expected to have a correlation around 1. However, for the correlation to be statistically significant, the computed correlation should be greater than 1.96/ (n-3) ^0.5 where '*n*' denotes the number of years of data used for computing correlation. Relative-RMSE denotes the average error in the conditional mean of the forecasts compared to the observed flows and it is computed using the following equation:

$$R-RMSE = \sqrt{n^{-1}\sum_{t=1}^{n}(1-\hat{Q}_t/Q_t)^2} \qquad \ldots (8)$$

A good forecast is expected to have R-RMSE closer to zero. Another way to summarize the performance of the mean of the forecast is using MSSS. Basically, MSSS is similar to R-RMSE but it compares the mean square error of the candidate forecast with the mean square error of the climatological forecast (which is just the mean monthly/seasonal streamflow ($\overline{Q}$). Expression for MSE of the forecast and climatology could be written as follows:

$$MSE(\hat{Q}_t) = \sqrt{n^{-1}\sum_{t=1}^{n}(Q_t-\hat{Q}_t)^2}\ ;\ MSE(\overline{Q}) = \sqrt{n^{-1}\sum_{t=1}^{n}(Q_t-\overline{Q})^2} \qquad \ldots (9)$$

Based on these two expressions, MSSS could be written as

$$MSSS = 1 - MSE(\hat{Q}_t)/MSE(\overline{Q}) \qquad \ldots (10)$$

For a good forecast, we would expect MSSS should be closer to one. A forecast is considered to be poorer than climatology if MSSS is lesser than zero.

Given that seasonal forecasts are better represented probabilistically using ensembles, expressing the skill of the forecasts using correlation requires summarizing the forecasts using some measures of central tendency such as mean or median of the conditional distribution, which does not give any credit to the probabilistic information in the forecast. Rank Probabilistic Skill Score (RPSS) computes the cumulative squared error between the categorical forecast probabilities and the observed category in relevance to a reference forecast (Wilks, 1995). In general, the correlation of the retrospective forecasts for all the above six sites are statistically significant for the winter season and it ranges from 0.5-0.8. For details on the skill evaluation of these forecasts, see http://www.nc-climate.ncsu.edu/inflowforecast.

3.0 Reservoir Inflow Forecasts Portal Development (Objective 3)

A nice web portal that can both upload and disseminate the streamflow forecasts from the NC-CRONOS database has been developed (http://hatteras.meas.ncsu.edu/ajmcnama/). The portal can display both retrospective forecasts and individual year forecasts along with detailed info on the forecast skill summary. Under individual year forecasts, the user has been provided with the option to download the forecast files under various file formats. Under retrospective forecasts, the skill of the forecasts are summarized using simple correlation, relative root mean square error, mean squared skill score and rank probability skill score. Details regarding the skill measures have also been provided in the website. Both these forecasts and web portal was developed by two graduate students, Harminder Singh and Andrew McNamara, from the

Department of civil, construction and environmental engineering. We have submitted a proposal to the NC-urban water consortium for a continuation project that focuses on the automation of seasonal to interannual streamflow forecasts for these target reservoirs. A manuscript based on the importance of disseminating seasonal inflow forecasts to water managers and their skill over NC will be prepared and submitted to the Journal of American Water Resources Association or to the Bulletin of American meteorological society.

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Appendix I

Notations are self-contained in the report

Appendix II

Two graduate students, Harminder Singh and Andrew McNamara (part-time), worked on this project.

Harminder Singh received third prize in the Annual NC WRRI conference for his poster presentation:
Singh, H., McNamara, A., Boyles, R. and Arumugam, Experimental Reservoir Inflow Forecast, NC Annual Water Conference, March 22-23, Raleigh, NC.

Journal Publication (in preparation):
Singh, H., and A. Sankarasubramanian, Systematic uncertainty reduction in streamflow forecasts development: Importance of Input and Hydrologic Model Uncertainty, Water Resources Research, 2011, to be submitted, 2011.

Using PCR-based Methods to Assess Microbial Contamination from Swine CAFOs in Surface and Groundwaters

Basic Information

Title:	Using PCR-based Methods to Assess Microbial Contamination from Swine CAFOs in Surface and Groundwaters
Project Number:	2009NC123B
Start Date:	3/1/2009
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	7
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Surface Water, Water Quality
Descriptors:	
Principal Investigators:	Bongkeun Song, Lawrence B. Cahoon, Michael A. Mallin

Publication

1. Arfken, A., M.I. Haltom, M.A. Mallin and B Song, 2010, Molecular Detection and Quantification of Swine Fecal Contamination in the Northeast Cape Fear River and Black River, Water Resources Research Institute Annual Conference, Raleigh, NC, March 30-31, 2010.

2011 WRRI Progress report May 2011

Project title: Using PCR-based methods to assess microbial contamination from swine CAFOs in surface and groundwaters

PIs – Dr. Bongkeun Song, Dr. Lawrence B. Cahoon, Dr. Michael A. Mallin,
University of North Carolina Wilmington

Activities and Findings:

We completed Quantitative PCR assays of water samples collected bimonthly from 5 sites (LCO, GCO, 6RC, B210 and COL) in the Black River watershed and 4 locations (PB, GS, SAR and BC117) in the Northeast Cape Fear River watershed. We conducted multiple correlation analyses between the Q-PCR data and the water quality parameters monitored at the sampling stations. The hog waste contamination in the Northeast Cape Fear River seemed to depend primarily on proximity of the sampling site from upstream hog related facilities. Sites furthest away from hog farms (i.e. COL – Colly Creek – only 6 CAFOs in watershed) had the least amount of contamination compared to those directly downstream from a hog facility. On a seasonal basis, all but one site had a spike in hog waste contamination during May 2010. This is most likely a result from run-off or leaching from seasonal spraying of fields with lagoon waste. Future monitoring efforts in this river should focus on sites located near hog CAFOs and processing plants, including sites PB (Panther Branch) and BC117 (Burgaw Creek – processing plant located upstream).

In comparison to the Northeast Cape Fear River, the contamination in the Black River appears to be more related to the sampling location on the river as well as rainfall events. Site 6RC (located on Six Runs Creek), had the highest overall contamination in the Black River watershed. Even though the sampling station is not located in immediate proximity from any CAFOs, there are numerous CAFOs in its watershed (153). With the exception of July 2009 and May 2010, contamination at site 6RC was higher than either GCO (on Great Coharie Creek) or LCO (on Little Coharie Creek). Site 6RC contamination levels were also significantly correlated to rain events on the day of sampling. It would be more informative if monitoring of hog waste contamination was conducted at additional sites located upstream in Great Coharie and Little Coharie Creeks in areas where high densities of CAFOs are located.

The number of students who worked on this project:

Two graduate students seeking MS in marine biology or marine science have worked on this project. One student completed her degree in 2010 and another is in the final stage of degree completion.

Awards or recognition of students:

One graduate student received a travel grant from Southeastern North Carolina local American Chemical Society branch.

Presentations:

1. Arfken, A.**, M. I. Haltom, M. A. Mallin and **B. Song**. 2010. Molecular Detection and Quantification of Swine Fecal Contamination in the Northeast Cape Fear River and Black River. American Chemical Society Meeting, Boston, MA.

2. Arfken, A.**, Haltom, M. I., Mallin, M. A., **Song, B**. 2010. Molecular Detection and Quantification of Swine Fecal Contamination in the Northeast Cape Fear River and Black River. Water Resource Research Institute Conference, Raleigh, N.C..

Publications:
None

Improved Statewide Soil Moisture Estimation for Hydrologic Assessment and Forecasting

Basic Information

Title:	Improved Statewide Soil Moisture Estimation for Hydrologic Assessment and Forecasting
Project Number:	2010NC145B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	NC-02
Research Category:	Climate and Hydrologic Processes
Focus Category:	Drought, Hydrology, Water Quantity
Descriptors:	None
Principal Investigators:	Joshua Heitman, Robert E Austin, Ryan Boyles, Jeffrey G White

Publication

1. Pan, W. 2010. Soil Moisture Characterization with North Carolina Environment and Climate Observing Network. M.S. Thesis, NCSU.

Improved Statewide Soil Moisture Estimation for Hydrologic Assessment and Forecasting

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WRRI Project 70251

Final Report

March 31, 2011

Abstract

Soil moisture is a dominant forcing variable in the terrestrial environment. Yet, routine monitoring of soil moisture at regional scales and with temporal continuity remains a challenging task. Recognizing the potential of the undeveloped framework provided by the NC Environment and Climate Observing Network (ECONet), the goal of this project was to enhance soil moisture monitoring and estimation for North Carolina. We focused on improvements for interpretation of ECONet soil moisture data and also considered the potential for coupling this network with data from NASA's Advanced Microwave Scanning Radiometer for Earth Observing System (AMSR-E). Objectives were to: 1) Characterize soil properties at the ECONet soil moisture monitoring sites, 2) Determine the distribution of NC ECONet stations with respect to soils, 3) Assess spatial and temporal relationships among ECONet and AMSR-E soil moisture observations, and 4) Gauge the potential of AMSR-E data to improve spatio-temporal estimation of soil moisture statewide. We investigated soil physical properties at 27 NC ECONet soil moisture monitoring stations in the piedmont and coastal plain regions of North Carolina. Soils at ECONet sites fall in seven textural classes. Porosities ranged from 0.36 to 0.58 cm^3 cm^{-3}, suggesting a wide range of upper boundaries for soil water content. Diversity was also found for other parameters, such as field capacity and wilting points. Strong correlations were found between the soil physical parameters. A principal component analysis reduced 10 soil physical parameters into three principle components that explained 85% of the variability within the dataset. Analysis of variance of select, semi-qualitative soil taxonomic classes for seasonal and whole-year ECONet soil moisture revealed that the greatest significance was for the taxonomic descriptor particle size class. Multiple linear regression analysis of ECONet seasonal soil moisture with measured soil physical properties suggested two water retention parameters, along with potential evapotranspiration, were most significant. The strong relationship between individual parameters revealed through correlation and principal component analysis, as well as the significance of only a few soil parameters in the multiple linear regression, suggests that the influence of soil physical properties on ECONet soil moisture might be explained by measurement of a subset of soil properties. Coupled with results based on analysis with soil taxonomy, the most appropriate soil property measurement may be particle size distribution (i.e. texture). Poor spatial correlation of daily, statewide ECONet soil moisture was observed and may indicate that interpolation of ECONet soil moisture data is not warranted. This result may be due to the relatively low number of ECONet sites available and the distances between these. Statewide spatial correlation did improve with longer time scales, which is reasonable given that these longer time scales integrate a highly spatially and temporally variable parameter. AMSR-E soil moisture data cannot presently be used with ECONet soil moisture for interpolation since they are not correlated on a statewide scale. This may be due in part to AMSR-E's low estimates and damped variation with respect to ECONet. The correlation did improve over seasonal and annual time scales. AMSR-E soil moisture data displayed strong spatial correlation. Continuing research will look at whether AMSR-E brightness temperature is more strongly correlated with ECONet soil moisture than is AMSR-E soil moisture. Overall, results provide opportunity for improvement of soil moisture data offerings from ECONet, but further research is warranted to support efforts at continuous statewide soil moisture estimation.

Acknowledgements

Two graduate students, Weinan Pan and Christopher D'Aiuto, contributed significantly to this work as part of their M.S. thesis research in the NCSU Soil Science Dept. Weinan Pan led field sampling of soil properties and assessment of data quality for the NC ECONet. Chris D'Aiuto led spatial and correlation analysis of NC ECONet and AMSR-E data.

Additionally, significant contributions were made by Ameenulla Syed, Sean Heuser, and Ashley Frazier from the State Climate Office of NC and Matthew Taggart, Adam Howard, and Chris Niewoehner of the NCSU Soil Science Dept.

We thank the NC WRRI for funding support and also recognize the Southeast Climate Consortium for partial support of student assistantships.

Introduction

North Carolina has recently been subject to both regional and statewide droughts. These droughts have required restrictions on water usage for more than half of the State's citizens and cost the State millions of dollars in drought-associated losses. Drought conditions are the result of large-scale climate patterns. However, rainfall's direct influence on water supplies is determined by the interaction between climate and local land conditions. Land cover, soil type, topography, and antecedent soil moisture combine to affect partitioning of rainfall between runoff, groundwater recharge, soil moisture storage, and evapotranspiration (Brocca et al., 2008; Zhang and Schilling, 2006; Maurer et al., 2004). While land cover, soil type, and topography are relatively constant on short timescales, antecedent soil moisture is a dynamic hydrologic state variable. Temporally fluctuating soil moisture conditions are important in determining the direct effects of rainfall events on water supplies. Without an adequate understanding of soil moisture conditions, predictions of event-based and seasonal variations in hydrologic response are unreliable (De Michele and Salvadori, 2002; Entekhabi et al., 1999). Soil moisture status also provides a primary indicator of drought recovery following lapses in normal rainfall (Basara et al., 1998).

The overall importance of soil moisture as a forcing variable in terrestrial environments is widely recognized (Vereecken et al., 2008; Robinson et al., 2008; Seneviratne et al., 2010; Legate et al., 2011). Soil moisture significantly influences weather and climate, plant growth and productivity, hydrology, and soil ecology (i.e., carbon/nitrogen dynamics, trace gas emissions). Because of these broad potential applications, the need for compilation of extensive and intensive soil moisture information has also been recognized for several decades (e.g., Robock et al., 2000; Western and Grayson, 1998).

Research efforts to develop new techniques for monitoring soil moisture also continue, often with focus on large scale monitoring. One prominent area of research is remote sensing (Engman and Chauhan, 1995; Jackson, 1993; Jackson and Schmugge, 2002). Remote sensing techniques offer promise; however, many provide information only for the top few centimeters of the soil (Robinson et al., 2008). Therefore application of remotely sensed soil moisture data may be limited for conditions at typical plant rooting depths or for other ecological and hydrological applications without significant complimentary information (Houser et al., 1998; Robinson et al., 2008). Most remote sensing techniques also require extensive ground-based validation before application (Arya et al., 1983; Njoku et al., 2003; Drusch et al., 2004, Cosh et al., 2004). Thus, ground-based observation of soil moisture remains important even as remote sensing techniques improve (Georgakakos and Baumer, 1996; Western et al., 2002; Robinson et al., 2008).

Efforts have also been made to develop regional-scale, ground-based soil moisture monitoring; examples include the Oklahoma Mesonet (Illston et al., 2008), the Illinois Soil Moisture Network (Hollinger and Isard, 1994), and the USDA Natural Resources Conservation Service Soil Climate Analysis Network (Schafer et al., 2007). A potential limitation of such networks is that they represent soil moisture only at the point of observation, which may differ significantly from surrounding areas (Scott et al., 2010).

Vachaud et al. (1984) proposed the concept of temporal stability for soil moisture, which attempts to explain patterns in soil moisture that persist in time. Vachaud et al. (1984) and other researchers (e.g., Martínez-Fernández and Ceballos, 2005; Western et al., 1999) have

demonstrated, beyond the idea of temporal stability, the role of soil and landscape properties in extending point soil moisture information to describe patterns in soil moisture across the landscape. It is critical that, as ground-based soil moisture networks continue to develop, soil moisture observations should be accompanied by careful inventory of soil and landscape properties in order to understand patterns in soil moisture. Furthermore, to apply or even to check quality of soil moisture monitoring data, collection of metadata is critical (Scott et al., 2010). However, a vast number of soil properties can potentially be considered in terms of characterizing soil moisture dynamics. Among the key soil parameters frequently assumed important are soil texture and particle size distribution (Loague, 1992; Saxton et al., 1986; Ritsema and Dekker, 1994; Western et al., 2002), bulk density and porosity (Gupta and Larson, 1979; Saxton et al., 1986, Rodriguez-Iturbe, 1995; Wagner et al., 1999), water retention characteristics (Rawls et al., 1982, Feddes et al., 1988; Wagner et al., 1999; Western et al., 2002), and hydraulic conductivity (Feddes et al., 1988, Western et al., 2002). Clearly, characterizing all these properties requires a significant investment in time and resources, and choice of properties to characterize must be considered carefully.

In North Carolina, the State Climate Office (SCO) currently provides soil moisture data to the public through the NC Environment and Climate Observing Network (ECONet; http://www.nc-climate.ncsu.edu). The ECONet is a near real-time, point-based, state-wide monitoring network providing soil moisture data at a single depth (20 cm). Data collection at the first sites began as early as 1998 with new sites added periodically since that time; there are currently 36 stations state-wide (Fig. 1). While this information is potentially useful, the current network was not designed to represent soil moisture conditions in major soil units. Instead, network monitoring sites were chosen to maximize spatial coverage and make use of existing meteorological monitoring frameworks irrespective of specific soil patterns. The connection between soil moisture status at these monitoring locations and regional soil moisture status for the diverse set of soil and land conditions in the State is not well defined. Thus, despite availability of soil moisture data, these data may be of limited use for characterizing conditions that contribute to regional storm response and water availability. Furthermore, within the existing monitoring framework, there have been no efforts made to characterize soil properties at the monitoring sites to aid interpretation of how monitored soil moisture conditions affect processes in the surrounding soils and landscapes.

Recognizing the potential of the undeveloped framework provided by the NC ECONet, the goal of this project was to enhance soil moisture monitoring and estimation for a diverse clientele in NC. We focused on improvements for interpretation of ECONet soil moisture data and also considered the potential for coupling this network with remote sensing data. Specific project objectives were to:

1) Characterize soil properties at the ECONet soil moisture monitoring sites to develop network metadata and new ECONet soil moisture products.

2) Determine the distribution of NC ECONet stations with respect to soils using site characterization data and existing geospatial data layers in order to define linkages between soil moisture observations at monitoring locations.

3) Assess spatial and temporal relationships among ECONet and NASA's Advanced Microwave Scanning Radiometer for Earth Observing System (AMSR-E) soil moisture observations.

4) Gauge the potential of the passive microwave radiometry data to improve spatio-temporal estimation of soil moisture status statewide.

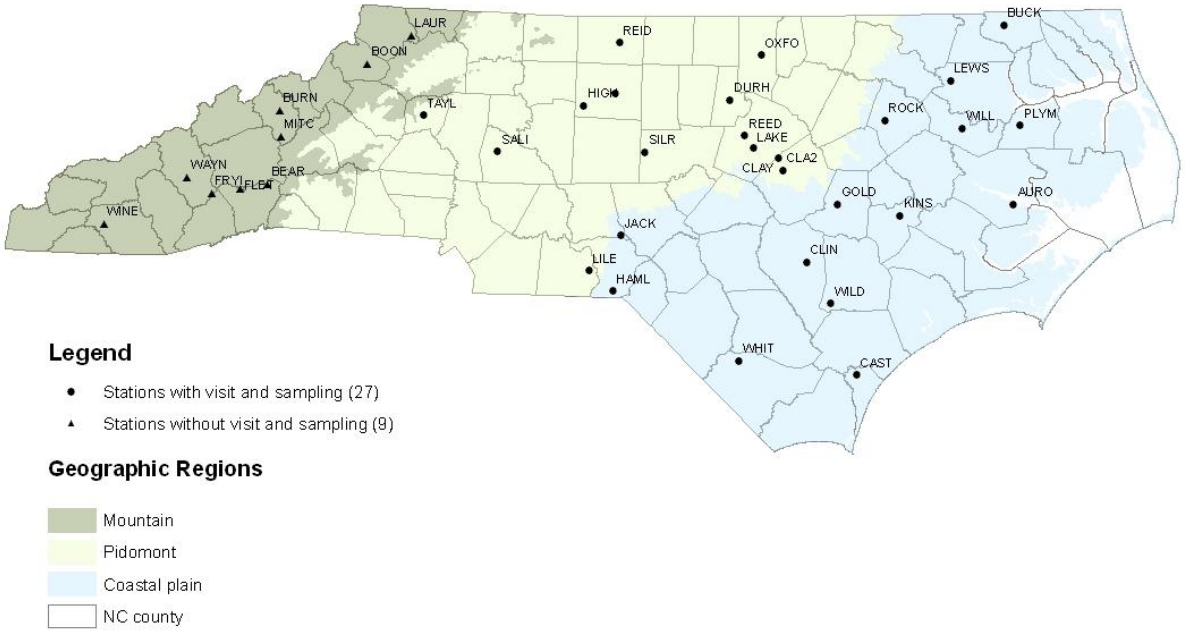

Figure 1. Study Area with Sampled and Unsampled ECONet Sites.

Methods

Soil Physical Property Characterization and Statistical Analysis

At the time of data collection for this study, there were 27 NC ECONet stations within the coastal plain and piedmont regions of NC (Fig. 1). Data were collected from each of these sites; data collection in the mountain region is on-going at the time of this report. The landscape at individual stations within the coastal plain and piedmont varies according to local topography, but sites are generally positioned on locally level (< 5% slope) terrain. Land use history at each site varies, but most sites can be assumed to have been used for agriculture practices at least some time during the past hundred years. Current vegetation at each site is a mix of native and introduced grasses and weeds.

For each station, soil moisture data are collected at the 20 cm depth every 30 min, producing 48 observations per station, per day. The soil moisture sensor currently installed for the NC ECONet is the Theta Probe ML2X (Delta-T Devices, Cambridge, UK). The volume measured by the

sensor is approximately 75 cm^3 (Kaleita et al., 2005). The sensor installation depth and approximate observation volume were used to guide the soil sampling protocol.

Sampling in the coastal plain and piedmont regions was conducted during the period between February 2009 and May 2010. Altogether, 81 intact soil cores, as well as additional bulk samples, were collected from the sites. Though it was not possible to sample at the exact location where sensors were installed, it was intended that the soil being collected have characteristics similar to the soil where the moisture sensor was installed. Sampling spots were randomly selected within a 3- meter radius circle centered at the approximate location of the sensor. Three 7.6 cm length, 6.3 cm diameter intact soil cores, centered at 20 cm soil depth, were collected as replicates at each site. Sampling was performed using an AMS soil sampler (AMS, Inc., American Falls, ID). A pilot hole was used to access the appropriate sampling depth. Upon retrieval, cores were sealed with caps to protect their integrity and immediately weighed in the field to determine field water content. Cores were then transported to the laboratory for the determination of water retention, saturated hydraulic conductivity and bulk density. Loose soil samples were also collected simultaneously at the 20 cm depth for additional water retention measurements and soil textural analysis.

Laboratory analyses on soils were performed during the same time period as soil sampling. The intact soil cores were used to determine saturated hydraulic conductivity values (Ks) by the constant-head method as described in Klute (1986). The falling head method (Klute, 1986) was applied to soil cores that did not exhibit measureable flow with the constant-head measurement during a 4 h period. After Ks measurements, water retention measurements at pressure of 10, 33, 66 kPa (hereafter referred to as P10, P33, and P66, respectively) were performed using a chamber method for the same intact cores (Klute, 1986). After saturation, gas pressure was applied in steps, and the volume of outflow after equilibrium at each pressure step was recorded. At the final pressure step, the samples were weighed, oven dried at 105 °C for 24 h and reweighed. Total porosity (TP) and bulk density (BD) were calculated from the dry weight and sample volume of the intact sample, assuming the particle density was 2.65 g cm^{-3}.

Water retention measurements at 100, 500 and 1500 kPa pressure (hereafter P100, P500 and P1500, respectively) were determined with disturbed samples following similar procedures as described by Klute (1986). An additional parameter, air-dried water content (AD), was measured by allowing saturated, disturbed soil samples to dry to a constant weight under constant temperature and humidity (approximately 22 ºC and 30%, respectively). Particle size distribution was determined using the hydrometer method (Klute, 1986) . Hydrometer reading were made at 0.5, 1.5, 360, and 960 minutes to determine the percentage of clay, silt and sand.

Parameter values for the three replicate cores at each site were arithmetically averaged to obtain a single value for each parameter except for Ks. The skewness test (Tabachnick and Fidell, 1996) revealed that Ks values are highly skewed among replicates compared with all the other variables. Thus, they were transformed using the log transfer method to a nearly normal distribution, then back transformed after averaging. Based on analyses, a soil properties dataset including 13 parameters for each of 27 ECONet station was generated. Selected variables were analyzed using classical statistical methods to obtain the minimum, maximum, mean, median, standard deviation and coefficient of variation (CV).

A correlation analysis was performed on 10 of the 13 parameters (excluding Ks, TP and silt content) via a correlation matrix. Values for Ks were excluded because of local heterogeneity amongst replicates. Porosity and silt content were excluded since they were derived from BD and total content of sand and clay, respectively, and were therefore directly related to other subsets of parameters. Following correlation analysis, a principle component analysis (PCA) was used to assess the overlap of individual parameters and collapse correlated parameters into a smaller subset of uncorrelated parameters. Prior to this analysis, the data were normalized to an average of zero and standard deviation of one.

Analysis of Relationships between ECONet Soil Moisture Observations and Soils

Continuous observations of soil volumetric moisture content (θ), along with climatological parameters of precipitation and potential evapotranspiration (PET), at the sampling sites were retrieved from the NC ECONet database. For this work, we used the ECONet dataset from May, 2008 to April, 2009, which was the most recently available complete annual cycle (Pan, 2010). The average one-year precipitation across all sites was 98 cm, which was 25 cm lower than the 30-year normal. However, this period was chosen because it provided the most complete dataset across all sites. With the exception of six stations with unavailable or problematic data (Pan, 2010), 21 stations provided a total of 7665 θ observations (on a daily basis) included in this study. We further subdivided this period into two intervals: 'growing season' from May, 2008 to October, 2008 and 'non-growing season' from November, 2008 to April, 2009. Whole-year and seasonal average soil moisture content at sampling sites were compiled from daily monitoring records for corresponding ECONet stations. Other desired parameters, precipitation and PET, were obtained in the same manner. A paired-sample T-test was performed for differences in precipitation, soil moisture and PET in discrete periods in the studied area.

Physical properties were also extracted from the taxonomic descriptions for each soil family. Rather than numeric parameters, physical properties at the family level were qualitative taxonomic descriptors shown in the form of classification. Soil moisture content at the sensor depth is not only controlled by soil properties at the measurement depth, but also by the characteristics of the soil profile including multiple horizons (Ghosh, 1980; Hillel, 1971). Thus, we chose these taxonomic descriptors based on the pedological horizon (20-100cm) that represents the major characteristic of the profile and, according to Wosten et al. (1985), are highly related to soil hydraulic properties. The taxonomic descriptors and their classes for soils are summarized in Table 4.1. Once the descriptor classification had been determined for all the sites, the analysis proceeded to investigate the correlation between soil moisture content and soil taxonomic descriptors.

One-way analysis of variance (ANOVA) was performed for each taxonomic descriptor to determine if θ varied over the classes of that descriptor. That is, we attempted to identify if some known taxonomic descriptor of the soils could be used as the determinant factor for the soil moisture pattern. ANOVA was chosen since the parameters for the entire soil profile were only available as qualitative descriptors. In ANOVA, means of θ with sites in the same descriptor category were used for comparison. If ANOVA results specified significant differences from one class (based on a single descriptor) to another, that descriptor was identified as a property associated with θ variation. Further analysis was performed to determine if the variation in θ

pattern could be better explained by the combination of two determined descriptors identified in the previous ANOVA test. For instance, results suggested θ was influenced by particle size and wetness class (in descriptor classifications) of the soil in individual one-way ANOVAs. A two-way ANOVA analysis could show the proportion of total variation in θ attributed to each descriptor. Here, a combination of descriptor classes was used instead of two-way ANOVA because of the absence of descriptors for two sites with "Udorthents" soil (classified as "other" in descriptors). It essentially serves the same purpose as two-way ANOVA by simultaneously including statistically important factors in the previous step. If the P-value is improved over results when using either descriptor alone, the information contained in one descriptor could not be enough to describe θ patterns in the studied area.

In addition to using soil descriptors available from soil maps, attempt was made to quantify the relationship between observed θ and measured soil physical properties. Forward stepwise (SPSS, 2000) multiple linear regression (MLR) analysis was performed using the means of daily θ at each sampling site. In order to include both locational and temporal variation in precipitation and PET, seasonal means were selected. The MLR was designed to pick the most important influences on θ (in the sense of the significance level for each parameter). In the preliminary test, 10 soil hydraulic parameters (the same parameters analyzed in PCA), and two climatological parameters (precipitation and PET) were included. The number of predictive variables was reduced by evaluating the corresponding P-value for each parameter leading to a reduced model containing only significant variables.

Spatial and Temporal Correlation of ECONet Soil Moisture Observations

Assessments of ECONet θ data quality by Pan (2010) suggest that there are stations that have had more than half of several years with either missing or poor quality data. Data quality was particularly bad before 2005. Three stations maintained poor quality through 2009: Durham, High Point, and Siler City (DURH, HIGH, SILR). Based on station number and data quality considerations, we chose to use data from 2007 through 2009 for this portion of the analysis. Also, the AMSR-E data (next section) are available beginning in 2004. There were 31 stations at the start of 2007, but two were removed from study because of poor data quality (HIGH and SILR), leaving 29 stations for analysis.

We began by examining the difference in spatial correlation between wet and dry days across the ECONet. To do this, we examined precipitation records from the State Climate Office to determine the months of highest and lowest rainfall. These were September 2008, and May and November 2009 for wet months, and November 2007, June 2008, and February 2009 for dry months. NC's Storm Event Database was used to find a large precipitation event that might have covered the whole state. We expected such an event to provide a short period of relatively uniform θ across the state. Tropical Storm Hanna in September 2008 was the only storm found in the study period that generally went east to west over the state.

Daily-averaged ECONet θ data were then used to find specific wet and dry days within the wet and dry months noted. These were chosen considering representative sites, peaks of wet and dry, and uniformity across the state. The SCO provided a subset of stations that represent average conditions for the state's three physiographic regions. These were: Waynesville (WAYN) and Fletcher (FLET) in the mountains; High Point (HIGH), Rockingham (ROCK), and Jackson

Springs (JACK) in the piedmont; and Plymouth (PLYM), Aurora (AURO), and Castle Hayne (CAST) in the coastal plain. Their daily averaged θ data were reviewed for peak dry and wet days within the considered months. The most coincident peaks (for wet and dry conditions) for all eight stations were chosen as the representative dates. The wet dates were 6 September 2008, 18 and 19 May 2009, and November 2009. The dry dates were 14 November 2007, 18 June 2008, and 17 February 2009. This task was inherently difficult in that what happens on the coast is not generally occurring in the mountains, and vice versa. The dates, therefore, were an average of the wettest days for most stations, and were weighted toward the date when most stations had received rainfall.

In order to quantify spatial correlation, a semivariogram is used. It is a graph of the semivariance, i.e., half the average variance between all pairs of points a selected lag distance h_i apart, as a function of h_i. Practically, the semivariance is calculate for pairs of points that lie within a range of lag distances, the bin, which results in a corresponding range of semivariances. These so-called semivariance clouds are plotted and modeled via regression to produce the semivariogram model. Conceptually the semivariogram tells us at what distances values are more alike, i.e., more correlated (low semivariance) and at what distance the semivariance reaches or approaches the population variance. This semivariance plateau is called the sill. The distance at which the sill occurs, i.e., where the variance between points approximates the sample variance, is called the range of spatial correlation. The nugget is the semivariance extrapolated to a lag distance $h = .0$. In theory the nugget should be zero; that it often is not is due to experimental error and spatial correlation at scales smaller than the shortest sampled lag distance. The degree of spatial correlation is indicated by the nugget:sill ratio, which tells us what proportion of the population variance is non-spatial. The smaller the nugget:sill, the greater the degree of spatial correlation; 1- (nugget/sill) is the proportion of variance attributable to spatial correlation. We used the geostatistical software GS+ (Gamma Design, Plainwell, MI) to generate our semivariograms.

Analysis of AMSR-E Soil Moisture Data and Comparison with ECONet

AMSR-E is one instrument on board NASA's AQUA satellite. AQUA's mission is to gain more understanding about Earth's water cycle in all its forms: ice, snow, ocean water, atmospheric water, soil moisture, etc. Also on board is the Moderate Resolution Imaging Spectroradiometer (MODIS), which gives vegetation indices that might be useful in refining AMSR-E's θ estimation. Accuracy of estimation of θ via passive microwave radiometers is affected by the extent and magnitude of vegetative cover. In addition, vegetation affects θ directly via evapotranspiration. These datasets are global in scale, so the information can be applied beyond NC if warranted. AMSR-E data are available without cost via a variety of data pulls from the National Snow and Ice Data Center (NSIDC) in Boulder, CO.

AMSR-E estimates soil moisture by sensing the microwaves emitted by the surficial 1 cm of soil. It records these as brightness temperature (Tb). Because of the contrast between the dielectric properties of water versus soil solids, the strength of the microwave, (i.e., the brightness temperature, Tb) is a function of θ. AMSR-E passes over NC every other day with a statewide view using the ascending pass. The data are sampled at varying spatial densities, but averaged and served in a standardized global Equal-Area Scalable Earth Grid (EASE grid) with 25- by 25-

km cells. The State contains 209 such cells. In theory, θ is sensed with an accuracy of 0.06 g cm^{-3} in low vegetation conditions. Large water bodies, high vegetation biomass, and changes in topography all negatively affect accuracy of estimation of θ via passive microwave radiometry.

To correct for these interferences, an algorithm that incorporates parameters for soil types, vegetation, surface roughness, and quality checks is used to estimate θ from the raw temperature brightness data. The data are also flagged for ice, permafrost, snow, precipitation, radio frequency interference, and vegetation density. To date, we have been unable to find the actual algorithm well described in the literature. For example, other than Tb, we do not know exactly which auxiliary parameters appear in the model and which of these are dynamic and which are static. An R script was used to pull Tb, θ, Date, Latitude, and Longitude from L3 data for a rectangular area over the entire state in order to examine relationships between θ estimated by the algorithm and Tb.

The AMSR-E θ data comes in hierarchical data files (.hdf) and requires special procedures to view and manipulate. Using grid georeferencing, we subset the data to select only the grid cells covering NC. So-called Level 3 data, which include the θ estimates in EASE grid cells, were viewed in ArcGIS. L2B data is also averaged into the EASE grid, but is stored in a table format. It can be loaded into ArcMap by adding it as XY data. Using L2B also has lower memory requirements (L2B: 1 MB; L3: 63 MB). We also used HDFView (HDF Group, 2011) to view the data, copy tables, and other limited options. Both data types and programs were used to analyze AMSR-E θ data.

Results and Discussion

Characteristics of Soil Physical Properties

It is necessary to recognize that there is natural variation amongst sampling locations at each station site which may limit representativeness of individual samples for describing the soil properties at the actual sensor location (Scott, 2010). For example, in the present dataset the CV for Ks among replicates at a given site exceeded 50%. The rest of the parameters, however, were relatively consistent between the three replicates at each site with CV's < 5% (data not shown). Limited local variation in soils data obtained from small soil cores obtained within a spatially confined area has also been reported by others in similar approaches (Basara and Crawford, 2000) or on similar soils (Cassel, 1983). Because variation among individual parameters was small for all parameters except Ks, we focus the remaining discussion on comparison of mean properties from site to site rather than local variation at a given site. The full data set for parameters measured at each site is provided in Pan (2010).

Descriptive statistics of selected soil physical properties among the 27 ECONet stations are shown in Table 1. Based on the skewness and CV, several of the variables can be described as having a normal distribution. Soil bulk density was normally distributed from 1.10 to 1.69 Mg m^{-3} with normality indicated by the slight difference between mean and median. Similarly TP, derived from BD, was normally distributed. While sand content was normally distributed, clay and silt content were skewed judging by their skewness values and the difference between mean and median. The texture distribution (i.e. combination of sand, silt, and clay) of sampling sites is shown within an alternative texture triangle in Fig. 2. The soil texture at ECONet sites is

distributed within seven classifications, with most points falling within the four classifications loam, sandy clay, sandy loam and loamy sand. Texture points clustered in the area with sand percentage greater than 40% and clay percentage less than 40%. The relatively higher CV (80%) for clay content could be explained by noting that one station had observed clay content of 55% while all other stations had clay content < 40%. The reason for a CV of 50% in AD may be caused by a similar reason since AD may be highly dependent on the content and mineralogy of the clay fraction (Sumner and Kamprath, 2000).

Table 1. Descriptive Statistics for Selected Physical Properties at ECONet sites in the Piedmont and Coastal Plain.

Parameter	Mean	Median	Max	Min	SD	Skewness	CV (%)
BD, Mg m^{-3}	1.42	1.43	1.69	1.10	0.17	-0.34	12
TP, m^{-3} m^{-3}	0.46	0.46	0.59	0.36	0.06	0.33	13
Log Ks, cm h^{-1}	0.65	0.70	1.15	-0.32	0.33	-1.1	47
Clay, %	15	11	53	2	12	1.54	80
Sand, %	63	64	90	24	17	-0.30	27
Silt, %	22	16	49	4	13	0.72	59
AD, m^3 m^{-3}	0.02	0.02	0.07	0.01	0.01	1.84	50
P33, m^3 m^{-3}	0.28	0.29	0.50	0.13	0.09	0.14	31
P1500, m^3 m^{-3}	0.10	0.09	0.19	0.04	0.04	0.56	44
PAW, m^3 m^{-3}	0.18	0.19	0.33	0.07	0.06	0.43	32

Field capacity and wilting point, corresponding approximately to P33 and P1500, are two commonly used reference points for soil moisture observations. There are wide ranges for both of these parameters among the 27 stations; P33 ranged from 0.13 to 0.50 m^3 m^{-3} and P1500 ranged from 0.04 to 0.13 m^3 m^{-3}. Strong positive correlations with clay content were observed for both P33 and P1500, with r^2 of 0.66 and 0.80, respectively, for the best fit power model (Fig. 3). Another common parameter of interest for soil moisture observation, plant available water content, the difference between field capacity and wilting points, is shown as the area between the two curves in Fig. 3 as well as in Table 1. The general trend for plant available water content is apparent as it increases with clay content for these sites. However, the correlation ($r^2 = 0.18$, fitted power model not shown) was much weaker.

Results from simple statistical analysis clearly indicate that soil physical properties are highly varied among the 27 studied ECONet stations of the piedmont and coastal plain. More importantly, the physical heterogeneity would be reflected in distinct hydraulic behavior. For example, the maximum possible θ (i.e., TP) at sites within the network ranges from 0.36 to 0.59 m^3 m^{-3}. The difference between the upper and lower end of this TP range would result in a very different interpretation for the same numerical value of θ observed at different sites. Though slightly less pronounced, differences at the dry end of the soil moisture range (e.g. P1500) are also substantial. The wide range in observed soil characteristics within the network illustrates the importance of collecting soil physical properties data for soil moisture monitoring in an expansive network such as NC ECONet. This information is not only potentially useful for

quality control of soil moisture data collected in the network but also enhances the potential for interpretation of soil moisture data.

Correlations and Parameter Reduction for Soil Physical Properties

The soil physical parameters are generally linearly correlated; Table 2 is the correlation matrix, listing the correlation coefficients and significance level. Bulk density is only weakly statistically correlated with most other parameters. The literature on the relationships between BD and other soil physical properties are not very conclusive. For Example, Manrique and Jones (1991) noted that the nature of the relationship between bulk density and clay content was different between soil types. While, Williams (1970) found that the relationship between bulk density and soil texture was dependant on landuse and management. Considering that ECONet sites are located in the different land parcels with variable soil type and historical land use, these prior observations are compatible with our observation of the weak relation between BD and other soil physical properties.

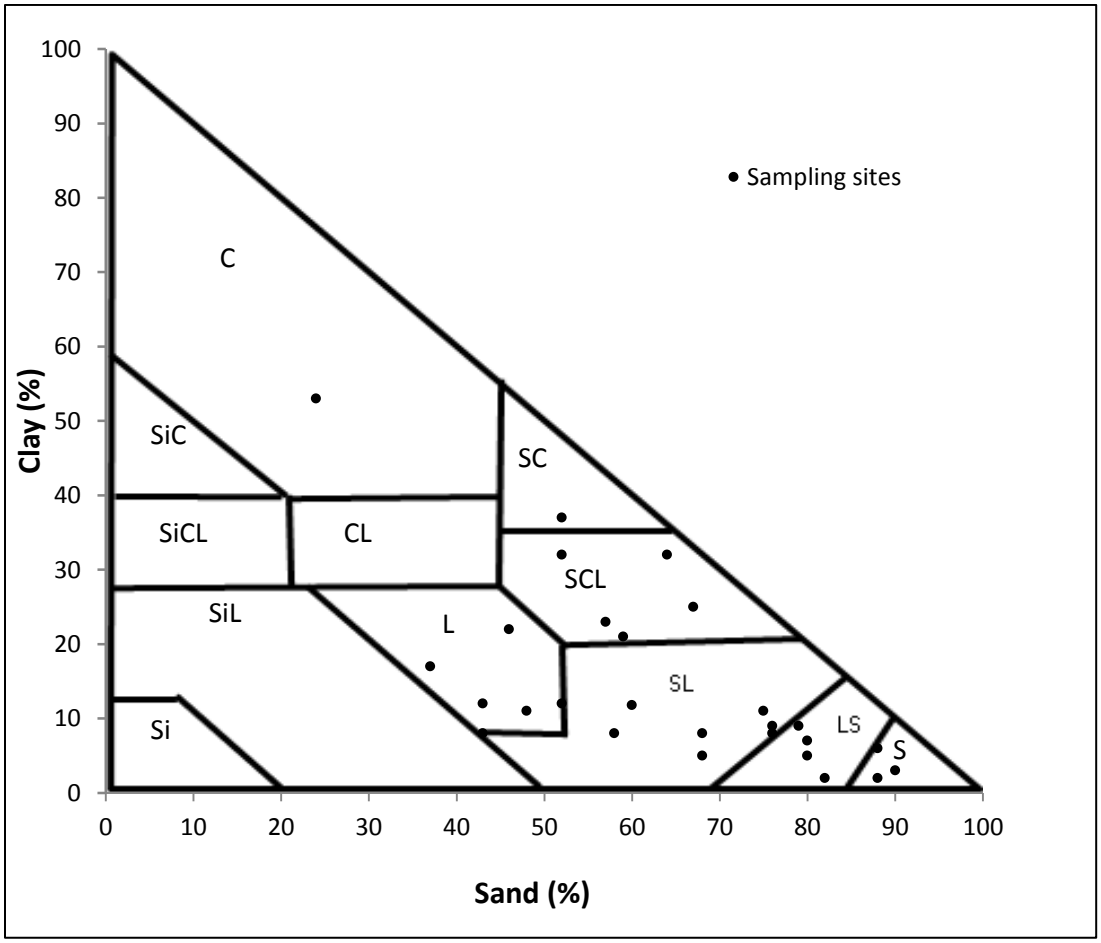

Figure 2. Textural Triangle with Distribution of Sampled ECONet Sites. Texture classes are as defined by the USDA classification system.

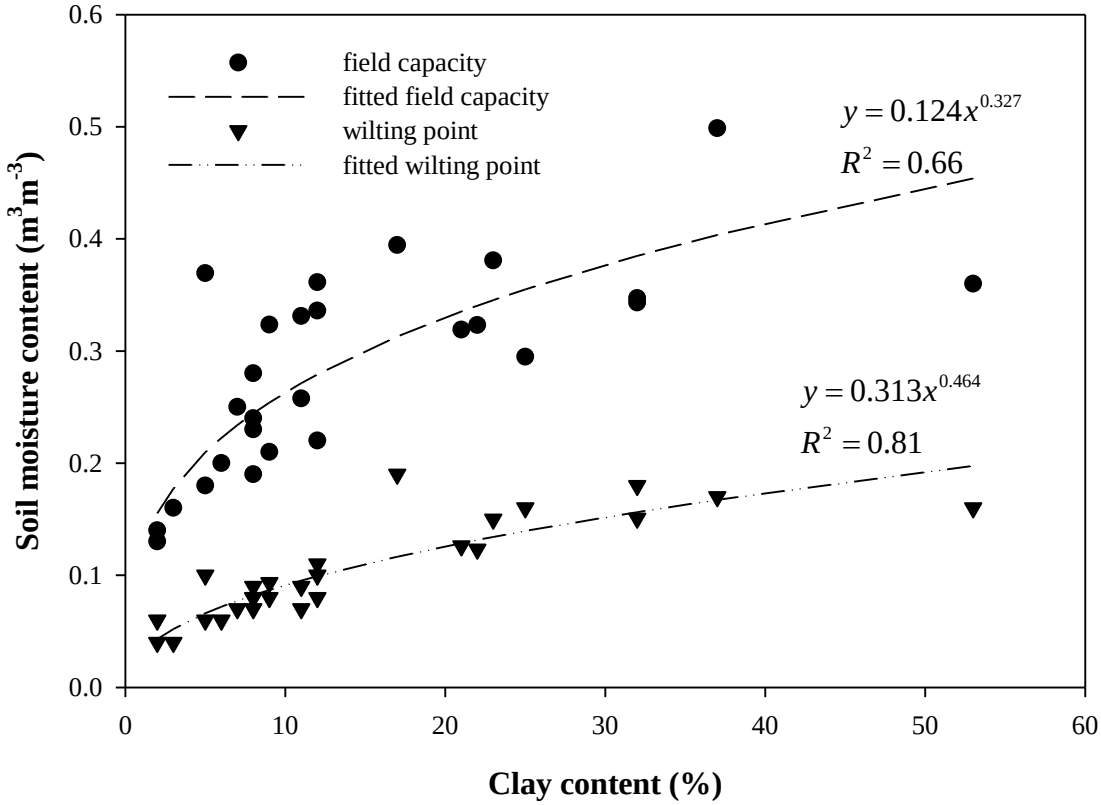

Figure 3. Field Capacity and Wilting Point Relationships to Clay Content. The equations for the fitted lines are given next to the lines.

Table 2. Correlation Matrix (lower triangle) for Measured Soil Physical Parameters.

Parameter	BD	Clay	Sand	AD	P10	P33	P66	P100	P500	P1500
BD	1.00									
Clay	0.047 ns	1.00								
Sand	-0.19 ns	-0.65***	1.00							
AD	0.018 ns	0.48***	-0.35**	1.00						
P10	-0.37**	0.54***	-0.50***	0.17ns	1.00					
P33	0.24ns	0.67***	-0.71***	0.21 ns	0.50***	1.00				
P66	0.22 ns	0.65***	-0.72***	0.18 ns	0.47***	0.96***	1.00			
P100	0.47***	0.68***	-0.68***	0.29 ns	0.25 ns	0.80***	0.78***	1.00		
P500	0.28*	0.72***	-0.70***	0.048 ns	0.35**	0.73***	0.70***	0.82***	1.00	
P1500	0.26*	0.83***	-0.68***	0.223*	0.44**	0.83***	0.81***	0.85***	0.89***	1.00

ns, non-significant; ***,** and *, significant at p = 0.01, 0.05, 0.1, respectively.

Water retention parameters are positiviely correlated to clay content with the strength of the correlation increasing at the highest pressures (e.g. P1500). This is as expected since the amount of water held at and after 1500 kPa pressure is primarily a function of soil texture, especially clay content (Stewart and Howell, 2003). The correlation for AD and clay content is weaker, but at very dry conditions mineralogy, not just clay content, may also be important. The more narrow range in observed AD also likely weakens the correlation. Individual water retention parameters are highly correlated in most cases, which is not surprising given that all represent a portion of the same pore-size distribution for a given soil. It may be noteworthy that P10 tended to be less strongly correlated with other parameters, or in the case of P100, uncorrelated. AD may also be viewed as another water retention parameter; AD showed no significant correlation to all other water retention parameters besides P1500 (P = 0.1), which is the next driest water retention parameter. As indicated above, AD may be more closely related to mineral type (and possibly specific surface area) than other water retention parameters.

There are two main exceptions to the positive correlation observed for most parameters. One is sand which is negatively correlated with all the other parameters. Strong negative correlation (P = 0.01) between sand and clay content observed in our study is well recognized (Coffin and Lauenroth, 1992; Kaiser et al., 1992; Rostagno, 1989). The negative correlations between sand content and water retention parameters are consistent with the positive correlations between clay content and water retention parameters. Another expection is negative correlation between BD and P10 (P = 0.05), which may be explained by the negative physical relationship between BD and soil porosity (i.e. void space) for retaining water at low pressures.

The dataset yields a KMO value of 0.778 which indicates that the degree of variance among the tested parameters is greater than the minimally accepted level of 0.7 to conduct a PCA (Pallant, 2001). A significance value of 0.000 for Bartlett's test of sphericity also reinforced that the parameters are suitable for a PCA (Pallant, 2001). In PCA, latent roots and vectors of the correlation matrix were extracted to reaveal a more clear relationship among the parameters. The first three eigenvalues are listed in Table 3. The first principle component (PC) accounts for more than 59% of the variance, whereas the second and the third PCs account for only an additional 15% and 10%, respectively. This confirms the results of the above correlation analysis that all the variables are generally strongly correlated as the first 3 PCs could explain 85% of the total variance.

Table 3. Eigenvalues of Correlation Matrix for Principal Component Analysis of Soil Physical Properties.

	Initial Eigenvalues		
Component	Parameters	Variance	Cumulative Variance
		%	%
1	6	60	60
2	2	15	75
3	1	10	85

In Table 4, the configuration rotated by varimax of the first three PCs is reported with the correlation coeffiecients between the original variates and the PCs. The parameters clay, sand, P33, P66, P100, P500, and P1500 appear closely related, loading on the first PC. The close correlation suggests that, as described above, soil texture has a strong influence in determination of soil water retention characteristics. Bulk density and P10 are strongly correlated with the second PC, but in opposed positions. Air-dried water content has the strongest association with the third PC.

Table 4. Correlations Between Original Variates and the First Three Principle Components.

	Component		
	1	2	3
Parameter	Weights[1]		
BD	27	87	18
Clay	85	-24	20
Sand	-83	9	-8
AD	33	-26	90
P10	53	-71	-22
P33	92	2	-14
P66	90	2	-16
P100	89	30	7
P500	87	16	-21
P1500	94	7	-8

[1]Values were muliplied by 100 and rounded to the nearest integer.

Loading plots (Fig. 4) project the linear objects onto the new reduced space representing the main part (85.1%) of total data variance, thus it is possible to investigate interelations through the cluster of points. If a variable is close to another, the variables will have influence on each other. Conversely, if a variable is distant from another, the influence will be inverse. The projections onto the axes indicate the relative contributions for the corresponding components (Norušis, 1993). The loading plots delineate separate groups of highly intercorrelated, or similar variables, allowing a visual observations of all the variables and investigation of the physical meaning of components. From Fig.4, it is noted that parameters clay, P10, P33, P66, P100, P500, P1500 are very close to each other. This cluster of points might represent the water retaining function of the soil. Parameter sand was distant form this cluster but negatively correlated ($P < 0.05$) with all the parameters comprising it. The strong negative correlation could be explained as sand is unfavorable for water storage. Bulk density and AD are clearly separated from the cluster of points. They can be considered as the two parameters that account for the last two PCs, since no apparent correlation is found between them. As for physical meanings, BD (via its

relationship to TP) and AD may be representative of the maxium and minium limits of water content in the soil, respectively. While a water content substantially below that observed at P1500 (e.g., corresponding to AD) may not be likely in the subsurface soil, the AD parameter may be of greater importance when considering near surface soil moisture content for soil exposed directly to atmospheric drying. When it is not feasible to measure all soil parameters, the analysis of parameters BD and AD along with soil texture (i.e. sand, silt and clay content) could be an option. These parameters could reveal the inherent locational differences in soil physical properties at soil moisture monitoring sites, thus aiding data interpretaion without the added costs of water retention measurements.

Relationships of ECONet Soil Moisture Observations to Soils

Table 5 presents the taxonomic classes and descriptors used for ANOVA tests. Figure 5 and Table 6 present the results of the ANOVA tests. The number of degree of freedom for each ANOVA test can be found from data given in Table 5 (number in parentheses). The height of each bar in Fig. 5 represents the F-ratio derived from the one-way ANOVA test for θ at sites with different descriptors. F is the ratio of the θ variance between groups to the θ variance within groups; a large value of F indicates a significant change in average soil moisture content from one soil classification to another. With the exception of suborder, θ varied ($P = 0.05$) by single descriptors (wetness class and particle size) for each time interval (Table 6). The finding that suborder was not a significant soil descriptor for moisture content is not surprising. Although, suborder could reduce the variance of soil properties in the dataset (Heuscher et al., 2005), it is a broader classification than family. It is not specific enough to account for moisture variation among the groups since the property differences existing within a suborder could cause heterogeneous in-group hydraulic behavior.

Generally, the F ratio was higher for the non-growing season than the growing season, which suggests that the soil properties play a more dominant role for θ in non-growing season (Fig. 5). This could be explained by the vegetation at the sampling sites. Soil moisture content is influenced by the actual evapotranspiration related to the vegetation cover (Douville, 2003). The vegetation cover is grasses for most sites, but the species differ (i.e. wild short grass, hay for cattle consumption). In the non-growing season, the vegetation is in the dormant stage with low and similar evapotranspiration rate. However, evapotranspiration increases and differs largely between species, and depending on site maintenance, in the growing season and thereby exerts different levels of control on water in the soil (Zavaleta et al., 2003). As a result, the significance of soil properties for θ is lessened in the growing season.

In all cases, the combination of wetness and particle size classes partitioned soil moisture best with a P-value less than 0.01. However, the F ratio only slightly changed by including two significant predictors at the same time (e.g. 4.17 compared to 4.81 in whole-year data). Because it provided the highest F ratio in all cases, the largest difference in θ between groups due to a single class was from particle size class. But its significance level may not be as much as wetness class groups, suggested by comparing their P-value. In the combination of particle size and wetness class, there was only a small portion of total variance explained by the additional descriptor wetness class when particle size was treated as the first parameter. This implies that the information about θ variability may be described by soil particle size alone. On the other

hand, wetness class alone should also suffice to describe θ if we treat it as the first factor. This led us to conclude that there is an overlap in information between wetness class and particle size class.

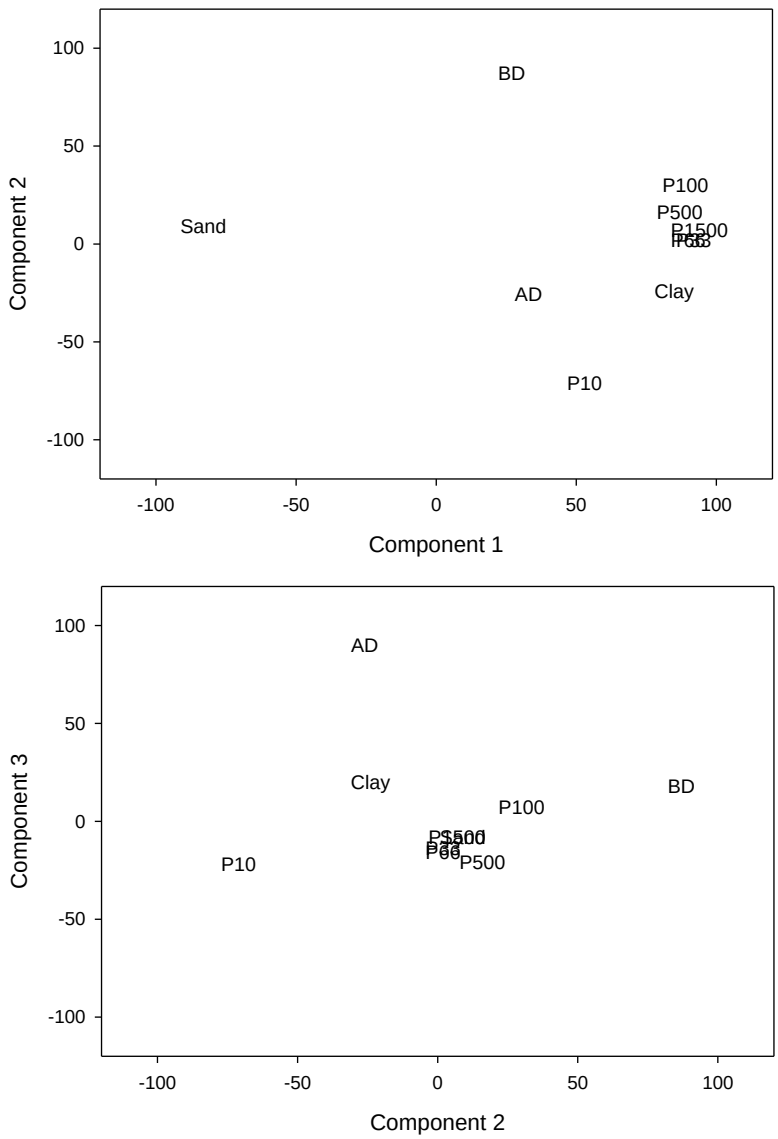

Figure 4. Two-dimensional Loading Plots of the Weights of the First Three Principle Components. Parameters labels indicate coordinates within the plots. Parameters are defined in the text.

Table 5. Site Descriptors and Classes for Each Descriptor Extracted from Family-level Soil Classification. Descriptor classes are treated as categories in one-way ANOVA.

Descriptor	Classes[1]
Suborder	Udic (13), Aguic (6), other (2)
Particle size class	fine (8), fine-loamy (7), coarse-loam (4), other (2)
Wetness class	poorly/very poorly drained (3), somewhat poorly drained (3), mod. well drained (4), well drained (2), somewhat excessively drained (2), other (2)
Combined wetness and particle size classes	poorly/ very poorly drained, fine (1); poorly/very poorly drained, loamy (2) somewhat poorly drained, fine (1); somewhat poorly drained, loamy (2); moderately well drained, loamy (4), well drained, fine (6); well drained, loamy(1); somewhat excessively drained, loamy (2); other (2)

[1]Numbers in parentheses are the number of sampling sites in each classification. Two sites designated with Udorthents were treated as "other" in every class.

Table 6. P-values from One-way ANOVA of Soil Moisture and Taxonomic Descriptors.

	P-value			
Period	Sub order	Particle size	Wetness class	Particle size and wetness class
Whole year	0.37	0.01	0.01	0.007
Non-growing season	0.28	0.007	0.005	0.0025
Growing season	0.52	0.04	0.05	0.039

Our next step was to investigate the dependence of soil properties based on hydraulic data obtained from lab measurements and to explore the relative significance of these parameters. Before proceeding, we should point out that we are interested in an exploratory statistical analysis which can lead us to determine the importance of soil property controls on θ. The choice of MLR model here is intended to compare the importance of soil with other factors known to influence θ. We are concerned with exposing "robust" parameters in the data, but not the precision of the predictive equation.

The prelimary MLR model included 12 parameters: precipitation, PET and 10 parameters representing measured soil physical properties (Table 7). After close examination of the importance for each parameter in the initial MLR, it was reduced to its three most important parameters with significance level at P = 0.10. After dropping the insignificant factors shown in the prelimary MLR model, the reduced MLR used to describe θ was:

$$\theta = 0.079 - (0.0291*PET) + (0.680*P10) + (0.503*P1500)$$

The development of this model was based on 42 seasonal (divided by growing and non-growing season) means in 21 stations which include 7665 daily observations altogether. The model includes both time stable (soil propety parameters) and non-stable (climate observations) influences on θ. The P value for this model is < 0.001 with an r^2 of 0.51. Results shows a linear combination of independent parameters PET (P = 0.002), P10 (P = 0.006), P1500 (P = 0.087) predict θ. This suggests that θ varied as a combined function of climate and soil properties. This is consistent with findings of others (e.g., Robock et al. 1995) that soil moisture is controlled by interactions between atmospheric and land surface conditions and soil characteristics.

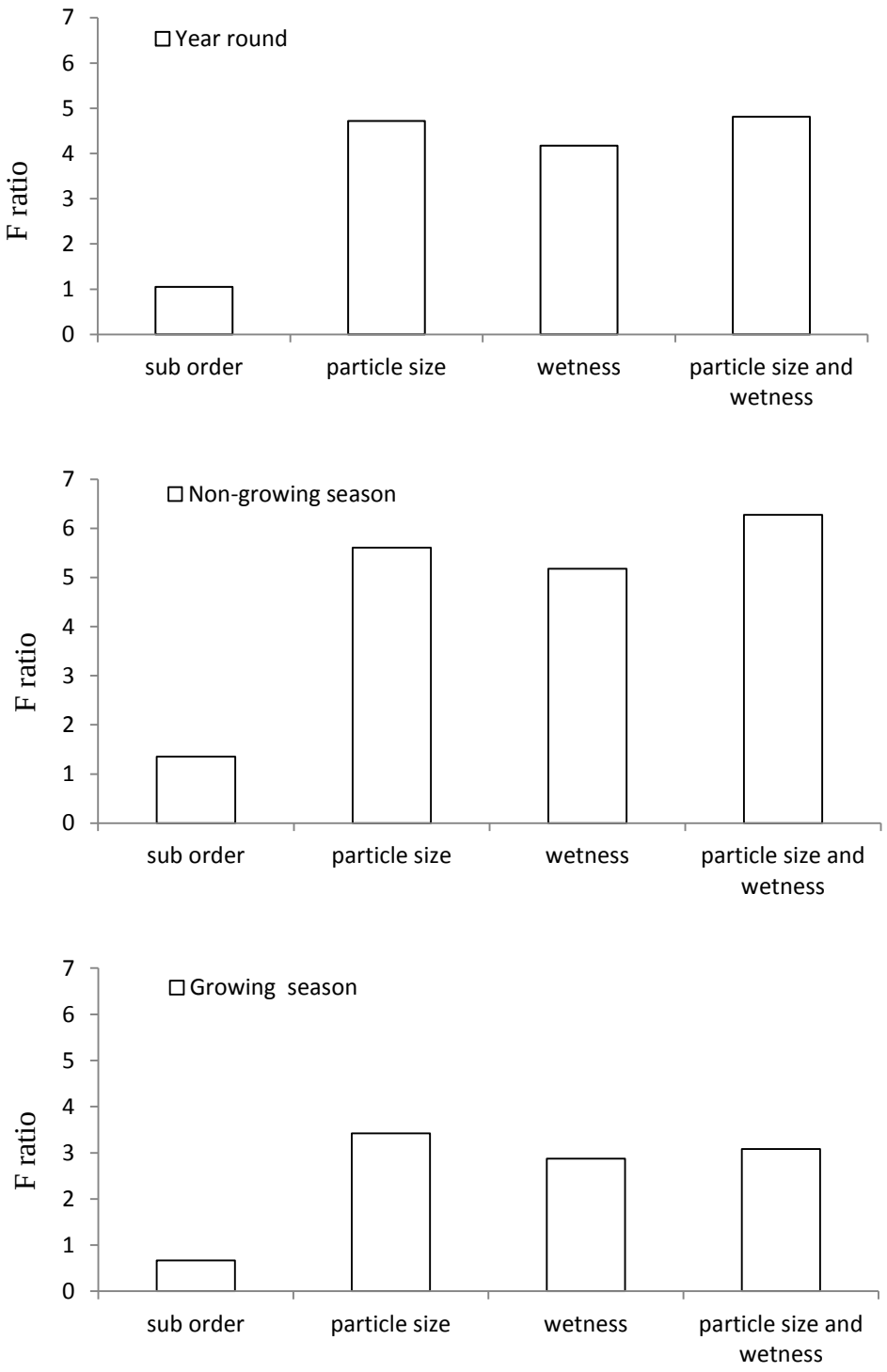

Figure 5. Values of the F ratio from One-way ANOVA with Whole Year (top), Non-Growing season (middle), and Growing-season (bottom) Soil Moisture Data based on Soil Taxonomic Descriptors.

Table 1. Multiple Linear Regression (MLR) Results of PET, Precipitation and Soil Physical Properties on Soil Moisture Content. Overall MLR model: P value = 0.004, r^2=0.51.

Parameter[1]	Estimate	P-value
Intercept	0.08	0.57
PET	-0.03	0.02
Precipitation	-0.01	0.65
TP	-0.05	0.81
Clay	-0.13	0.59
Sand	-0.02	0.83
AD	-1.60	0.22
P10	0.85	0.01
P33	0.46	0.26
P66	-0.78	0.05
P100	0.24	0.64
P500	-0.79	0.18
P1500	2.19	0.06

PET represents the amount of water that could evaporate and transpire from the landscape based on atmospheric demand (Lu et al., 2005). It accounts for part of atmospheric and land surface conditions with temperature and solar radiation as inputs for its calculation (Allen et al., 1998). The slope of -0.029 suggests PET is negatively related to θ which is consistent with water loss from soil by evapotranspiration.

Another dominant part of atmospheric and land surface conditions is precipitation (Koster et al., 2004). The dominant role precipitation plays in controlling soil moisture conditions cannot be overlooked, although the parameter precipitation is not significant as one of the three parameters in the MLR model. In the experimental area, the locational variability is similar for PET and precipitation, with coefficients of variation of 0.34 and 0.31. But the impact of event-driven, short-term differences in precipitation is not apparent when dealing with seasonal θ data. Soil moisture content could increase greatly after a rainfall event, but the seasonal mean data used in the model smooths the change following individual events.

P10 and P1500 represent control on θ from soil. The simultaneous appearance of these two variables could be explained by their weak correlation in the first PC which is highly related to the water retaining function of soil (Table 4). However, as indicated by the correlation matrix (Table 2), P10 and P1500 are both highly dependent on clay and sand content (P = 0.01). Thus, the two parameters may essentially represent the same source of influence from soil that could be interpreted as soil texture.

The regression equation accounted for 51% of the variability of the soil moisture content over different soils. The remaining variability might be reduced if the actual evapotranspiration rate

were known rather than the approximate values estimated from other climate parameters. There could be alternative explanations. For example, the model tested here may not completely describe all the soil property factors that influence θ since not only the value but also the co-variation of the testing parameters could be affected by soil properties (refer to PCA section).

Besides PET, combined results from MLR and PCA suggest soil texture (via water retention behavior) is the most important factor for describing the observed θ variation between stations, at least on a longer-term basis (i.e. seasonal and whole-year patterns). This result is of high practical value since soil texture information could be easily extracted from soil survey datasets at multiple taxonomic classification levels. Currently, texture information is restricted to qualitative estimates based on the properties of "representative" profiles. Quantitative values for soil parameters rather than qualitative estimates will be more favorable for increasing the accuracy of soil moisture interpolation. Even with qualitative classification, it may be feasible to develop regional soil moisture maps with the combination of climate influence (monitored on station) and soil property influence (integrated by GIS).

Spatial and Correlation of ECONet Soil Moisture Observations

Basic descriptive statistics for ECONet daily average θ on the dates chosen for spatial analysis are shown in Table 8. Soil moisture on days chosen as wet was generally wetter than for dry days. The variability of θ was similar for wet and dry days. We first conducted semivariography of ECONet θ using these daily averages (Table 9). The active lag distance used was 257,400 m, keeping with a convention to limit consideration to approximately half the maximum lag in the data, which removes noise at greater distances and to keep a minimum of 10 pairs in the first lag class. This resulted in a reasonable number of points with which to assess spatial correlation. On the daily scale, spatial correlation was found to be poor (Table 9). Two of the dry dates (18 Jun 2008; 17 Feb 2009) were found to have no spatial correlation, showing linear models. The latter is plotted in Fig. 6. GS+ forced the nugget to = 0, resulting in a spherical. The semivariogram, however, is all nugget effect and would be better modeled as linear. Of the dates examined, 12 Nov 2009, a wet day, exhibited the strongest spatial correlation (Fig. 7) with a nugget:sill of 0.08, or 92% spatial correlation. All other models exhibited spatial correlation < 77%.

Longer time scales (seasons and years) were then examined to see how spatial correlation might change. Spatial correlation for the seasons and year examined (Table 10) had a narrower range of generally lower nugget:sill ratios, indicating stronger correlation than the individual days examined. Among the time periods examined, the yearly data (Fig. 8, 2009) generally had the strongest spatial correlation. Spatial correlation was found, on average, to increase with the time scale: the average daily nugget:sill was 0.313 versus 0.20 for the monthly average, with higher maximum values also occurring at the longer time scales.

Table 8. Summary Statistics for ECONet θ on Select Wet and Dry Days, 2007 through 2009.

Date	N	Mean	SD	Minimum	Maximum	CV
		---------- cm^3 cm^{-3} ----------				%
Wet						
6/9/2008	29	0.32	0.11	0.11	0.65	0.34
18/05/2009	29	0.30	0.10	0.12	0.49	0.34
19/05/2009	29	0.29	0.09	0.12	0.46	0.32
12/11/2009	28	0.35	0.11	0.17	0.57	0.31
Dry						
14/11/2007	28	0.25	0.08	0.12	0.42	0.33
18/06/2008	29	0.23	0.08	0.09	0.38	0.36
17/02/2009	29	0.28	0.09	0.13	0.45	0.31

Table 9. Semivariogram Parameters for ECONet θ on Select Wet and Dry Days, 2007 through 2009.

Date	Active Lag	Lag Class	Best-Fit Model	r^2	Nugget	Sill	Range	Nugget: Sill
	------ m ------				--- cm^6 cm^{-6}---		--- m ---	
Wet								
6/9/2008	257400	32175	Gaussian	0	0.003	0.013	5,543	0.231
18/05/2009	"	"	Gaussian	0.68	0.005	0.010	144,799	0.510
19/05/2009	"	"	Gaussian	0.65	0.004	0.009	180,999	0.444
12/11/2009	"	"	Spherical	0	0.001	0.012	20,300	0.083
Dry								
14/11/2007	"	"	Exponential	0.67	0.000	0.007	166,800	0.000
18/06/2008	"	"	Linear	0.19	0.006	0.006	239,257	0.925
17/02/2009	"	"	Spherical	0	0.000	0.007	20,300	0.000

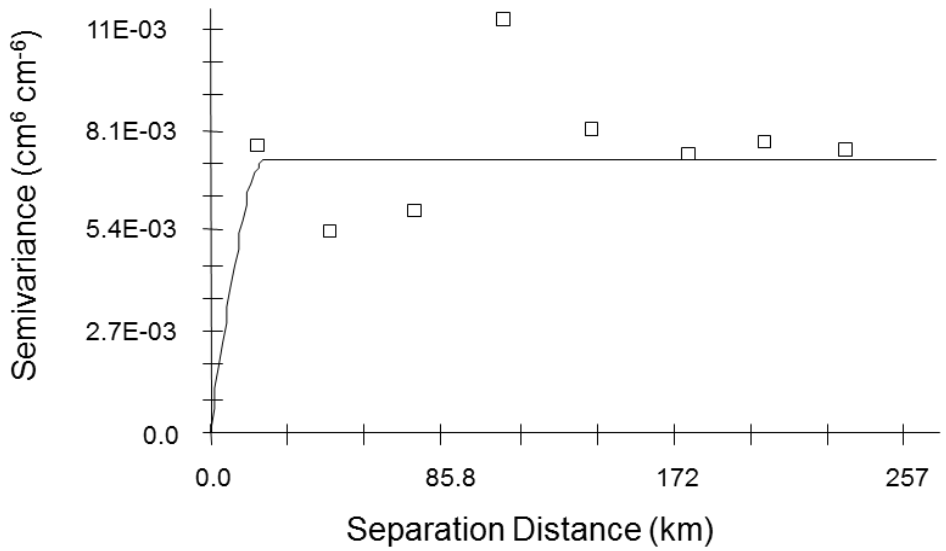

Figure 6. Semivariogram of Statewide ECONet θ for 17 Feb 2009, a Dry Day.

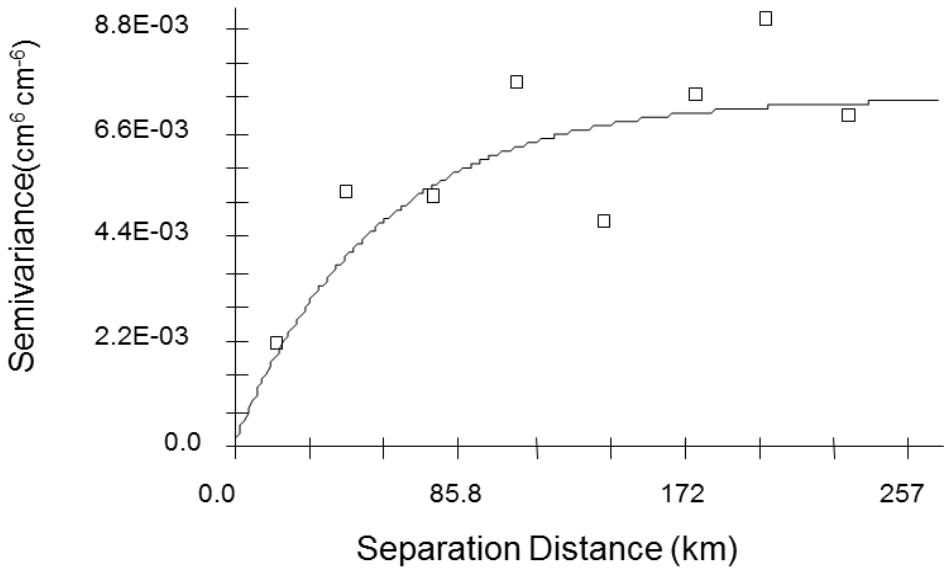

Figure 7. Semivariogram of Statewide ECONet θ for 12 Nov 2009, a Wet Day; Nugget:Sill = 0.08.

Table 10. Semivariogram Parameters for ECONet θ for Months Containing Select Wet and Dry Days, 2007 through 2009.

Date	Active Lag	Lag Class	Best Fit Model	r^2	Nugget	Sill	Range	Nugget: Sill
	------ m ------				--- cm^6 cm^{-6}---		--- m ---	
Wet								
Sep-08	257400	32175	Gaussian	0	0.003	0.010	5,716	0.300
May-9	"	"	Exponential	0.67	0.001	0.009	229,500	0.111
Nov-09	"	"	Exponential	0.50	0.005	0.015	11,820,000	0.333
Dry								
Nov-07	"	"	Exponential	0.7	0.001	0.007	204,000	0.143
Jun-08	"	"	Exponential	0.25	0.001	0.006	63,000	0.167
Feb-09	"	"	Exponential	0	0.001	0.007	17,400	0.143

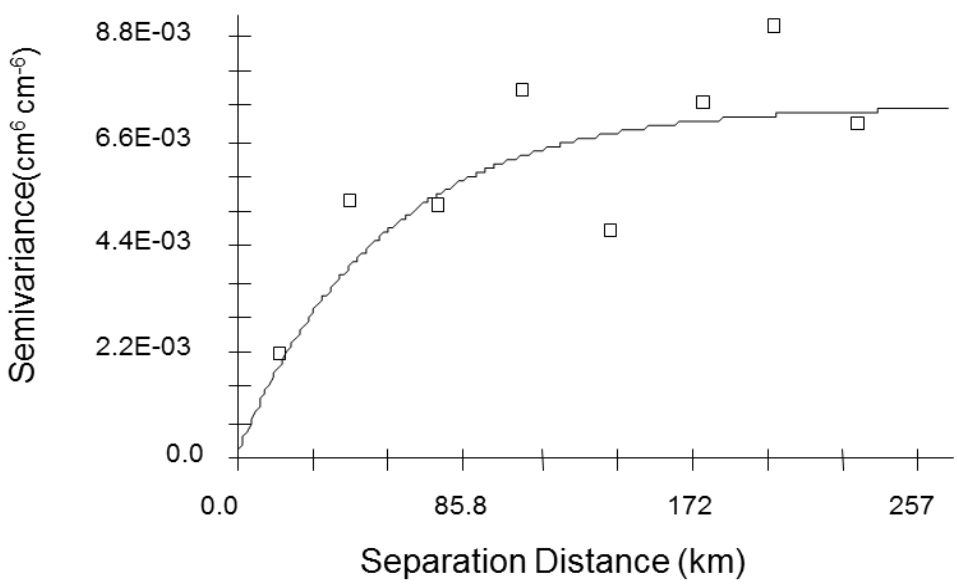

Figure 8. Semivariogram of 2009 Annual Average Statewide ECONet θ.

AMSR-E and ECONet Comparisons

Descriptive statistics for AMSR-E θ for the 209 NC cells on the same wet and dry days used in the ECONet analyses are summarized in Table 11. AMSR-E θ were lower and less variable than ECONet θ. Semivariograms of AMSR-E θ were well modeled (r^2 = 0.89 – 0.99; Table 12) and showed very strong spatial correlation that ranged from 90 to 99% of the total variability (nugget:sill from 0.0004 to 0.02, respectively). Figure shows one semivariogram that demonstrates the strong spatial correlation of AMSR-E θ. The nugget is very low with a well-defined sill. Compared to the ECONet's spatial correlation, AMSR-E had upwards of 183 data

points on the study days, leading to the first lag classes having more than 50 pairs. The average range of spatial correlation was greater on dry days than wet days (732 vs. 502 km, respectively). Comparing the ECONet and AMSR-E θ datasets was difficult due to not having AMSR-E data on the majority of the study days, or only partial data over the state. AMSR-E data from the day before and after were compared to the study day. We found no correlation of ECONet θ with AMSR-E in any date pairs. Figure 10 shows the best simple linear regression, which had an r^2 of 0.07. While disappointing relative to the objectives of this research, the lack of correlation is not unexpected considering that the ECONet θ are point observations at ~ 20-cm depth and AMSR-E senses surficial (0 – 1 cm) θ integrated over large-area cells.

Table 11. Summary statistics for AMSR-E θ on Select Wet and Dry Days, 2007 through 2009.

Date	N	Mean	SD	Minimum	Maximum	CV
		----------cm^3 cm^{-3}----------				%
Wet						
5/9/2008	195	0.129	0.021	0.031	0.195	16
7/9/2008	205	0.143	0.018	0.077	0.218	13
17/05/2009	183	0.135	0.026	0.01	0.18	19
19/05/2009	201	0.151	0.019	0.081	0.201	13
11/11/2009	184	0.130	0.026	0.026	0.173	20
13/11/2009	209	0.139	0.018	0.064	0.196	13
Dry						
13/11/2007	206	0.128	0.016	0.053	0.17	13
15/11/2007	208	0.132	0.028	0.009	0.175	21
17/06/2009	206	0.138	0.017	0.074	0.191	12
19/06/2008	207	0.139	0.021	0.074	0.204	15
17/02/2009	186	0.122	0.021	0.082	0.174	17

We examined the temporal correlations of ECONet θ with AMSR-E θ from the individual cells that contained each ECONet stations to see if their variability through time was similar. Representative sites were selected using the added criteria of being two AMSRE footprints away from water (Njoku et al., 2003). Among the potential representative sites, WAYN, FLET, ROCK and JACK remained applicable choices. Of these, FLET is near Asheville which has higher potential of radio frequency interference (RFI), so it was eliminated. Then taking into account potential for observation distortion in the mountains, JACK was eliminated. ROCK is mostly viable except that the Tar River Reservoir, not much larger than the river itself, may be in the footprint. Looking outside of the suggested stations, CLIN seemed the best option in the state, being distant from the ocean, mountains, large cities, and reservoirs and having one of the better data histories. Thus, we began the analysis on temporal correlation using CLIN, OXFO, ROCK, and WAYN.

Table 12. Semivariogram Parameters for AMSR-E θ on Select Wet and Dry Days, 2007 through 2009.

Date	Active Lag	Lag Class	Best-Fit Model	r^2	Nugget	Sill	Range	Nugget: Sill
	------- m ------				$cm^3\ cm^{-3}$		m	
Wet								
5/9/2008	405947	27063	Spherical	0.99	21	612	458,900	0.03
7/9/2008	"	"	Spherical	0.89	28	370	232,700	0.08
17/05/2009	"	"	Spherical	0.99	30	1650	908,900	0.02
19/05/2009	"	"	Exponential	0.99	14	435	404,100	0.03
11/11/2009	"	"	Gaussian	0.99	83	1177	522,213	0.07
13/11/2009	"	"	Exponential	0.98	38	391	482,700	0.10
Dry								
13/11/2007	"	"	Exponential	0.98	18	347	674,100	0.05
15/11/2007	"	"	Gaussian	0.99	102	1554	586,299	0.07
17/06/2009	"	"	Spherical	0.98	52	506	782,800	0.10
19/06/2008	"	"	Exponential	0.99	28	650	716,700	0.043
17/02/2009	"	"	Gaussian	0.98	1	2112	902,572	0.005

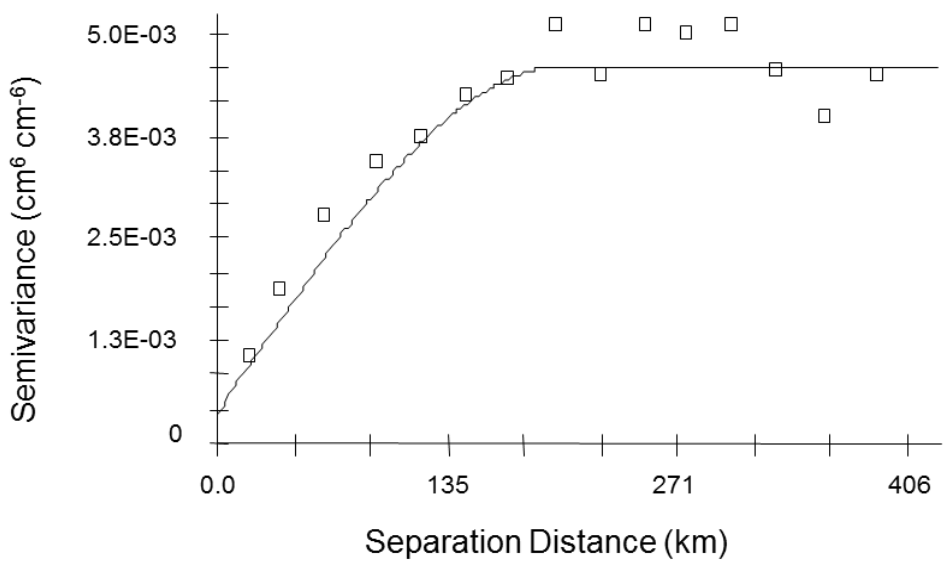

Figure 9. Semivariogram of AMSR-E θ on 5 Sep. 2008, a Wet Day; Nugget:Sill = 0.03.

The closest AMSRE cells to ECONet sites were not always predictable. The lat and long in the L2B datasets are not coincident with the L3 cell's centroid location, but offset by about (-0.04663˚, 0.01534˚). We choose to use L2B data because L3 data does not allow you to access the EASE Grid cell locations through HDFView, nor by subsetting in ArcMap. HDFView does not have a "Find" function, so visual scanning for the points nearest the ECONet sites is

necessary. However, since the AMSRE Lat/Long are not in the center of the cell, the wrong cells may be selected and validation is needed (Figure 11).

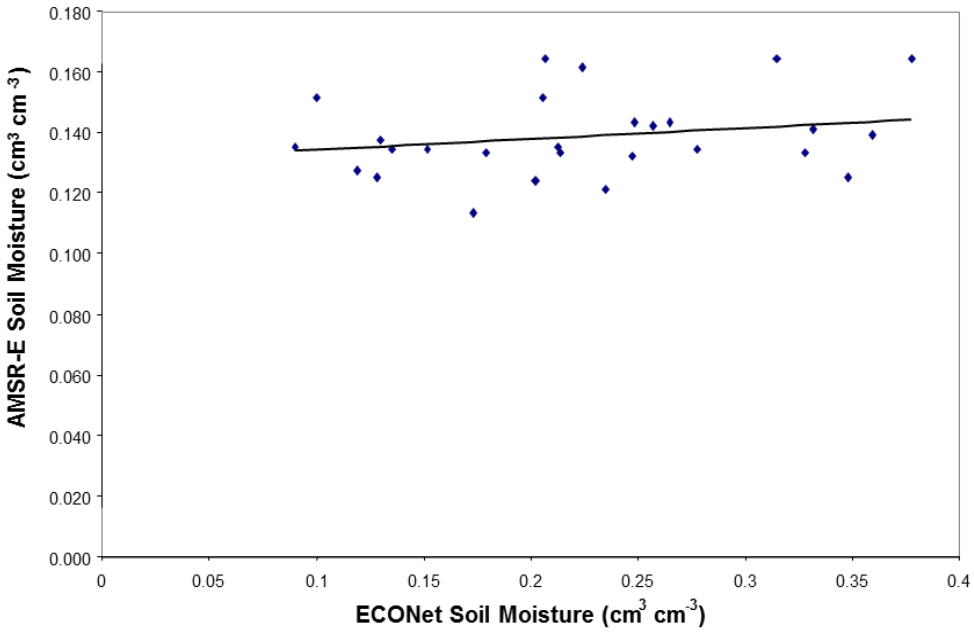

Figure 10. Simple Linear Regression of AMSR-E vs. ECONet θ on 17-18 June 2008, r^2=0.07.

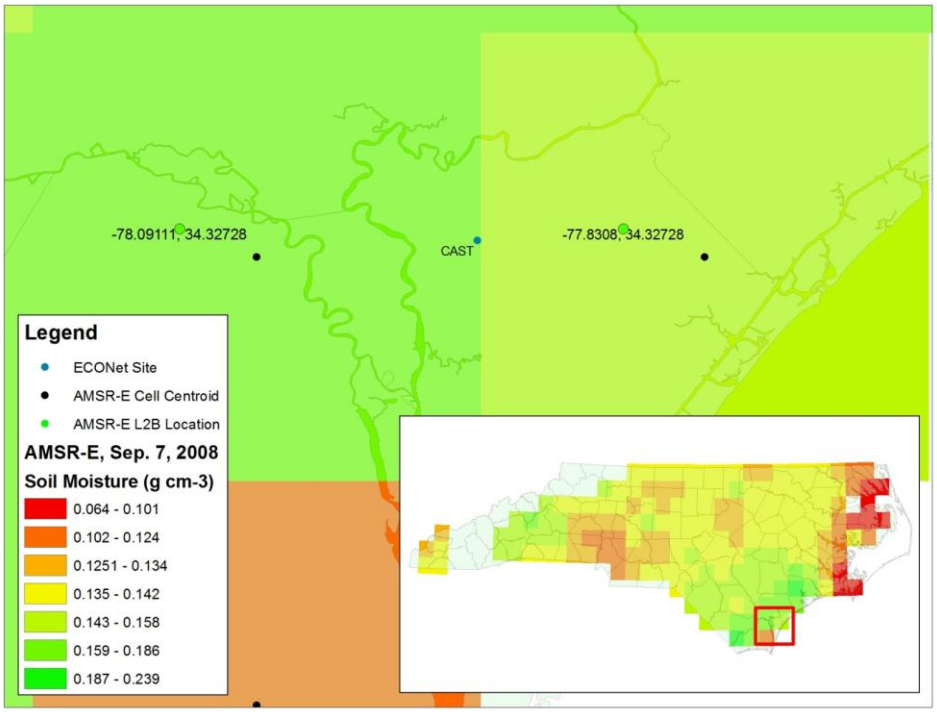

Figure 11. Spatial Offset of AMSR-E L3 Data (cell centroid) and AMSR-E L2B data. Inset Map Shows AMSR-E L3 θ as Interpolated into the Equal-Area Scalable Earth (EASE) grid. Red Bounded Area on Inset Map is Shown Behind at Larger Scale.

Table 13 shows the temporal correlations of AMSR-E and ECONet θ by season in 2008, starting with January to March as winter at select, individual ECONet sites. Correlations ranged from 0.02 to 0.52, a large improvement from statewide SLR. A scatterplot of ECONet and AMSR-E θ for winter, 2008 at Clinton is shown in Fig. 12. Though the regression of Clinton's θ values gave a moderate correlation ($r^2 = 0.44$), the numerical agreement was somewhat poor. A time series comparison is shown in Figure 13. First, ECONet θ shows clearly defined wetting and drying cycles, whereas AMSR-E was much less variable. Secondly, the physical values of AMSR-E were very low compared to ECONet values, and lower than physically expected over many rain events. The regression model did not improve with removal of extreme ECONet values. Similar results were observed at other sites. Figure 14 shows daily θ for spring 2008 for the Oxford ECONet station and the AMSR-E cell containing it. The ECONet data exhibit dynamic moisture release, while the AMSR-E data showed very little variation and very low magnitude relative to ECONet θ.

Table 13. Coefficients of Determination (r^2) of Site-specific ECONet θ versus AMSR-E θ from Grid Cell Containing the ECONet Station Over Seasons and Year, 2008.

Period	Wayne (WAYN)	Oxford (OXFO)	Clinton (CLIN)	Rockingham (ROCK)
Winter	0.02	0.02	0.44	0.04
Spring	0.50	0.13	0.46	0.09
Summer	0.08	0.11	0.52	0.19
Fall	0.04	0.05	0.13	0.01
2008	0.21	0.05	0.25	0.00

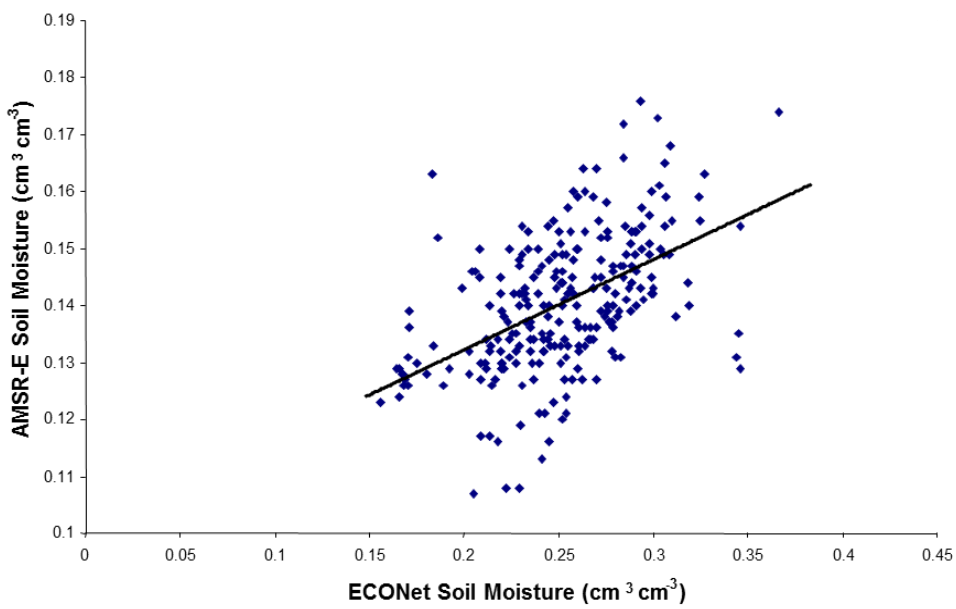

Figure 12. Simple Linear Regression of AMSR-E Soil Moisture from the Grid Cell Containing the Clinton ECONet Station versus Clinton ECONet Soil Moisture, Winter 2008; r^2=0.44.

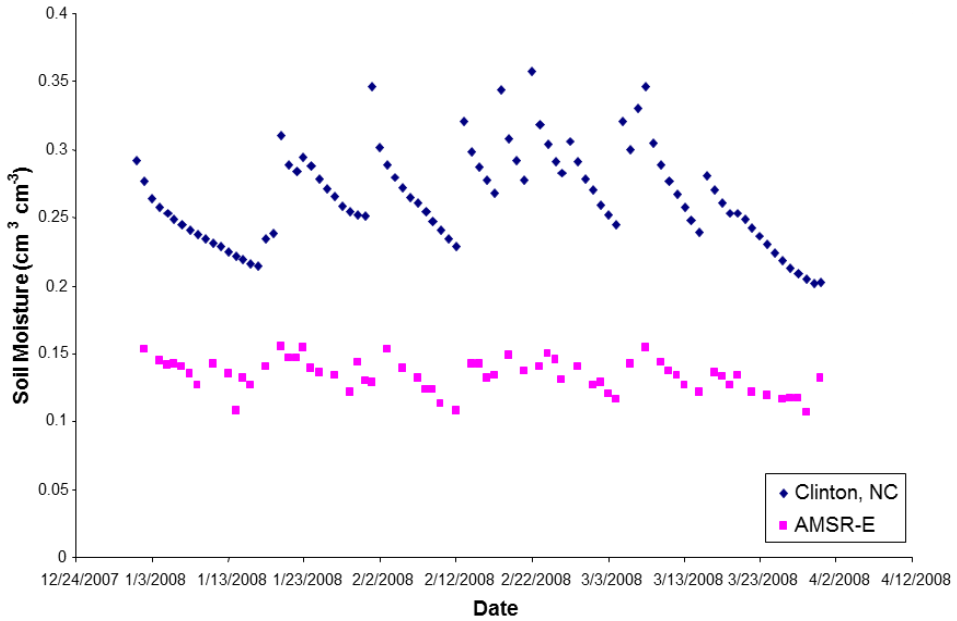

Figure 13. Daily Soil Moisture from ECONet Station at Clinton, NC and from the AMSR-E Grid Cell Containing the Clinton Station, Winter into Spring 2008.

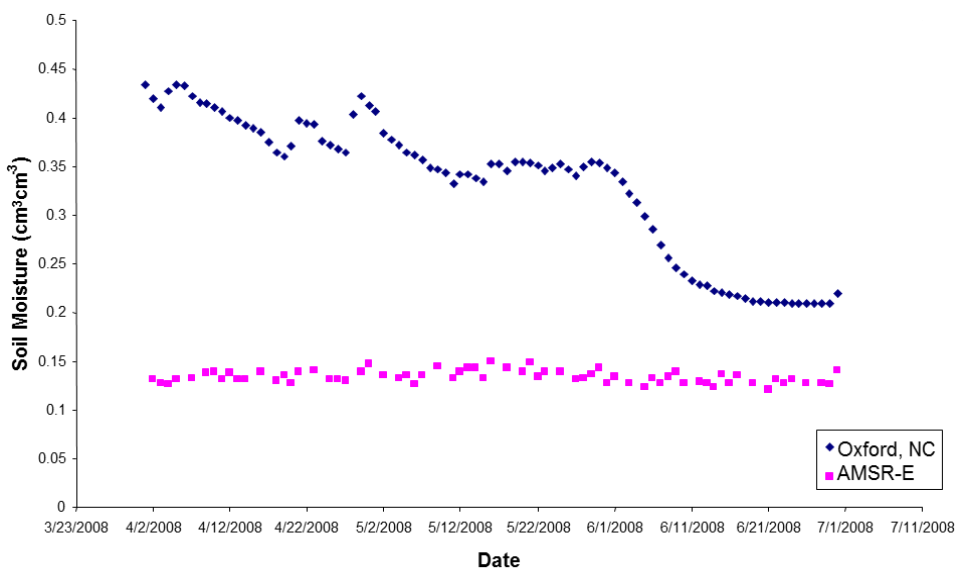

Figure 14. Daily ECONet Soil Moisture at the Oxford, NC Station and for the AMSR-E Cell Containing It for Spring 2008. Linear Regression of the Two had $r^2 = 0.13$.

While the lack of spatial and temporal correlation between ECONet and AMSR-E θ may be due to the grossly different sampling of area (point vs. large cell) and depth (20 vs. 1 cm), the accuracy and precision of the algorithm used to estimate θ is also in question. There has been little actual validation of this AMSR-E algorithm, which estimates θ as a function of AMSR-E Tb and other parameters. According to the National Snow and Ice Data Center (http://nsidc.org/data/docs/daac/ae_land_l2b_soil_moisture.gd.html), which serves the data:

> "The soil moisture algorithm uses Polarization Ratios (PR), which are sometimes called normalized polarization differences of the AMSR-E channel Tbs. PR is the difference between the vertical and horizontal Tbs at a given frequency divided by their sum. This effectively eliminates or reduces surface temperature effects, which is necessary since no dynamic ancillary surface temperature data are input to the algorithm. The algorithm first computes a vegetation/roughness parameter g using PR 10.7 GHz and PR 18.7 GHz, plus three empirical coefficients. Soil moisture is then computed using departures of PR 10.7 GHz from a baseline value, plus four additional coefficients. The baseline values for PR 10.7 GHz are based on monthly minima at each grid cell over an annual cycle. AMSR-E/Aqua L2A Global Swath Spatially-Resampled Tbs (Tb) are used as input to calculating soil moisture variables. Static input databases are used for surface classification and to identify valid grid points for retrieval. Surface topography data are derived from the United States Geological Survey (USGS) GTOPO30 global digital elevation model. Horizontal grid spacing is 30 arc seconds. Preprocessing of these data enables screening out points over ocean, mountains, and areas where the topographic variability within a grid cell is likely to degrade geophysical retrievals. Sand and clay fraction are derived from a 1 degree x 1 degree latitude/longitude global soil type database that estimates soil dielectric properties as a function of soil moisture content. A mask of permanent ice and snow is used to screen out these areas over land. Vegetation type is derived from the USGS 1 km global land cover characteristics database. These data estimate the dependence of vegetation type on the model coefficient that relates vegetation water content to vegetation opacity. Finally, precipitable water and surface air temperature are derived from National Center for Environmental Prediction (NCEP) or European Centre for Medium-Range Weather Forecasts (ECMWF) global reanalysis climatologies, or from real-time forecast model outputs. These data are used for estimating atmospheric contributions in the geophysical retrieval algorithm (Njoku 1999)."

Our understanding of this description is that the algorithm uses temporally and spatially variable AMSR-E Tbs from at least two frequencies, as well as ancillary data that are spatially variable but static. We have sought, but not yet obtained, the actual program code of the AMSR-E soil moisture algorithm.

Given that the accuracy and precision of the AMSR-E soil moisture algorithm is unknown, we decided to examine the relationship between AMSR-E θ and the 10.7 GHz Tb that is the basis of the estimation. This might indicate how well the algorithm estimates soil moisture via model parameters other than Tb, as well as indicate whether and how model fidelity to Tb changes over time and space.

Tables 14 and 15 show summary statistics for both vertical and horizontal Tb on the wet and dry dates studied, as well as their coefficients of determination (r^2) with AMSR-E θ. For both polarizations, the ranges of Tb for wet and dry days were similar except for two dry days (15 November 2007 and 17 February 2009) when the ranges were about one third lower. The r^2 for correlations of Tb with AMSR-E θ ranged from 0.04 to 0.56. The correlations were somewhat stronger on wet versus dry days, with an average r^2 of 0.33 for wet days and 0.24 for dry days.

Table 14. AMSR-E Vertical Brightness Temperature (Tb) Summary Statistics and r^2 for Correlation with AMSR-E θ on Select Wet and Dry Days, 2007 through 2009.

Date	N	Min.	Max.	Range	Mean	SD	CV	r^2
		----------K----------					%	
Wet								
9/5/2008	330	220	291	71	282	10	3.6	0.20
5/17/2009	305	215	285	71	273	9	3.4	0.44
5/19/2009	341	207	285	78	276	12	4.3	0.32
11/13/2009	356	206	280	74	269	12	4.4	0.32
Dry								
11/13/2007	349	209	284	76	275	11	4.1	0.37
11/15/2007	353	231	281	50	267	8	3.2	0.46
6/17/2008	351	215	296	81	287	12	4.1	0.10
6/19/2008	344	212	293	81	284	12	4.1	0.04
2/17/2009	322	221	275	53	268	6	2.1	0.07

Table 15. AMSR-E Horizontal Brightness Temperature (Tb) Summary Statistics and r^2 for Correlation with AMSR-E θ on Select Wet and Dry Days, 2007 through 2009.

Date	N	Min.	Max.	Range	Mean	SD	CV	r^2
		----------K----------					%	
Wet								
9/5/2008	330	167	287	121	275	17	6.1	0.21
5/17/2009	305	159	279	120	264	16	5.9	0.50
5/19/2009	341	148	278	130	266	20	7.7	0.33
11/13/2009	356	149	274	126	258	20	7.7	0.32
Dry								
11/13/2007	349	150	279	129	266	19	7.2	0.45
11/15/2007	353	196	275	79	258	13	5	0.56
6/17/2008	351	153	291	138	277	20	7.3	0.15
6/19/2008	344	151	288	138	275	20	7.4	0.06
2/17/2009	322	176	269	93	260	10	3.7	0.13

On average and across polarization (Tables 16 and 17), the spatial correlation of Tb was somewhat stronger for dry days than wet days with nugget:sill of 0.20 and 0.04 (i.e., proportion of variability that was spatial was 80 and 96%, respectively). This stronger spatial correlation

compared to AMSR-E θ suggests that there may be some promise in using these data for interpolation, but interpretation will be aided when additional information on the AMSR-E algorithm can be obtained.

Table 16. Semivariogram Parameters for AMSR-E Vertical Brightness Temperature (Tb) on Select Wet and Dry Days, 2007 through 2009.

Date	Active Lag	Lag Class	Best Fit Model	r^2	Nugget	Sill	Range	Nugget: Sill
	---degrees---				---- K^2 K^{-2} ----		degrees	
Wet								
9/5/2008	2	0.294	Exponential	0.99	2590	6465	5.571	0.401
5/17/2009	“	“	Spherical	0.99	1950	5669	3.709	0.344
5/19/2009	“	“	Spherical	0.99	10	7385	1.984	0.001
11/13/2009	“	“	Spherical	0.99	10	5850	2.041	0.002
Dry								
11/13/2007	2	0.294	Spherical	0.99	10	7372	1.823	0.001
11/15/2007	“	“	Exponential	0.97	110	4297	2.262	0.026
6/17/2008	“	“	Gaussian	0.99	770	7350	1.306	0.105
6/19/2008	“	“	Gaussian	0.99	740	8013	1.320	0.092
2/17/2009	“	“	Spherical	0.62	1	2267	0.370	0.000

Table 17. Semivariogram Parameters for AMSR-E Horizontal Brightness Temperature (Tb) on Select Wet and Dry Days, 2007 through 2009.

Date	Active Lag	Lag Class	Best Fit Model	r^2	Nugget	Sill	Range	Nugget: Sill
	---degrees---				----- K^2 K^{-2} -----		degrees	
Wet								
9/5/2008	2	0.294	Exponential	0.99	8500	18510	5.316	0.459
5/17/2009	"	"	Exponential	0.97	6280	17750	9.363	0.354
5/19/2009	2.3	"	Spherical	0.99	10	22600	2.275	0.000
11/13/2009	2	"	Spherical	0.99	10	17860	1.946	0.001
Dry								
11/13/2007	2	0.294	Spherical	0.99	10	19070	1.730	0.001
11/15/2007	"	"	Exponential	0.95	10	8803	1.338	0.001
6/17/2008	"	"	Gaussian	0.987	2080	20130	1.297	0.103
6/19/2008	"	"	Gaussian	0.991	2160	22210	1.342	0.097
2/17/2009	"	"	Spherical	0.378	10	6717	0.344	0.001

Summary, Conclusions, and Recommendations

We investigated soil physical properties at 27 NC ECONet soil moisture monitoring stations in the piedmont and coastal plain regions of North Carolina. Prior to this study, and despite collection of soil moisture data for the past twenty years, few soils metadata existed to support NC ECONet. Soils at ECONet sites fall in seven textural classes. Porosities ranged from 0.36 to 0.58 $cm^3\ cm^{-3}$, suggesting a wide range of upper boundaries for soil water content. Diversity was also found for other parameters, such as field capacity and wilting points. As these properties individually and cumulatively influence soil moisture dynamics, it is beneficial to understand soil properties for each monitoring site as well as the potential range of characteristics across monitored sites within the network.

Strong correlations were found between the soil physical parameters tested in the dataset. A PCA reduced 10 soil physical parameters into three PCs that explained 85% of the variability within the dataset. We interpret the first PC to represent the soil water retaining function (closely related to soil texture), and the second and third PCs, associated with bulk density (and TP) and air-dried water content, respectively, represent the upper boundary and lower boundaries for soil moisture values under field conditions. The PCA results suggests that soil texture, bulk density and air-dried water content may be three of the most important physical properties to characterize because they accounted for much of the variance for soil physical properties considered here. Thus, it may not be necessary to test a large number of parameters in order to develop understanding of soil physical properties at a given location within the network.

We highly recommend including basic soil physical information in monitoring station metadata in similar regional networks. Based on results obtained here, it may be possible to limit data collection to a subset of relatively easy to obtained soil physical properties. Nonetheless we expect that the data can be very helpful to evaluate soil moisture data quality on a physically realistic basis and/or for extending network products for additional applications. Information obtained in this study is currently being implemented into routine reporting procedures for the NC ECONet (see Appendix 2).

Analysis continued with direct examination of soil relationships with ECONet θ observations. Evaluation of the relationship of select, semi-qualitative soil taxonomic classes to seasonal and whole-year ECONet θ (via ANOVA) revealed that the greatest significance was for the taxonomic descriptor particle size class. Additional MLR analysis of ECONet seasonal θ with measured (i.e. quantitative) soil physical properties suggested two water retention parameters, along with potential evapotranspiration, were most significant. The strong correlation of individual parameters revealed through correlation analysis and PCA, as well as the significance of only a few soil parameters in the MLR, again suggests that the influence of soil physical properties on ECONet θ might be explained by measurement of a small subset of soil properties. Coupled with results based on analysis with soil taxonomy, the most appropriate soil property measurement may be particle size distribution (i.e. texture).

Poor spatial correlation of daily, statewide ECONet θ was observed and may indicate that interpolation is not warranted. However, this result may be due to the relatively low number of

ECONet sites available and the distances between these. As the network grows and increases in density, the resulting larger datasets will need to be examined to determine whether stronger spatial correlation is evident, increasing the likelihood that interpolation would yield reasonable θ estimates. Statewide spatial correlation did improve with longer time scales, which is reasonable given that these longer time scales integrate a highly spatially and temporally variable parameter, θ. In continuing research, we will analyze correlation of θ with other parameters like precipitation and evapotranspiration, for which data are available from many more stations (~12,000). If soil moisture is correlated with either or both of these, co-kriging θ with them should improve estimation.

AMSR-E θ cannot presently be used with ECONet θ to interpolate θ since they are not correlated on a statewide scale. At least in part, this was due to AMSR-E's low θ estimates and damped variation with respect to ECONet. The correlation did improve over seasonal and annual time scales. AMSR-E θ displayed strong spatial correlation. This might be due to the "drop-in-the bucket" processing which averages the multiple raw data returns within an EASE grid cell to determine the cell's θ. AMSR-E θ was weakly correlated to its Tb across the state, somewhat more strongly on wet versus dry days. Brightness temperature had longer ranges on dry days, whereas θ showed no trend. Brightness temperature was more spatially correlated on drier than wetter days, and on par with the spatial correlation of its θ.

Continuing research will look at whether Tb is more strongly correlated with ECONet θ than is AMSR-E θ. We will also see if we can improve estimation by incorporating auxiliary parameters like precipitation and evapotranspiration, which are monitored much more intensively ($n \approx 12{,}000$) than are ECONet and AMSR-E θ. Vegetation characteristics such as type and biomass can be estimated from vegetation indices based on data from the Moderate Resolution Imaging Spectroradiometer (MODIS), also aboard AQUA, to improve AMSR-E θ estimation. The accuracy and precision of θ estimation via passive microwave radiometry generally decreases as vegetation biomass increases. The temporal and spatial correlation could be expanded to more sites and years.

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Appendix 1

AD: Air-dried water content

AMSR-E: Advanced Microwave Scanning Radiometer

ANOVA: Analysis of variance

AURO: Aurora ECONet Station

BD: Bulk density

CAST: Castle Hayne ECONet Station

CLIN: Clinton ECONet Station

CV: Coefficient of variation

DURH: Durham ECONet Station

ECONet: Environment and Climate Observing Network

FLET: Fletcher ECONet Station

EASE-Grid: Equal-Area Scalable Earth Grid

HIGH: High Point ECONet Station

JACK: Jackson Springs ECONet Station

Ks: Saturated hydraulic conductivity

MLR: Multiple linear regression

MODIS: Moderate Resolution Imaging Spectroradiometer

NC: North Carolina

NSIDC: National Snow and Ice Data Center

OXFO: Oxford ECONet Station

PLYM: Plymouth ECONet Station

P10: Water retained at 10 kPa

P33: Water retained at 33 kPa

P66: Water retained at 66 kPa

P100: Water retained at 100 kPa

P500: Water retained at 500 kPa

P1500: Water retained at 1500 kPa

PC: Principal component

PCA: Principal component analysis

PET: Potential evaportranspiration

ROCK: Rockingham ECONet Station

SCO: North Carolina's State Climate Office

SILR: Siler City ECONet Station

SD: Standard deviation

Tb: Brightness Temperature

WAYN: Waynesville ECONet Station

θ: Soil moisture content

Appendix 2

Publications

Theses

Pan, W. 2010. Soil Moisture Characterization with North Carolina Environment and Climate Observing Network. M.S. Thesis, NCSU.

Presentations (listed chronologically)

Pan, W., J.L. Heitman, R.P. Boyles, and J.G. White. Soil Moisture Characterization with the North Carolina Environmental and Climate Observing Network. Soil Sci. Soc. Am. Meeting. Pittsburgh, PA. Nov. 5-9, 2009.

Pan, W., J.L. Heitman, R.P. Boyles, and J.G. White. Soil Moisture Characterization with the North Carolina Environmental and Climate Observing Network. Soil Sci. Soc. of NC Annual Meeting. Raleigh, NC. Jan. 19-20, 2010.

Pan, W. Soil Moisture Characterization with NC Environment and Climate Observing Network. NCSU Graduate Student Research Symposium, Raleigh, NC. March 10, 2010.

Pan, W., J.L. Heitman, R.P. Boyles, and J.G. White. A Study to Improve Soil Moisture Observations with the NC ECONet. NC WRRI Annual Conference, Raleigh, NC. March 30-31, 2010.

Heitman, J.L. Soil Physics Research at NCSU: Evapotranspiration, Heat Flux, Temperature, and Water. Southern Region Environmental Soil Physics (SDC333) Annual Meeting, Nashville, TN. May 20, 2010.

Heitman, J.L., C. D'Aiuto, W. Pan, J.G. White, and R. Boyles. Soil Moisture Maps for Agricultural Management Decision Support. Southeast Climate Consortium (SECC) Annual Program Review, Raleigh, NC. May 24-25, 2010.

D'Aiuto, C. 2010. Passive Microwave Remote Sensing of North Carolina Soil Moisture for Hydrologic Assessment and Forecasting. NCSU Soil Science Department Seminar. Raleigh, Sep. 29, 2010.

D'Aiuto, C., J. White, J.L. Heitman and R.P. Boyles. Passive Microwave Remote Sensing of NC Soil Moisture for Hydrologic Assessment and Forecasting. ASA-CSSA-SSSA Int'l Annual Meetings. Long Beach, CA. Nov. 2, 2010.

Pan, W., J.L. Heitman, J. White, R. Boyles and R. Austin. Improved Soil Moisture Products From the North Carolina Environment and Climate Observing Network. ASA-CSSA-SSSA Int'l Annual Meetings. Long Beach, CA. Nov. 3, 2010.

Pan, W., J.L. Heitman, J. White, R. Boyles and R. Austin. Improved Soil Moisture Products From the North Carolina Environment and Climate Observing Network. Soil Sci. Soc. of NC Annual Meeting. Raleigh, NC. Jan. 18-19, 2011.

D'Aiuto, C., J. White, J.L. Heitman, and R.P. Boyles. Passive Microwave Remote Sensing of NC Soil Moisture for Hydrologic Assessment and Forecasting. NC WRRI Annual Conference, Raleigh, NC. Mar. 22-23, 2011.

Technology Transfer

Soil moisture indices based on ECONet data and data reported herein are available online through the State Climate Office database CRONOS < http://www.nc-climate.ncsu.edu/cronos>. These include a saturation index, defined as the ratio between observed soil moisture content and measured porosity, and plant available water, defined as the observed water content minus the measured water retention at 1500 kPa (set with max at water retention at 33 kPa minus water retention at 1500 kPa, min at zero). Metadata for soil observations will also be made available through the SCO to aid in data interpretation. Development of additional products based on incorporation of AMSR-E data may be pursued pending outcomes of ongoing analyses.

Microbial Contaminants Associated with Urbanization of a Drinking Water Reservoir

Basic Information

Title:	Microbial Contaminants Associated with Urbanization of a Drinking Water Reservoir
Project Number:	2010NC147B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	NC-04
Research Category:	Water Quality
Focus Category:	Non Point Pollution, Water Quality, Water Supply
Descriptors:	None
Principal Investigators:	Jill Stewart

Publications

1. Rowny, JG (2011). Characterization of nonpoint source microbial contamination in an urbanizing watershed serving as a municipal water supply. MS thesis. University of North Carolina, Chapel Hill.
2. Wang, AT (2011). Influence of land use and storm events on dissolved organic matter quantity and quality in the Jordan Lake watershed. MSPH technical report. University of North Carolina, Chapel Hill.

Microbial Contaminants Associated with Urbanization of a Drinking Water Reservoir

WRRI Project # 70252

Jill R. Stewart and Jakob G. Rowny
University of North Carolina, Chapel Hill

Second Project Report
Submitted to:
The University of North Carolina Water Resources Research Institute (WRRI)
02/28/2011

This report summarizes progress and planned activities by researchers at the University of North Carolina, Chapel Hill for WRRI Project # 70252, *Microbial Contaminants Associated with Urbanization of a Drinking Water Reservoir*. The period of performance for this project is 03/01/2010 though 02/28/2011, and this report includes progress for the first 11.5 months, through 02/15/11.

Project Activities:

Sample Collection and Analysis. As of February 16th, 2011, we have collected 271 dry-weather samples during the course of 19 sampling runs. We plan to collect the final 15 dry-weather samples 3/02/2011. We have also collected an additional 135 storm samples from three separate precipitation events. The following measurements for all samples have been completed: temperature, dissolved oxygen, conductivity, total dissolved solids, pH and turbidity. Completed microbial assays include measurements of fecal coliforms (bi-monthly), *E. coli* (bi-monthly), male-specific coliphages (monthly) and somatic coliphages (monthly). Molecular analysis for pathogens and source tracking markers is on-going. Also, samples for nutrient analysis have been collected and prepped, and shared with project collaborators as originally planned. However, nutrient analysis has been delayed, making it unlikely that the microbial measures determined for our project will be directly compared to nutrient concentrations from the same samples during the project period. Comparisons will proceed once the nutrient concentrations are determined. Although not included in the original proposal, samples have also been shared with Dr. Rose Cory at UNC for analysis and characterization of dissolved organic matter.

Student Involvement. Three graduate students are using this project as the basis of their thesis or dissertation. Jakob Rowny, who led the field campaign, will use this work as the basis of his masters thesis which he plans to defend in March. Angela Wang, supervised by Dr. Cory, is also basing a masters thesis on this project. Finally, Jen Shields, a PhD candidate at UNC, will use this work as the basis for one chapter of her dissertation focused on pathogen detection and microbial source tracking. Additional undergraduate (4) and graduate students (3) have been involved in sample collection and sample processing, particularly during labor-intensive processing of rain event samples.

Statistical Analysis. We began preliminary statistical analysis during this reporting period. Final analysis will occur once the final samples set has been collected and processed during the first week of March, 2011. Planned analysis includes the characterization of both dry-weather and storm event microbial loading patterns, as well as fecal indicator bacteria (FIB) concentration correlations with antecedent precipitation, stream flow, water temperature and land cover metrics such as watershed imperviousness. The effects of sample type (dry-weather vs. storm), watershed imperviousness and watershed area on FIB concentrations will be evaluated using a 3-factor analysis of variance, with sample type, watershed imperviousness and watershed area as fixed factors.

Land Cover Update. On February 15th, 2011, the Multi-Resolution Land Characteristics Consortium released more current National Land Cover Data (2006) and updated the last most recent release (2001). For the extent of our study area, the 2001 data made use of satellite imagery captured in October 1999, while the 2006 data were based on imagery from October, 2005. Unlike earlier iterations, these data are directly comparable because NLCD has finalized their standard methodology. Measures

of land cover and impervious surfaces in all upstream watersheds were updated to both 1999 and 2005 values.

Preliminary Project Findings:

Land Cover Update: Comparisons of land cover data from the 2001 and 2006 NLCD indicate rapid changes in land use both within individual creek watersheds and across the entire study area (Table 1).

While percent changes on the scale of individual watersheds varied considerably, the overall pattern is of net increases in development, agricultural use and impervious surfaces and a net decrease in forested lands. The smallest increases in percent development and imperviousness occurred in watersheds that were already highly developed in 1999 (TFWP, SC) or where local land use policy and regulations limit new building (CBC, MCWC).No watershed decreased in either developed lands or impervious surfaces. Forest land cover decreased in 12 of the 15 watersheds and across the entire study area. These rapidly occurring land use trends are in accordance with other data, such as economic indicators and census data that also reflect sustained local patterns of recent growth.

Table 1: Land cover and imperviousness of individual creek watersheds in Oct. 1999, Oct. 2005 and percent change.

		Land cover classification											
		Developed			Agricultural			Forested			Imperviousness		
Creek	**Area (ha)**	**1999**	**2005**	**% change**	**1999**	**2005**	**% change**	**1999**	**2005**	**% change**	**1999**	**2005**	**% change**
MCWC	2197.5	5.27	5.31	0.9	22.04	22.55	2.3	71.92	71.50	-0.6	0.46	0.46	0.0
MWC	231.1	83.51	85.71	2.6	0.00	0.00	0.0	16.49	14.29	-13.4	33.33	34.01	2.0
MCCH	10420.3	18.23	18.29	0.4	14.32	14.87	3.8	66.28	65.73	-0.8	3.98	4.01	0.9
LCPGC	4929.5	54.05	55.15	2.0	5.14	4.59	-10.7	39.81	39.27	-1.3	9.92	10.24	3.2
MC1726	12008.8	19.07	19.16	0.5	13.47	14.08	4.6	64.86	64.16	-1.1	4.07	4.13	1.4
NHCB	19733.6	39.32	40.41	2.8	7.85	8.30	5.7	47.28	45.79	-3.2	8.33	8.78	5.4
NECG	5463.5	55.06	57.10	3.7	4.84	4.67	-3.4	35.59	33.85	-4.9	13.67	14.43	5.6
NECLG	779.1	61.54	67.15	9.1	2.68	2.26	-15.8	34.86	29.90	-14.2	13.04	14.95	14.6
TFWP	3839.8	84.40	85.35	1.1	0.78	0.76	-2.6	10.68	9.79	-8.3	17.75	18.25	2.8
TFFHP	151.0	99.31	99.31	0.0	0.00	0.00	0.0	0.69	0.69	0.0	17.14	17.14	0.0
SC	1224.4	78.52	78.52	0.0	0.94	0.94	0.0	20.35	20.35	0.0	21.58	21.90	1.5
MUD	1383.7	33.07	34.55	4.5	8.20	10.89	32.9	55.91	51.80	-7.4	4.72	4.97	5.4
NHCE	8165.4	7.73	7.97	3.1	13.58	14.49	6.7	77.14	76.00	-1.5	1.01	1.08	6.5
NHCTF	5846.5	8.00	8.33	4.2	15.57	16.88	8.4	74.41	72.79	-2.2	1.21	1.30	7.6
CBC	141.8	11.76	11.76	0.0	9.97	9.97	0.0	76.98	76.98	0.0	3.61	3.61	0.0
Total	**42135.4**	**37.31**	**38.24**	**2.5**	**8.74**	**9.04**	**3.4**	**49.90**	**48.71**	**-2.4**	**7.99**	**8.36**	**4.6**

Preliminary Loading Characterization:

Dry-weather FIB loads demonstrated considerable seasonal variation. Both FC and EC dry-weather loading per 24 hour period (day) was an order of magnitude greater during spring months in comparison to all other seasons (Table 2).

Table 2: Seasonal dry-weather FIB loading, all creeks combined

Season	Total Loading (FC CFU/24 hrs)	Total Loading (EC CFU/24 hrs)	EMC (FC CFU/100 ml)	EMC (EC CFU/100 ml)
Spring (n = 33)	3.79×10^{11}	2.10×10^{11}	919.93	541.05
Summer (n = 36)	8.84×10^{10}	5.51×10^{10}	546.6	283.81
Autumn (n = 23)	4.97×10^{10}	2.69×10^{10}	160.22	97.75
Winter (n = 17)	1.62×10^{10}	1.63×10^{10}	59.82	58.31
Average	**1.48×10^{11}**	**8.56×10^{10}**	**502.16**	**289.15**

Average storm event loading of both FC and EC greatly surpassed average 24 hour dry-weather loading at all creek sites (Table 3). FC event loading was consistently greater than EC event loading. The average storm event FC load was equivalent to 249 days of dry-weather loading. The average storm event EC load would require 52 days of dry-weather loading.

Table 3: Average dry-weather (DW) and average storm event FIB loads for all creeks and equivalent days of dry-weather necessary to equal event loading of both FC and EC.

	FC Loading			EC Loading		
Creek	**DW (CFU/24 hrs)**	**Storm (CFU/Storm)**	**DW days**	**DW (CFU/24hrs)**	**Storm (CFU/Storm)**	**DW days**
MCWC	9.78×10^{9}	1.43×10^{12}	146.01	5.51×10^{9}	5.78×10^{11}	104.96
MWC	1.54×10^{11}	2.45×10^{13}	159.11	9.91×10^{10}	3.05×10^{12}	30.72
MC1726	2.24×10^{11}	1.30×10^{13}	58.28	2.08×10^{11}	3.81×10^{12}	18.31
NHCB	4.41×10^{11}	1.72×10^{14}	390.39	1.84×10^{11}	8.90×10^{12}	48.31
NECG	1.11×10^{11}	2.05×10^{13}	184.01	5.12×10^{10}	4.79×10^{12}	93.65
TFWB	5.91×10^{10}	1.92×10^{13}	324.58	3.78×10^{10}	7.73×10^{12}	204.46
SC	3.85×10^{10}	7.61×10^{12}	197.42	1.36×10^{10}	2.62×10^{12}	192.84
All creeks combined	**1.48×10^{11}**	**3.69×10^{13}**	**249.02**	**8.56×10^{10}**	**4.50×10^{12}**	**52.49**

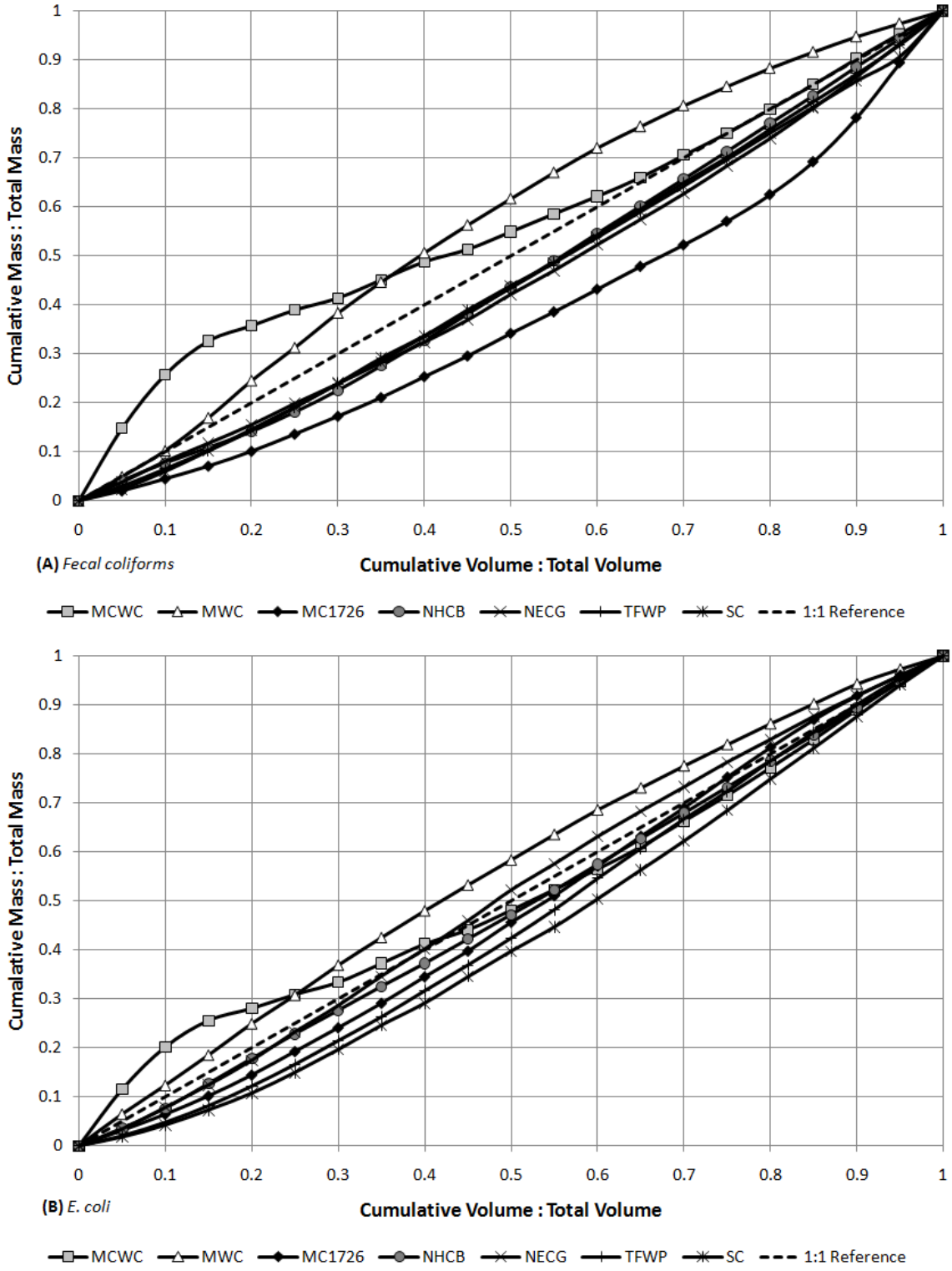
Average mass to volume (M/V) curves for each creek indicate that loading of both FC and EC remains relatively constant over the course of storms (Figure 1). The average creek data do not provide evidence to support first flush loading of either FC or EC pollutants in the sampled watersheds. Averaged individual creek FC and EC loading after the initial 30% runoff volume for all storms was 27.3% and 27.4% of total mass, respectively (Table 4).

Table 4: Range and average of FC and EC mass loading after initial 30% volume storm runoff for individual creeks and all creeks combined.

	FC		EC	
Creek	**Range**	**Average**	**Range**	**Average**
MCWC	10.8 - 81.4%	41.4%	8.1 - 66.6%	33.4%
MWC	30.1 - 43.2%	38.3%	31.5 - 44.8%	36.9%
MC1726	13.4 - 21.7%	17.3%	20.7 - 29.6%	24.1%
NHCB	12.4 - 29.2%	22.5%	22.9 - 32.2%	27.7%
NECG	14.6 - 32.5%	23.9%	24.0 - 31.3%	28.6%
TFWP	14.9 - 33.2%	23.9%	16.6 - 24.4%	21.4%
SC	18.0 - 31.8%	24.0%	15.7 - 22.9%	19.6%
All creeks combined	**10.8 - 81.4%**	**27.3%**	**8.1 – 66.6%**	**27.4%**

Interestingly, the two creeks with the greatest initial average FC and EC loading, MCWC and MWC, differ considerably in watershed land use and impervious surface coverage. The watershed upstream of MCWC is predominantly forested (71.5%) and has the least impervious surface coverage (0.46%) of all sampled watersheds. In contrast, the MWC watershed contains the main campus of the University of North Carolina at Chapel Hill and is highly developed (85.7%). Additionally the MWC watershed has the greatest impervious surface coverage (34.0%) of all sampled watersheds. These results are largely consistent with other studies that have found no strong pattern of first flush loading of microbial contaminants (Stumpf et al, 2010; Krometis et al, 2007; Surbeck et al, 2006).

Figure 1: Average mass to volume (M/V) curves for (A) FC and (B) EC at each gauged creek site.



FIB Concentration Patterns

Antecedent precipitation, streamflow, water temperature:

Measures of total precipitation, storm event duration, 2-hour, 24-hour, 48-hour and 7 day antecedent precipitation (AP) were highly variable between storms. Total precipitation ranged from 0.28 to 9.84 cm. Storm event duration ranged from 7 to 32 hours. Most measures of AP were moderately and positively correlated with both EC and FC concentrations. Across all watersheds, there were significant correlations between both EC and FC concentrations and all measures of AP (Tables 4 and 5).

At gauged creeks, correlations between streamflow (m^3/sec) and FIB concentrations were inconsistent. Three of seven creeks (NECG, TFWP and SC) demonstrated moderate correlations between FIB concentrations and streamflow, but the remaining four had flat responses. Interestingly, the three creek sites where these relationships were significant had higher measures of upstream surface imperviousness than the creeks where streamflow correlations were not significant, although the creek with the highest measure of upstream impervious surfaces (MWC) did not follow this pattern.

Table 4: Spearman's rank correlations (R^2) for all creeks combined and individual creek sites for measures of streamflow and antecedent precipitation vs. EC concentrations (log 10 (x + 1) CFU/100 ml)

		Antecedent precipitation			
Creeks	**Streamflow**	**2 hr**	**24 hr**	**48 hr**	**7 day**
All creeks combined	**0.005**	**0.030****	**0.274****	**0.412****	**0.328****
MCWC	0.002	0.292**	0.412**	0.514**	0.340**
MWC	0.000	0.052	0.356**	0.354**	0.196*
MCCH	-	0.032	0.473**	0.348**	0.144
LCPGC	-	0.010	0.494**	0.588**	0.472**
MC1726	0.001	0.013	0.163	0.264**	0.125
NHCB	0.073	0.006	0.125	0.354**	0.245*
NECG	0.359**	0.048	0.419**	0.458**	0.222*
NECLG	-	0.002	0.248*	0.549**	0.453**
TFWP	0.412**	0.036	0.292**	0.536**	0.520**
TFFHP	-	0.043	0.549**	0.610**	0.387**
SC	0.413**	0.023	0.591**	0.719**	0.430**
MUD	-	0.026	0.297**	0.551**	0.501**
NHCE	-	0.013	0.206*	0.460**	0.387**
NHCTF	-	0.082	0.367**	0.533**	0.661**
CBC	-	0.000	0.125	0.114	0.287*

*Significant at $p < 0.05$ ** Significant at $p < 0.01$

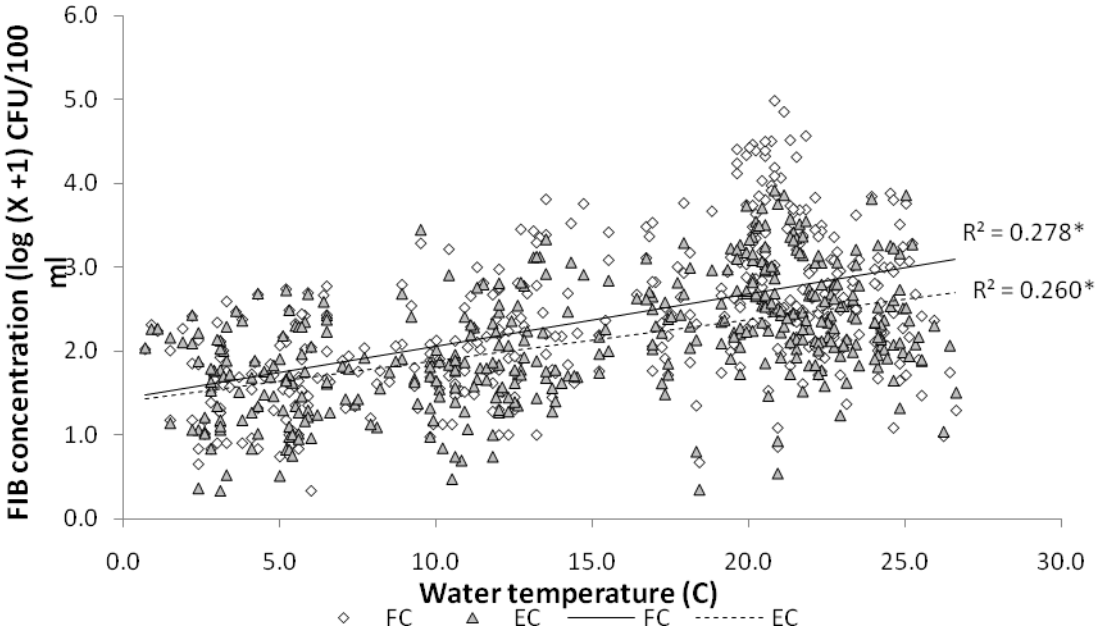
Table 5: Spearman's rank correlations (R^2) for all creeks combined and individual creek sites for measures of antecedent precipitation vs. FC concentrations (log 10 (x + 1) CFU/100 ml)

		Antecedent precipitation			
	Streamflow	**2 hr**	**24 hr**	**48 hr**	**7 day**
All creeks combined	**0.016**	**0.034****	**0.317****	**0.464****	**0.387****
MCWC	0.002	0.299**	0.433**	0.471**	0.340**
MWC	0.002	0.052	0.540**	0.507**	0.320**
MCCH	-	0.053	0.543**	0.491**	0.308**
LCPGC	-	0.010	0.573**	0.587**	0.440**
MC1726	0.025	0.007	0.210*	0.341**	0.292**
NHCB	0.085	0.032	0.183*	0.448**	0.305**
NECG	0.218*	0.021	0.282**	0.454**	0.339**
NECLG	-	0.002	0.318**	0.552**	0.506**
TFWP	0.397**	0.020	0.307**	0.554**	0.526**
TFFHP	-	0.038	0.520**	0.712**	0.484**
SC	0.333**	0.027	0.466**	0.557**	0.311**
MUD	-	0.007	0.316**	0.672**	0.551**
NHCE	-	0.053	0.196*	0.387**	0.336**
NHCTF	-	0.087	0.331**	0.588**	0.706**
CBC	-	0.007	0.272*	0.253	0.392*

*Significant at $p < 0.05$ ** Significant at $p < 0.01$

Both FC and EC log-transformed concentrations were moderately but significantly correlated with water temperature (Figure 2).

Figure 2: Relationship between log-transformed FIB concentrations and water temperature. *Spearman's rank correlations significant at p < 0.001.



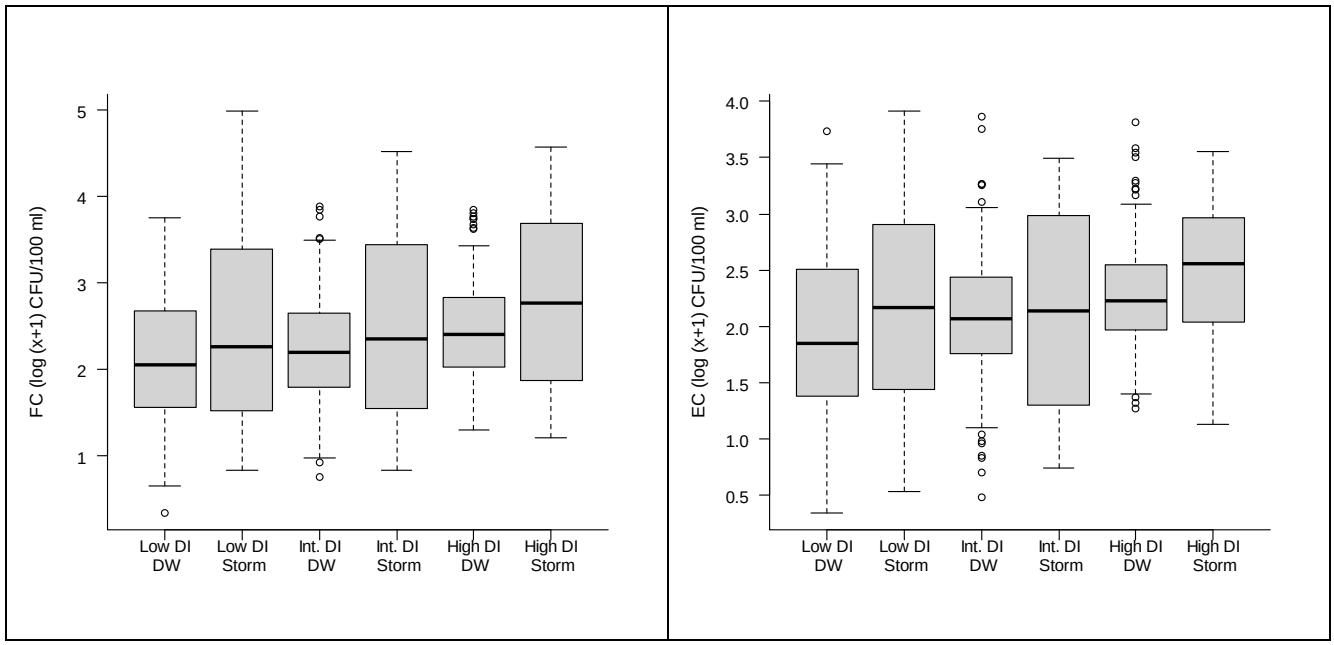
Land Cover and Impervious Surfaces:

Sites were divided into three levels of development intensity, as measured by % IS in the watershed upstream of each sampling point. The five sites with the lowest % IS were assigned to the 'Low intensity' development class (0 to 3.93%), the five sites with intermediate % IS were assigned to the 'Intermediate intensity' class (3.94 to 12.89 %) and the five sites with the largest % IS were assigned to the 'High intensity' class (12.90 to 33.10%). These % IS measures were derived from the earlier 2001 NLCD, but will be updated to the 2006 release.

Table 6: Summary statistics of FC and EC concentrations (CFU/100 ml) by development intensity class and sample type

			Development intensity class		
			Low n = 131	**Intermediate** n = 137	**High** n = 138
Sample Type	**DW FC** n = 271	Mean	421.04	611.05	836.64
		Std dev	*825.68*	*1322.07*	*1514.17*
	Storm FC n = 135	Mean	7348.75	3578.38	4876.40
		Std dev	*18818.83*	*7353.11*	*8956.49*
	DW EC n = 271	Mean	272.68	384.77	482.65
		Std dev	*677.62*	*996.91*	*948.27*
	Storm EC n = 135	Mean	900.87	515.56	718.64
		Std dev	*1783.11*	*770.03*	*903.95*

Figure 3: Summary Tukey box plots divided by development intensity (DI) class and sample type (a) FC and (b) EC



FIB concentrations varied by sample type and development intensity class (Table 6). During dry-weather, mean concentrations of both FC and EC in the most developed watersheds were about twice those in the least developed watersheds. Mean storm concentrations of both FC and EC deviated from this pattern, but log-transformed median storm concentrations were consistently greater than corresponding dry-weather measurements and increased with development intensity (Figure 3).

3-Factor ANOVAs:

For all FIB parameters, 3-factor analyses of variance were used to determine the significance of relationships between log-transformed concentrations, sample type, development intensity and watershed area. Both sample type and development intensity were shown to have significant main effects on all FIB concentrations (Table 7). Watershed area did not have a significant main effect on any of the FIB parameters. However, there was a significant interaction effect between watershed area and development intensity on EC concentrations.

Table 7: Results of 3-factor ANOVA and pair wise comparisons performed on log-transformed FIB concentrations.

	Factor			Pair wise comparisons	
Parameter	**Sample type (Storm vs. DW) *p***	**Development intensity *p***	**Watershed area *p***	**Sample type**	**Development intensity**
EC[1]	0.02	3.32×10^{-5}	0.16	DW[a] Storm[b]	Low[a] Int[a] High[b]
FC	4.91×10^{-5}	0.0008	0.12	DW[a] Storm[b]	Low[a] Int[a] High[b]
EC (EMC)	0.02	0.01	0.67	DW[a] Storm[b]	Low[a] Int[a,b] High[b]
FC (EMC)	0.01	0.09	0.34	DW[a] Storm[b]	-

Tukey pair wise comparisons were performed on significant factors. Factor levels with same superscripts were not significantly different at $p < 0.05$.
DW= dry-weather; Int = Intermediate
[1] There was a significant interaction effect ($p = 0.01$) between development intensity and watershed area (see Table 8 for pair wise comparisons).

For all parameters, upstream watersheds having low (0-3.93% IS) and intermediate (3.94-12.89% IS) levels of imperviousness did not differ significantly. However, FIB concentrations were significantly greater in watersheds assigned to the high intensity development class (12.90-33.10 % IS). While these results do not necessarily support a specific watershed imperviousness threshold, they do indicate that watersheds with higher levels of imperviousness have greater FIB concentrations.

Analysis of the significant interaction effect between development intensity and watershed size reveals that small watersheds with high %IS had significantly greater EC concentrations than most other watershed types (Table 8). Three creeks fall into this category: MWC, TFFHP and SC. The presence of this higher order interaction effect suggests that development and increasing watershed imperviousness does not have a uniform effect on EC concentrations. Instead, the influence of watershed imperviousness is heightened in smaller watersheds.

Table 8: Pair wise comparisons of development intensity | watershed area interaction effect on EC concentrations

Interaction	difference	lower	upper	*p*
High DI:Small | High DI:Large	NA	NA	NA	NA
High DI:Small | Low DI:Small	0.147	-0.389	0.682	0.99
High DI:Small | High DI:Medium	0.201	-0.169	0.572	0.75
High DI:Small | Int. DI:Large	0.462	0.091	0.833	0.004
High DI:Small | Low DI:Large	0.497	0.162	0.832	0.0002
High DI:Small | Low DI:Medium	0.540	0.070	1.011	0.01
High DI:Small | Int. DI:Small	0.558	0.067	1.048	0.01

No other pair wise comparisons of the interaction effect were significant at $p < 0.05$.

References:

Krometis, L., Characklis, G., Simmonsiii, O., Dilts, M., Likirdopulos, C., Sobsey, M., 2007. Intra-storm variability in microbial partitioning and microbial loading rates. Water Research. Vol. 41, No. 2 (1): 506-516.

Stumpf, C. H., Piehler, M. F., Thompson, S., Noble, R.T., 2010. Loading of fecal indicator bacteria in North Carolina tidal creek headwaters: hydrographic patterns and terrestrial runoff relationships. Water Research. Vol. 44, No. 16 (9): 4704-4715.

Surbeck C.Q., Jiang, S.C., Ahn, J.H., Grant, S.B., 2006. Flow fingerprinting fecal pollution and suspended solids in stormwater runoff from an urban coastal watershed. *Environ. Sci. Technol.* Vol. 40(14): 4435-4441.

Fate of Fats, Oils, and Grease (FOG) Deposit Forming Precursors in Sewer Systems

Basic Information

Title:	Fate of Fats, Oils, and Grease (FOG) Deposit Forming Precursors in Sewer Systems
Project Number:	2010NC148B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	NC-02
Research Category:	Engineering
Focus Category:	Wastewater, Treatment, Water Quality
Descriptors:	None
Principal Investigators:	Francis de los Reyes, Joel J Ducoste

Publication

1. He, X., M. Iasmin, L. Dean, S. Lappi, J. J. Ducoste and F. L. de los Reyes III (2011). Evidence for How Fat, Oil, and Grease (FOG) Deposits Form in Sewer Lines. Environmental Science and Technology, in press.

Progress Report (as of 4/2011)
Submitted to
NC Water Resources Research Institute

Project Title: Factors Affecting the Formation of Fats, Oils, and Grease Deposits in Sewer Systems
and
Fate of FOG Deposit Forming Precursors in Sewer Systems

PI: Francis L. de los Reyes III, Associate Professor,
Joel J. Ducoste, Professor,
Department of Civil, Construction, and Environmental Engineering, North Carolina State University

Background
We are combining the reports for the two WRRI projects, as they are related, and being conducted by the same research team (PIs, grad student and undergraduate assistants).

The **overall objective** of the first project is to quantify the effects of kitchen wastewater characteristics on FOG deposit formation mechanism and rate. Specifically, we propose to determine the impacts of the : (1) the nature of food particles (carbohydrate, protein, and lipid) from food grinders/disposal units; (2) type of oil (e.g., animal fats, vegetable oils); (3) hydraulic changes; (4) type of pipe material; and (5) addition of cations such as Ca^{2+}.

The **overall objective** of the second project is to test the hypothesis that FOG formation in sewers is caused via a saponification-like reaction involving major chemical precursors: free fatty acids, a metal cation, and surfactant. The specific objectives are:
(1) To determine the effect of type and amount of free fatty acids in kitchen wastewater on the saponification reaction; (2) To demonstrate that calcium leaching from concrete (for example, from pre-cast concrete grease interceptors) at realistic conditions is the source of calcium for the saponification reaction; (3) To determine the effect of surfactant levels on FOG formation; (4) To develop a new FOG Deposit Formation Potential Test (FFP) that can be used to determine the propensity of a given food service wastewater to form FOG deposits, and to determine the applicability of this test to several full-scale grease interceptor effluents.

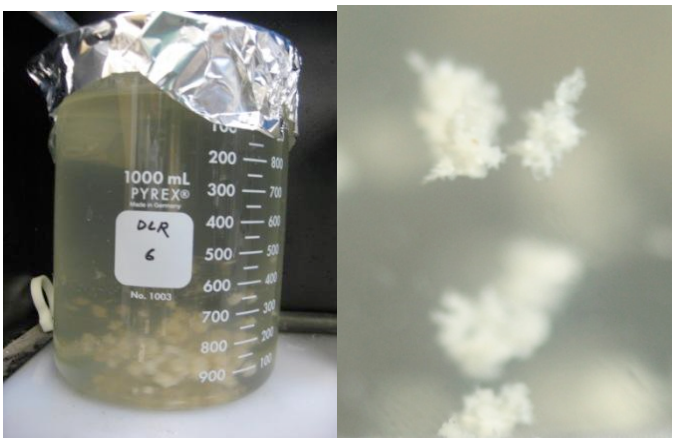
Progress to Date
One peer reviewed publication is now in press: **He, X., M. Iasmin, L. Dean, S. Lappi, J. J. Ducoste and F. L. de los Reyes III (2011). Evidence for How Fat, Oil, and Grease (FOG) Deposits Form in Sewer Lines. *Environmental Science and Technology*, in press (see attached pdf).**

Majority of the work in this paper was conducted to meet the objectives of these projects, in particular, to elucidate the mechanisms by which FOG deposits form. The work reported in the paper was mostly funded by the WRRI grant; additional funding from EPA funded another student (Mahbuba Iasmin), who is the second autor of the paper.

A. FOG DEPOSIT FORMATION MECHANISMS

1. Formation of FOG deposits in lab-scale

We have achieved the formation of FOG deposits using GI effluent, under laboratory conditions. To our knowledge, this is the first time that this has been achieved. This study and the related components (Nos. 2 and 3 below) are reported in the ES&T paper.



(a) (b)

FIGURE 1. FOG deposits formed under laboratory conditions. (a) Photo was taken at day 10 when free fatty acids reacted with calcium salt in 1L beaker; (b) Close-up of FOG deposit particles.

2. Comparison with natural FOG deposits

We found a high similarity between FOG deposits formed in lab scale and natural FOG deposits using fatty acid analysis and calcium & total fat analysis.

a. Fatty acid analysis

TABLE 1. Fatty acid composition of FOG deposits

Sample	Total fat[a] (g/g)	Saturated fat[b] (%)	Primary saturated fat	Mono-unsaturated fat[c] (%)	Primary mono-unsaturated fat	Poly-unsaturated fat[d] (%)	Primary poly-unsaturated fat
R1	0.344	78.8	Palmitic	9.8	Oleic	0.8	Linoleic
R2	0.255	57.5	Palmitic	9.0	Oleic	0.6	Linoleic
R3	0.18	70.6	Palmitic	14.0	Oleic	0.7	Linoleic
Apartment	0.261	56.5	Palmitic	38.3	Oleic & palmitoleic	1.0	Linoleic
Shopping center 1	0.393	38.7	Palmitic	37.2	Oleic	15.3	Linoleic
Shopping center 2	0.489	64.7	Palmitic	31.7	Palmitoleic	0.6	Linoleic

[a] Total fat content was calculated from 1 g FOG deposit sample
[b] Saturated fat is shown in percentage of the total fat
[c] Monounsaturated fat is shown in percentage of total fat
[d] Polyunsaturated fat is shown in percentage of total fa

b. Calcium and total fat analysis

TABLE 2. Calcium and total fat amounts in FOG deposits

Sample	FOG deposit weight (mg)	Calcium in FOG deposit (mg)	Total fat in FOG deposit (mg)	Total fat/ calcium (mg/mg)	Calcium/ FOG deposit (mg/mg)
R1	52.6	2.15	18.07	8.40	0.0409
R2	93.5	4.61	23.81	5.16	0.0493
R3	123.5	6.06	22.23	3.67	0.0491
Apartment	415.2	21.35	108.16	5.07	0.0514
Shopping center 1	145.5	0.13	57.22	438.42	0.0009
Shopping center 2	143.5	1.78	70.10	39.41	0.0124

3. Evidence of saponification

To prove that FOG deposit formation is the result of a saponification reaction between free fatty acids and metal ions such as calcium, Fourier transform infrared (FTIR) spectrometry was used to provide evidence of saponification.

There are four regions that can be attributed to the formation of calcium soaps: region 1: 4000-3000 cm^{-1}, the band has been associated with O-H stretching vibration of hydrated water; region 2: 1800-1350 cm^{-1}, two modes of vibration, attributed to the carboxylate group of the fatty acid metallic salt; region 3: 1350-1180 cm^{-1} and additional side band near 720 cm^{-1}, the spectral region of the aliphatic chains is sensitive to the crystallization of soap; region 4: near 670 cm^{-1}, the calcium-oxygen bond absorption band at 665 cm^{-1}.

FTIR analysis demonstrated a strong similarity between the lab-scale FOG deposit and calcium soap as shown in their infrared spectra, particularly in the absorption bands of four characteristic regions previously identified for calcium soap. Analysis of these four infrared spectral band regions indicated that FOG deposits are likely metallic salts of fatty acid made of calcium and formed as a result of saponification. However, the differences among FOG deposit samples, such as different total fat to calcium ratios and appearance of additional bands due to the un-reacted fatty acids (e.g., palmitic, oleic and linoleic), indicated that some FOG deposits are not only formed by the reaction between free fatty acids and a metal but are also aggregates made of excess calcium or fatty acids based on DLVO theory.

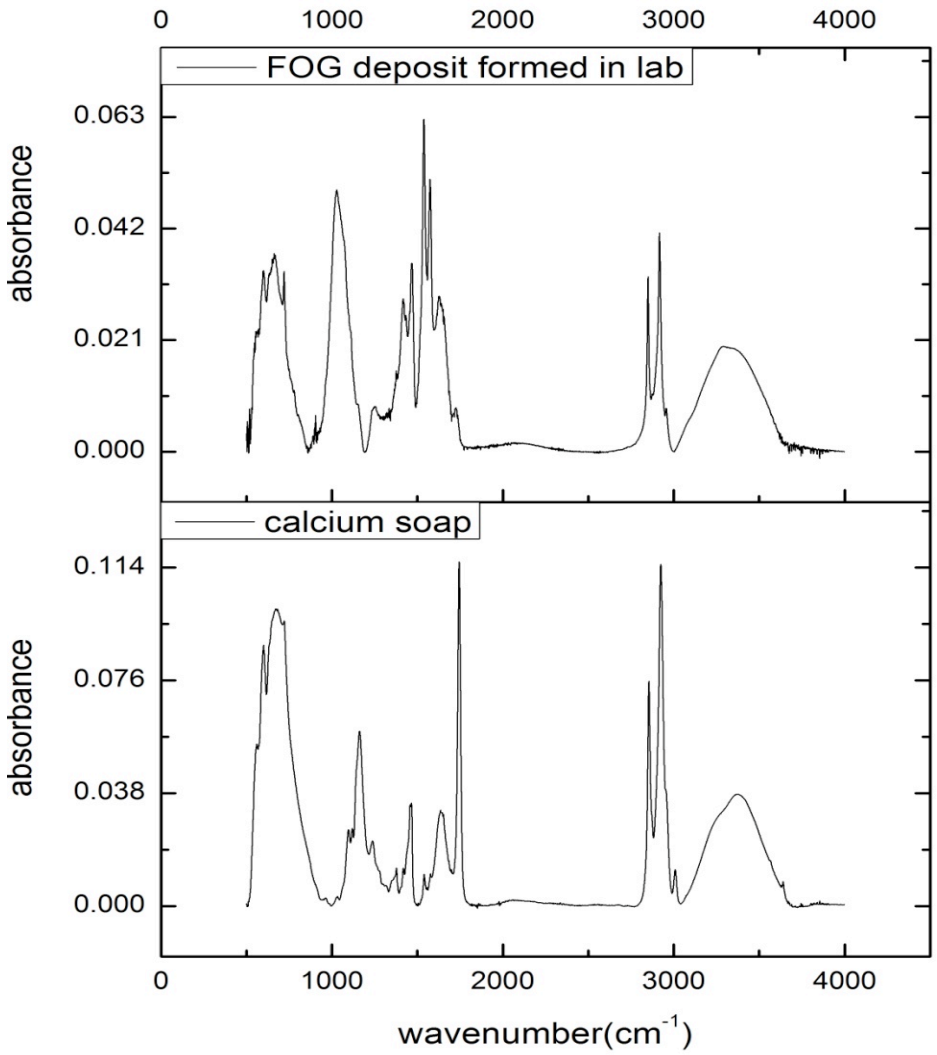


FIGURE 2. Baseline corrected infrared spectra of FOG deposit formed in the lab and calcium soap

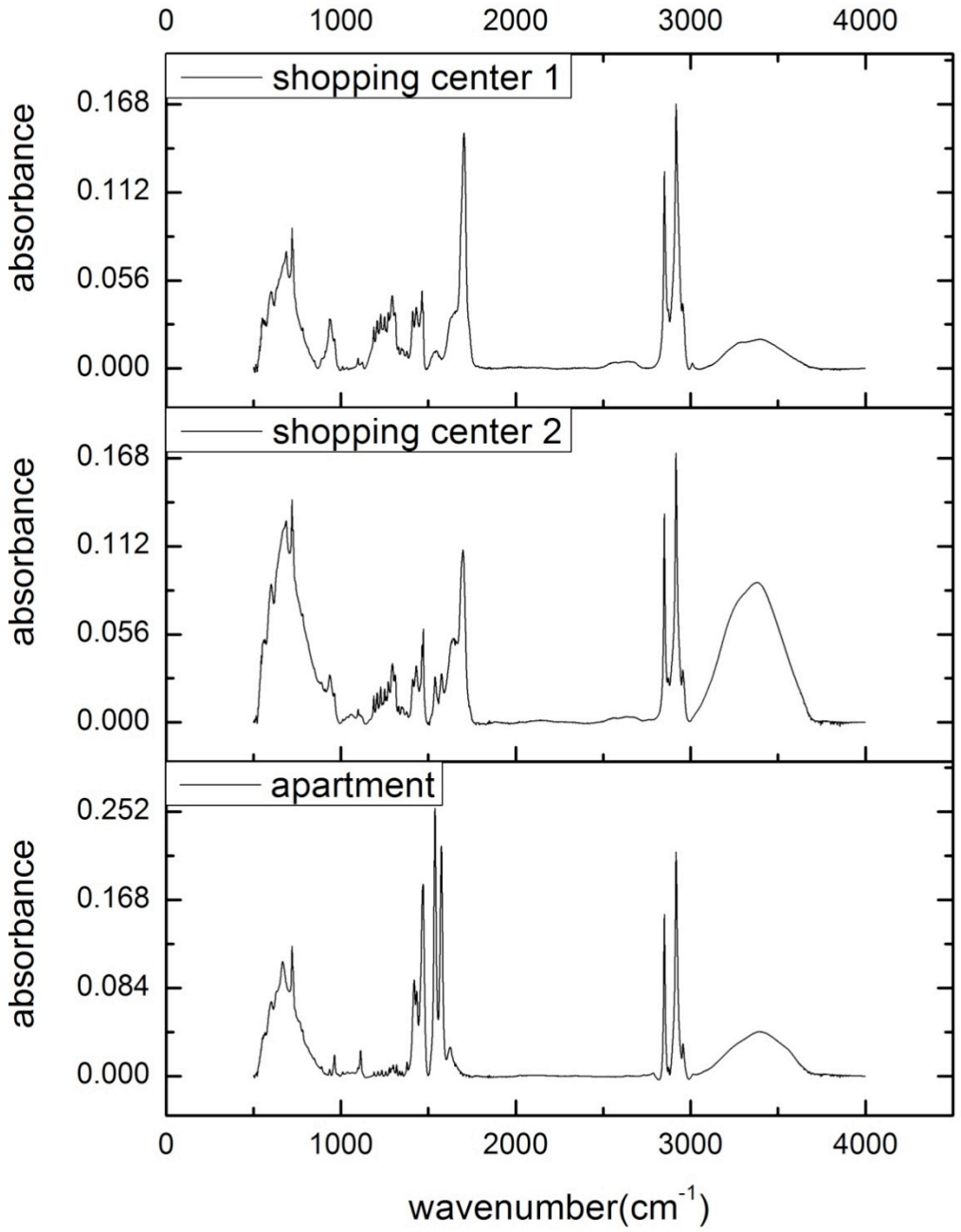


FIGURE 3. Baseline corrected infrared spectra of three FOG deposit samples from sewer lines

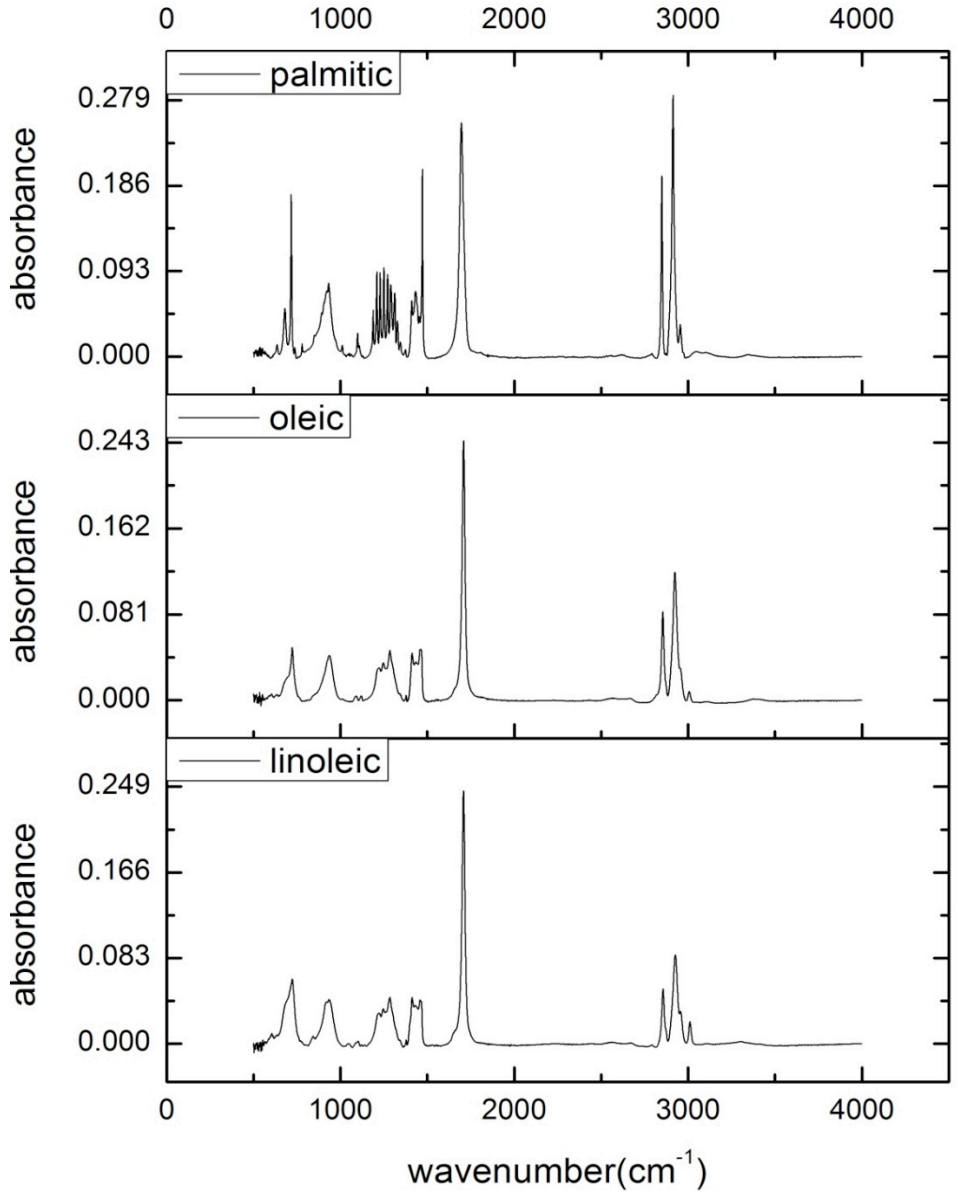


FIGURE 4. Baseline corrected infrared spectra of palmitic, oleic and linoleic acid

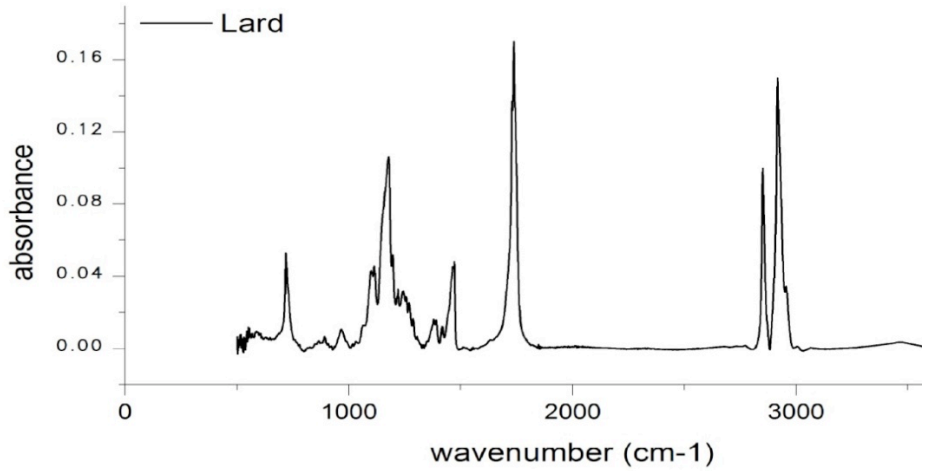


FIGURE 5. Baseline corrected infrared spectrum of lard

4. Metal leaching from concrete

We hypothesize that concrete may be the major source corresponding to the high amount of calcium in FOG deposits. The amount of metal leaching from concrete was monitored under different pH conditions.

a. Metal leaching from concrete in deionized water

Concrete specimens were placed in deionized water with different pH as shown in Figure 6. The pH was maintained by adding sulfuric acid and sodium hydroxide for 3 weeks.

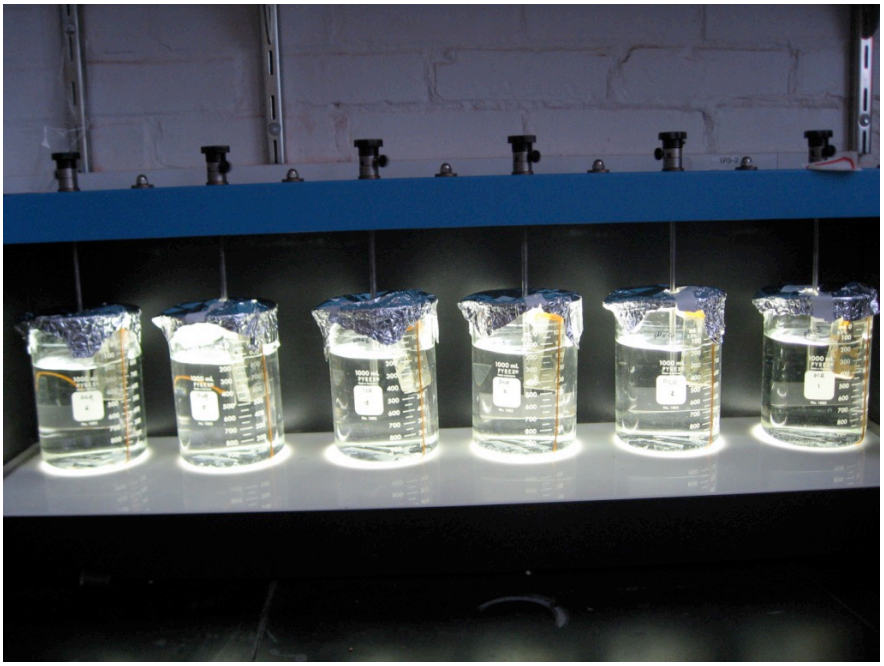


FIGURE 6. Metal leaching from concrete in deionized water at pH3, 4, 5, 6, 7, 8 from right to left

High amounts of calcium were leached under acid conditions. Even under base condition (pH=8), 50 mg/L calcium was leached from concrete (Figure 7). The amounts of potassium, iron and magnesium were also measured. Compared to calcium, these concentrations are much lower (Figure 8, 9, 10).

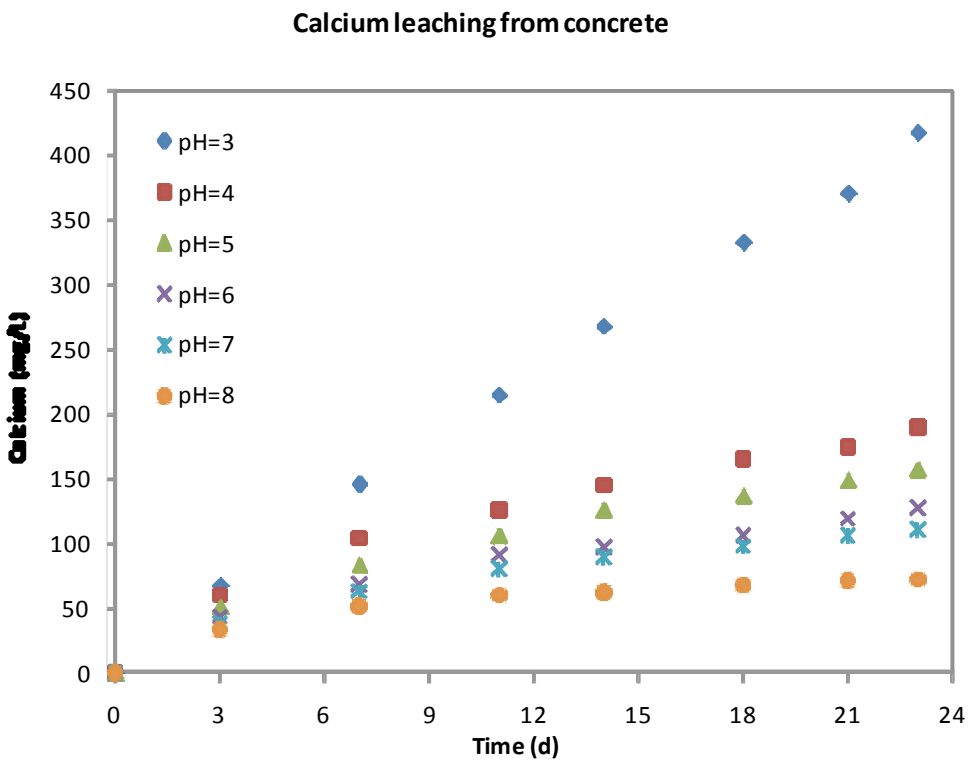


FIGURE 7. Calcium leaching from concrete at different pH in deionized water

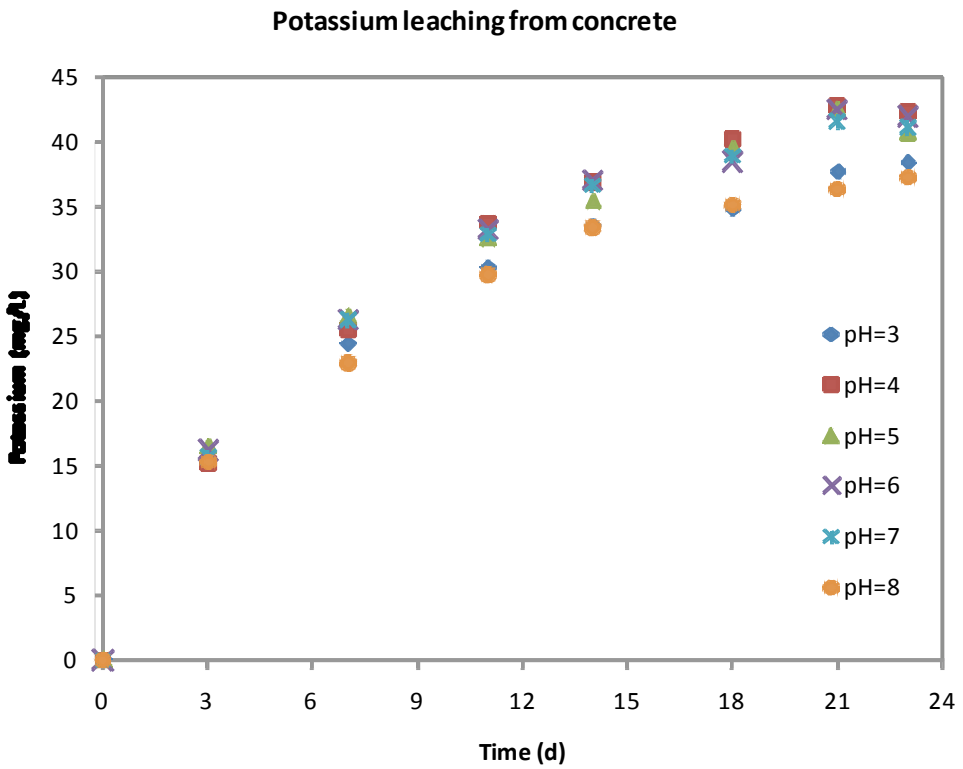


FIGURE 8. Potassium leaching from concrete at different pH in deionized water

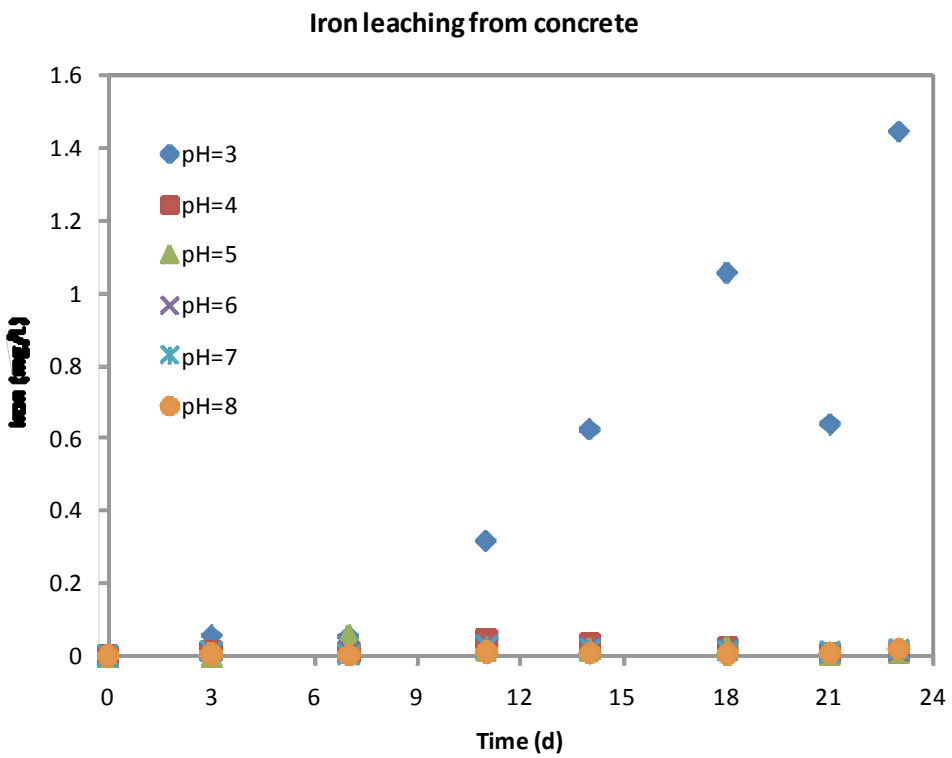


FIGURE 9. Iron leaching from concrete at different pH in deionized water

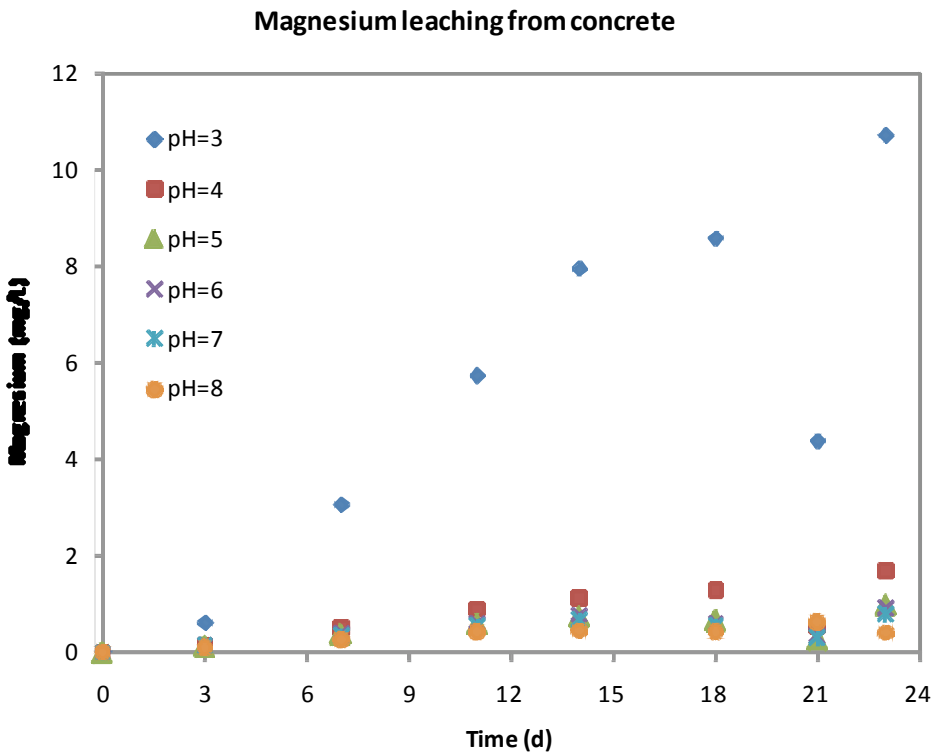


FIGURE 10. Magnesium leaching from concrete at different pH in deionized water

b. Metal leaching from concrete in grease interceptor effluent

Half of the concrete specimen was put in grease interceptor at pH 3, 4, 5, 6, 7 and 8 (Figure 11). Grease interceptor effluent without concrete specimen was used as control. The pH was maintained by sulfuric acid and sodium hydroxide for 3 weeks.

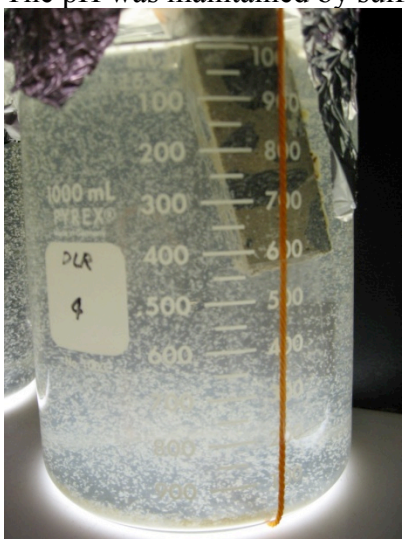


FIGURE 11. Metal leaching from concrete in grease interceptor effluent

Compared to deionized water, a high similarity of metal leaching was found in grease interceptor effluent (Table 3).

TABLE 3. Metal leaching from concrete in grease interceptor effluent after 3 weeks

	Ca (mg/L)	K (mg/L)	Fe (mg/L)	Mg (mg/L)
GI effluent	7.99	6.12	0.376	2.89
B(pH=3)	389	37.3	0.832	12.1
B(pH=4)	138	36.1	0.056	4.12
B(pH=5)	96.8	34.5	0.032	3.04
B(pH=6)	98.5	34.4	0.047	2.96
B(pH=7)	60.5	36.6	0.060	2.90
B(pH=8)	53.4	40.2	0.102	3.01
B(GI only)	8.70	6.57	0.151	2.85

B. EFFECT OF SURFACTANT

1. Surfactant as source of fatty acids

Here, we tested the hypothesis that surfactants may serve as a source of free fatty acids for the saponification reaction. No solid was formed with additional calcium at 500 mg/l and 0.7 ml of additional detergents as shown in Figure 12.

FIGURE 12. The mixture of surfactant and calcium chloride

2. Effect of surfactant in FOG deposit formation and adhesion

Another hypothesis is that surfactants could prevent free fatty acids from reacting with calcium. Surfactants have the tendency to form micelles in the water. When micelles form in the water, their tails form a core that can encapsulate the oil and lipids, and their heads form an outer shell that maintains favorable contact with water and prevent the lipids from reacting with calcium in the water.

Beaker #	GI effluent (liter)	Calcium (mg/l)	Detergent (ml)
1	1	500	0.7
2	1	500	0.3
3	1	500	0
4	1	250	0.7
5	1	250	0.3
6	1	250	0

FIGURE 13. Beaker #1 to #6 from right to left at the beginning

FIGURE 14. Beaker #1 to #6 from right to left after 5 days

After 5 days, in beaker 3 (no detergent was added), the solution was clear as the FOG deposit sunk to the bottom. In beaker 2, with 0.3 ml detergent, the FOG deposit particles that sank to the bottom were smaller than the ones in beaker 3, and the solution was cloudier. In beaker 1, with 0.7 ml detergent, almost no FOG deposits sank to the bottom. The particles were the smallest as pinpoint particles and the solution was the cloudiest. The same phenomenon was observed in beaker 4 to 6. Thus, the results supported the hypothesis that surfactant could be considered as an inhibitor preventing the formation of FOG deposit.

Very small amounts of FOG deposits adhered to PVC coupons in all beakers. The PVC coupon in beaker #3 had more adhered FOG deposits than the PVC coupons in beaker #2 and #1. The PVC coupon in beaker #6 had more adhered FOG deposits than the PVC coupons in beaker #5 and #4 (shown in Figure 15)

.

FIGURE 15. Adhesion of FOG deposits to PVC coupon

C. PIPE LOOP SYSTEM

A pilot scale sewer collection system has been built for simulating a sewer line as shown in Figure 16. The pipe loop system has two tanks (base: 1.5 ft x 1.5 ft, height: 2.5 ft) connected by a 10 ft long, 3 inch diameter pipe (three sections). The flow rate in the pipe loop system is controlled by a variable speed pump which will be adjusted to allow a velocity of at least 2 ft/sec. Grease interceptor effluent and calcium salt (500 mg/L $Ca^{2+)}$ were mixed in the system. The objective of this section is to study the FOG deposit buildup in the pipe loop system.

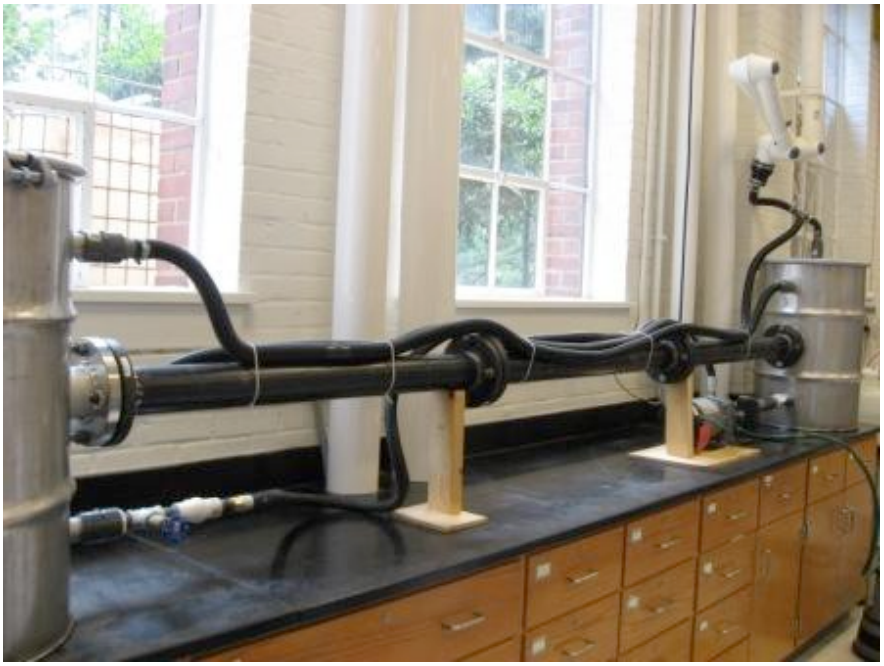


FIGURE 16. The pipe loop system in pilot scale

a. Cast iron pipe

After 40 days, deposits were formed in the cast iron pipe as shown in Figure 17. Iron became the biggest interference factor as most of deposit was rust. Metal analysis showed that the amount of iron in deposits was much higher than calcium and the percentage of total fat in the deposit was low (~ 0.2%)(Table 4).

FIGURE 17. Deposits were formed in cast iron pipe loop system

TABLE 4. Metal and total fat analysis of deposit formed in the cast iron pipe loop system

Pipe sections	Metal analysis				Total fat
	Ca (10000mg/kg)	Fe (10000mg/kg)	K (mg/kg)	Mg (mg/kg)	(%)
1	9.32	56.72	2548	1047	0.23
2	9.63	54.54	4008	1030	0.29
3	9.05	52.05	3009	963	0.25

b. PVC pipe

PVC pipe was used instead of cast iron pipe to prevent the interference with iron (Figure 18).

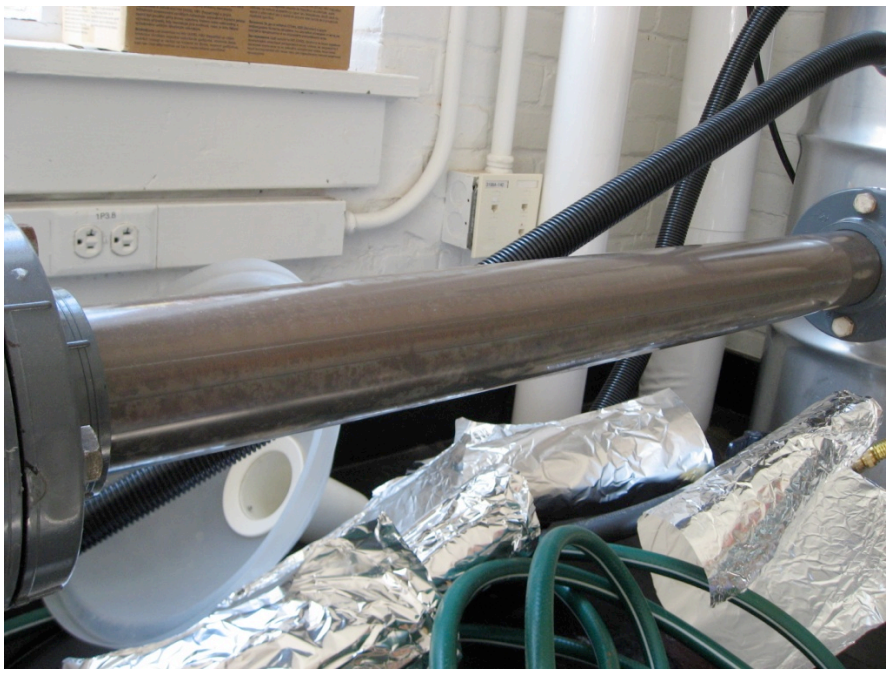


FIGURE 18. PVC pipe loop system

After 40 days, deposit ere formed as shown in Figure 19. Though PVC pipe was used, the color of deposit was still brown. Metal analysis showed that high amount of iron was still found in the deposit (Table 5), presumably from other iron components in the system. Compared to the cast iron pipe loop system, the amount of iron in the PVC pipe loop system is lower, and the total fat percentage in the deposit is higher.

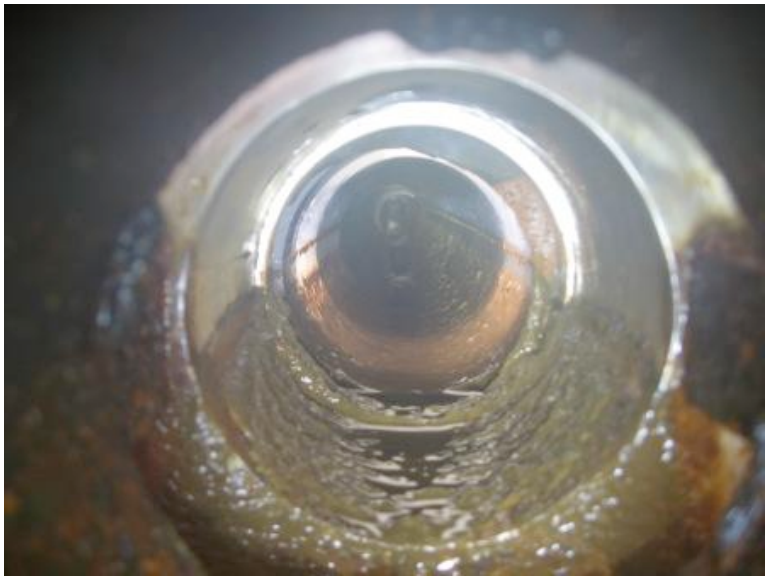


FIGURE 19. Deposits were formed in PVC pipe loop system

TABLE 5. Metal and total fat analysis of deposit formed in the PVC pipe loop system

Pipe sections	Metal analysis				Total fat
	Ca (10000mg/kg)	Fe (10000mg/kg)	K (mg/kg)	Mg (mg/kg)	(%)
1	6.25	30.59	419	392	2.41
2	9.42	32.54	567	367	2.30
3	7.41	32.67	567	398	3.07

D. FUTURE RESEARCH PLANS

We intend to determine the effects of different kitchen wastewater components on FOG deposit formation, now that we have determined the mechanisms of FOG deposit formation. We also intend to successfully simulate the deposit formation in the pipe loop system. If successful, we will have a complete picture of FOG deposit formation, the different factors affecting formation, and hopefully, rational control methods for preventing deposits from forming in sewer lines.

Mineralization, Plant Availability, and Water Quality Consequences of Nitrogen and Phosphorus in Land-Applied Municipal Biosolids

Basic Information

Title:	Mineralization, Plant Availability, and Water Quality Consequences of Nitrogen and Phosphorus in Land-Applied Municipal Biosolids
Project Number:	2010NC149B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	NC 02
Research Category:	Water Quality
Focus Category:	Wastewater, Nutrients, Non Point Pollution
Descriptors:	None
Principal Investigators:	Jeffrey G White, David H. Hardy, Daniel Israel, David L Lindbo, Deanna Osmond

Publications

1. White, J.G., D. Israel, R. Walters, D. Osmond, D. Lindbo, and D. Hardy. 2010. Mineralization and Plant Availability of Nitrogen and Phosphorus in Land-Applied Municipal Biosolids. In Annual Meetings Abstracts [CD-ROM]. ASA, CSSA, and SSSA, Madison, WI.
2. Shaffer, K., J.G. White, and D. L. Lindbo. 2010. Use of Municipal and Industrial Biosolids. p. 71 in Chapt. 4: Fertilizer Use. 2010 North Carolina Agricultural Chemicals Manual. CALS, NCSU, Raleigh. http://ipm.ncsu.edu/agchem/4-toc.pdf

Mineralization, Plant Availability, and Water Quality Consequences of Nitrogen and Phosphorus in Land-Applied Municipal Biosolids

WRRI Project Number: 70253

Second Progress Report

February 28, 2011

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Project Activities

Substantial effort was devoted to recruiting and engaging a M.S. graduate research assistant, Ryan Dodd, whose assistantship began on August 16, 2010. In the meantime, he was hired as an hourly employee to participate in the final planning and preparation for laboratory incubations, analyses, and greenhouse experiments. This project and the continuation of project activities after termination are Ryan's thesis research. All Soil Science (SSC) graduate students are required to serve as teaching assistants for two semester-sections of a SSC course. Ryan is serving in this capacity this semester, Spring 2011, which has decreased the time that he has been able to devote to this project and resulted in his project assistantship being offset this semester by CALS/SSC teaching assistant funds. Given that this grant will expire 28 February 2011 and we have been notified that a no-cost extension will not be possible, we sought and obtained additional funding to continue Ryan's assistantship through the completion of his degree in 2012, which will allow us to continue the research initiated in this project. Delays in the establishment of project accounts (established 4/22/10, notification received 5/3/2010) and difficulties in locating appropriate North Carolina Dept. of the Environment and Natural Resources, (NCDENR)-permitted sites for the field trials resulted in us not being able to initiate them in summer 2010 as planned; below we detail one field trial that was initiated in Fall 2011. Special apparatus required for the amino sugar nitrogen (N) test went missing during recent lab renovation. Replacement equipment was fabricated and tested. Given these issues, were have yet to establish the greenhouse trials.

The lab incubation phase of this project was initiated in September 2010. We began by identifying suitable sites from which the soils for these experiments could be obtained.This was done using USDA-NRCS soil maps, detailed experimentation soil maps, and aerial photographs. We excavated two representative piedmont soils, Vance sandy clay loam and Wedowee sandy loam from Rockingham and Nash County, respectively; and two representative coastal plain soils, Norfolk loamy sand and Noboco loamy sand from Johnston and Duplin County, respectively. We collected ~130 L of soil from each site through a depth of ~20 cm. The soil consisted primarily of the surficial Ap horizon ("plow layer"), but for the piedmont soils, included some of the clayey Bt horizon. We sieved field soils to pass a 2-mm screen and submitted a moist sample of each to the North Carolina Dept. of Agriculture and Consumer Services Agronomic Division (NCDA&CS) Soil Test Section laboratory for routine fertility and chemical analysis. The remainder of the soil was air dried prior to incubation described below.

Three biosolids were selected and acquired for testing: a dry pellet from Cary's wastewater treatment plant (WWTP): Cary "Enviro Gems", a Class A exceptional quality (EQ) biosolids residual of a biological nutrient removal process (hereafter: "Cary pellets"); "Raleigh Plus," a lime-stabilized twice-dewatered, Class A EQ product from the City of Raleigh's Neuse River WWTP aerobic process; and "OWASA cake," a moist product generated from the anaerobic biological nutrient removal process of the Orange County Water and Sewage Authority (OWASA) WWTP. Chemical analysis of these products was provided by the generators except for the OWASA cake, which was analyzed by the NCDA&CS Waste Analysis laboratory because the generator (OWASA) was not required to analyze the biosolids, as their disposal was contracted out to a composter, who need only analyze the final compost product.

Three different laboratory methods for estimating plant available nitrogen (PAN) in biosolids were proposed for this project: aerobic and anaerobic incubation (Bundy and Meissinger, 1994),

and the amino sugar nitrogen test (ASNT, a.k.a, the Illinois Soil Nitrogen Test, ISNT; Mulvaney and Khan, 2001; Mulvaney et al., 2001). The aerobic incubations are relatively long-term (several months) and are in progress. Here we comment on the anaerobic incubation for which partial data are available for the coastal plain soils. Incubation and analysis of the piedmont soils are in progress. The ASNT has only been carried on a trial basis. From the results of these trials, we concluded that some fabricated equipment needed to be adapted and titration equipment with greater accuracy and precision purchased. Some of these materials have arrived, but others are on backorder.

The anaerobic test involved a 7-day incubation at 40°C of soil plus biosolids or fertilizer plus 50 mL of dioionized water in sealed plastic specimen cups. The experimental design was a 4 X 5 X 4 factorial arrangement of treatments: N source X N rate X soil. The four N sources were: 1) NH_4NO_3 fertilizer reference (reagent grade; assumed to be 100% plant available) and the three biosolids: Cary pellets, Raleigh Plus, OWASA cake. The five N rates were multiples (0X, 0.5X, 1.0X, 1.5X, and 2.0X) of the agronomic N rate determined from the North Carolina Realistic Yield Expectation (RYE) Datebase (North Carolina Nutrient Management Workgroup, 2003) N for corn averaged over the four soil types Norfolk, Vance, Wedowee, Noboco. For the statistical analyses, the soil factor will be analyzed as described above as well as two regional classes, i.e., Piedmont versus Coastal Plain. Each treatment combination was replicated four times. After the 7-day incubation, 50 mL of 2M KCl was added to the soil + biosolids + water mixture and shaken for 1 hr. The extract was filtered through No. 42 filter paper and analyzed for NH_4 and NO_3 on a multi-channel flow injection auto-analyzer (Lachat QuikChem 8500 Series 2; Lachat Instruments, Loveland, CO).

A field trial was initiated in Fall 2010 on a cooperating grower's field near Spring Hope in Nash County to test the efficacy of the different N sources and agronomic N rates on tall fescue (*Festuca arundinacea*) growth and productivity. This trial is being facilitated by a private nutrient management consultant, Scott Carpenter of SoilPlus. An initial meeting was held with the landowner to explain our purpose, obtain permission, and secure a suitable site for the experiment. The research site, under established fescue, does not have a history of biosolids application. We used a split-plot factorial treatment structure in a randomized complete block design with four replications. The main plot factor consists of two N sources: 1) Cary pellets and 2) fertilizer grade NH_4NO_3 prills, applied at multiples (0, 0.5X, 1.0X, 1.5X, and 2X) of the agronomic RYE N rate for fescue on the experimental site soil, which is mapped as a Wedowee sandy loam soil. Main plots are 12- by 12-ft. After Year 1, each plot will be split; one split plot will receive a second pellet application while the other will not in order to determine residual N from the initial application. Nitrogen treatments were applied on 15 November 2010.

Results and Discussion

Caveat: All results herein are preliminary and require confirmation by additional statistical analyses.

Analyses of the three biosolids, shown in part in Fig. 1., revealed that the Cary pellets contained the greatest amount of total nitrogen (N), followed by OWASA cake, and Raleigh Plus. This implies that Cary pellets would likely provide more plant-available N (PAN) than OWASA cake or Raleigh Plus, which had substantially lower total N than the other two biosolids. The results shown in Fig. 2A1 and 2B1 confirm this. The proportion of biosolids total N that was organic

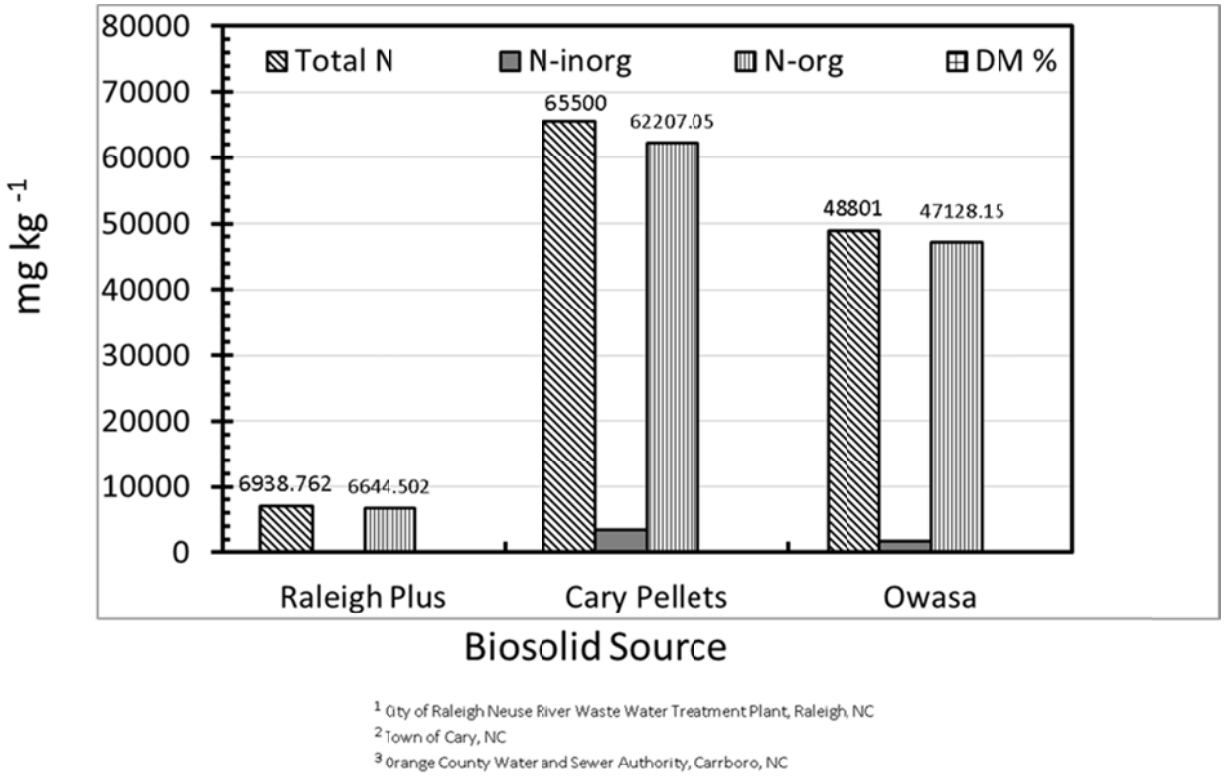

Figure 1: Analysis of three biosolid products used, displaying Total N, inorganic N, organic N, and % dry matter.

was similar in all sources, averaging 95%. This is typical of biosolids from modern WWTP, which are very effective at removing/reducing inorganic (mineral) N (i.e., NO_3 and NH_4) from wastewater. While these mineral forms are considered immediately plant available, they are only a small proportion of total biosolids N, hence the overarching objective of this research: to estimate the rates at which and amounts of biosolids organic N that will mineralize to become plant available N (PAN = NH_4 + NO_3). The dry matter proportions of the biosolids varied as could be predicted from their natures: the dried Cary pellets had the highest dry matter, OWASA's dewatered cake intermediate, and the double-dewatered Raleigh Plus, the lowest.

After anaerobic incubation, the Norfolk unamended control released approximately double the total PAN compared to the Vance soil, 23 versus 11 mg kg^{-1}, respectively. We will compare the humic matter contents of the soils to determine if this was likely due to a greater amount of organic N in the Norfolk versus the Vance soil prior to incubation, or if the Norfolk soil inherently released more N via anaerobic incubation. If so, this would have important implications for mineralization of biosolids added to these soils (see below).

Based on the initial N analyses, it was hypothesized that the Cary pellets would yield the greatest amount of N after the 7-day anaerobic incubation. In the results provided here for the two coastal plain soils, Norfolk loamy sand (Fig. 2A_) and Vance sandy clay loam (Fig. 2B_), the Cary pellets did yield the greatest amount of total PAN on the Norfolk soil, followed by the Owasa cake, NH_4NO_3, then Raleigh Plus. For the Norfolk soil, the N-release responses of all but Raleigh-plus were similar; the latter demonstrated no response to increasing N rate, an unusual

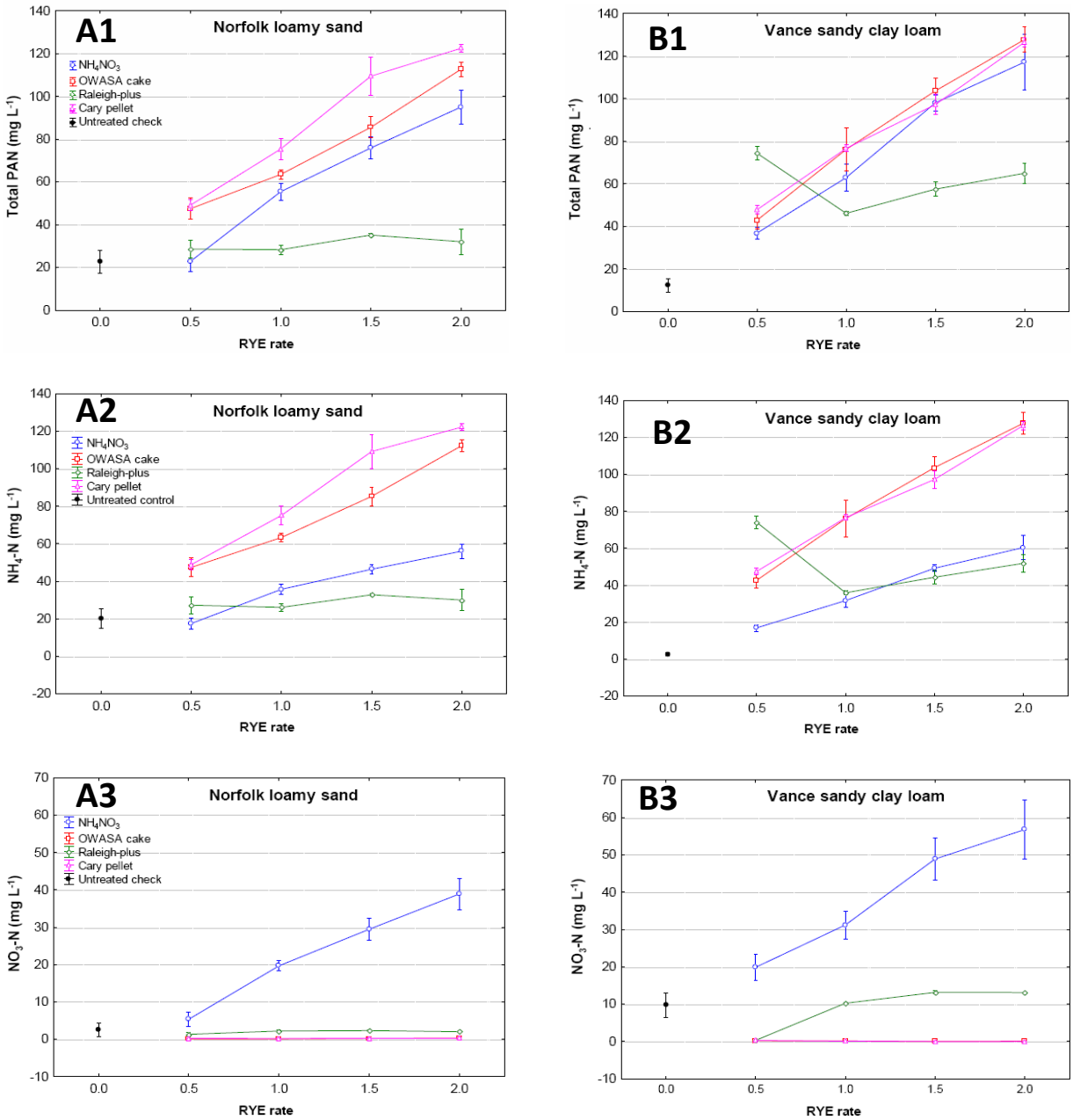

Fig. 2. Total plant-available N (PAN = NH_4 + NO_3; #**1**), ammonium (NH_4: #**2**), and nitrate (NO_3: #**3**) released during a 7-day anaerobic incubation of three biosolids and NH_4NO_3 applied at five rates to two representative coastal plain soils: Norfolk loamy sand (**A**) and Vance sandy clay loam (**B**). Nitrogen rates were determined as 0, 0.5 X, 1.0 X, 1.5 X, and 2.0 X the North Carolina Realistic Yield Expectation Datebase (North Carolina Nutrient Management Workgroup, 2003) N rate for corn averaged over the four soil types (Norfolk, Vance, Wedowee, Noboco), i.e., ~148 kg N ha^{-1}. Not that the y-axis scale for NO_3 (Fig. A3 & B3) is half that of those for PAN and NH_4. Error bars are standard errors.

result that we are unable to explain at this time. On the Vance soil, all N sources except Raleigh-Plus had similar PAN release rates and amounts.

The greater proportion of organic N that is mineralized via anaerobic incubation is typically NH_4 rather than NO_3. This was true for all the biosolids tested (Fig. 2). For both soils, the NH_4 released from all biosolids paralleled and dominated PAN release (Fig. A2 vs A1). However, for NH_4NO_3 on both soils, only about half of the total PAN was NH_4, which was to be expected given the nature of this inorganic source. On the Vance soil, there were anomalies in the relative amounts of NH_4 released from Raleigh Plus relative to the other treatments. We believe that this was due to a labeling error: the 0.5 X RYE treatment was likely in fact the 2 X RYE treatment, and all the other treatments were actually the next lower N rate. We are rerunning this incubation to confirm this.

On the Norfolk soil, there was essentially no NO_3 released from anaerobic incubation of the biosolids. On the Vance soil, there were small amounts of NO_3 released only with Raleigh Plus. However, if we consider the NO_3 released from the unamended control soil as a blank to be subtracted from the biosolids treatments, then Raleigh Plus mineralized no NO_3, and the other biosolids appear to have lost NO_3. Nitrate in these soils may have been assimilated by microorganisms and potentially re-released as NH_4. At this point, we have no hypotheses as to why the dynamics of NO_3 mineralization for Raleigh Plus on the Vance soil were different from all other treatments. A closer inspection of existing soil analyses and addition analyses of soil chemical and physical characteristics may inform these results.

Different biosolids appeared to have different mineralization rates and amounts among themselves and on different soils. Biosolids mineralized N slightly faster in the Vance versus the Norfolk soil. A primary objective of this research is to determine if different PAN availability coefficients should be used for land application of municipal biosolids from different sources and/or on different soils. These preliminary results indicate that different PAN availability coefficients may be needed for biosolids from different sources applied to different soils.

These preliminary results also indicate that the Cary pellets would be the best N source among the three biosolids tested. The Cary pellets had the highest initial N content, mineralized the most PAN, and had a low moisture content which makes their transport and application less expensive than the other biosolids. In principle, anaerobic incubation provides a relatively quick (7 days) and easy estimate of PAN. However, the longer-term aerobic incubation better mimics field conditions and may provide a better estimate of total PAN as well as an estimate of the temporal rate of N mineralization. The latter is important in order to understand whether mineralization of PAN from biosolids is in temporal synchrony with and of sufficient magnitude to meet crop demand, which typically increases over time as a sigmoidal/logistic function. The better this synchrony, the greater the N-use efficiency and crop uptake, and the less surplus N that is available to leach to groundwater.

Our most recent (Feb. 18, 2011) visit to the field trial revealed some distinctly visible effects on fescue growth and color (Fig. 3), manifested primarily as darker green foliage in some treatments due presumably to greater amounts of PAN. However, the grass has not yet been sampled. Once the fescue breaks dormancy and puts on growth sufficient to warrant a first cutting, sampling for yield and nutrient content will be done followed by appropriate tissue analysis.

Fig. 3. Trial of Cary Pellets versus NH_4NO_3 applied at five different rates to an established stand of tall fescue in Nash Co., NC. Treatment effects are manifested as different shades of green, with darker green associated primarily with greater plant-available N (PAN). No fescue sampling has been done yet; sampling will commence once sufficient growth occurs after fescue breaks dormancy.

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Appendix 1: Abbreviations

Ap: plow layer
ASNT: amino sugar nitrogen test
Bt: argillic horizon
DM: dry matter
EQ: exceptional quality
H: hydrogen
inorg: inorganic
org: organic
ISNT: Illinois soil nitrogen test
KCl: Potassium chloride
N: nitrogen
NCDA&CS: North Carolina Department of Agriculture and Consumer Services
NCDENR : North Carolina Dept. of the Environment and Natural Resources
NH_4NO_3: ammonium nitrate
O: Oxygen
OWASA: Orange County Water and Sewer Authority
PAN: plant available nitrogen
RYE: realistic yield expectation
SSC: Dept. of Soil Science, NCSU
USDA-NRCS: U.S. Dept. of Agriculture-Natural Resources Conservation Service
WWTP: Waste water treatment plant

Appendix 2: Publications, presentations, efforts at technology transfer or communication of results to end users, policy makers, or others

White, J.G., D. Israel, R. Walters, D. Osmond, D. Lindbo, and D. Hardy. 2010. Mineralization and Plant Availability of Nitrogen and Phosphorus in Land-Applied Municipal Biosolids. *In* Annual Meetings Abstracts [CD-ROM]. ASA, CSSA, and SSSA, Madison, WI.

White, J.G., D. Israel, R. Walters, D. Osmond, D. Lindbo, and D. Hardy. 2010. Mineralization and Plant Availability of Nitrogen and Phosphorus in Land-Applied Municipal Biosolids. Poster presented at the 2010 Annual International Meetings of the American Society of

Agronomy, Crop Science Society of America, and Soil Science Society of America, Oct. 31-Nov. 3, 2011, Long Beach, CA.

White, J.G., D. Israel, R. Walters, D. Osmond, D. Lindbo, and D. Hardy. 2010. Mineralization and Plant Availability of Nitrogen and Phosphorus in Land-Applied Municipal Biosolids. Poster presented at the 2011 Annual Meeting of the Soil Science Society of North Carolina, Jan. 18-19, 2011, McKimmon Center, NCSU, Raleigh.

White, J.G. 2010. Biosolids: Where Are We Going? Current Issues, Future Vision. Invited presentation. Fork to Farm: A Biosolids Educational Summit. April 27-28, 2010. McKimmon Center, NCSU, Raleigh.

White, J.G. Biosolids: Fork to Farm to Fury. 2010. Invited presentation. Southern States Growmaster Program, August 8, 2010, Holiday Inn Brownstone, Raleigh, NC.

Shaffer, K., J.G. White, and D. L. Lindbo. 2010. Use of Municipal and Industrial Biosolids. p. 71 *in* Chapt. 4: Fertilizer Use. 2010 North Carolina Agricultural Chemicals Manual. CALS, NCSU, Raleigh. http://ipm.ncsu.edu/agchem/4-toc.pdf

Dr. White was a primary organizer and Co-Coordinator of "Fork to Farm: A Biosolids Educational Conference." April 27-28, 2010. McKimmon Center, NCSU. Raleigh NC. The conference featured nineteen nationally and internationally recognized experts speaking on biosolids to a registered audience of ~100, and a half-day field trip to a local wastewater treatment plant and biosolids land application site.

Dr. White had substantial engagement with biosolids producers, land appliers, regulators, environmental activists and was/is a frequent contributor to sludge@lists.ibiblio.org, a listserv for discussing issues related to wastewater treatment residuals (biosolids).

Dr. White met with scientists from USGS North Carolina Water Science Center to discuss collaborative activities to characterize water quality impacts of land application of OWASA biosolids. He engaged the services of a USDA-NRCS geophysicist/soil scientist to assist in the characterization of soils and stratigraphy at the study site.

Drs. White, Osmond, and Lindbo met with representatives from the NCDENR Division of Water Quality to discuss regulation and research and extension needs related to phosphorus from land-applied biosolids. Grant proposal in preparation: White, J.G. and D.L. Osmond. Ground and surface-water phosphorus risk coefficients from land-applied municipal biosolids. NCDENR/USEPA 319.

Dr. White serves as member of the North Carolina American Water Works Association/Water Environment Association Residual and Groundwater Committee.

Information Transfer Program Introduction

The Water Resources Research Institute (WRRI) is heavily geared to providing water resources information to the water professional. 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.

The professionals targeted by this program include private entrepreneurs, federal, state and local government staff and officials, and representatives of industry, agriculture, consulting, and environmental groups. The main forms of information transfer are through an Institute internet site, bi-monthly newsletter, conferences, seminars, forums, workshops, luncheons, and research publications.

The workshops conduced through WRRI's partnership with the Department of Environment and Natural Resources Division of Land Resources constitute the primary means by which the Division meets its educational obligations on sediment control under the state's Sediment Control Act.

WRRI continues to be a sponsor of continuing education credits by the NC Board of Examiners of 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 also submits information for approval to the N.C. Board of Landscape Architects to offer contact hours to landscape architects. This allows WRRI to offer Professional Development Hours (PDHs) to engineers and surveyors, and Continuing Education Units (CEUs) to landscape architects for attendance at the WRRI Annual Conference and other workshops, seminars and forums that WRRI sponsors.

During this reporting year, WRRI provided 83 PDHs and 62.5 CEUs through the workshops, seminars, and other events described below.

WRRI Information Transfer Program

Basic Information

Title:	WRRI Information Transfer Program
Project Number:	2010NC154B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	NC-02
Research Category:	Not Applicable
Focus Category:	Water Quality, Management and Planning, Sediments
Descriptors:	
Principal Investigators:	Nicole Saladin

Publications

There are no publications.

FY 2010 Information Transfer Progress & Achievements

I. WRRI Annual Conference

The WRRI Information Transfer Program includes the WRRI Annual Conference, which the Institute has sponsored since 1998. It is North Carolina's premier water research conference where research is presented by university and corporate researchers, students, local, state, and federal government agency representatives, and environmental professionals. The 2010 Annual Conference was held on March 30-31, 2010. The theme was "The State of Water Resources in North Carolina", and the conference was accompanied by the NC Water Resources Association (NCWRA) Symposium entitled "Water Energy Nexus: The Future of Two Valuable Resources." The event featured 67 oral presentations and 21 poster presentations. 193 people attended the conference, and the event qualified for 9.5 PDHs. Dr. Richard Whisnant of UNC-Chapel Hill's School of Government delivered the keynote address "Fire and Water: Making Meaning Out of Water Resource Policy."

II. Newsletter

Published the *WRRI News* five 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, water-related workshops and conferences, and reviews of water-related publications. The WRRI News is now sent electronically to 911 federal and state agencies, university personnel, multi-county planning regions, city and local officials, environmental groups, consultants, businesses and individuals. It is also posted on the WRRI website http://www.ncsu.edu/wrri/newsletter/index.html#news

III. Internet Services

The Water Resources Research Institute of The University of North Carolina maintains an internet site: http://www.ncsu.edu/wrri. The purposes of the internet site are:

a. to provide wider dissemination of research results, such as WRRI research reports, and information produced for our newsletter
   - http://www.ncsu.edu/wrri/reports/index.html
   - http://www.ncsu.edu/wrri/newsletter/index.html
b. to provide researchers quick and easy access to proposal and project related materials (proposal guidelines and forms, guidelines for authors, etc)
   - http://www.ncsu.edu/wrri/cfp/
c. to provide links to other water-related organizations that might be of use to the research and management communities in North Carolina
   - http://www.ncsu.edu/wrri/uwc/index.html
   - http://www.ncsu.edu/wrri/stormwater/index.html
   - http://www.bae.ncsu.edu/programs/extension/wqg/ncwra/

d. to provide timely information on workshops, conferences, seminars and other educational opportunities, and presentations from WRRI sponsored events
   - WRRI Annual Conference Programs (http://www.ncsu.edu/wrri/conference/past.html)
   - Erosion and Sedimentation Control Planning and Design Workshops (http://www.ncsu.edu/wrri/events/esc_workshops/pastescworkshops.html)
   - Local Programs: (http://www.ncsu.edu/wrri/events/localprograms/index.html)
   - North Carolina Water Resources Association Forums (http://www.ncsu.edu/wrri/events/ncwra/pastforums.html)
   - Progress Energy Water Resources Seminars (http://www.ncsu.edu/wrri/events/progressenergyseminars/pastforums.html)

IV. WRRI Electronic Lists

WRRI maintains the following electronic mail lists (listservs) for information transfer purposes:

a. Water-Research list - 208 subscribers – inform water researchers from NC universities about calls for papers, grants, upcoming conferences, student internships, etc.;
b. WRRI-News list - 911 subscribers - informs researchers, local governments, municipalities, interest groups etc. about calls for papers, grants, upcoming conferences and events, etc.;
c. NCWRA-info list - 246 subscribers - provides information of the North Carolina Water Resources Association sponsored events;
d. Urban Water Consortium (UWC) for Urban Water Consortium member communications;
e. and UWC-Stormwater Group list for the UWC Stormwater Group member communications.

V. Audio-Visual Productions

The Water Resources Research Institute designed a tabletop exhibit to display at conferences, workshops, and other events in which we participate. The exhibit is a 7' x 4', 4-panel display bearing our name and logo along with photos and descriptions of several current research projects. This display highlights our current research and publications at our annual conference and at other events.

Most presentations given at workshops and seminars sponsored by WRRI are uploaded to the WRRI website for public viewing (see under WRRI Internet Services). Investigators or their graduate students have presented or will present an oral or poster presentations at a WRRI Annual Conference. Many of these presentations are available from past WRRI Annual Conferences at: www.ncsu.edu/wrri/conference/past.html

VI. NC Urban Water Consortium

WRRI administers the NC Urban Water Consortium (UWC) and meets with the 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. There are 12 member cities/special districts in North Carolina, and several members hosted quarterly meetings on the following dates: March 18, 2010 in Huntersville; June 04, 2010 in Cary; October 15, 2010 in Durham; and December 13, 2010 in Greensboro.

The UWC also provided partial funding to USGS 104(b) projects, further supporting the research and the resulting dissemination of project results through presentations and publications. During this project year, they supported projects 2010NC147B (PI Stewart) and 2010NC148B (PI de los Reyes). In addition, they funded a project at UNC-Chapel Hill by PI Hughes entitled "Ensuring Water Supply Reliability and Financial Stability for NC Water Utilities", the results of which are provided in individual profiles for participating utilities, as well as presented at WRRI events.

VII. NC Urban Water Consortium - Stormwater Group

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 selective representation on the WRRI advisory board, determining stormwater-related research priorities, participation in the design of requests for proposals and review of proposals submitted to WRRI directly or to the SWG. Currently there are eight members in the SWG, and quarterly meetings were held on the following dates: March 25, 2010 in High Point; June 10, 2010 in Greensboro; September 09, 2010 in Raleigh; and December 09, 2010 in Huntersville.
The UWC-SWG provided funding for a project at NC State University by PI Hunt entitled "Long-term Modeling of Bioretention Hydrology with DRAINMOD", the results of which are being presented to the SWG in FY11 and will also be presented at the 2012 WRRI Annual Conference.

VIII. Other WRRI Sponsored Workshops, Forums and Seminars

a. The WRRI Information Transfer Program includes workshops supported by the NC Department of Environment and Natural Resources (DENR), Division of Land Resources Land Quality Section along with the NC Sedimentation Control Commission (SCC). Workshops held during this period include:

- Two Spring Erosion and Sediment Control Planning and Design Workshops, March 3-4, 2010 in Clemmons, NC and April 12-13, 2010 in Raleigh, NC
- Two Fall Planning and Design Erosion and Sedimentation Control Workshops, October 26-27, 2010 in Mills River, NC and November 8-9, 2010 in Raleigh, NC
- Erosion and Sedimentation Control Local Programs Training Workshop, January 26-27, 2011 in Raleigh, NC.

Information on these workshops can be found at
http://www.ncsu.edu/wrri/events/esc_workshops/pastescworkshops.html

b. WRRI formed a new partnership with NC DENR Division of Water Quality (DWQ) to begin the NC DWQ Stormwater Programs Workshops
(http://www.ncsu.edu/wrri/events/dwq/):

- One DWQ Stormwater Programs Workshop, April 22, 2010 in Clemmons, NC
- One DWQ Stormwater Programs Workshop, December 2, 2010 in Raleigh, NC

c. Another way WRRI provides Information Transfer is through the North Carolina Water Resources Association (NCWRA) Luncheon and Forums
(http://www.ncsu.edu/wrri/events/ncwra/):

- April 19, 2010: "The Little Sugar Creek Stream Restoration Project"; Crystal Taylor, PE, CFM, Project Manager Mecklenburg County Storm Water Services Engineering Department
- September 13, 2010: "Incorporating the Value of Ecosystem Services and Uncertainty into Water Supply Planning"; Douglas J. MacNair, PhD, Vice President, ENTRIX
- December 6, 2010: "Determining Ecological Flows for River Basin Planning in North Carolina"; Jim Mead, NC Division of Water Resources
- February 7, 2011: "What You Need to Know about the NC Phase I and Phase II MS4 Programs"; Mike Randall, NC Division of Water Quality- Stormwater Permitting Unit.

d. In addition, one seminar was sponsored by Progress Energy at NCSU's Jane S. McKimmon Center to provide Information Transfer
(http://www.ncsu.edu/wrri/events/progressenergyseminars/pastforums.html)

- March 31, 2010: "Regulation of Nutrients in North Carolina Surface Waters", by Connie Brower, Classification & Standards Coordinator; Rich Gannon, NonPoint Source Planning Supervisor; Jeff Manning, Classification & Standards Supervisor; Matt Matthews, Surface Water Protection Section Chief; Dianne Reid, Basinwide Planning Supervisor

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	9	0	0	0	9
Masters	9	0	0	0	9
Ph.D.	2	0	1	0	3
Post-Doc.	0	0	0	0	0
Total	20	0	1	0	21

Notable Awards and Achievements

During FY 2010, WRRI has made a number of internal achievements, as well as enjoyed the stories of success communicated by PIs about their own successes and those of their students. A number of these achievements relate to restructuring, strengthening, and streamlining WRRI as an organization through staff changes and enhanced partnerships. WRRI also seeks additional funds from partners across the state to enhance its research and outreach activities beyond base federal and state appropriations

I. ORGANIZATIONAL AWARDS & ACHIEVEMENTS

a. USDI/USGS Determination of Recertification and Continued Eligibility of WRRI-UNC

Based upon a report submitted by WRRI for the period 2002-2007, USGS re-certified WRRI as eligible to receive grants under the provisions of Section 104 of the Water Resources Research Act of 1984, as amended. The USGS-appointed review panel, in particular, found that WRRI "….continues to be exemplary, with enviable programs of research and information transfer." In a letter to the NCSU Chancellor, USGS also stated "We commend the current Director, Dr. Michael Voiland, for continuing an outstanding program."

b. Designation as Center of Excellence in Watershed Management

The U.S. Environmental Protection Agency designated NC State University, through the Water Resources Research Institute, as a Center of Excellence for Watershed Management. The EPA and university officials signed a memorandum of understanding to help communities identify watershed problems and find sustainable solutions. The designation will allow NC State to continue to develop strong partnerships with other institutions, organization and agencies required to protect and restore watersheds. Currently, WRRI is partnering with NC DENR, NCSU Extension, and UNC-Chapel Hill to assess the current status of watershed efforts in NC, and develop new strategies aimed at statewide coordination of these efforts.

c. Staffing Efficiencies & Consolidation

Beginning in 2009, efforts have been made to consolidate and achieve cost- savings at two water resource-related and federally designated and supported centers within ORI — NC Sea Grant and WRRI. This staffing initiative continues an approach that began in 2009 with the establishment of a single director position for these two centers/institutes and also a part-time (0.25 FTE) position of associate director for research. Estimated WRRI state salary (with fringe benefit) savings accruing from all such staffing consolidations since 2009 and through June 30, 2011 are calculated to total over $400K.

Accounting Support: In June 2010, to address a vacancy of an accounting technician position at WRRI while seeking greater cost savings and efficiencies at both WRRI and NC Sea Grant, the two centers (WRRI and NC Sea Grant) took action to share equally (50:50) a single accounting/administrative position. The position is key to the administrative functioning of both centers.

Business Officer: In September 2010, the previous full-time position of WRRI Business Officer was subject to a Reduction in Force (RiF). In December 2010, the full time fiscal officer position for NC Sea Grant was ultimately split to allocate 0.30 FTE as the WRRI Business Officer. The position is key to the administrative functioning of both centers.

Coordinator for Research and Outreach (CRO): With a vacancy in its Environmental Education and Communications Coordinator position occurring in June of 2010, the duties of that position were re-evaluated, based upon how the position had changed in its work focus over the last 6 years and how EPA staffing needs

at WRRI had shifted given the Institute's new leadership structure. The position was redescribed and retitled "Coordinator for Research and Outreach (CRO)," and this position was filled in October 2010.

II. EXTERNAL FUNDING AWARDS & ACHIEVEMENTS

a. External Research Support from the Urban Water Consortium and Stormwater Group

New interaction and operational procedures were mutually agreed to by WRRI and the Urban Water Consortium (UWC) and its affiliated Storm Water Group (SWG). Together, these two stakeholder organizations, composed of representatives from the state's larger municipal drinking, waste, and storm water utilities, contribute $160,000 annually in fees that can then be allocated to university-based water research projects managed by WRRI. In 2010-11, the groups will have supported almost $550K in research administered by WRRI and carried out by university faculty.

b. External Education and Outreach Funding from NC DENR

To carry out the Erosion and Sediment Control and Local Program workshops, WRRI secured two contracts from the NC Department of Environment and Natural Resources (DENR) for a combined total of $94,390 to cover the costs associated with the workshops. This includes funding to cover 7 months of salary of WRRI's 0.5 FTE Workshop Assistant position. These contracts are the primary means by which the Division of Land Resources meets its educational obligations on sediment control under the state's Sediment Control Act.

III. RESEARCH AWARDS & ACHIEVEMENTS

The following awards were made to students and researchers whose work was supported through WRRI/USGS funding:

a. Project #2010NC147B (PI Stewart): PhD Candidate Jennifer Gentry Shields received an honorable mention in a student poster competition at the 2011 WRRI Annual Conference and NCWRA Symposium (Raleigh NC) for poster presentation entitled "Alternative indicators to predict water quality in a North Carolina drinking water reservoir based on land-use characteristics".

b. Project #2010NC148B (PI de los Reyes): Xia He won 2nd place for a poster presentation at the 2011 WREE Research Symposium.

c. Project #2010NC145B (PI Heitman): M.S. student Chris D'Auito was a finalist for top student presentation for an oral presentation at the 2010 Conference for the Soil Science Society of America.

d. Project #2009NC122B (PI Arumugam): M.S. student Harminder Singh received third prize in the 2011 WRRI Annual Conference and NCWRA Symposium for the poster presentation entitled "Experimental Seasonal Inflow Forecasts for North Carolina".

Publications from Prior Years