Connecticut Institute of Water Resources
Annual Technical Report
FY 2013

Introduction

The Connecticut Institute of Water Resources is located at the University of Connecticut (UCONN) and reports to the head of the Department of Natural Resources and the Environment, in the College of Agriculture and Natural Resources. The current Director is Dr. Glenn Warner and Associate Director is Mr. James Hurd.

Although located at UCONN, the Institute serves the water resource community throughout the state. It works with all of Connecticut's water resource professionals, managers and academics to resolve state and regional water related problems and to provide a strong connection between water resource managers and the academic community.

The foundation for this connection is our Advisory Board, whose composition reflects the main water resource constituency groups in the state. CT IWR staff also participates on statewide water-related committees whenever possible, enabling our Institute to establish good working relationships with agencies, environmental groups, the water industry and academics.

The USGS 104B program is the financial core of the CT IWR. The Institute does not receive discretionary funding from the state or the university, although it does receive approximately two thirds of the Associate Director's salary per year as match for our program administration and other activities.

Research Program Introduction

The majority of our 104B funds are given out as grants initiated in response to our annual RFP, with the majority of those funds going to research projects. To solicit research proposals, the Institute sends an announcement to Connecticut institutions of higher learning requesting the submission of pre-proposals. These are reviewed by the CT IWR Director and Associate Director. When selecting potential projects for funding, the Institute considers three main areas: 1. technical merit, 2. state needs and 3. CT IWR priorities (use of students, new faculty, seed money for innovative ideas). Investigators submitting pre-proposals meeting the initial requirements are invited to submit a full proposal. Each full proposal received is reviewed by two to four outside individuals with expertise in the field described in the proposal. Proposals and reviewer comments are presented to the CT IWR Advisory Board, composed of 11 individuals that reflect the main water resource constituency groups in the state, and a determination is made on which projects are to be funded.

Post-audit Verification of the Model SWMM for Low Impact Development

Basic Information

Title:	Post-audit Verification of the Model SWMM for Low Impact Development
Project Number:	2011CT231B
Start Date:	3/1/2011
End Date:	5/31/2013
Funding Source:	104B
Congressional District:	2
Research Category:	Water Quality
Focus Category:	Hydrology, Models, Non Point Pollution
Descriptors:	None
Principal Investigators:	Michael Dietz, John Campbell Clausen

Publications

1. Rosa, D. 2012. Modeling the Effectiveness of Low Impact Development Using SWMM. Connecticut Conference on Natural Resources, 3/12/12, University of Connecticut.
2. Rosa, D. 2013. Post-audit Verification of the Model SWMM for Low Impact Development College of Agriculture and Natural Resources Graduate Research Forum, 4/6/13. University of Connecticut.
3. Rosa, D. 2012. Modeling the Effectiveness of Low Impact Development Using SWMM. Connecticut Conference on Natural Resources, 3/12/12, University of Connecticut.
4. Rosa, D. 2013. Post-audit Verification of the Model SWMM for Low Impact Development College of Agriculture and Natural Resources Graduate Research Forum, 4/6/13. University of Connecticut.

Post-audit Verification of the Model SWMM for Low Impact Development

ANNUAL REPORT

May 24, 2013

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Introduction/Research Objective

The impact of traditional development on local waters is well known; increases in stormwater runoff volume, rate, and pollutant export have documented effects on receiving waters. Typical stormwater design only protects channel integrity by mitigating for increased flow rates; the volume and quality of stormwater are not typically considered.

Implementation of Low Impact Development (LID) techniques (Prince George's County, 1999) has increased steadily since the 1990s. The overall goal of LID is to have post-development hydrologic function mimic that of pre-development, thereby minimizing impacts to downstream channels and aquatic life. This is accomplished through proper site planning, preservation of existing vegetation, and directing runoff from impervious areas to pervious areas where possible. Individual practices used to accomplish these items include bioretention, grassed swales, water harvesting, green roofs, and pervious pavements. Numerous states and local municipalities have included LID in stormwater manuals (e.g. CT DEP, 2005; MA DEP 2008; RI DEM & CRMC 2010), although LID use is only recommended, not required, in most cases.

Since its inception, LID design was aimed at capturing and treating smaller, more frequent storms. For larger storms, some runoff would infiltrate close to its source, but the majority would bypass distributed LID features, and would need to be routed out of the area. Provisions for management of this size event need to be demonstrated to meet flood control requirements designed to protect public safety, however engineering design often has not given credit for the runoff reduction benefit provided by LID. Much research has been performed on individual LID practices, but little effort has been put into integrating the hydrologic and water quality benefits of LID techniques into engineering design models.

The main objective of this project was to determine how a residential watershed with LID features responds to larger, less-frequent precipitation events. Specific objectives were the following:

a. Calibrate and validate a distributed, continuous model simulation using the Storm Water Management Model (SWMM) for the Jordan Cove LID and traditional watersheds, using existing precipitation, discharge, and pollutant (nitrogen and phosphorus) export data.

b. Compare the runoff volume and peak flow rate response of LID and traditional watersheds for hypothetical 10, 25, 50 and 100-year (24 hr) precipitation events using a calibrated SWMM model.

Materials/Procedures/Progress

Study Site

The Jordan Cove Urban Watershed Project is located in Waterford, CT (Figure 1). The project consisted of a traditionally built subdivision and a low impact development subdivision. A control watershed was also monitored to statistically evaluate the effects of the two types of construction methods using a paired watershed design (Clausen & Spooner, 1993). Monitoring methods for the project have been described previously (Clausen, 2008). Land cover, surface infiltration rates, precipitation, continuous flow measurements, and pollutant export data are available for the pre-construction, construction, and post-construction phases of the traditional and LID watersheds. Only the results from the fully built-out (post-construction period) were used in this study.

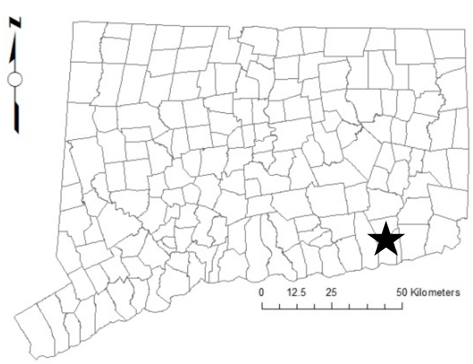

Figure 1. Location of Jordan Cove study site in State of Connecticut.

SWMM Model

A georeferenced aerial image of the watersheds was imported into SWMM (version 5.0.022) to allow for subcatchment digitization and automatic calculation of watershed areas (Figures 2,3). The LID watershed was modeled using a distributed parameter approach that resulted in the digitization of 105 subcatchments representing roofs, lawns, driveways, sidewalks, and individual LID controls. Field verification of impervious surfaces, drainage paths, and currently installed LID features was performed in both watersheds. LID controls included 11 rain gardens, 1 bioretention area in the cul-de-sac, 2 grassed swales, 1 permeable paver road, 2 permeable paver driveways, 2 crushed stone driveways, and a rain barrel. Subcatchments ranged in size from 0.3 m^2 to 20,396.2 m^2.

Initial input parameter values were estimated through a combination of field data, literature sources, and model defaults (Table 1). Field visits, as-built drawings, and manufacturer specifications were used to calculate slopes, pervious pavement parameters, and the percent of impervious area routed over pervious. Green-Ampt infiltration parameters were based on Natural Resource Conservation Service (NRCS) hydraulic conductivity values for Udorthents-urban land and soil suction and initial soil moisture deficit values for sandy loam (USDA-NRCS, 2012; Rawls *et al*., 1983; Maidment, 1993).

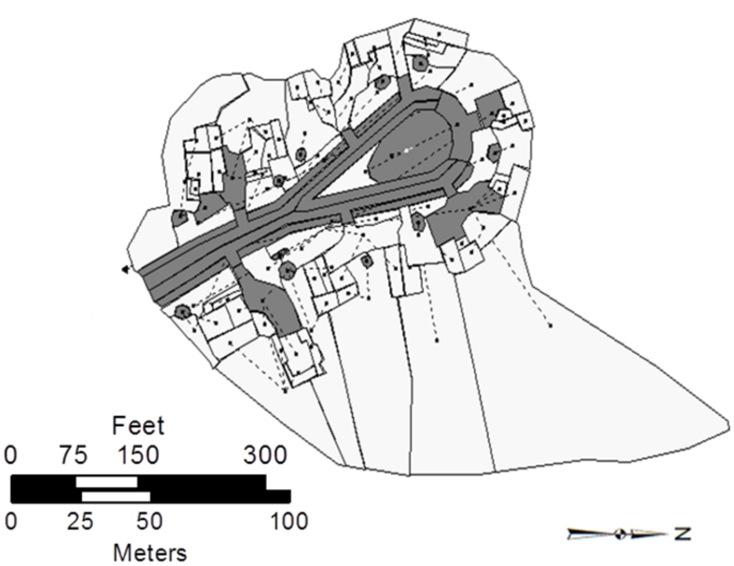

Figure 2. SWMM representation of the Jordan Cove LID watershed.

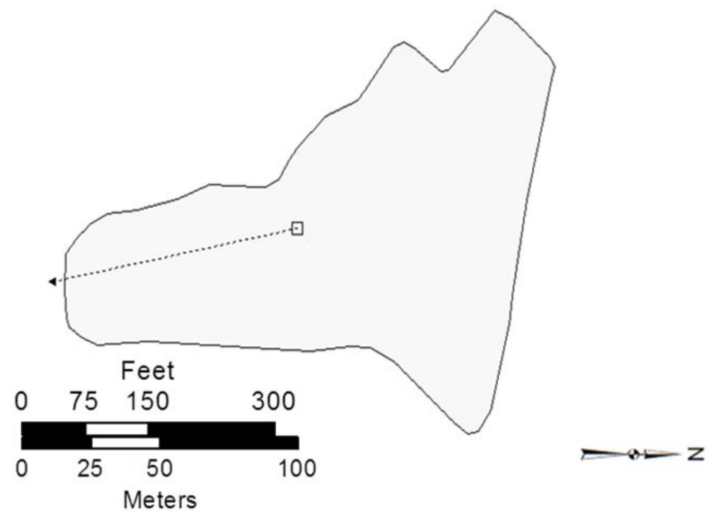

Figure 3. SWMM representation of the Jordan Cove Traditional watershed.

Sensitivity analysis was performed in order to identify which parameters would be most effective in minimizing differences between observed and predicted results. Parameters were adjusted over a range of ± 50% of their original value while keeping all other parameters unchanged and the corresponding difference in runoff volume and peak flow was calculated. Relative sensitivity was computed according to the method outlined in James and Burges (1982).

Calibration and Validation

The time period of August 12, 2004 to June 30, 2005 was used to conduct a manual calibration. Total rainfall for this period was approximately 111 cm. Sensitive parameters were systematically adjusted one at a time until differences between the simulated and observed values were minimized. A separate 46 week period from August 14, 2003 to July 08, 2004, which had approximately 91 cm of total rainfall was used for validation. Validation simulations used calibrated parameter values without further adjustment. Runoff was not simulated when there was a lack of observed data as a result of equipment malfunction or during periods of snowmelt. Agreement between predicted and observed data was assessed using coefficients of determination (R^2) and Nash Sutcliff Efficiency (NSE) coefficients (Nash and Sutcliffe, 1970).

Table 1. SWMM parameters and initial values for uncalibrated simulation of the LID and traditional Jordan Cove Watersheds.

Parameter (units)	Initial Value	Data Source
Subcatchments		
Area (ha)	0.0008 - 2.0396	Automatically calculated
Width (m)	0.9 - 1,247.0	Calculated (Rossman, 2010)
% Slope	0.5 - 30%	As-built drawings
% Imperv	0 - 100%	Bedan and Clausen, 2009
N-Imperv	0.01	Rossman, 2010
N-Perv	0.24	Rossman, 2010
Dstore-Imperv (in/mm)	0.07	Rossman, 2010
Dstore-Perv (in/mm)	0.15	Rossman, 2010
% Zero-Imperv	25%	Rossman, 2010
Percent routed	34%	Field observations
Suction head (mm)	110.1	Rawls, W.J. *et al*., 1983
Conductivity (mm/hr)	25.1	USDA, NRCS, 2012
Initial deficit (a fraction)	0.246	Maidment, 1993
Snow melt		
Snow vs rain (degrees C)	1.1°	default
ATI Weight (fraction)	0.5	default
Negative Melt Ration (fraction)	0.06	default
Porous pavement - surface		
Storage Depth (mm)	1.52	Rossman, 2010
Manning's n	0.03	James and von Langsdorff, 2003
Surface Slope (percent)	1 - 20	As-built drawings
Porous pavement - pavement		
Thickness (mm)	79.37	Manufacturer specifications
Void ratio (Void/Solid)	0.75	Maidment, 1993
Impervious Surface Fraction	0.878	Manufacturer specifications
Permeability (mm/hr)	22.8 - 88.9	Clausen, 2008
Clogging factor	0.0	default
Porous pavement - storage		
Height (mm)	0 - 304.8	As-built drawings
Void Ratio (voids/solids)	0.75	default
Conductivity (mm/hr)	254	default
Bioretention cell - surface		
Storage Depth (mm)	15.2	As-built drawings
Bioretention cell - soil		
Thickness (mm)	609.6	As-built drawings
porosity (volume fraction)	0.45	Maidment, 1993
Bioretention cell - soil		
Field capacity (volume fraction)	0.1	Dunne and Leopold, 1978
Wilting point (volume fraction)	0.05	Dunne and Leopold, 1978
Conductivity (mm/hr)	25.1	USDA, NRCS, 2012
Conductivity Slope	10	default
Suction Head (mm)	110.1	Rawls, W.J. *et al*., 1983
Bioretention cell - storage		
Conductivity (mm/hr)	25.1	USDA, NRCS, 2012
Vegetative Swale - surface		
Storage Depth (mm)	30.5	As-built drawings
Manning's n	0.24	Rossman, 2010

Rare Events

In order to simulate watershed response to rare rainfall events, synthetic 10, 25, 50, and 100-year 24 h storms were developed from Miller *et al*. (2002). A Type-III Soil Conservation Service (SCS) rainfall distribution was used to disaggregate total precipitation amounts over the 24 h period at 15 min intervals (Akan and Houghtalen, 2003).

Results/Significance

Uncalibrated discharge volumes and peak flows showed poor agreement with observed values in the LID watershed, but good agreement with observed values in the traditional watershed (Table 2). Sensitive parameters were identified and adjusted to optimize agreement between modeled and observed weekly discharge values (Table 3). Detail on sensitive parameters and calibration can be found in Rosa (2013).

Table 2. Observed and predicted runoff for the LID and traditional watersheds for uncalibrated simulation.

	LID			Traditional		
	Observed	Predicted	% Difference	Observed	Predicted	% Difference
Weekly Volume (m^3)	1,076	188	82.5%	3,647	3,021	17.2%
Average Peak Flow (m^3/s)	0.0048	0.0007	86.0%	0.0127	0.0113	11.0%

Table 3. Initial and final values of parameters adjusted during calibration.

Parameter	Initial Values for both watersheds	LID calibrated	Traditional calibrated
Ksat (mm/hr)	25.15	3.05	4.57
Suction head (mm)	109.98	101.60	228.60
Initial soil moisture deficit	0.25	0.40	0.40
N-Imperv	0.011	0.011	0.015
N-Perv	0.24	0.15	0.15
Manning's n for swale†	0.24	0.15	-
Dstore-Perv	3.81	2.54	5.08
Dstore-Imperv (mm)	1.78	1.27	2.54
Width‡	1,638	-	600
Washoff Coefficients			
Nitrogen	5.00	3.00	2.00
Phosphorus	5.00	0.03	0.01

†Applies only to LID watershed

‡Applies only to traditional watershed

Runoff Volume and Peak Flow

The model simulated weekly runoff volume and peak flow well for both the calibration and validation periods, with high R^2 values (>0.8) for all regressions (Figure 4). A hydrograph of weekly modeled runoff volume (LID watershed) showed good agreement during the calibration period (Figure 5). High NSE values were also found for the calibration period (Table 4). NSE values >0.5 have been suggested as an indication of good model prediction (Santhi, *et al.,* 2001). Observed and predicted values of total volumes and average peak flows for both the calibration and validation periods also showed good agreement (Table 5). These findings suggest that the calibrated model is performing well in predicting runoff volumes and peak flows from the two study watersheds.

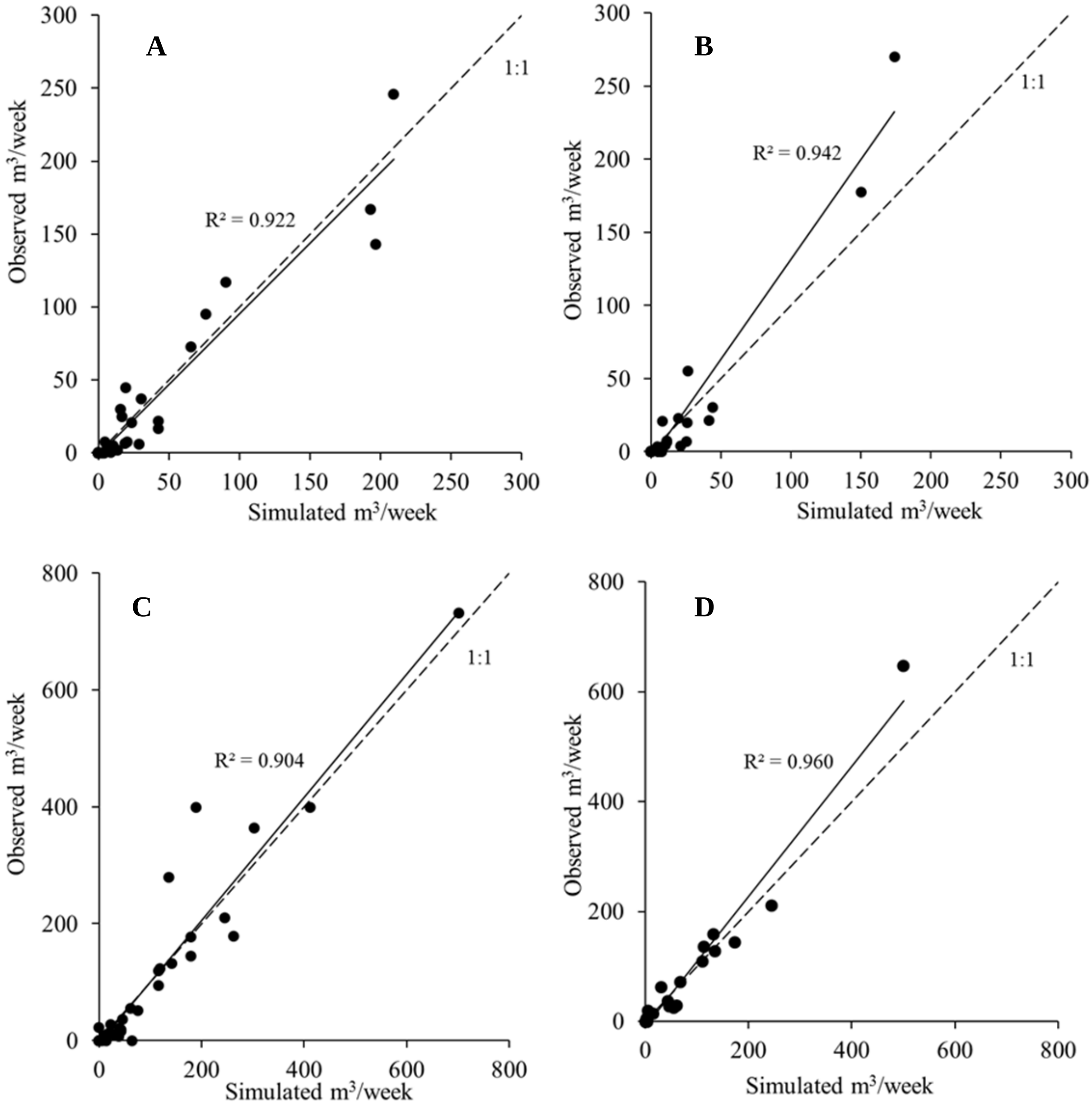

Figure 4. Weekly runoff volume for the LID and traditional Jordan Cove watersheds. A: LID Runoff volume calibration; B: LID runoff volume validation; C: Traditional runoff volume calibration; D: Traditional runoff volume validation.

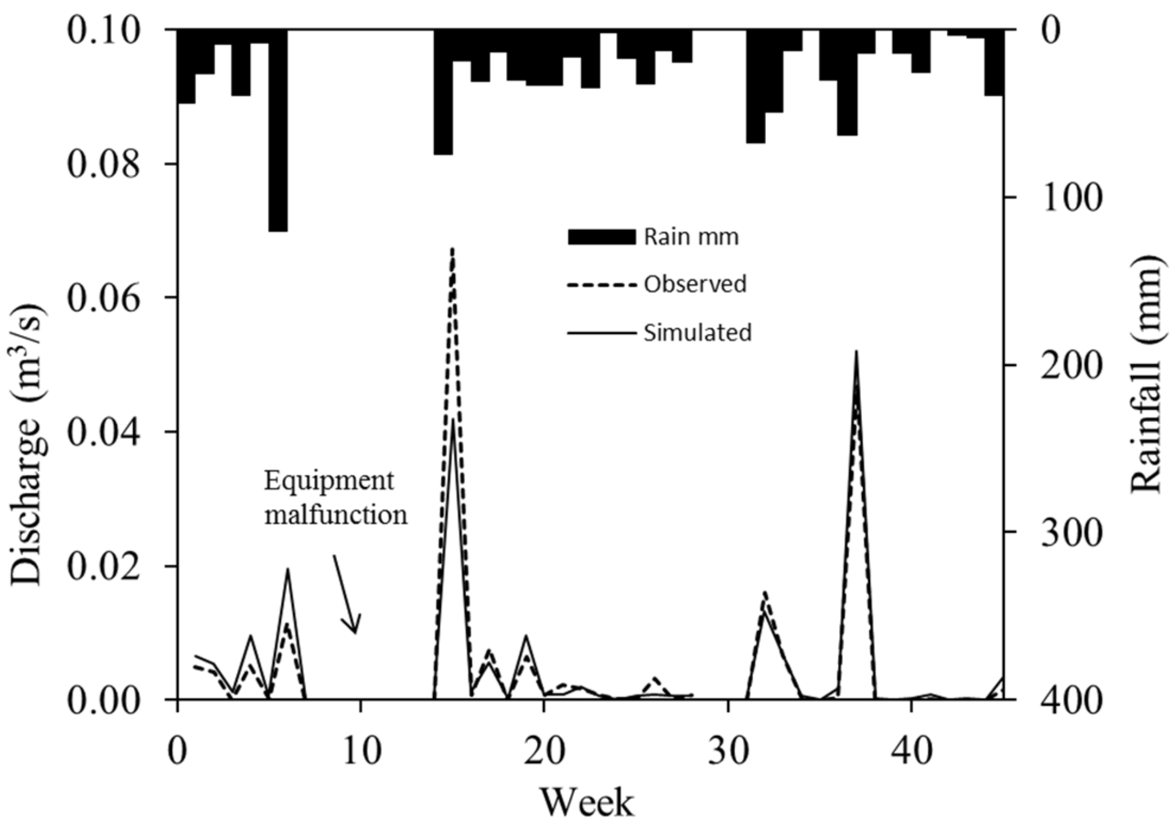

Figure 5. Weekly discharge and precipitation for the LID watershed calibration period (Aug. 2004-Jun. 2005).

Table 4. Nash-Sutcliffe Efficiency (NSE) coefficients for runoff volume and peak flow for Jordan Cove LID and traditional watersheds.

	LID		Traditional	
	Runoff Volume	Peak Flow	Runoff Volume	Peak Flow
Calibration	0.918	0.876	0.901	0.684
Validation	0.875	0.741	0.936	0.885

Table 5. Observed and predicted runoff for the LID and traditional watersheds.

	LID			Traditional		
	Observed	Predicted	% Difference	Observed	Predicted	% Difference
Calibration						
Total Volume (m^3)	1,076	1,162	8.0%	3,647	3,615	0.9%
Average Peak Flow (m^3/s)	0.0048	0.0047	2.1%	0.0127	0.0112	11.8%
Validation						
Total Volume (m^3)	664	625	5.9%	1,839	1,757	4.5%
Average Peak Flow (m^3/s)	0.0017	0.0015	11.8%	0.0116	0.0103	11.2%

Nutrient Export

In general, prediction of TN and TP export by the model was not as accurate as flow predictions; only TN export from the LID watershed had reasonable performance with NSE coefficient > 0.5. The model overestimated export of TN and TP from the LID watershed by 21% and 13%, respectively. For the traditional watershed, the model underestimated TN by 20%, and overestimated TP by 9%. The cause of the poor prediction of nutrient export is not known, but is likely due to homeowner activities such as lawn fertilization that were not accounted for in the model. Fluxes of nitrogen and phosphorus from homeowner activities could cause variability in the model that would not be accounted for by model algorithms.

Rare Events

The calibrated model was used to simulate runoff for the 10, 25, 50, and 100-year 24 hour rainfall events for the traditional and LID watersheds. A hydrograph of the 100-year 24 hour storm appears to show little difference in runoff per unit area from the two watersheds (Figure 6). The peak runoff rate from the LID watershed (34.5 $m^3/s/km^2$) was slightly lower than the rate from the traditional watershed (36.0 $m^3/s/km^2$). However, a steeper receding limb for the LID watershed resulted in less runoff compared to the traditional watershed. Although this difference appears to be slight, the LID watershed had consistently lower runoff coefficients (event runoff :

event rainfall) than the traditional watershed for all events modeled (Table 6). The percent difference decreased with increasing storm size, but was still substantial (22% less runoff from the LID watershed compared to the traditional) for the 100-year event. This is especially significant considering that in the predevelopment condition, the LID watershed had a higher runoff coefficient than the traditional watershed (Dietz and Clausen, 2007). It is not known what the predevelopment hydrologic response was to these large events, so pre- vs. post-development analyses cannot be performed. However, it is evident that there is some benefit of LID to reduce runoff from large events, despite common thinking that it only helps with small events.

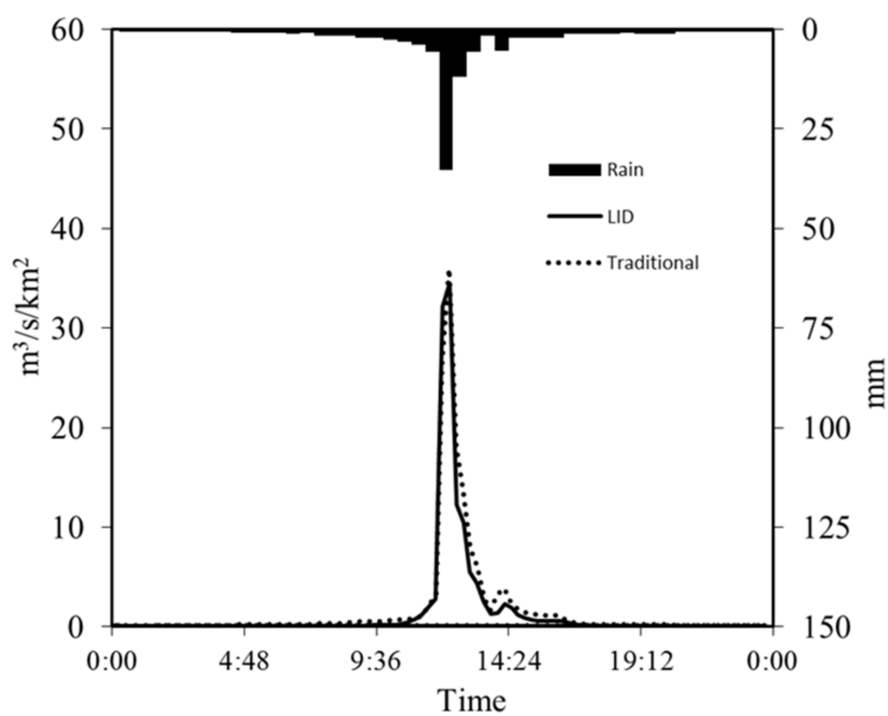

Figure 6. Traditional and LID watershed hydrographs and hyetograph for the 100-year 24 hour event.

Table 6. Rare event rainfall, runoff depth, and runoff coefficients for the Jordan Cove LID and traditional watersheds.

Recurrence interval (year)	Rainfall (mm)	LID Watershed		Traditional Watershed		Percent difference
		Runoff depth (mm)	Runoff coefficient	Runoff depth (mm)	Runoff coefficient	
10	132	44	0.34	60	0.46	26
25	163	62	0.38	82	0.51	25
50	198	84	0.42	110	0.55	24
100	234	107	0.46	138	0.59	22

Conclusions

The calibrated SWMM models for the LID and traditional Jordan Cove watersheds showed excellent predictive capabilities for runoff volume and rate according to standard metrics of accuracy. However, less accuracy was found for nitrogen and phosphorus loading estimates from the model as compared to observed values.

Simulation of the 10, 25, 50, and 100-year 24 hour events results in consistently lower runoff coefficients for the LID watershed compared to the traditional watershed, indicating that LID practices likely have stormflow control benefits even during large storms.

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APPENDIX A: Graduate Student Involvement and Conference Presentations

Graduate students involved in this project:

Name: David Rosa

Department: UConn department of Natural Resources and the Environment

Degree: M.S.

Expected graduation date: August 2013

Thesis title: Post-audit verification of the model SWMM for Low Impact Development

Conference presentations:

Rosa, D. 2012. Modeling the Effectiveness of Low Impact Development Using SWMM. Connecticut Conference on Natural Resources, 3/12/12, University of Connecticut.

Rosa, D. 2013. Post-audit Verification of the Model SWMM for Low Impact Development College of Agriculture and Natural Resources Graduate Research Forum, 4/6/13. University of Connecticut.

Accepted presentations:

2013 International Low Impact Development Symposium. August 18-21, St. Paul, MN.

The Impacts of Wastewater from a Retirement Community on Fish Health

Basic Information

Title:	The Impacts of Wastewater from a Retirement Community on Fish Health
Project Number:	2012CT257B
Start Date:	3/1/2012
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	CT-002
Research Category:	Water Quality
Focus Category:	None, None, None
Descriptors:	None
Principal Investigators:	Thijs Bosker, Thijs Bosker

Publications

There are no publications.

The impacts of wastewater from a retirement community on fish health

NOTE: Due to personal family matters requiring his attention in his native country of the Netherlands, the PI, Dr. Thijs Bosker, has resigned from the University of Connecticut and is no longer in a position to continue work on this project as of the start of the 2013 fiscal year. The director of CT IWR, Dr. Glenn Warner, attempted to find a suitable replacement for Dr. Bosker to take over as PI for this project. While a qualified replacement was found at the University of Connecticut, scheduling unfortunately did not allow for continuation of the work started during the 2012 fiscal year. In a brief correspondence with Earl Greene, he agreed that the remaining funds from this project could be applied to a future project selected by the director of CT IWR. As such, we anticipate using these funds to fund a project during the next funding cycle.

The progress report from fiscal year 2012 is provided here.

Progress Report March 1, 2012 – February 28, 2013

Principal Investigator:
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Introduction

Many contaminants have the ability to disrupt the reproductive system of fish and potentially cause effects at population levels (Tyler et al. 1998; Kidd et al. 2007). These contaminants are found in a wide variety of sources, including municipal (Jobling et al. 2002) and industrial (Munkittrick et al. 1992) effluents, and agricultural run-off (Orlando et al. 2004). A group of contaminants of emerging concern are pharmaceuticals and personal care products (PPCPs) found in municipal wastewater effluent (MWWE) (Diamond et al. 2011). PPCPs are omnipresent in sewage effluent (Kolpin et al. 2002), as current sewage treatment does not effectively remove them (Fent et al. 2006).

One of the main concerns about PCPPs is their ability to affect fish reproduction by disrupting endocrine signaling (Hotchkiss et al. 2008; Burkhardt-Holm 2010), causing effects such as sex reversal and intersex condition in fish and amphibians (Hutchinson et al. 2006). Effects of PCPPs on reproduction have been observed at different levels of biological organization, including molecular (Garcia-Reyero et al. 2011; Ings et al. 2011), physiological (Dinizi et al. 2010; Ings et al. 2011), organismal (Ma et al. 2005) and population (Jobling et al. 2002; Jobling et al. 2002; Kidd et al. 2007) level endpoints. For example, a recent long-term, whole-lake study demonstrated a collapse of a fish population when exposed to environmentally-relevant levels of 17α-ethinylestradiol (EE_2), a potent estrogen used in birth-control pills, and commonly measured in MWWE (Kidd et al. 2007). As current sewage treatment does not effectively remove PCPPs, effects on organisms have been observed downstream of wastewater treatment plants (WWTPs). This is true even for facilities that support advanced treatment. Changes in physiology, gene expression and reduced competitive behavior have been observed in fish exposed after secondary treatment (Garcia-Reyero et al. 2011). Moreover, fish exposed to tertiary treated MWWE have shown changes in physiological endpoints, as well as altered gene expression (Ings et al. 2011).

Interestingly, there has been limited research on the impact of PPCPs on ecosystem health within Connecticut, even though it has the fourth highest population density of all US states, with 738.1 inhabitants/per square mile (US Census Bureau 2010). The investigator is aware of only one study on the *presence* of PCPPs and non-traditional compounds released from a WWTP into Connecticut water bodies. Scientists from the United States Geological Survey (USGS) conducted a pilot assessment of the Farmington River and characterized a subset of persistent pollutants and PCPPs (John Mullaney, unpublished data). This study found the presence of plant and animal steroids, fragrances, personal care products, pesticides, cosmetics, detergent by-products, and flame retardants in the WWTP effluent as well as from downstream samples. Importantly, many of these compounds were not found in detectable concentrations upstream of the MWWE.

Currently a second study is being conducted in Connecticut. Dr. Allison MacKay (Civil and Environmental Engineering, University of Connecticut [UCONN]) is studying the fate and transport of PCPPs discharged from *Heritage Village* WWTP into Pomperaug River (Southbury, CT). The effluent from the *Heritage Village* WWTP has some distinguishing characteristics; (1) the sole source feeding into the *Heritage Village* WWTP is a retirement community (discharge estimated at ~500k gallon/day), (2) the MWWE input is the only significant point-source discharging in the system (environmental concentrations reach 10%, but average 1-3%), (3) the watershed has been well studied by both Dr. MacKay and the Pomperaug River Watershed Coalition and (4) there is an active and open collaboration with the operators of the *Heritage Village* WWTP. **The combination of these characteristics provide an excellent opportunity to study *impacts* of effluent from a retirement community on fish reproduction, using both laboratory and field tools.**

To date there are no published studies on the impacts of MWWE of retirement communities on fish reproduction. Based on the elderly population's higher dependence on various medications, a disproportional amount of PPCPs are expected in their wastewater. The expected higher levels of PPCPs have been confirmed by preliminary data on the presence of pharmaceuticals in the final treated effluent of this retirement community. Ibuprophen was detected at 1µg/L in the final effluent, which is comparable to the highest levels ever reported in final treated effluent (Dr. McKay, unpublished data). Moreover, ibuprophen has been demonstrated to impact fish health and reproduction in recent laboratory studies on Japanese Medaka (*Oryzias latipes*) (Flippin et al. 2007; Han et al. 2010). The composition of pharmaceuticals within MWWE of a retirement community will also be likely to be different compared to MWWE from more diverse sources. For example higher levels of hormones used in estrogen replacement therapies are expected, compared to lower levels of pharmaceuticals used in birth-control.

In addition to the increased dependence of elderly on medication, the percentage of people age 65 and older is increasing rapidly. The percentage of people 65 and older is estimated to be 13.9% of the population in Connecticut, which is above the US average of 12.4% (Bureau 2010). This percentage is projected to increase to 21.5% of the CT population by 2030 [projected US average is 19.7%] (Department of Health & Human Services 2010). Furthermore, it is likely that there will be an increase of retirement communities within Connecticut and the US. This is because the house prices are relatively high (generating increased property tax revenues), while people living in retirement communities require less education related services. As a result, the development of retirement communities is an attractive option for municipalities.

Objectives of the project

The overall objective of this study is to perform a comprehensive evaluation of the potential of waste water from a retirement community to affect fish reproduction at different levels of biological organization. To address this, we will evaluate a number of interconnected hypotheses, associated with two specific objectives.

Objective 1. — To quantify the impacts of increased concentrations of final treated effluent from a retirement community on reproductive endpoints in fish under standardized laboratory conditions

- H_{01}: There are no molecular, physiological, organismal or functional responses in fish exposed under laboratory conditions to different concentrations of final treated effluent of an WWTP from a retirement community.

Objective 2. — Quantify the impact of MWWE discharge within the Pomperaug River on reproductive endpoints in two fish species collected in the field

- H_{02}: There are no molecular, physiological, organismal or population level responses in two fish species collected upstream and downstream of an WTTP discharge from a retirement community.
- H_{03}: There is no difference in sensitivity between two fish species collected downstream of an WTTP discharge from a retirement community.

Methods/Procedures/Progress

To assess the impact of the Heritage Village WWTP on fish reproduction both field and laboratory studies will be applied. Laboratory and field studies have different advantages and disadvantages. For example, field studies have a direct environmental relevance compared to lab studies. However, there are many confounding factors within field studies which can make data interpretation a challenge (Munkittrick 2009). The standardized conditions of lab exposures will minimize these confounding variables. Using both field and laboratory studies will allow a comprehensive evaluation on the potential of MWWE of a retirement community to affect fish reproduction.

Objective 1: Quantifying impacts under laboratory exposure

In year 1 a laboratory exposure will be conducted on fathead minnow (*Pimephales promelas*) using a test developed by US EPA (Ankley et al. 2001). Fathead minnow are one of the most widely used small fish species for ecotoxicology in North America, with a toxicity database encompassing more than 10,000 chemicals tested over 50 years. They are a small fish native to North America and a member of the ecologically-important Cyprinidae (minnow) family.

In order to assess the impact of the final effluent on fathead minnow, a short-term reproductive test will be conducted. Short-term reproductive tests have been developed for a variety of freshwater and saltwater species, including fathead minnow (Ankley et al. 2001). In these tests, the reproductive effects of contaminants on molecular, physiological, organismal and functional endpoints are measured, to study and compare effects at different levels of biological organization. Recently a series of refinements has been proposed for use in short-term reproductive tests to optimize statistical power (Bosker et al. 2009). These refinements will be used in the proposed experiment, and include (1) tank selection after a pre-exposure phase, and (2) an increased sample size (n=6 tanks/treatment) to ensure adequate statistical power (a required power level of 80% [β=0.2]), to detect a 40% decrease in egg production (Bosker et al. 2009).

Adult fish are exposed under static conditions, with a complete daily renewal of the water. Fathead minnow are exposed either on-site in a toxicity trailer or in the Animal Facilities at the University of Connecticut. Exposure conditions (temperature, dissolved oxygen, pH and water hardness) will be regularly monitored. During a 14-d pre-exposure phase all fish will be kept in control water, and eggs will be collected daily. Based on initial egg production, tanks will be selected based on a set of pre-defined criteria (Bosker et al. 2009) and randomly distributed over the different treatments (n=4 treatments, with n=6 tanks/treatment). Fish will be exposed for 21-d to concentration of 0, 1, 5 and 25% of final treated effluent of the *Heritage Village* WWTP. Both 1% and 5% are environmental relevant concentrations within the Pomperaug River. Eggs will be collected daily to determine cumulative number of eggs spawned per female, and number of spawning events.

Objective 2: Quantifying impacts under field conditions

Blacknose dace (*Rhinichthys atratulus*) and creek chub (*Semotilus atromaculatus*) are both members of the Cyprinidae family. They will be used to study potential impacts of the wastewater effluent on fish reproduction. Selection of these species for use as sentinel species is based on a series of criteria, which include (1) abundance, (2) small home range and (3) sensitivity to stressors of concern (Canada 1997). Both blacknose dace and creek chub meet these criteria. The Pomperaug River Watershed Coalition has done extensive fish surveys in the Pomperaug River, and identified blacknose dace and creek chub as two of the most abundant species (Parasiewicz et al. 2007). In addition, blacknose dace are a small-bodied fish, with a small home range (Galloway and Munkittrick 2006). They have been successfully used to monitor impacts of urban inputs (Fraker et al. 2002; Nelson et al. 2008) and metal contamination (Jardine and Kidd 2011). Creek chub are a larger species, which mainly feed on small fish and invertebrates (Fitzgerald et al. 1999). Creek chub have a small home range (Fitzgerald et al. 1999), and have been successfully used to study impacts of effluents (Weber et al. 2008; Driedger et al. 2009).

To adequately assess impacts on reproduction, it is of great importance to sample fish during the right period of their reproductive cycle. For example, a review of data submitted in Canada under the Federal Environmental Effects Monitoring (EEM) program for adult fish surveys showed that 72% of studies were not conducted optimal time, potentially misinterpreting potential responses in fish (Barrett and Munkittrick 2010). Therefore, in year 1 of the proposed study, data on the reproductive cycle of blacknose dace and creek chub will be collected, with assistance from volunteers of the Pomperaug River Watershed Coalition. Collections will occur from April until the end of their spawning cycle at three uncontaminated, spatially distributed sites. Specimens will be collected using electrofishing and/or minnow traps (10 fish/sex/species) to determine the natural variation within the population in relative gonad size and sex steroid hormone levels, and to determine appropriate sample sizes for these endpoints based on power calculations (Munkittrick et al. 2009). For both species primers will be designed for a suite of molecular biomarkers that have been shown to respond to chemical stressors. In the second year, data from year 1 will inform a more rigorous statistical design. Fish are collected from an upstream site and three sites downstream from the discharge location of the *Heritage Village* WWTP. Fish numbers will be based on power calculations, using a critical effect size of 25% for gonad size (Munkittrick et al. 2009), and 60% for steroid levels (Bowron et al. 2009). Fish are either transported back to the laboratory or dissected on location.

Results/Significance

After the grant was awarded, approval was secured from the Institutional Animal Care and Use Committee (IACUC) to conduct animal research. An electrofishing permit was obtained from the Connecticut Department of Energy and Environmental Protection (CT DEEP).

In the first year the main goal was to identify the optimal collection time of the target species within the Pomperaug River. To achieve this fish were collected at three sites, which were selected in collaboration with James Belden and Carol Haskins of the Pomperaug River Watershed Coalition.

Sampling ran from April 4 to June 26. Collection sites were fished seven times (spaced 1,5 weeks apart) using a backpack electrofisher. Blacknose dace were collected during this period of time in sufficient numbers (20 fish/site), however, we did not have success securing sufficient numbers of creek chub at all sites. For this reason our efforts were focused on blacknose dace. After collection fish were transported to the laboratory at the University of Connecticut, to determine relative gonad size (Fig. 1 and 2). Gonads were incubated to determine sex steroid levels in males and females, and are currently being processed.

Gonad size and sex steroid levels data will be used to determine appropriate sampling times, as well as sample size requirements for both males and females. In addition, gonad and liver samples were stored to develop molecular primers for use in year 2 of the project.

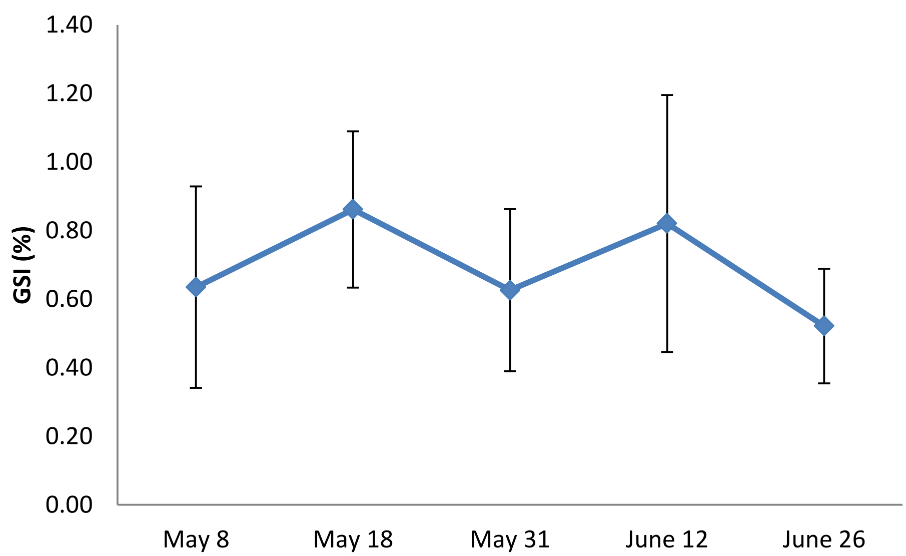

Figure 1. Average gonadal somatic index (GSI; +/- STDEV) of male blacknose dace (*Rhinichthys atratulus*) collected within the Pomperaug River at three different sides

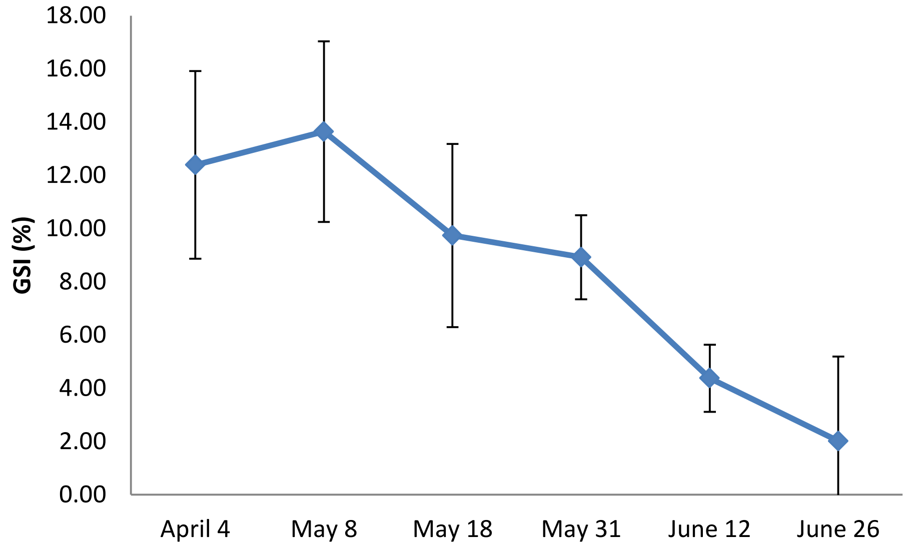

Figure 2. Average gonadal somatic index (GSI; +/- STDEV) of female blacknose dace (*Rhinichthys atratulus*) collected within the Pomperaug River at three different sides

Chemical characterization of effluent

Methods for the quantification of pharmaceuticals and personal care products are currently being finalized, consistent with the approach in the proposal. The target compound list has been finalized (Table 1), and we have evaluated and modified the preparation method to maximize the extraction efficiency for the targeted compounds. All that remains is the finalization of the instrument analysis method.

The study design is to collect effluent samples concurrent with spawning fish collections. Through collaborators at Pomperaug River Watershed Coalition we have contacted the managers of the Heritage Village WWTP to ensure that water samples can be collected. Water samples will be collected during the laboratory experiment and when conducting the field assessment (upstream-downstream sampling).

Table 1. Representative list of compounds and elements that will be analyzed in this study.

Compound	Pharmaceuticals (12 of 80 possible) Category/ Use	Metals (8 of 20 possible)
Caffeine	Stimulant	Arsenic
Carbamazepine	Anticonvulsant	Cadmium
Digoxigenin	Steroid	Chromium
Diltiazem	Calcium channel blocker	Copper
Digoxin	Cardiac glycoside	Lead
Doxycycline	Antibiotic	Nickel
Fluoxetine	Antidepressant	Selenium
Gemfibrozil	Lipid regulator	Zinc
Ibuprophen	Anti-inflammatory	
Norgestimate	Contraceptive	
Triclosan	Antibacterial	
Warfarin	Anticoagulant	

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Influence of dynamic copper speciation on bioavailability in streams

Basic Information

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Proposal Title: Influence of dynamic copper speciation on bioavailability in streams

Introduction

Copper is both an essential micronutrient for biology and a potential toxicity issue at high concentrations. Besides the natural sources of Cu in ecosystems that provide nutrition, there are many additional anthropogenic sources that are reaching receiving water bodies, including dissolved Cu from roofing materials, household water distribution pipes, applications of copper sulfate algicides, abrasion of brake pads and other commercial uses (Marsalek et al., 1999). Within a given reach of a stream, there are potentially four contributing sources of Cu, including wastewater treatment plant effluent (industrial or municipal), stormwater inputs, legacy pollution in the sediments, and Cu in baseflow that may be contributed by natural sources or e.g., by algicide application upstream.

Although for impaired water bodies regulations focus on total pollutant input to receiving water bodies regardless of its chemical form, Cu speciation influences bioavailability, and thus stream impairment due to toxicity and changes in ecosystem function. Cu speciation is controlled primarily by organic matter and introduces a level of complexity in understanding bioavailability. While in select cases, uptake of DOC-metal complexes may have occurred (Campbell et al., 2002; Vadas and Ahner, 2009), in most cases, uptake is thought to be controlled by diffusion, lability and transfer of the free metal to a transporter on the cell surface. Based on that, the major conditions that control the uptake of Cu in urban streams are either the diffusion of labile complexes or the kinetics of metal-ligand complex exchange. The equilibrium condition of this model is considered in the biotic ligand model. However, when considering the biological structure of a stream ecosystem, dietary uptake needs to be considered. While biological uptake may still be controlled by the strength and kinetics of the organic ligand, both the dynamic conditions in streams and the food web structure can influence biouptake and trophic transfer, e.g. metal attachment and uptake in periphyton and trophic transfer to grazers.

The research conducted focuses on Cu contamination, which is of widespread concern across the state of Connecticut, including for example the Eagleville Brook watershed surrounding part of UConn campus, the Hockanum River or the Tankerhoosen River watershed. Many TMDLs developed or in development in the state currently utilize acute and chronic water quality standards to set total copper loads and/or whole effluent toxicity studies. However, these have not always been sufficient to reduce impairment, most likely due to differences in chronic toxicity. Future analyses will be better served to assess loads based on aqueous phase copper speciation criteria with a causal link to biological impacts. This can only be accomplished by understanding the dynamic conditions in urban streams, and the relationship of Cu speciation with biological uptake.

With respect to metal source, the current assessment of total and dissolved Cu ignores relevant speciation information that may inform mechanisms of impairment. Speciation measurements are not simple or routine and thus would not be appropriate for regulatory use. In an effort to get around that issue, chemical surrogates such as diffusive gradients in thin film (DGT) devices have been developed that measure "bioavailable" metals (Zhang and Davison 2000). These have been validated for soil systems and plant root bioavailability, but their use in waters and sediments as stream organism uptake indicators has not been validated (Warnken et al., 2008). Ultimately, what DGT devices will measure in streamwater are labile species, i.e. readily exchangeable Cu that could potentially interact with a biotic ligand as an indicator of biologically available metals.

In addition to passive chemical sensors, periphyton have been used to assess metal uptake in streams (Meylan et al 2003). Periphyton is the most important primary producer in running waters and responsible for the uptake and retention of organic carbon and inorganic nutrients. Periphyton, being one trophic level below macroinvertebrates, should more accurately capture the dynamic conditions in streams and help pinpoint the source and timing of contaminants that lead to impairment of the water body.

In summary, the goal of the research was to assess two tools to measure bioavailable metals in streams, DGT and periphyton cultures. These were assessed in combination with water chemistry measurements as well as characterization of metal size distribution in different source waters to the stream. These were assessed both as a function of distance downstream of the inputs in the case of effluent as well as over the course of several storm events, two pieces of information that are not currently captured using grab samples or macroinvertebrate surveys. The data suggests a strong difference between bioavailability of effluent sources versus stormwater sources and further studies should be conducted to assess a wider range of source waters and seasonal variability. These simple assessment tools could be used to provide justification for management decisions based on Cu speciation, not just total Cu, and mitigation options based on source and location of inputs.

Research Objectives:
Results from this work have implications for improving risk assessment at impacted sites, enhancing dynamic bioaccumulation models, and providing evidence for reducing their impacts through treatment or restoration activities that manage carbon or metal sources. This research addressed three specific questions:

1) What is the impact of the dynamic urban stream environment on metal size speciation?
2) Can a chemical surrogate readily predict biouptake in a benthic organism?
3) Do anthropogenic metal sources drive excess biouptake in stream organisms?

Methods

Site description
The Hockanum River (Connecticut, USA) originates at the outlet of Shenipsit Lake and flows 36.4 km through Vernon, Ellington, Manchester, and East Hartford before it spills into Connecticut River. This research mainly investigated the reach flowing through Vernon, which is primarily a suburban area. The Hockanum River was contaminated by Cu inputs from base flow, stormwater, and treated wastewater. The Hockanum River which flows through the towns of Vernon and Manchester had an average flow rate of 3.94 m^3/s over the last few years. A water pollution control facilities (WPCF) in Vernon discharges treated effluent into the river, with an average effluent discharges of 0.21 m^3/s. In addition, separate storm sewers exist and discharge into the river in several locations along its course. Six sampling locations were selected to deploy the diffusive gradient in thin film (DGT) and periphyton samples from upstream to downstream along the Hockanum river, including one in Rockville, the wastewater treatment plant (WWTP) upstream and downstream, Dart Hill Road, Hockanum Blvd, and Pleasant View Dr. The storm runoff was collected from the discharge pipe at Pleasantview Dr (Figure

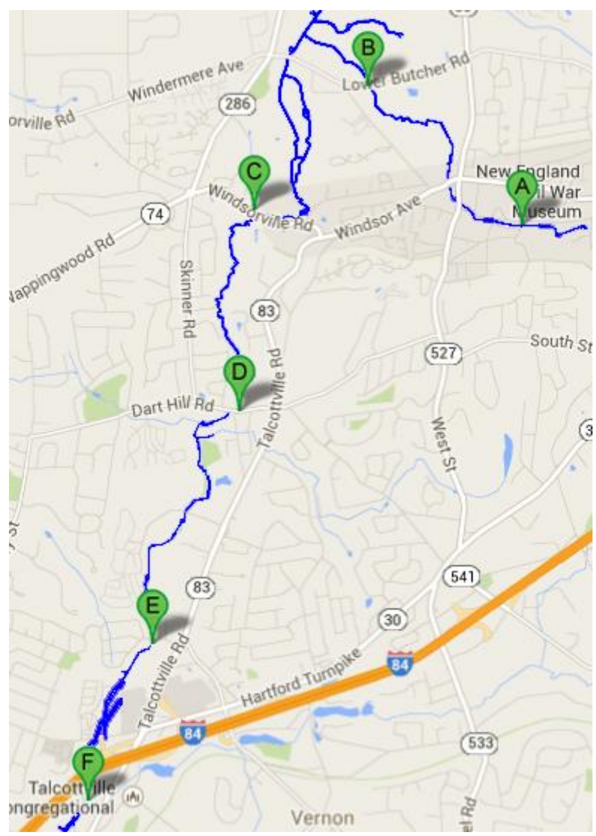

Figure 1: Hockanum River sampling locations

1). Additonal grab samples for size distribution comparison were taken from the Quinnebaug River, Willimantic River, and associated wastewater treatment plants.

Passive sampler preparation

Microscope slides pre-loaded to acrylic racks were used to colonize periphyton. To minimize collection of suspended particles, the racks were deployed vertically about 10 cm below the water surface. 4 racks holding 16 microscope paired slides each were placed next to each other parallel to the water current. A 3-week colonization period in a clean water source prior to use was necessary to obtain sufficient periphyton. DGT-devices were made following the procedure described by Zhang (2000). To get a consistent performance, the thickness of diffusive gel was modified to 1.0 mm.

Sampling and sample preparation

Water samples were collected in acid washed low density polyethylene (LDPE) bottles for dissolved, colloidal and total metal concentration, dissolved organic carbon (DOC) and alkalinity. DGT devices were deployed 10 cm above the bottom of the river and retrieved after 24 h exposure. Periphyton slides were deployed in the same way but retrieved at certain time intervals along the storm event. Water, periphyton and DGT sampling was performed before, during and after several storm events as well as a function of distance downstream from the WWTP during baseflow. At the time of sampling, 4 microscope slides were thoroughly rinsed with filtered river water (0.45 μm). The natural algal biofilm was then scratched from the slide with a clean microscope slide and was suspended in filtered river water. The suspension was afterward divided into two fractions. One fraction (20 mL) was treated for 10 min with 4.0 mM EDTA to remove the metals adsorbed to the cell wall and most of the inorganic complexes embedded in the biofilm. This process allowed for the measurement of the intracellular metal content of periphyton. The other fraction was used to measure the total metal accumulated in periphyton. The difference between total and intracellular metal content is considered to be adsorbed metal on periphyton. Three aliquots of each fraction were filtered with acid-washed and preweighed filters (cellulose nitrate 0.45 μm) to obtain the dry weight (dw) of each sample after drying to a constant weight at 50 °C. The filters were digested following standard methods (EPA Method 3050B). Briefly, the filters were soaked in 4 mL of concentrated nitric acid (ACS) in a 15 mL digestion tube. Digestion samples were heated at 95 ℃±5℃ until no brown fumes were given off. Subsequently, hydrogen peroxide (30%) was added stepwise until the effervescence was minimal or until the general sample appearance was unchanged. The digested sample was diluted for ICP analysis. Water samples for dissolved metals and DOC were also filtered through 0.45 μm nitrocellulose filters then pH adjusted to 2 with nitric or hydrochloric acid, respectively. For DGT devices, after retrieval from the field, the resin gel was peeled off and transferred to an acid-cleaned 2 mL microcentrifuge tube containing 1mL of 1M HNO_3 and soaked overnight. The elution solution was diluted 5 times with 1% HNO_3 matrix prior to analysis on ICP-MS.

Size distribution by AFFFF coupled to ICP-MS

Concentration and size distribution of colloidal metal complexes was characterized by asymmetric flow field flow fractionation (AF4, Postnova Analytics, Landsberg, Germany) coupled on-line to UV detection at 254 nm for aromatic DOC determination and ICP-MS for trace metal determination. The AF4 2000 Control software (Postnova Analytics) was used for data collection and analysis of UV signals and size calculations, while Agilent Chemstation (MassHunter) software was used for time resolved analysis of metals. Prior to injection into the ICP-MS introduction system, a 6% nitric acid solution containing 500 ppb Sc was mixed in as an internal standard and to acidify the neutral samples. The AF4 system was metal free and equipped with a 275 mm long trapezoidal channel cartridge and different size spacers depending on the method. The mobile phase was 10mM $NaNO_3$ with pH matched to the source water. Samples were analyzed in two different modes, to capture more resolution in the large or small size colloidal fractions. Capture of the large size fraction was achieved using a 10 kDa cut-off polyethersulfone (PES) membrane and a 350 μm spacer. Samples were injected to the channel using a 1 mL sample loop at an injection flow of 0.2 mL min^{-1} for 6 min. After a 1 min transition time, samples were separated using a channel flow of 1 mL min^{-1} and a constant cross flow of 1 mL min^{-1} over 40 minutes. To capture the small size fraction, a 300 Da cut-off PES membrane was used with a 500 µm spacer. The 300 Da membrane was selected over the typically used 1 kDa PES or 1 kDa regenerated cellulose membranes because it had the most metal recovery, i.e. limited metal retention on the membrane, from the various water sources when analyzed without crossflow.

Sample analysis

Inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7700x, Agilent, USA) was applied for determination of the metals in this work. A total organic carbon analyzer (Apollo 9000, Tekmar-Dohrmann, USA) was used to measure dissolved organic carbon (TOC).

Results:

Metal distribution between particulate, colloidal and truly dissolved fractions

The bulk metal distributions in in stream, effluent and stormwater samples showed large variations. Upstream and stormwater samples usually had more total Fe and higher colloidal Fe fractions than the effluent, with the exception of H_up (Fig 2). More than 30% of Fe was present in the particulate form especially for the stormwater (above 60%) which strongly correlates with particulate Pb concentrations in solution. On the other hand, the effluent and stormwater samples had much higher Cu and Zn concentrations than the upstream samples. Cu and Zn were mostly found in the truly dissolved fractions (usually >50%), 20-50% in the colloidal phase, and a typically smaller fraction in the particulate phase

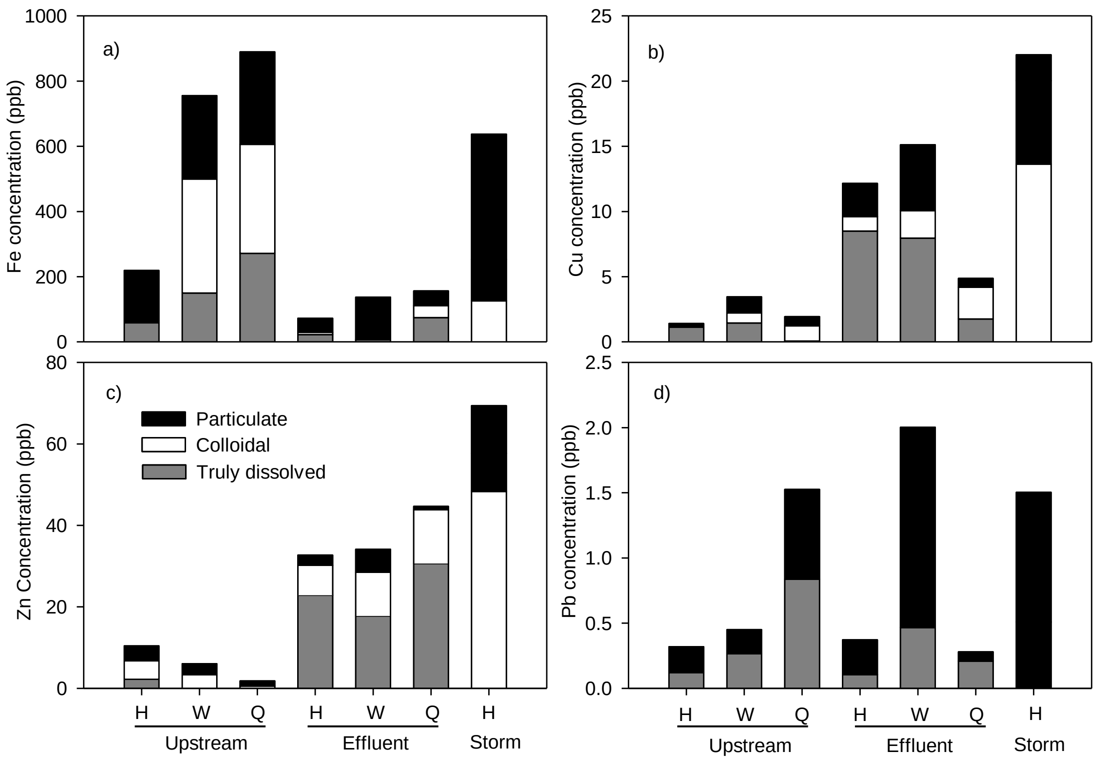

Figure 2: Size distribution between particulate, colloidal and truly dissolved in stream, effluent and storm runoff samples

which is similar to previous observations of effluent sources (Worms et al., 2010). The colloidal size fraction, which can contain up to 50% of the dissolved metals, covers a large size distribution, and samples were further analyzed to assess the metal association between organic matter and iron colloids.

Colloidal size distribution of metals

The colloidal fractions of Fe in Q_up and W_up showed both small (0.5-3 nm; 10-20% of the mass) and much more dominant large (3-80 nm; 70-80% of the mass) size distributions (data not shown), whereas Fe in effluent samples was only observed in the small size range. The large size fraction of Fe never co-eluted with UV measurable organic matter or other metals measured in this study, and was likely primarily composed of iron oxides (Perret et al., 2000; Stolpe et al., 2013). The only observable difference in the large size range Fe was a broader peak in the Q_up compared to the W_up which could have been due to differences in stream velocity or water chemistry. Further analysis focused on a higher resolution analysis of the smaller size range colloids with both metals and organic matter present.

For all samples measured via AF4-ICP-MS, the majority of colloid associated metals, besides Fe, were found in the less than 3 nm size range. However, the distribution and association with OM or Fe was different depending on the metal. The size distributions of UV-absorbance, as a surrogate for OM, showed two peaks in both effluent and upstream samples, one centered around 0.5 nm and one typically larger peak centered around 2 nm (Fig. 3, upstream data not shown). The Fe signal exhibited a similar pattern for upstream samples, but the magnitude of the 0.5 nm peak was larger for Fe. The smaller size range of OM corresponded to molecular weights of less than 1 kDa, while the larger size range fell between 1 kDa and 50 kDa. The smaller size fraction is likely more fulvic-rich, while the larger size is likely a mixture of fulvic and humic acids? (Beckett et al., 1987). Only a few subtle differences existed between effluent and upstream samples. In effluent samples, while the size distribution of UV absorbance still showed two peaks, the magnitude of the signals decreased and the maximum of the second peak shifted to a lower kDa size range in W_eff and H_eff samples. Even though DOC concentrations were of the same order of magnitude for upstream and effluent samples, organic matter from effluent is typically skewed to the smaller size range. The fulvic acid signal observed in the EEMs spectra for effluent samples was not as strong as upstream samples, thus this smaller size contribution likely comes from the much larger protein enriched signals observed in effluent. The size distribution of the Q_eff organic matter remained similar to the upstream waters. The first peak of Fe was mostly absent or non-detectable in the effluent samples as expected from the size distribution results (Fig 2), and the maximum of the second peak was more closely associated with organic carbon. While the relative metal mass in the two size ranges differed between samples, they each overlapped, suggesting the presence of either an organic matter bound Fe ion, or an iron oxide and organic matter aggregate.

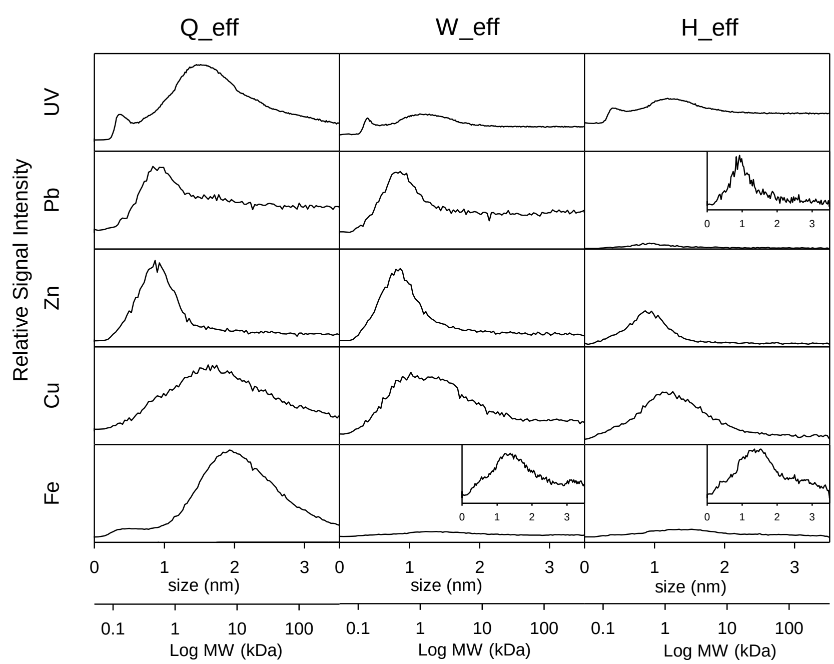

Figure 3: Colloidal size fractionation of metals and organic matter in effluent samples

Most of the single peaks of Pb and Zn in effluent and upstream samples fell between the peaks of Fe and OM, suggesting some binding to both size ranges of colloids, while the single peak of Cu lined up directly with the UV signal, but also overlaps a portion of the Fe signal (Fig. 3, upstream data not shown). The Zn and Pb signals in particular had long shoulders in the larger size range, similar to the UV signal. Only in the H_up samples were the Pb and Zn peaks aligned with the UV signal, but these were much lower concentrations and in that case there was very little colloidal Fe present. The strong association with organic matter was expected for Cu (Tipping, 1998) , while Pb typically associates with iron oxides, and Zn association falling somewhere in between. However, since all signals overlap, there are likely a variety of associations present, e.g. mixed aggregates of iron oxides, organic matter, and metals bound to organic ligands or iron oxide surfaces.

During the storm event, all colloidal metal and UV peaks showed variation in magnitude, and Fe and Pb in particular showed shifts in size distributions over time. The colloidal size distributions of Fe in stormwater samples collected during the first hour were predominated by a single peak centered at about 2 nm, extending over a slightly larger range of sizes compared to the upstream or effluent samples. More than an hour after the storm started, Fe in even larger size ranges were observed, with a peak around 5 nm with a long tail extending into larger size distributions increasing over time. Meanwhile, the size distribution of UV-absorbance only exhibited one single peak at all times centered around 1-10 kDa, similar to the upstream and effluent samples, but the magnitude increased by a factor of 3 from the earlier to later times of stormwater runoff. This is consistent with the generally higher SUVA values observed later in the storm (Table 1). The colloidal size distributions of Cu and Zn are similar throughout the storm event, only varying in magnitude with the highest concentrations observed later in the storm and the lowest observed in the first 45 min? During the storm, both Cu and Zn are more closely associated with organic matter, though Zn peaks at a slightly lower size. The size distribution of Pb is a lot less uniform and varies significantly over time. In the first 30 min, the size distribution was very broad, spanning a size range of about 1-5 nm, and exhibited a double peak (data not shown). The two peaks correspond to the peaks in UV and Fe, suggested a role of both organic matter and iron oxides in binding Pb during a storm. Over time, the peaks change and shift in relative magnitude and are shifted to the lower size range later in the storm. The colloidal metal concentrations decreased for the first 45 minutes then increased, following the same trend as the dissolved metal concentrations in storm runoff. This shift in metal concentrations was likely due to differences in sources and transport times in the stormdrain system. The appearance of larger size colloidal Fe and the increased Fe and DOC concentrations could have been released from the upper organic-rich soil horizons because the size of the second peak was similar to the typical colloids found in the soil pore-water (Pokrovsky et al., 2005; Stolpe et al., 2013). It is also possible that iron oxide formation or aggregation processes during the travel time resulted in the about 3-fold increase in colloidal Fe concentration over the course of the storm.

Alterations in colloidal distributions upon mixing and spiking

Since these source waters all mix in the receiving stream, we assessed changes in colloidal metal distribution and size upon mixing with stream water or upon addition of metals or competing cations. The size distributions of mixed samples (H_up:H_eff of 7:3 or H_up:H_st of 1:1) were similar to the calculated distribution based on the previously measured individual sample distribution and mixing ratio. This suggests the colloids originally present in the source water are maintained upon entering stream waters. Spiking samples with Cu, Zn and Pb at 10-fold background concentrations revealed differences depending on the metal. Colloidal Cu increased proportionally, but the size distribution and association with organic matter changed little with the exception of a longer tail on the peak. The percentage of colloidal Cu remained the same in effluent, but decreased from 30 to 15% in stormwater samples, suggesting that even though the concentration of organic matter was lower in effluent mixture, it still had excess binding capacity compared to the stormwater. The percent colloidal Zn was already low in the samples and spiking did not significantly increase its concentration and it remained in the small size range. The addition of excess Ca did not alter the size distribution or colloidal phase concentrations in effluent mixtures, but did significantly change the stormwater mixtures. At a doubling of the Ca concentration, the total colloidal metal concentration slightly increased, possibly due to enhanced bridging of smaller organic matter. However, at a 10-fold increase in Ca concentration, the total colloidal metal concentration was reduced and the size distribution shifted to the smaller size range, likely due to competition at ligand binding sites.

Periphyton and DGT response during baseflow

During baseflow, water, DGT, and periphyton samples were collected as a function of distance downstream. These samples were collected during July and August, when WWTP effluent contributed approximately 35% of the stream flow. Dissolved and total Cu concentrations were approximately 2 ppb upstream of the wastewater treatment plant and 5 ppb downstream of the wastewater treatment plant. The DGT labile portion of the streamwater Cu was about 25-30% upstream of the WWTP and increased to about 40% immediately downstream of the effluent outfall (Fig. 4). The DGT labile portion continued to increase as water flowed downstream, up to a maximum of about 50%. This occurred even though the Cu concentration did not change significantly as water traveled downstream. This suggests some transformation of the effluent organic matter that binds Cu, resulting in more Cu lability further downstream. The periphyton body burden for the most part followed the same trend as DGT labile Cu, with the exception of the furthest location downstream. Upstream periphyton had body burdens of about 15-30 ug/g intracellular Cu, while immediately downstream they increased to about 40 ug/g and total periphyton Cu increased further downstream. However, the furthese location had body burdens similar to the upstream site.

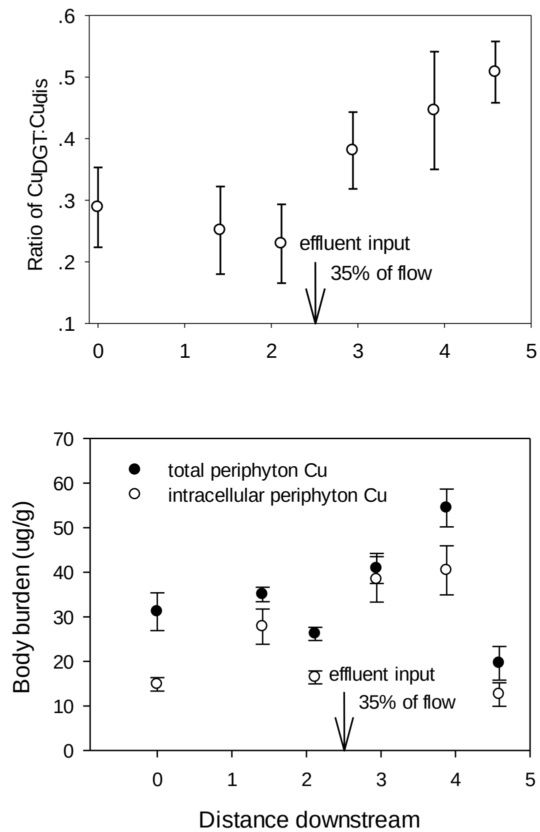

Figure 4: Labile Cu ratio and periphyton body burden as a function of distance downstream

Periphyton and DGT response during stormflow

A total of five different storm events were observed during the fall of 2012 and 2013. Results from one example event are shown in Figures 5 and 6. Prior to the storm, the periphyton body burdens upstream of the WWTP were similar to baseflow conditions from the previous summer, arounb 30 ug g^{-1}. Following a storm even, the total and dissolved Cu and DOC concentrations spiked for a period of about 2 days and periphyton body burdens increased to more than 50 ug g^{-1}. This level remained over 50 ug g^{-1}, but varied over time, decreasing four days after the storm, but increasing again following another small increase in water column Cu concentration. Generally, total periphyton Cu concentrations were elevated, but followed intracellular Cu concentrations over time. Each time the periphyton body burden increased, the DGT labile Cu concentration from the previous days was elevated, suggesting it was a reliable indicator of bioavailable Cu at the upstream site.

At the site furthest downstream of the WWTP, periphyton body burden was initially about 50 ug g^{-1}, again similar to the baseflow conditions downstream of the WWTP. Following the storm event, there was a smaller spike in DOC and Cu concentrations, and the DOC concentration remained slightly elevated around 4 to 5 mg L^{-1}, but the Cu concentration generally remained similar, about 3 to 4 ug L^{-1}. This concentration was still elevated compared to the upstream site, however periphyton body burden did not start to significantly increase until about 4 days after the storm, increasing to about 120 ug g^{-1} at the highest point. However, there was significant day to day variability, with intracellular body burdens ranging from about 70 to 120 ug g^{-1}, and remaining elevated for more than a week following the storm. In this event, the DGT labile Cu concentration was highest initially, and started to decrease following the storm, possibly due to dilution with less labile Cu sources. This might suggest the largest increase in periphyton body burden should have occurred during the days during and immediately following the storm event, but that didn't happen. Perhaps the increase in periphyton body burden over time occurred due to either some transformation of the particulate Cu concentrations over time, or a kinetically limited uptake process dependent on the Cu speciation or size distribution embedded in the extracellular matrices.

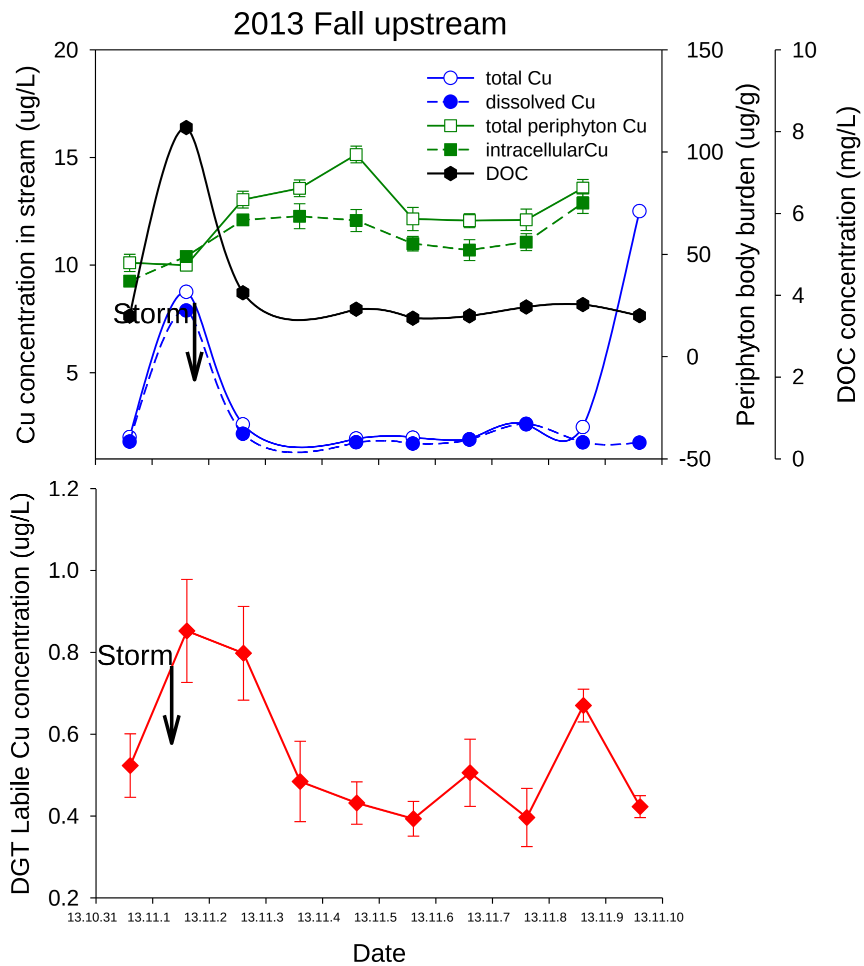

Figure 5: Dynamics of water chemistry and periphyton response to a storm even upstream of the wastewater treatment plant

Environmental Significance

The DGT devices generally followed the periphyton body burden during baseflow and upstream water exposure. However, following storm events there was not a clear relationship between the two. Based on the size distribution analysis of mixed source waters, it was common for effluent to have excess Cu binding capacity, while stormwater did not, even though it had higher concentrations. In that respect, DGT labile concentrations might be expected to increase in streams following the storm, but they generally did not. This could be due to seasonal differences in organic matter lability, i.e. grab samples for metal size distribution were taken during the peak of the growing season, while storms were monitored during the fall. In addition, following the storm event, the changes in DGT labile concentrations upstream followed the dissolved Cu concentrations, but downstream of the WWTP, there was a more prolonged change in DGT labile concentrations, much longer after the flow returned to baseflow levels. This could be due to differences in colloid transport and settling, or dynamics of metal repartitioning onto to newly exposed or transported surfaces within the stream. The periphyton also had a much larger lag time in response to metal exposure downstream during storm events. It is difficult to identify the specific reasons in-situ, but we expect some of the response is due to differences in colloidal phase organic matter over time, interactions with periphyton surfaces, and kinetic exchange limitations on periphyton uptake. These types of interactions need to be further studied in controlled laboratory environments.

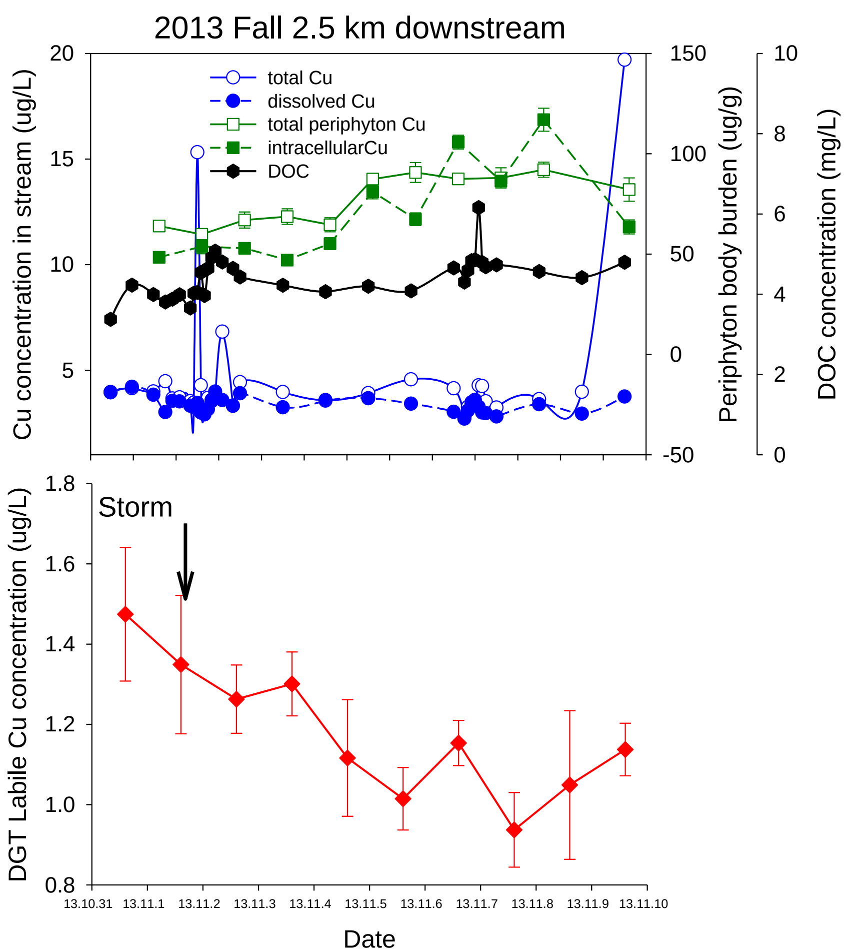

Figure 6: Dynamics of water chemistry and periphyton response to a storm even downstream of the wastewater treatment plant

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Information Transfer Program Introduction

The Connecticut Institute of Water Resources Information transfer program has several components: 1. CT IWR web site; 2. Publications; 3. Seminar Series; 4. Conferences and Workshops; 5. Service and Liaison Work.

Field Testing the Educational and Land Use Planning Value of a New Nitrogen Modeling Tool in the Niantic River Watershed

Basic Information

Title:	Field Testing the Educational and Land Use Planning Value of a New Nitrogen Modeling Tool in the Niantic River Watershed
Project Number:	2012CT256B
Start Date:	3/1/2012
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	2
Research Category:	Not Applicable
Focus Category:	Nitrate Contamination, Models, Education
Descriptors:	
Principal Investigators:	Juliana Barrett, Chester Arnold, Emily Wilson

Publication

1. Arnold, C. D.Q. Kellogg, K. Forshay, C. Damon, E. H. Wilson, A. Gold, E.A. Wentz, and M.M. Shimizu. 2013. Tracking the fate of watershed nitrogen: the “N-Sink” web tool and two case studies. Final Technical Report submitted to the EPA Office of Research and Development. 39pp.

State: CT

Project Number: 2012CT256B

Title: Field Testing the Educational and Land Use Planning Value of a New Nitrogen Modeling Tool in the Niantic River Watershed

Project Type: Information Transfer

Focus Category: Nitrate Contamination, Models, Education

Keywords: nitrogen source/sink

Start Date: 3/1/2012

End Date: 2/28/2014

Congressional District: 2

PI: Barrett, Juliana
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Arnold, Chester
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Wilson, Emily
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Introduction/Research Objective:
We propose to deploy and test a relatively easy to use desktop GIS model that estimates N sources and sinks in a watershed, and that can estimate N delivery from a particular location in the watershed to the outlet. This will be a valuable tool for local land use decision makers and communities wishing to reduce N pollution to their waters.
There are two principal objectives of this project. Our first objective is to provide useful and actionable information to the four towns in the Niantic River watershed on existing and future N source and sink areas, coupled with planning, development and conservation strategies to minimize N export from the former and maximize N processing by the latter.

Our second objective is to use this as a pilot project to test the efficacy of the maps and data created by the N-Sink model. CLEAR's *Nonpoint Education for Municipal Officials* (NEMO) program has a long and successful history of taking geospatial environmental information and folding it into educational programs and products that assist local land use decision makers. The role of UConn CLEAR/NEMO in the development of N-Sink is to review and critique the tool, both with respect to its technical GIS functionality and the projected usefulness of the information it produces.

Our team's feeling is that N-Sink will prove to be a very useful tool at the local level. However, what is truly needed is a pilot project to test this assumption, and to see what improvements can be made both to model outputs and to the educational programs that use them, based on our own observations and feedback from our municipal clientele. Our expectation is that the proposed project will serve to fine-tune and improve the educational and planning value of the N-Sink model, which will then be ready to be expanded in its geographic scope.

Methods/Procedures/Progress:
The N-Sink prototype model was transformed from an ArcMap desktop tool to a web-based tool using ArcGIS Viewer for Flex. The tool highlights N sources and sinks within a watershed, and allows non-technical users to estimate relative N removal efficiencies from any chosen point within the project area's coastal HUC-12 watersheds (the Niantic River watershed in southeastern Connecticut and the Saugatucket River watershed in southern Rhode Island on the west side of Narragansett Bay).

Presentations at any conferences or workshops related to research project.
1) Webinar for EPA June 27, 2013 by Chet Arnold and Dorothy "Q" Kellogg

2) Workshop on N-Sink for the Niantic River Watershed Nitrogen Workgroup October 28, 2013. This workgroup consists of technical and scientific representatives from federal, state, academic, and NGO's (including The Nature Conservancy, Millstone Nuclear Power Plant, Connecticut Eastern Conservation District and private consulting firms). The group meets regularly to discuss monitoring challenges and knowledge gaps pertaining to managing nitrogen in the Niantic system. The Niantic River watershed is on the state's impaired waters list, due in part, to nitrogen pollution. The presentation looked at nitrogen reduction/delivery from several sites within the watershed. The examples were placed near each other so as to explore nitrogen delivery estimates based on small but important changes in the flow path. The post presentation discussion was very helpful to furthering the use of N-Sink as a tool. There is a great deal of workgroup interest in N-Sink. Numerous offers were made to share nitrogen data collected within the watershed that could be used to test N-Sink. Also, discussed was how the tool could best be used by practitioners, and who is the best audience for the tool. This information, as well as input from other groups, will be used by the N-Sink team to optimize the user interface for easy navigation and comprehension.

3) Presentation, National Land Grant/Sea Grant Water Conference, Portland, OR, April 22, 2012 by Q Kellogg and Chet Arnold

Tool Access.
The N-Sink web tool is published through a UConn CLEAR website:
http://clear.uconn.edu/projects/nsink/

In addition, the University of Rhode Island has a website for N-Sink which includes a demo of the N-Sink tool and a draft guidance document:
http://www.uri.edu/cels/nrs/whl/Research/n_mgmt/

Future Work on N-Sink:
Christine Kirchhoff and J. Barrett have submitted a CT IWR proposal to further work on the N-Sink tool (FY 2014-15) Title: Evaluating and enhancing communities' willingness to adopt N-Sink as a community based pollution mitigation decision tool

A meeting was held at University of Rhode Island on November 13, 2013 to discuss funding, outreach and next steps related to N-Sink. EPA, USDA's Natural Resources Conservation Service (NRCS), The Nature Conservancy and RI Coastal Resources Management Council are very interested in furthering the uses of this tool.

Chet Arnold and Q. Kellogg are submitting a proposal to EPA Office of Research and Development to continue the testing of N-Sink and determine its geographic extensibility.

CTIWR Technology Transfer

Basic Information

Title:	CTIWR Technology Transfer
Project Number:	2013CT281B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	2nd
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	None
Principal Investigators:	Glenn Warner, James D Hurd

Publication

1. Payne, D.W., A.C. Bagtzoglou, G.S. Warner and L.Liu. 2013. Management Alternatives to Reduce Pumping Effects in the Fenton River During Low Stream Flow. Special Report. 67 p. http://www.ctiwr.uconn.edu/SpecialReports/Fenton%20River%20Report%2008APR2013.pdf

Web Site: Our Institute maintains the CT IWR web site, which we update as needed. It includes information about the WRI program, our institute and its board, a listing of the current year's seminars, a list of sponsored projects and publications, and access to electronic copies of our "Special Reports" series. We also use the web to announce special events and our RFP in addition to secure access to grant proposals and information for the Advisory Board's review. We continue to cooperate with the University of Connecticut's digital archives department, which maintains our electronic reports as a part of its "Digital Commons @ University of Connecticut" project. This past year we created a new entrance page to the CT IWR website (Figure 1) which is more visually pleasing with the inclusion of new graphics, links, and information. Work will continue on upgrades throughout the coming year.

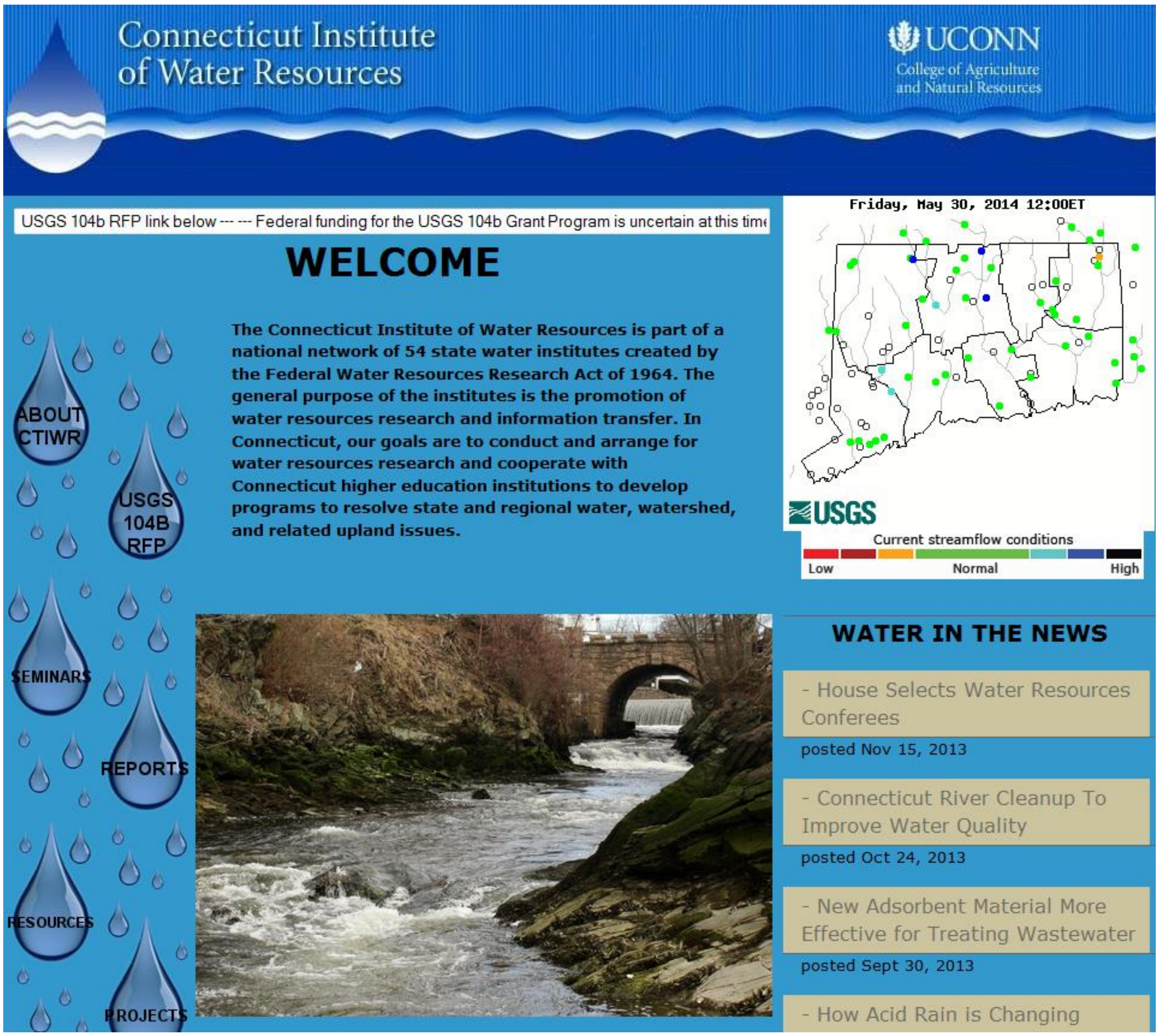

Figure 1. Entrance page to the Connecticut Institute of Water Resources website.

Publications. While we will continue to explore new information transfer options, we will also need to ensure that the legacy of the program is not lost, and that the projects and publications generated by this program are preserved, digitally archived when at all possible, and that they continue to remain available as a resource to water professionals and academics in the future. We have begun to add publications to the Publications section of the CT IWR website in addition to preparing publications for inclusion into the University of Connecticut's Digital Commons. This work will continue into the next fiscal year in conjunction with the CT IWR website redesign.

Conferences. The Institute co-sponsored the annual Connecticut Conference on Natural Resources (CCNR) held each March during spring break recess at the University of Connecticut. CT IWR contributes $500 to support the conference. Other conferences supported include The Connecticut Rivers Alliance Annual Conference, May 16, 2013, Berlin, CT and a Regional Water Forum, July 29, 2013, Willimantic, CT. Discussion topics included regional water resources, regional water systems, water, economic development and regional planning, water planning laws, and water management, population and business trends.

Service and Liaison Work. Currently**,** the Director actively serves on the following water related panels or workgroups:

- Panel participant, The Connecticut Rivers Alliance Annual Meeting, May 16, 2013, Berlin, CT. Discussion topics included
- Panel participant, League of Women Voters / Connecticut Institute of Water Resources Regional Water Forum, July 29, 2013, Willimantic CT.
- Panel participant, Connecticut Strategic Water Resources Planning Conference, February 3, 2014, Hartford, CT.

Special Meetings. This past December 2013, CT IWR hosted an informal workshop in the College of Agriculture and Natural Resources at the University of Connecticut. The presentation focused on the use of Unmanned Aerial Vehicles (UAVs) for potential research in the area of natural resources. The agenda included discussion of the technology, current flight regulations, potential imaging payloads, applications of the technology focused on natural resources, and a live demonstration. Following the presentation and demonstration, a discussion was held to discuss the potential for acquiring a UAV system and the logistics for its use at the University. CT IWR personnel will continue to pursue the use of this technology at the University.

USGS Summer Intern Program

None.

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	3	0	0	0	3
Masters	2	0	0	0	2
Ph.D.	3	0	0	0	3
Post-Doc.	0	0	0	0	0
Total	8	0	0	0	8

Notable Awards and Achievements

Publications from Prior Years