

**Connecticut Institute of Water Resources  
Annual Technical Report  
FY 2012**

# 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. Associate Director Patricia Bresnahan retired in the summer 2012 after 12 years of service to The Connecticut Institute of Water Resources. New Associate Director Mr. James Hurd was hired October 2012.

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. 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

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

**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

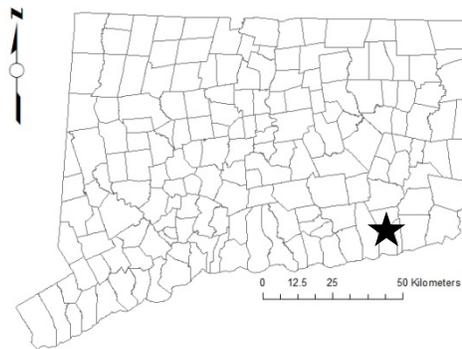
watersheds, using existing precipitation, discharge, and pollutant (nitrogen and phosphorus) export data.

- 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.

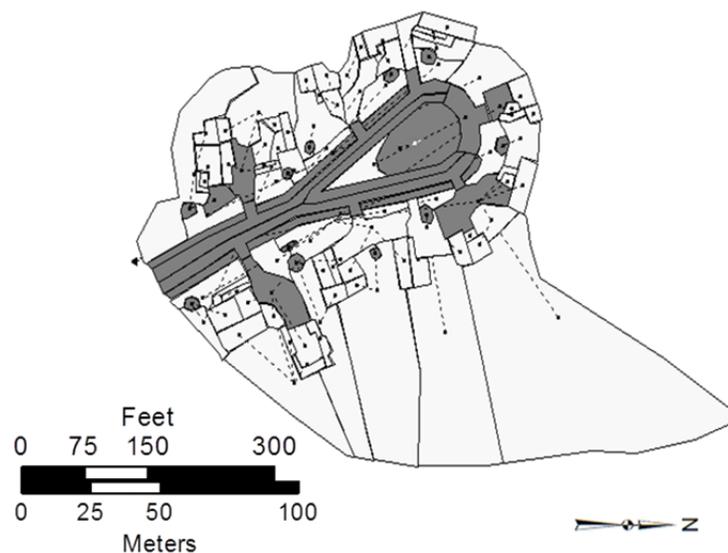


**Figure 1. Location of Jordan Cove study site in State of Connecticut.**

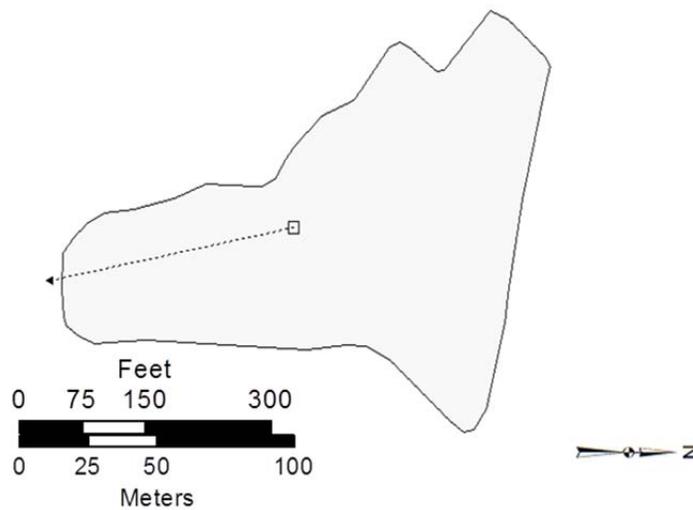
### *SWMM Model*

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<sup>2</sup> to 20,396.2 m<sup>2</sup>.

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  $\pm 50\%$  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 Sutcliffe 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.**

<b>Parameter (units)</b>	<b>Initial Value</b>	<b>Data Source</b>
<b><u>Subcatchments</u></b>		
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. <i>et al.</i> , 1983
Conductivity (mm/hr)	25.1	USDA, NRCS, 2012
Initial deficit (a fraction)	0.246	Maidment, 1993
<b><u>Snow melt</u></b>		
Snow vs rain (degrees C)	1.1°	default
ATI Weight (fraction)	0.5	default
Negative Melt Ration (fraction)	0.06	default
<b><u>Porous pavement - surface</u></b>		
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
<b><u>Porous pavement - pavement</u></b>		
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
<b><u>Porous pavement - storage</u></b>		
Height (mm)	0 - 304.8	As-built drawings
Void Ratio (voids/solids)	0.75	default
Conductivity (mm/hr)	254	default
<b><u>Bioretention cell - surface</u></b>		
Storage Depth (mm)	15.2	As-built drawings
<b><u>Bioretention cell - soil</u></b>		
Thickness (mm)	609.6	As-built drawings
porosity (volume fraction)	0.45	Maidment, 1993
<b><u>Bioretention cell - soil</u></b>		
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. <i>et al.</i> , 1983
<b><u>Bioretention cell - storage</u></b>		
Conductivity (mm/hr)	25.1	USDA, NRCS, 2012
<b><u>Vegetative Swale - surface</u></b>		
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 <sup>3</sup> )	1,076	188	82.5%	3,647	3,021	17.2%
Average Peak Flow (m <sup>3</sup> /s)	0.0048	0.0007	86.0%	0.0127	0.0113	11.0%

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

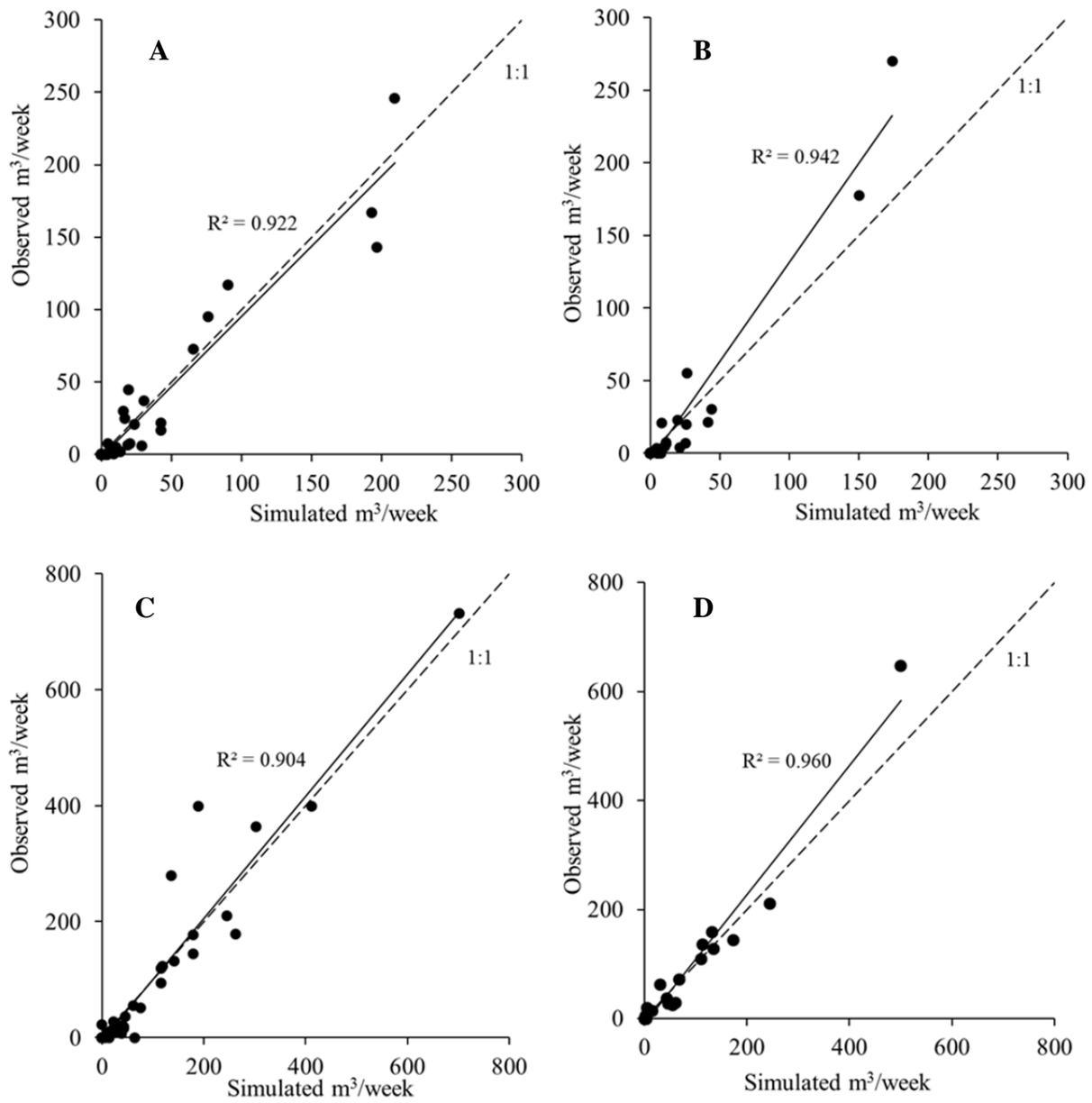
Parameter	Initial Values for both watersheds	LID calibrated	Traditional calibrated
Ksat (mm/hr)	25.15	3.05	4.57
Suction head (mm)	109.98	101.60	228.60
Initial soil moisture deficit	0.25	0.40	0.40
N-Imperv	0.011	0.011	0.015
N-Perv	0.24	0.15	0.15
Manning's n for swale†	0.24	0.15	-
Dstore-Perv	3.81	2.54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

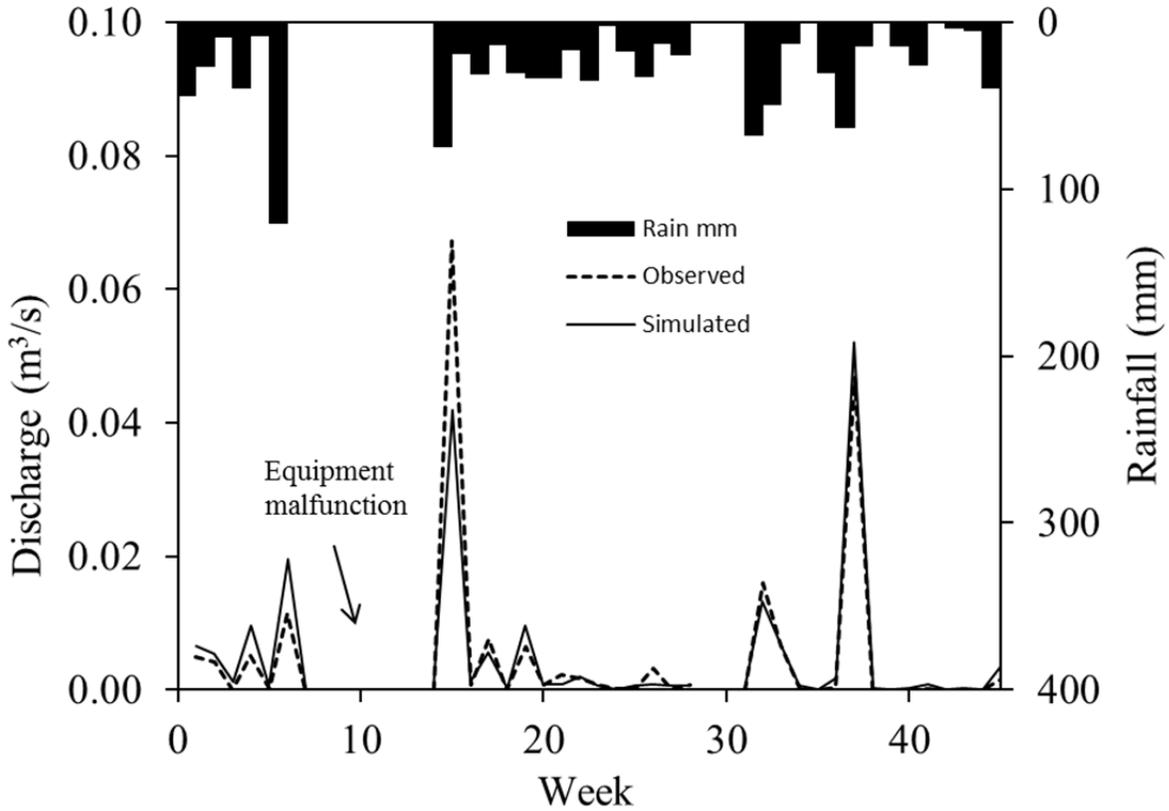


Figure 5. Weekly discharge and precipitation for the LID watershed calibration period (Aug. 2004-Jun. 2005).

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
<u>Calibration</u>						
Total Volume (m <sup>3</sup> )	1,076	1,162	8.0%	3,647	3,615	0.9%
Average Peak Flow (m <sup>3</sup> /s)	0.0048	0.0047	2.1%	0.0127	0.0112	11.8%
<u>Validation</u>						
Total Volume (m <sup>3</sup> )	664	625	5.9%	1,839	1,757	4.5%
Average Peak Flow (m <sup>3</sup> /s)	0.0017	0.0015	11.8%	0.0116	0.0103	11.2%

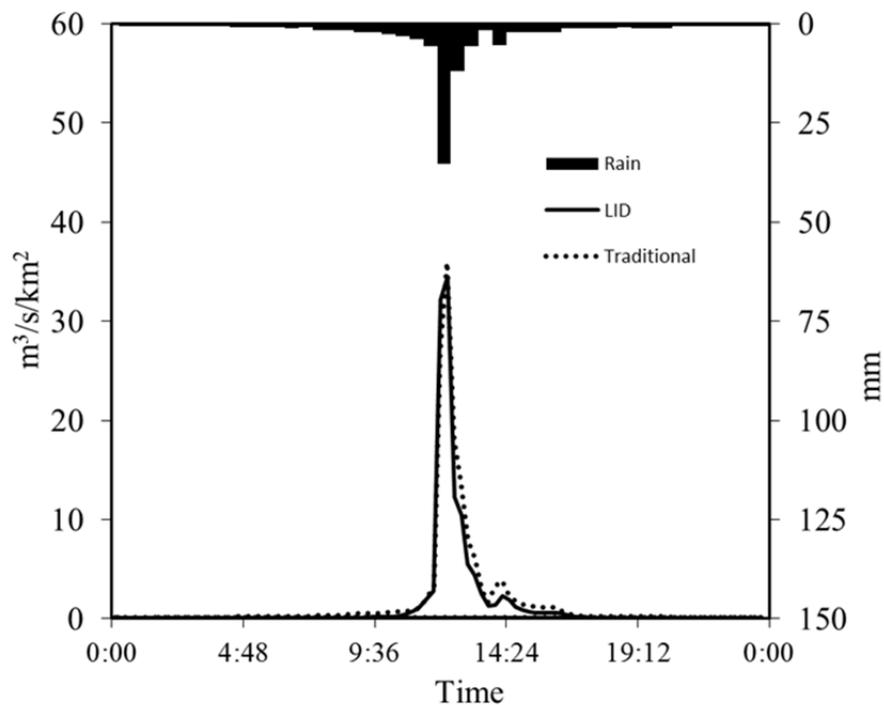
### *Nutrient Export*

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<sup>3</sup>/s/km<sup>2</sup>) was slightly lower than the rate from the traditional watershed (36.0 m<sup>3</sup>/s/km<sup>2</sup>). 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.

## Literature Cited

Akan, A.O., R.J. Houghtalen. 2003. Urban hydrology, hydraulics, and stormwater quality: Engineering applications and computer modeling. John Wiley and sons, Hoboken, NJ, ISBN: 978-0-471-43158-9.

Baffaut, C. and J. Delleur, 1989. Expert system for calibrating SWMM. *Journal of Water Resources Planning and Management*, 115(3), 278-298, doi: 10.1061/(ASCE)0733-9496(1989)115:3(278).

Bedan, E. S. and J. C. Clausen. 2009. Stormwater runoff quality and quantity from traditional and low impact development watersheds. *Journal of the American Water Resources Association (JAWRA)* 45(4), 998-1008.

Clausen, J.C. 2008. Final Report Jordan Cove watershed project section 319 National Monitoring Program Project. Department of Natural Resources Management and Engineering, College of Agriculture and Natural Resources, University of Connecticut. Storrs, CT.

Clausen, J.C. and Spooner, J. 1993. Paired watershed study design. United States Environmental Protection Agency, EPA 841-F-93-009.

CT DEP. 2005. Connecticut Stormwater Quality Manual. Connecticut Department of Environmental Protection, 79 Elm St., Hartford, CT.

Dietz, M.E., and Clausen, J.C. 2007. Stormwater Runoff and Export Changes with Development in a Traditional and Low Impact Subdivision. *Journal of Environmental Management*, Vol. 87(4): 560-566.

Dunne, T., and L. B. Leopold. 1978. Water in environmental planning. W.H. Freeman and Company. New York, NY.

James, L. D. and S. J. Burges, 1982. Selection, calibration, and testing of hydrologic models. Chapter 11 in: Hydrologic Modeling of Small Watersheds, C.T. Haan (Editor). American Society of Agricultural Engineers, St. Joseph, Michigan, 437-472.

Maidment, D.R., 1993. Handbook of Hydrology. McGraw-Hill, New York, New York, ISBN-13: 978-0070397323.

MA DEP. 2008. *Massachusetts Stormwater Handbook. Chapter 1: Overview of Massachusetts Stormwater Standards*. Massachusetts Department of Environmental Protection.

Miller, D. R., G. S. Warner, F. L. Ogden, A. T. DeGaetano. 2002. *Precipitation in Connecticut*. University of Connecticut College of Agriculture and Natural Resources. Connecticut Institute of Water Resources, Storrs, CT.

Nash, J. E. and J. V. Sutcliffe, 1970. River flow forecasting through conceptual models part I — A discussion of principles. *Journal of Hydrology*, 10(3), 282-290, doi: 10.1016/0022-1694(70)90255-6.

Prince George's County. 1999. Low-impact development design strategies: An integrated design approach. Prince George's County, MD Department of Environmental Resources.

Rawls, W.J., D. L. Brakensiek, N. Miller. 1983. Green-Ampt infiltration parameters from soils data. *Journal of Hydraulic Engineering*, 109, 62-70, doi: 10.1061/(ASCE)0733-9429(1983)109:1(62).

RI DEM & CRMC. 2010. *Rhode Island Stormwater Design and Installation standards Manual*. Rhode Island Department of Environmental Management and Coastal Resources Management Council.

Rosa, D. 2013. Post-audit verification of the model SWMM for Low Impact Development. M.S. Thesis, University of Connecticut Department of Natural Resources and the Environment.

Rossman, L. A., 2010. Storm Water Management Model user's manual version 5.0. United States Environmental Protection Agency, Water Supply and Water Resources Division, National Risk Management Research Laboratory. Cincinnati, OH.

Santhi, C., J. G. Arnold, J. R. Williams, W. A. Dugas, R. Srinivasan, and L. M. Hauck, 2001. Validation of the SWAT model on a large river basin with point and nonpoint sources. *Journal of the American Water Resources Association (JAWRA)*, 37(5), 1169-1188, doi: 10.1111/j.1752-1688.2001.tb03630.x.

Soil Conservation Service, 1986. *Urban hydrology for small watersheds*. U.S. Department of Agriculture Technical Release No. 55 (revised), 210-VI-TR-55.

U.S. Department of Agriculture, Natural Resources Conservation Service (USDA-NRCS), 2012. Web Soil Survey. Available online at <http://websoilsurvey.nrcs.usda.gov/>. Accessed 10/2/2012.

**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.

# A Dye Displacement Method to Characterize Water Contributing Fractures in Wells in Crystalline Bedrock

## Basic Information

<b>Title:</b>	A Dye Displacement Method to Characterize Water Contributing Fractures in Wells in Crystalline Bedrock
<b>Project Number:</b>	2012CT233B
<b>Start Date:</b>	3/1/2012
<b>End Date:</b>	2/29/2013
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	2
<b>Research Category:</b>	Ground-water Flow and Transport
<b>Focus Category:</b>	Water Quality, Groundwater, Toxic Substances
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Gary A. a Robbins

## Publications

1. Libby, Jill L., "An Unsteady State Tracer Dilution Method for Characterizing Water Contributing Fractures in Crystalline Bedrock Wells" (2012). Master's Theses. Paper 314, M.S., Geosciences, University of Connecticut, G.A. Robbins, Major Advisor.  
[http://digitalcommons.uconn.edu/gs\\_theses/314](http://digitalcommons.uconn.edu/gs_theses/314)
2. Chlebica, Dariusz, "Modifying Borehole Dissolved Oxygen Levels as a Tool in Deciphering Fracture Flow Conditions" (2013). Master's Theses. Paper 390. M.S., Geosciences, University of Connecticut, G.A. Robbins, Major Advisor.
3. Libby, L., and Robbins, G.A., 2013, An Unsteady State Tracer Method for Characterizing Fractures in Bedrock Wells, Accepted for Publication, Groundwater Journal.
4. Chlebica, D., and Robbins, G.A., 2013, Dissolved Oxygen to Determine Flow Conditions in Fractured Bedrock Wells, Accepted for Publication, Groundwater Monitoring and Remediation
5. Libby, J. and Robbins, G.A., 2012, Verifying an Unsteady State Tracer Dilution Method in Fractured Bedrock Wells Using Physical and Computer Models, Geol. Soc. of Amer., Northeastern Section Meet., abstracts with programs, March 18 , Hartford, CT.
6. Libby, J., Robbins, G., 2012, Characterization of Water Contributing Fractures Intersecting a Well in Crystalline Bedrock Through Monitoring Changes In a Tracer Profile during Slug Test Recovery, International Conference on Groundwater in Fractured Rocks, Prague, Czech Republic, May 23.
7. Robbins, G.A., Libby, J., and Chlebica, D, 2012, Deciphering Fractured Rock Hydrogeology and Contaminant Conditions Using Dye and Oxygen Dilution Methods, Presented at Italian National Research Council, Sept. 10, Bari, Italy.
8. Chlebica, D. W., and Robbins, G.A., 2013, Modifying Ambient Dissolved Oxygen Levels to Locate Intersecting Fractures and Determine Borehole Flow Conditions in Bedrock Wells, Geol. Soc. of Amer., Northeastern Section Meet., submitted abstract, March 18-20, Bretton Woods, NH.

Connecticut Institute of Water Resources Funded Project

Proposal Title

**A DYE DISPLACEMENT METHOD TO CHARACTERIZE WATER CONTRIBUTING FRACTURES IN WELLS IN CRYSTALLINE BEDROCK**

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**PROGRESS REPORT**

**May, 11 2013**

Introduction/Research Objective

The main objective of this research builds on Brainerd and Robbins (2004) and entails the development of an unsteady state tracer approach involving limited pumping that can provide information on the depths of water contributing fractures, their transmissivities, which fractures are contaminated and contaminant concentrations.

Methods/Procedures/Progress

The method was tested and perfected in the laboratory using a scale model of a fractured rock well. Then the method was tested at a bedrock well that had been characterized in the past by more conventional downhole geophysical methods. Specific elements of the method were refined and further tested and proved successful (Libby and Robbins, 2013).

An outgrowth of the approach was the development of another new approach for locating water contributing fractures by oxygen dilution. The oxygen method is not as quantitative as the tracer method but it is a major cost effective advance to both locate water contributing fractures and decipher borehole flow between fractures. The method was successfully tested in two wells on the University of Connecticut campus (Chlebica and Robbins, 2013)

Results/Significance

Testing to date has shown that the new methods provide technically sound and cost effective approaches for borehole characterization. They can be used alone or as supplements to more conventional approaches. Thus far the work has resulted in two graduate theses. We have two papers accepted for publication in peer reviewed journals. We have given 5 presentations on the research, including being invited to the International Conference on Groundwater in Fractured Rocks, Prague, Republic of Czechoslovakia. and to the Italian National Research Council, in

Bari, Italy. We have another presentation accepted at the September 2013 Fracture Rock Conference in Vermont.

Using the initial work from the grant as demonstration of the viability of the methods, we have submitted three research proposals to further develop and test the methods. These were: a proposal to the DOD SERDP program with Dr. Lanbo Liu, Civil and Environmental Engineering; a proposal to Loureiro Engineering as a subcontractor to conduct a fracture rock investigation at a State superfund site for the Connecticut Department of Energy and Environmental Protection; and as an invited subcontractor on a U.S. Geological Survey Proposal to the DOD SERDP program to conduct borehole characterization at contaminated military facilities. These latter research efforts would give us the opportunity to not only compare our methods with conventional test methods but to test out the contaminated sampling aspects of the proposed work.

We also planning on conducted further work with the oxygen method this summer to complete the grant research. This work entails use of a different oxygen gas source and the use of the method to determine how bedrock wells may be interconnected by fractures. These tests will be conducted on our campus bedrock well test site used for our previous tests.

### Research Bibliography

#### **Theses**

Libby, Jill L., "An Unsteady State Tracer Dilution Method for Characterizing Water Contributing Fractures in Crystalline Bedrock Wells" (2012). *Master's Theses*. Paper 314, M.S., Geosciences, University of Connecticut, G.A. Robbins, Major Advisor.  
[http://digitalcommons.uconn.edu/gs\\_theses/314](http://digitalcommons.uconn.edu/gs_theses/314)

Chlebica, Dariusz, "Modifying Borehole Dissolved Oxygen Levels as a Tool in Deciphering Fracture Flow Conditions" (2013). *Master's Theses*. Paper 390. M.S., Geosciences, University of Connecticut, G.A. Robbins, Major Advisor.  
[http://digitalcommons.uconn.edu/gs\\_theses/390](http://digitalcommons.uconn.edu/gs_theses/390)

#### **Referred Papers**

Libby, L., and Robbins, G.A., 2013, An Unsteady State Tracer Method for Characterizing Fractures in Bedrock Wells, Accepted for Publication, Groundwater Journal.

Chlebica, D., and Robbins, G.A., 2013, Dissolved Oxygen to Determine Flow Conditions in Fractured Bedrock Wells, Accepted for Publication, Groundwater Monitoring and Remediation

## **Presentations**

Libby, J. and Robbins, G.A., 2012, Verifying an Unsteady State Tracer Dilution Method in Fractured Bedrock Wells Using Physical and Computer Models, Geol. Soc. of Amer., Northeastern Section Meet., abstracts with programs, March 18, Hartford, CT.

Libby, J., Robbins, G., 2012, Characterization of Water Contributing Fractures Intersecting a Well in Crystalline Bedrock Through Monitoring Changes in a Tracer Profile during Slug Test Recovery, International Conference on Groundwater in Fractured Rocks, Prague, Czech Republic, May 23.

Robbins, G.A., Libby, J., and Chlebica, D., 2012, Deciphering Fractured Rock Hydrogeology and Contaminant Conditions Using Dye and Oxygen Dilution Methods, Presented at Italian National Research Council, Sept. 10, Bari, Italy.

Robbins, G.A., Libby, J., and Chlebica, D., 2012, Deciphering Fractured Rock Hydrogeology and Contaminant Conditions Using Dye and Oxygen Dilution Methods, U.S. EPA December 18, Boston, MA.

Chlebica, D. W., and Robbins, G.A., 2013, Modifying Ambient Dissolved Oxygen Levels to Locate Intersecting Fractures and Determine Borehole Flow Conditions in Bedrock Wells, Geol. Soc. of Amer., Northeastern Section Meet., submitted abstract, March 18-20, Bretton Woods, NH.

## **Research Proposals Based on IWR Project**

Robbins, G.A., Liu, Lanbo, Development of New Tracer Dilution and Dissolved Oxygen Addition Approaches for Evaluating Flow and Contaminant Conditions in Fractured Bedrock, submitted to DOD Strategic Environmental Research and Development Program (SERDP), submitted 1/8/13, \$549,719, 2 Yr., Not funded.

Robbins, G.A., Tylerville State Superfund Site in Haddam, CT, Loureiro Engineering Associates, Inc., 100 Northwest Drive, Plainville, CT, submitted 3/7/13, \$64,077, 1 Yr, under review (CT DEEP Project).

Harte, P. et al., (USGS), and Robbins, G., Testing, Development, and Application of a New Innovative Discrete Groundwater Sampling System, Called ZONFLO, for Fine-Resolution Delineation of Contaminant Plumes, submitted to DOD Strategic Environmental Research and Development Program (SERDP), submitted 3/13, \$39,963, 2 Yr., under review.

# The Impacts of Wastewater from a Retirement Community on Fish Health

## Basic Information

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

## Publications

There are no publications.

Connecticut Institute of Water Resources Funded Project

Proposal Title

**The impacts of wastewater from a retirement community on fish health**

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*Progress Report March 1, 2012 – February 28, 2013*

***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 17 $\alpha$ -ethinylestradiol (EE<sub>2</sub>), 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. Ibuprofen was detected at 1 µg/L in the final effluent, which is comparable to the highest levels ever reported in final treated effluent (Dr. McKay, unpublished data). Moreover, ibuprofen 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 MWWWE 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 MWWWE 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% [ $\beta=0.2$ ]), 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.

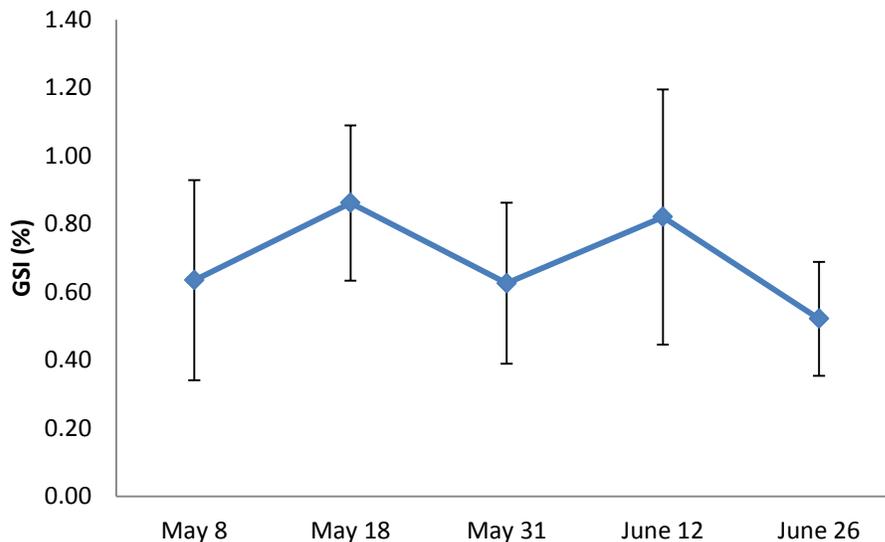
## Results/Significance

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).

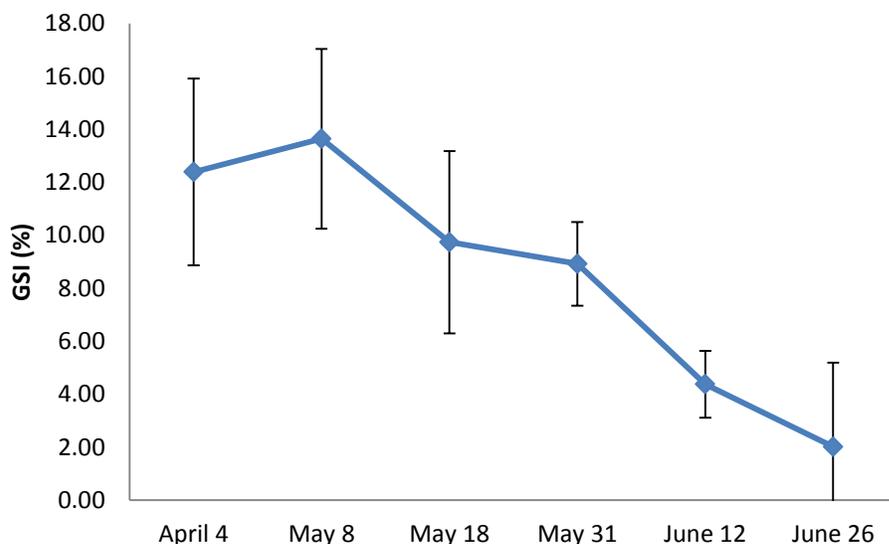
In the first year the main goal was to identify the optimal collection time of the target species within the Pomperaug River. To achieve this fish were collected at three sites, which were selected in collaboration with James Belden and Carol Haskins of the Pomperaug River Watershed Coalition.

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 sites



**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.

<b>Compound</b>	<b>Pharmaceuticals (12 of 80 possible) Category/ Use</b>	<b>Metals (8 of 20 possible)</b>
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	

## References

- Ankley, G.T., K.M. Jensen, M.D. Kahl, J.J. Korte and E.A. Makynen (2001). "Description and evaluation of a short-term reproduction test with the fathead minnow (*Pimephales promelas*)." *Environmental Toxicology and Chemistry* 20(6): 1276-1290.
- Barrett, T.J. and K.R. Munkittrick (2010). "Seasonal reproductive patterns and recommended sampling times for sentinel fish species used in environmental effects monitoring programs in Canada." *Environmental Reviews* 18: 115-135.
- Bosker, T., K.R. Munkittrick and D.L. MacLachy (2009). "Challenges in current adult fish laboratory reproductive tests: Suggestions for refinement using a mummichog (*Fundulus heteroclitus*) case study." *Environmental Toxicology and Chemistry* 28(11): 2386-2396.
- Bowron, L.K., K.R. Munkittrick, M.E. McMaster, G. Tetreault and L.M. Hewitt (2009). "Responses of white sucker (*Catostomus commersoni*) to 20 years of process and waste treatment changes at a bleached kraft pulp mill, and to mill shutdown." *Aquatic Toxicology* 95(2): 117-132.
- Burkhardt-Holm, P. (2010). "Endocrine disruptors and water quality: A state-of-the-art review." *International Journal of Water Resources Development* 26(3): 477-493.
- Canada, E. (1997). Fish monitoring, Fish Survey Section 5.1 technical guidance document for pulp and paper environmental effects monitoring. O. Ottawa, Canada.
- Department of Health & Human Services (2010). "Administration of aging: Projected future growth of the older population." Retrieved October 10, 2011, from [http://www.aoa.gov/AoARoot/Aging\\_Statistics/future\\_growth/future\\_growth.aspx#age](http://www.aoa.gov/AoARoot/Aging_Statistics/future_growth/future_growth.aspx#age).
- Diamond, J.M., H.A. Latimer, 2nd, K.R. Munkittrick, K.W. Thornton, S.M. Bartell and K.A. Kidd (2011). "Prioritizing contaminants of emerging concern for ecological screening assessments." *Environmental toxicology and chemistry / SETAC* 30(11): 2385-2394.
- Dinizi, M.S., R. Mauricio, M. Petrovic, M.J.L. De Alda, L. Amaral, I. Peres, D. Barcelo and F. Santana (2010). "Assessing the estrogenic potency in a Portuguese wastewater treatment plant using an integrated approach." *Journal of Environmental Sciences-China* 22(10): 1613-1622.
- Driedger, K., L.P. Weber, C.J. Rickwood, M.G. Dube and D.M. Janz (2009). "Overwinter alterations in energy stores and growth in juvenile fishes inhabiting areas receiving metal mining and municipal wastewater effluents." *Environmental Toxicology and Chemistry* 28(2): 296-304.
- Fent, K., A.A. Weston and D. Caminada (2006). "Ecotoxicology of human pharmaceuticals." *Aquatic Toxicology* 76(2): 122-159.
- Fitzgerald, D.G., R.P. Lanno and D.G. Dixon (1999). "A comparison of a sentinel species evaluation using creek chub (*Semotilus atromaculatus* Mitchill) to a fish community evaluation for the initial identification of environmental stressors in small streams." *Ecotoxicology* 8(1): 33-48.
- Flippin, J.L., D. Huggett and C.M. Foran (2007). "Changes in the timing of reproduction following chronic exposure to ibuprofen in Japanese medaka, *Oryzias latipes*." *Aquatic Toxicology* 81(1): 73-78.
- Fraker, M.E., J.W. Snodgrass and F. Morgan (2002). "Differences in growth and maturation of blacknose dace (*Rhinichthys atratulus*) across an urban-rural gradient." *Copeia* 2002(4): 1122-1127.

- Galloway, B.J. and K.R. Munkittrick (2006). "Influence of seasonal changes in relative liver size, condition, relative gonad size and variability in ovarian development in multiple spawning fish species used in environmental monitoring programmes." *Journal of Fish Biology* 69(6): 1788-1806.
- Garcia-Reyero, N., C.M. Lavelle, B.L. Escalon, D. Martinovic, K.J. Kroll, P.W. Sorensen and N.D. Denslow (2011). "Behavioral and genomic impacts of a wastewater effluent on the fathead minnow." *Aquatic Toxicology* 101(1): 38-48.
- Han, S., K. Choi, J. Kim, K. Ji, S. Kim, B. Ahn, J. Yun, K. Choi, J.S. Khim, X. Zhang and J.P. Giesy (2010). "Endocrine disruption and consequences of chronic exposure to ibuprofen in Japanese medaka (*Oryzias latipes*) and freshwater cladocerans *Daphnia magna* and *Moina macrocopa*." *Aquatic Toxicology (Amsterdam)* 98(3).
- Hotchkiss, A.K., C.V. Rider, C.R. Blystone, V.S. Wilson, P.C. Hartig, G.T. Ankley, P.M. Foster, C.L. Gray and L.E. Gray (2008). "Fifteen years after "Wingspread" - Environmental endocrine disrupters and human and wildlife health: Where we are today and where we need to go." *Toxicological Sciences* 105(2): 235-259.
- Hutchinson, T.H., G.T. Ankley, H. Segner and C.R. Tyler (2006). "Screening and testing for endocrine disruption in fish - Biomarkers as "signposts," not "traffic lights," in risk assessment." *Environmental Health Perspectives* 114: 106-114.
- Ings, J.S., M.R. Servos and M.M. Vijayan (2011). "Hepatic Transcriptomics and Protein Expression in Rainbow Trout Exposed to Municipal Wastewater Effluent." *Environmental Science & Technology* 45(6): 2368-2376.
- Jardine, T.D. and K.A. Kidd (2011). "Low concentrations of selenium in stream food webs of eastern Canada." *Science of the Total Environment* 409(4): 785-791.
- Jobling, S., N. Beresford, M. Nolan, T. Rodgers-Gray, G.C. Brighty, J.P. Sumpter and C.R. Tyler (2002). "Altered sexual maturation and gamete production in wild roach (*Rutilus rutilus*) living in rivers that receive treated sewage effluents." *Biology of Reproduction* 66(2): 272-281.
- Jobling, S., S. Coey, J.G. Whitmore, D.E. Kime, K.J.W. Van Look, B.G. McAllister, N. Beresford, A.C. Henshaw, G. Brighty, C.R. Tyler and J.P. Sumpter (2002). "Wild intersex roach (*Rutilus rutilus*) have reduced fertility." *Biology of Reproduction* 67(2): 515-524.
- Kidd, K.A., P.J. Blanchfield, K.H. Mills, V.P. Palace, R.E. Evans, J.M. Lazorchak and R.W. Flick (2007). "Collapse of a fish population after exposure to a synthetic estrogen." *Proceedings of the National Academy of Sciences of the United States of America* 104(21): 8897-8901.
- Kolpin, D.W., E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber and H.T. Buxton (2002). "Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999-2000: A national reconnaissance." *Environmental Science & Technology* 36(6): 1202-1211.
- Ma, T.W., X.Q. Wan, Q.H. Huang, Z.J. Wang and J.K. Liu (2005). "Biomarker responses and reproductive toxicity of the effluent from a Chinese large sewage treatment plant in Japanese medaka (*Oryzias latipes*)." *Chemosphere* 59(2): 281-288.
- Munkittrick, K.R. (2009). "Ubiquitous Criticisms of Ecological Field Studies." *Human and Ecological Risk Assessment* 15(4): 647-650.

- Munkittrick, K.R., C.J. Arens, R.B. Lowell and G.P. Kaminski (2009). "A review of potential methods of determining critical effect size for designing environmental monitoring programs." *Environmental Toxicology and Chemistry* 28(7): 1361-1371.
- Munkittrick, K.R., G.J. Vanderkraak, M.E. McMaster and C.B. Portt (1992). "Response of hepatic MFO activity and plasma sex steroids to secondary-treatment of bleached kraft pulp-mill effluent and mill shutdown." *Environmental Toxicology and Chemistry* 11(10): 1427-1439.
- Nelson, J.A., P.S. Gotwalt, C.A. Simonetti and J.W. Snodgrass (2008). "Environmental correlates, plasticity, and repeatability of differences in performance among blacknose dace (*Rhinichthys atratulus*) populations across a gradient of urbanization." *Physiological and Biochemical Zoology* 81(1): 25-42.
- Orlando, E.F., A.S. Kolok, G.A. Binzcik, J.L. Gates, M.K. Horton, C.S. Lambright, L.E. Gray, A.M. Soto and L.J. Guillette (2004). "Endocrine-disrupting effects of cattle feedlot effluent on an aquatic sentinel species, the fathead minnow." *Environmental Health Perspectives* 112(3): 353-358.
- Parasiewicz, P., J. Legros, J. Rogers and M. Wirth (2007). Assessment and restoration of instream habitat for the Pomperaug, Nonnewaug and Weekepeemee Rivers of Connecticut, Northeast Instream Habitat Program, University of Massachusetts, Amherst.
- Tyler, C.R., S. Jobling and J.P. Sumpter (1998). "Endocrine disruption in wildlife: A critical review of the evidence." *Critical Reviews in Toxicology* 28(4): 319-361.
- US Sensus Bureau (2010). "2010 Census: State & County QuickFacts." Retrieved October 10, 2011, from <http://quickfacts.census.gov/qfd/states/090001k.html>.
- Weber, L.P., M.G. Dube, C.J. Rickwood, K. Driedger, C. Portt, C. Brereton and D.M. Janz (2008). "Effects of multiple effluents on resident fish from Junction Creek, Sudbury, Ontario." *Ecotoxicology and Environmental Safety* 70(3): 433-445.

# Influence of dynamic copper speciation on bioavailability in streams

## Basic Information

<b>Title:</b>	Influence of dynamic copper speciation on bioavailability in streams
<b>Project Number:</b>	2012CT259B
<b>Start Date:</b>	3/1/2012
<b>End Date:</b>	2/28/2014
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	CT-002
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	None, None, None
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Timothy Vadas

## Publication

1. Luan, H. and T.M. Vadas. 2012. Cu lability and bioavailability in an urban stream during baseflow versus stormflow. American Geophysical Union Annual Conference. San Francisco, CA. Dec 2012.

Connecticut Institute of Water Resources Funded Project  
Proposal Title

**Influence of dynamic copper speciation on bioavailability in streams**

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**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 water body, for example a river flowing through an urban setting, 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 (i.e. that may be contributed by algicide application upstream).

Although some regulations focus on total pollutant input to receiving water bodies regardless of its chemical form, Cu speciation may influence bioavailability, and thus stream impairment due to toxicity. 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, availability and binding of the free metal at the cell surface. The major cases that may control the uptake of elevated metals in urban streams, particularly Cu, are either the diffusion of labile complexes or chemical kinetics of metal-ligand complexes. The equilibrium condition of this model is considered in the biotic ligand model. However, dietary uptake is not explicitly considered, which may also be influenced by complexation with organic matter or surface sorption onto stream organisms, e.g. periphyton.

The proposed work 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 for total aqueous phase copper concentrations or whole effluent toxicity studies. 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, diffusive gradients in thin film (DGT) devices have been developed that measure so-called 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, an indicator of ambient uptake.

In addition, 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 [16]. Periphyton, being one trophic level below some macroinvertebrates, will 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 proposed research will assess two tools to measure bioavailable metals in streams, DGT and periphyton cultures. When paired with biouptake assays and macroinvertebrate surveys, it is expected that these will provide an indication of water quality impairment in relation to speciation dynamics, both in distance downstream of the inputs as well as dependent on the source of contaminant, something that is not currently captured in grab samples or macroinvertebrate surveys. If strong correlations are found, 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 of the work will have implications for improving risk assessment at impacted sites, enhancing dynamic bioaccumulation models, and providing evidence for reducing their impacts through best management practices or restoration activities that manage carbon and metal sources. This research will address three specific questions:

- 1) What is the impact of the dynamic urban stream environment on metal speciation?**
- 2) Can a chemical or biological surrogate more readily predict stream impairments due to Cu than biological toxicity assessments?**
- 3) Do anthropogenic carbon 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 part flowing through Vernon and Manchester which are urban 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 has an average flow rate of 3.94 m<sup>3</sup>/s over the last three years. Water pollution control facilities (WPCF) from each of those towns discharge treated effluent into the river, with average effluent discharges of 0.21 and 0.28 m<sup>3</sup>/s, respectively. In addition, separate storm sewers exist and discharge into the river in several locations along its course. Six sampling spots were selected to deploy the diffusive gradient in thin film (DGT) and periphyton samples from upstream to downstream along the Hockanum river, which are Rockville, 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 in Pleasantview Dr (Figure 1).



**Figure 1:** Hockanum River sampling locations

### *Periphyton colonization*

Microscope slides pre-loaded to acrylic racks were used to colonize periphyton. To keep from collecting 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. 3-week colonization prior to sampling was necessary to obtain sufficient periphyton. Within a few days of exposure in the water, a thin biofilm was observed on the slides, and the periphyton layer was sufficient for the experiment after about 3 weeks.

### *Sampling and treatment*

Water samples were collected by low density polyethylene (LDPE) bottles for metal concentration, total organic carbon (TOC) and alkalinity. Sampling was performed before, during and after several storm events. Forty mL of TOC sample was also filtered through 0.45  $\mu\text{m}$  nitrocellulose filters then pH adjusted to 2 with hydrochloric acid. The alkalinity of water sample was determined by titration with sulfuric acid to pH=4.5.

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. At the time of sampling, 4 microscope slides were thoroughly rinsed with filtered river water (0.45  $\mu\text{m}$ ). 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  $\mu\text{m}$ ) to obtain the dry weight (dw) of each sample after 15 h drying at 50  $^{\circ}\text{C}$ . Then 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  $^{\circ}\text{C}\pm 5^{\circ}\text{C}$  until no brown fume were given off. Subsequently, hydrogen peroxide (31%, suprapure) was added stepwise until the effervescence is minimal or until the general sample appearance was unchanged. The digestion sample of 0.5 mL was diluted into 5 mL with MilliQ water for ICP analysis.

#### *Determination of Labile Metals by DGT*

Labile metal concentrations in water were measured with DGT. 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. After retrieval from the field, the resin gel was peeled off and transferred to 2 mL microcentrifuge containing 1 mL of 1M HNO<sub>3</sub> and left overnight. The elution solution was diluted 5 times with 1% HNO<sub>3</sub> matrix before measurement. The metal concentrations were then measured by inductively coupled plasma mass spectrometry (ICP-MS).

#### *Metal fractionation*

Total metals were determined by digested 15 mL of the acidified samples (2% HNO<sub>3</sub>) at 90 degree C for 1 h. To obtain dissolved metal concentration, the water samples were filtered with a plastic syringe and filter cartridge (0.45 µm filters, cellulose nitrate). An aliquot of 15 mL filtered metal samples were acidified by adding 0.3 mL concentrated trace metal grade nitric acid before ICP measurement. Then the filtered samples were divided into the truly dissolved fractions (permeate) and colloidal fractions (retentate) by using the Amicon Ultra-2 mL Centrifugal Filters with a 10 kDa nominal molar mass cut-off membrane. The total metal concentration (Mt), the colloidal metal concentration (Mc), and the truly dissolved metal concentration (Md) were determined by ICP-MS. The metal concentration in particulate phase was calculated by the difference between total metal concentration and dissolved metal concentration.

#### *Size distribution by AFFFF coupled to ICP-MS*

The size distribution of colloidal metals was characterized by AF2000 Focus (Postnova Analytics, Landsberg, Germany) coupled on-line to a UV detector and an Agilent 7700x ICP-MS (Agilent Technology, Tokyo, Japan). The AFFFF 2000 Control software (Postnova Analytics) was used for data collection and analysis. A 275 mm long trapezoidal channel cartridge with a 500 µm spacer, and a 300 Da and 1000 Da cut-off polyethersulfone membrane (PES, Postnova Analytics) were performed in this experiment. The mobile phase was 10mM NaNO<sub>3</sub> without any pH buffer. An aliquot of 1 mL filtered water samples (0.45µm) was manually injected in the AFFFF channel via a 1mL sample loop at injection flow of 0.1 mL/min for 13 min. During the injection, the colloids were focused under a focus flow rate of 4.4 mL/min and a cross flow rate of 4 mL/min. There was one minute of transition time between focus step and elution step. The separation of the colloids was undergone for 20 minutes elution time using a channel flow of 0.5 mL/min and a cross flow of 4 mL/min. For the 300 Da membrane, the cross flow rate of 3 mL/min was used. The runs ended with a 5 min purge time. The metal signal was measured by ICP-MS. A solution containing internal standard elements in 10 % nitric acid was prepared to monitor the stability of flow rate.

#### *Instrumentation*

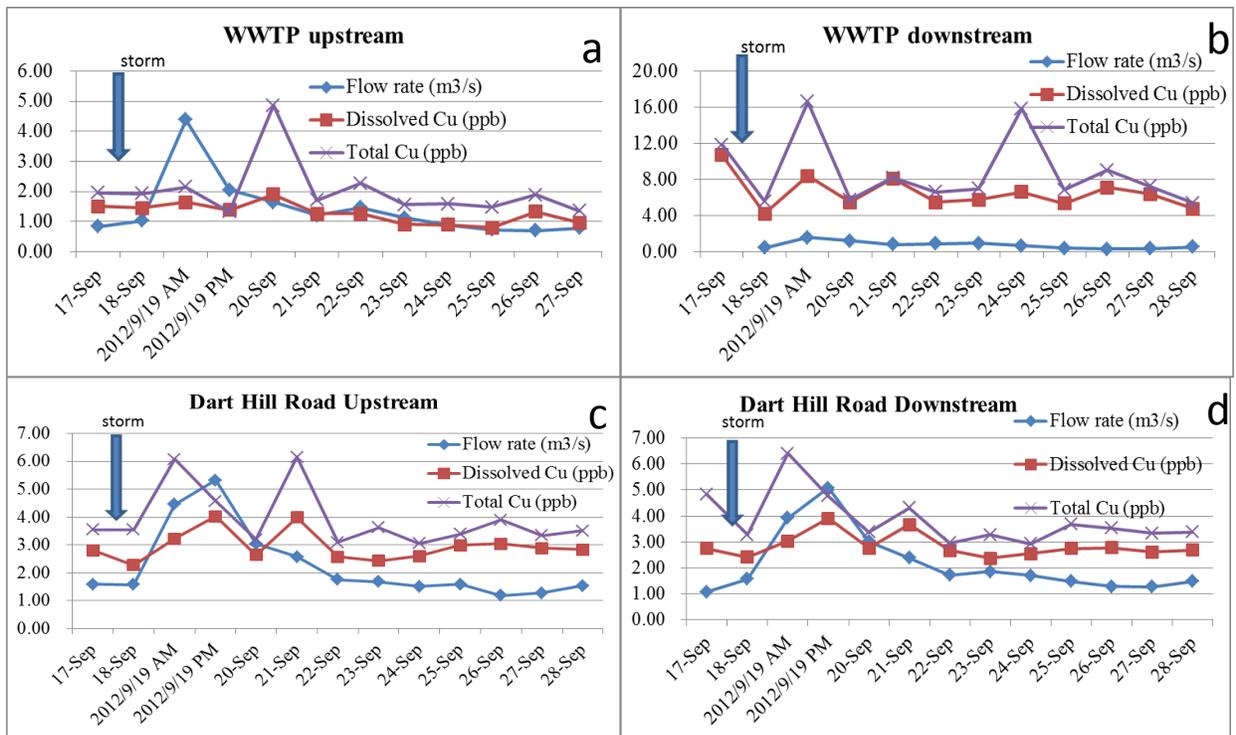
Inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7700x, Agilent, USA) was applied for determination of the elements in this work. A total organic carbon analyzer (Apollo 9000, Tekmar-Dohrmann, USA) was used to measure Total organic carbon (TOC).

### **Results:**

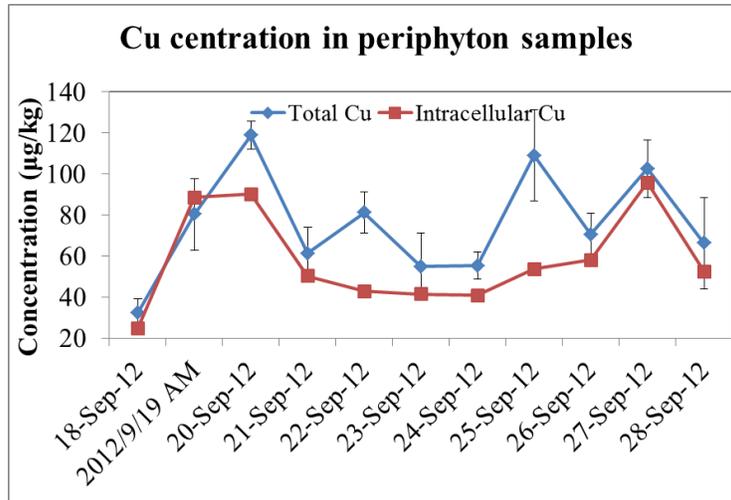
#### *Variation of Cu concentrations in stream along the storm event*

Figure 1 shows the variation of the stream flow rate, total Cu and dissolved Cu concentrations during a storm event along the river course. The storm event occurred on September 18, 2012 and continued until next afternoon on September 19, 2012. The flow rate achieved its peak value in the morning of September 19, 2012. The storm event resulted in an increase of total and dissolved Cu at all locations but the peak time was different from each location. Two days after the storm event, the Cu concentration dropped back to the levels during the baseflow conditions. At about 500 m upstream of wastewater treatment plant effluent, the total Cu increased greatly right after the flow rate peak was over (Figure 2(a)). This delay

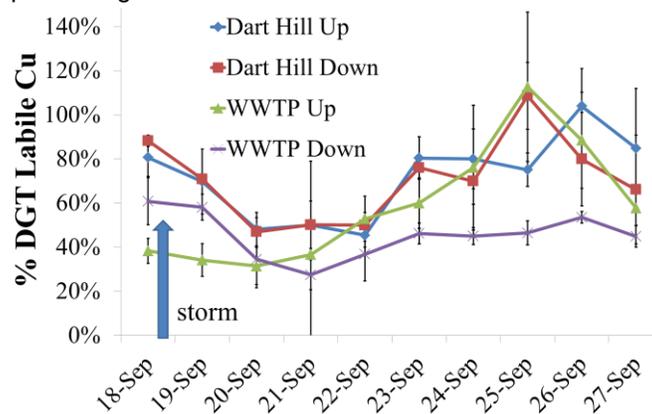
may because it took a while for the particulate Cu to travel from further upstream to this area considering wastewater treatment plant upstream is a forest-covered area and relatively clean for Cu. Not too much Cu was washed out by the storm runoff in this area. The dissolved Cu concentration seemed constant along the whole storm event but there was a slight increase during the storm and at the time of the peak of total Cu concentration. As for the location 500 m downstream from the WWTP effluent, the total Cu and dissolved Cu concentration decreased when the storm started partially due to the dilution effect of increased flow led by storm (see Figure 2(b)). Then the total and dissolved Cu concentrations reached their peaks accompanied by the peak of flow rate. This suggests that the increased flow rate resulted from the storm water disturbed the legacy Cu sank in the sediment at this location. Besides the slight increase after the peak of flow rate, there was another sharp increase of total Cu concentration 4 days after the storm event. These Cu may come from treated effluent since it would take a couple of days for the Cu-elevated influent from this storm event to discharge into the Hockanum River. The total and dissolved Cu concentration showed similar trends at Dart Hill Road upstream and downstream, 2 km and 2.5 km downstream WWTP respectively (Figure 2(c) and 2(d)). Both the total and dissolved Cu increased greatly with the increasing of the flow rate at these two locations. This is likely because this is an urban residential area and there was more Cu in the runoff due to heavy traffic. The Cu concentration displayed another peak as well right after the flow rate peak was over. This may attributed to the same reason of the delay of Cu traveled from upstream to downstream as the other locations. Therefore, the storm event can increase the total and dissolved Cu concentrations for all locations. The elevated dissolved Cu concentration during the storm and immediately after the flow rate peak revealed more available Cu in the stream.



**Figure 2:** Variation of flow rate, total Cu and dissolved Cu concentrations along the storm event at (a) 500 m upstream WWTP; (b) 500 m downstream WWTP; (c) 2000 m downstream WWTP; (d) 2500 m downstream WWTP.



**Figure 3:** Variation of Cu concentrations in periphyton samples along the storm event



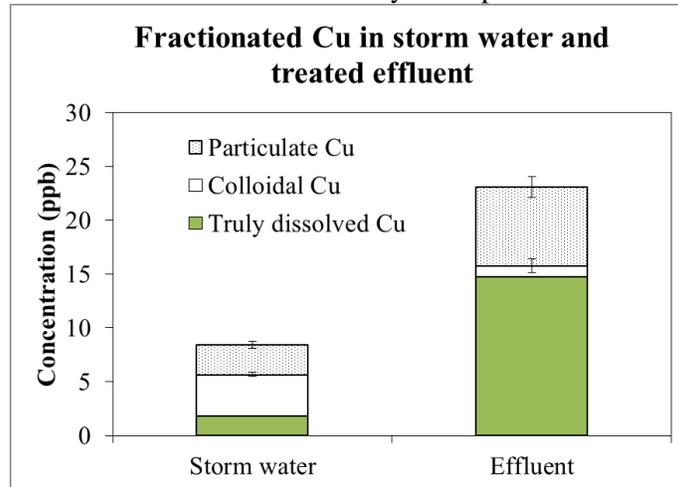
**Figure 4:** Variation of DGT labile Cu ratio along the storm event

#### Periphyton and DGT results

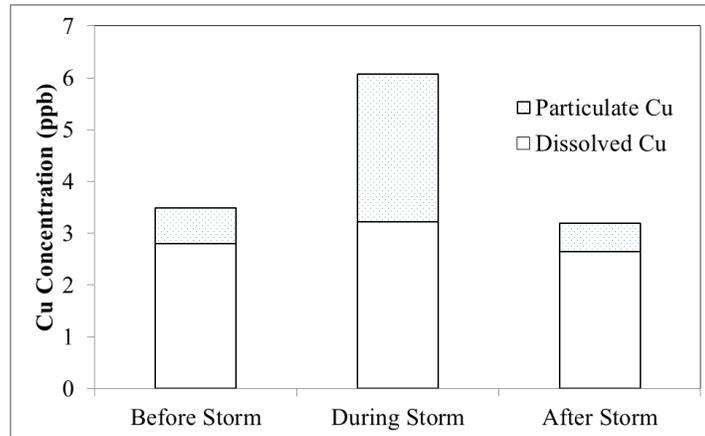
Both the total Cu and intracellular Cu in periphyton samples were correlated to the Cu concentrations in water samples. The total Cu and intracellular Cu increased with the growing Cu concentration in stream water after the storm started. But the peak of Cu concentrations in periphyton samples displayed a day later than the peaks of flow rate and Cu concentrations in stream water, indicating there was a delay for the biouptake of Cu. Moreover, the difference of Cu concentration in periphyton samples before and during the storm was much larger than that in water samples. The total Cu concentration in periphyton samples increased from 32 µg/kg to 118 µg/kg, close to 4 times increase (Figure 3). There was also more than 4 times increase of intracellular Cu from 22 µg/kg to 90 µg/kg. Compared to less than a 2-fold increase of Cu in stream water, there was an amplifying effect in the biological process of Cu uptake. This suggests the significance of storm events on the Cu bioavailability for the bottom level organisms in the food chain. In addition, the difference between total Cu and intracellular Cu in periphyton samples was very small at the beginning of the storm but it became larger over time. This meant more particulate Cu or non-bioavailable Cu was attached on the periphyton samples rather than taken up by the periphyton during the storm. Thus the storm may introduce larger size fractions of Cu which cannot be taken up by periphyton.

The DGT results showed similar trends for all locations. The ratio shown in Figure 4 is the labile Cu concentration measured by DGT over the dissolved Cu concentration in stream water. Figure 4 shows the ratio of labile Cu decreased with the increase of flow rate during the storm then grew after the peak of

flow rate. This indicates the storm event decreased the Cu lability in urban stream. The change of lability was opposite to that of bioavailability shown by periphyton results which indicated the labile Cu measured by DGT was not a direct indicator of bioavailability. The ratio of labile Cu before storm shows an increasing trend along the stream course. The WWTP upstream had the lowest ratio of 38% while the Dart Hill road location downstream had the highest ratio of 88%. The increase ratio of labile Cu along the stream course may be because more Cu ions dissociated from the organic matter or were released by biological processes with the increased travel distance. The labile Cu ratio of WWTP upstream increased significantly after the flow rate peak and exceeded those of other locations. This suggests the labile Cu at the WWTP upstream location remained for a longer time than the other locations and were more available for exchange. However, the labile Cu ratio of WWTP downstream remained lower the entire time. The strong chelating ligands from the WWTP like EDTA may be responsible for this result.



**Figure 5:** Fractionated Cu concentrations in storm water and treated effluent



**Figure 6:** Fractionated Cu concentration in stream water along the storm event

*Metal fractionation*

The elevated Cu concentrations in storm water (8.4 ppb) and treated effluent (23.1 ppb) indicated the potential contamination led by these two source waters (See Figure 5). Wastewater treatment plant contributed highest Cu concentration. The percentage of particulate Cu over total Cu in storm water was 33%, which is very similar to that in treated effluent (32%). The colloidal fraction in storm water

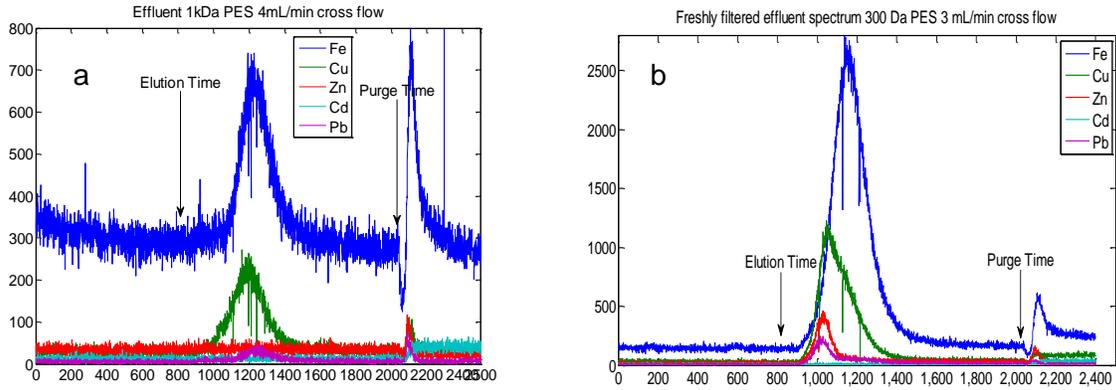
accounted for 45%, much larger than that in treated effluent which is only 4.4%. This indicated the dissolved Cu in the storm were mainly associated with larger size colloidal organic matter. On the contrary, 94% of dissolved Cu in the treated effluent was found in the truly dissolved fraction which meant free Cu ion and Cu associated with smaller organic matter less than 10 kDa were dominant in the treated effluent. In addition, the Cu fractionation in stream water was affected by the storm event. Although the dissolved Cu didn't change too much, the particulate Cu increased nearly 3 times during the storm event (see Figure 6). This may be because the storm runoff flushed the particulate Cu on the road and carried them to the river. Another reason was the storm runoff disturbed the sediment and released the Cu sinked during the baseflow.

#### *Size distribution of metals in storm water and effluent*

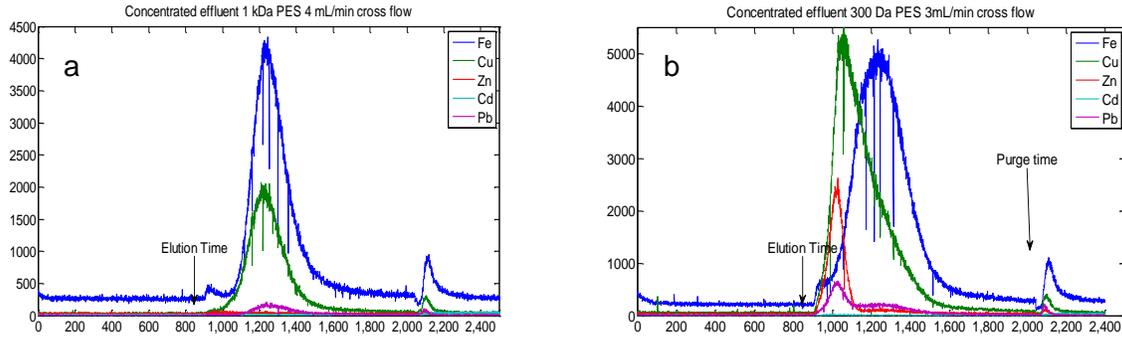
Effluent of Vernon wastewater treatment plant and storm runoff at Pleasantview Dr. were sampled in November 2012. Samples were collected in 20 L plastic carboys that had previously been acid wash with 0.1 M ACS grade HNO<sub>3</sub> and rinsed with deionized water (> 18.2 MΩ) to prevent from metal contamination. Water samples were filtered through 0.45 μm pore size cellulose acetate membrane before injection to FFF system. The effluent was also concentrated by a factor of 10 using a tangential flow ultrafiltration system (TFF), holding a regenerated cellulose membrane with 650 Da nominal molar mass cut-off. The size distribution of metals in these three samples were obtained at first with a 1 kDa PES membrane in FFF. The cross flow rate was set as 4 mL/min correspondingly. Then the membrane was changed to 300 Da cut-off for better performance. The cross flow rate was decreased to 3 mL/min to keep enough backpressure in FFF system.

Figure 7(a) shows the size distribution of metals in effluent using 1 kDa membrane. The Cu displayed only one peak and the peak time is earlier than that of Fe and Pb thus Cu was dominant in smaller size while the size of Fe was larger in effluent. The distribution of Cu was in accordance with the UV signal of organic matter, indicating the Cu was mainly associated with colloidal organic matter in effluent. The peak correspondence of Fe and Pb implied that colloidal Pb larger than 1 kDa was binding with Fe oxides rather than colloidal organic matter. There was no Zn captured by the 1 kDa membrane which demonstrated Zn was distributed in smaller than 1 kDa size fraction. The size distribution of metals in effluent using 300 Da membrane exhibited more interesting information (See Figure 7(b)). It is apparent that there were more metals captured by using 300 Da membrane. The peak height increased by a factor of 4 for Cu, Zn, and Fe. Fe displayed a wider peak at the lower end than on the 300 Da membrane partially because 300 Da membrane captured more metals with smaller size. The peak of Cu also shifted to the lower size fraction. Moreover, the Zn and Pb showed another peak which is not in the 1 kDa results right after the transition time. These fractions were in the range of 300 Da and 1 kDa molar mass. Figure 9 presents the size distribution of metals in concentrated effluent samples. Fe showed another peak which was not in the original effluent before the peak of Zn. This meant the distribution of Fe can be divided into two sections, one in a smaller size and the other in a larger size. There were no big differences between the original and concentrated effluent on 1 kDa membranes except more mass captured and another peak of Fe, suggesting the aggregate size does not change during concentration. The Zn and Pb results showed two peaks with the 300 Da membrane in Figure 7(b), a larger peak at the lower size fraction and a smaller peak at the larger size fraction. The larger peaks correspond with the peak of Cu and the smaller peaks correspond to the peak of Fe. This suggests the small size Zn and Pb may be associated with colloidal organic matter (for which an absorbance peak is observed corresponding to the Cu peak; data not shown) but the large size fraction is associated with Fe oxides. Figure 8(a) shows the size distribution of metals in storm runoff using 1 kDa membrane. Compared to the FFF results of the effluent, the metals in storm runoff exhibited a broader distribution which meant the metals in storm runoff had a larger size range than those in effluent, especially for Fe. There were two peaks for Fe in storm runoff as well. The size distribution of Cu has a similar trend as that in effluent samples. However, Zn and Pb showed very different results. There was another small peak of Zn associated with the first peak of Fe, indicating the really small size of Fe and Zn may combine together. Also, the largest peak of Zn shifted earlier than that in effluent samples and showed a long tail in the storm runoff. It is reasonable

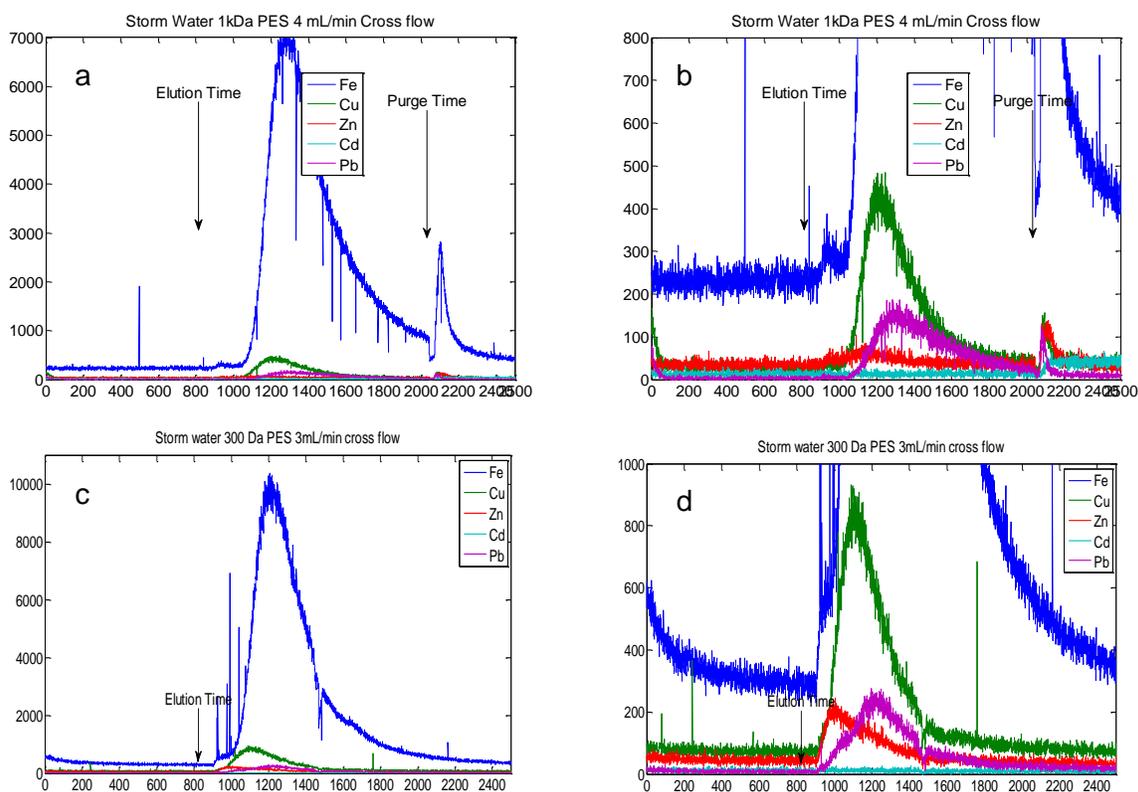
that Zn may correspond to Fe in storm runoff. The peak of Pb showed an obvious delay in elution and a split from the peak of Zn with the 300 Da membrane in storm runoff.



**Figure 7:** size distribution of metals in effluent by FFF (a) on 1 kDa membrane and at 4 mL/min cross flow rate; (b) on 300 Da membrane at 3 mL/min cross flow rate



**Figure 8:** size distribution of metals in concentrated effluent by FFF (a) on 1 kDa membrane and at 4 mL/min cross flow rate; (b) on 300 Da membrane at 3 mL/min cross flow rate



**Figure 9:** size distribution of metals in storm water by FFF (a) on 1 kDa membrane and at 4 mL/min cross flow rate; (b) enlargement of (a); (c) on 300 Da membrane at 3 mL/min cross flow rate; (d) enlargement of (c).

## References

- Campbell, P.G.C., Errecalde, O., Fortin, C., Hiriart-Baer, V.P., and Vigneault, B., 2002, Metal bioavailability to phytoplankton - applicability of the biotic ligand model: Comparative Biochemistry and Physiology Part C, v. 133, p. 189-206.
- Marsalek, J., Rochfort, Q., Brownlee, B., Mayer, T., and Servos, M., 1999, An explanatory study of urban runoff toxicity: Water Science and Technology, v. 39, p. 33-39.
- Meylan, S., Behra, R., and Sigg, L., 2003, Accumulation of copper and zinc in periphyton in response to dynamic variations of metal speciation in freshwater: Environmental Science & Technology, v. 37, p. 5204-5212.
- Vadas, T.M., and Ahner, B.A., 2009, Cysteine and glutathione-mediated uptake of Pb and Cd into *Zea mays* and *Brassica napus* roots: Environmental Pollution, v. 157, p. 2558-2563.
- Warnken, K.W., Davison, W., and Zhang, H., 2008, Interpretation of in situ speciation measurements of inorganic and organically complexed trace metals in freshwater by DGT: Environmental Science & Technology, v. 42, p. 6903-6909.
- Zhang, H., and Davison, W., 2000, Direct in situ measurements of labile inorganic and organically bound metal species in synthetic solutions and natural waters using diffusive gradients in thin films: Analytical Chemistry, v. 72, p. 4447-4457.

## **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. In addition, CT IWR provides financial support to select conferences and workshops with a water resources component. These are supported through a separate 104B information transfer project, described below.

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

## Basic Information

<b>Title:</b>	Field Testing the Educational and Land Use Planning Value of a New Nitrogen Modeling Tool in the Niantic River Watershed
<b>Project Number:</b>	2012CT256B
<b>Start Date:</b>	3/1/2012
<b>End Date:</b>	2/28/2013
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	2
<b>Research Category:</b>	Not Applicable
<b>Focus Category:</b>	Nitrate Contamination, Models, Education
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Juliana Barrett, Chester Arnold, Emily Wilson

## Publications

There are no publications.

Connecticut Institute of Water Resources Funded Project

Proposal Title

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

PI Juliana Barrett  
Co-I Chester Arnold  
Co-I Emily Wilson  
Department of Extension  
1066 Saybrook Road  
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**Introduction/Research Objective:**

We propose to develop 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 is being transformed from an ArcMap desktop tool to a web-based tool using ArcGIS Viewer for Flex. The programming for the tool will be completed by the end of June, 2013. The web tool will allow non-technical users to estimate nitrogen removal efficiencies from any chose point within the project area (Eastern CT and Rhode Island coastal HUC-12 watersheds).

# CTIWR Technology Transfer

## Basic Information

<b>Title:</b>	CTIWR Technology Transfer
<b>Project Number:</b>	2012CT283B
<b>Start Date:</b>	3/1/2012
<b>End Date:</b>	2/28/2013
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	2nd
<b>Research Category:</b>	Not Applicable
<b>Focus Category:</b>	Education, None, None
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Glenn Warner, Patricia Bresnahan

## Publications

There are no publications.

## **CT IWR INFORMATION TRANSFER**

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.

**Web Site:** Our Institute maintains the CT IWR web site, which is typically updated 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. 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. We are planning an upgrade to the CT IWR website during FY 2013.

**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. Due to staff changes, no publications were added to the list during FY2012. Several publications are being reviewed for inclusion in the near future.

**Seminar Series.** The CTIWR typically co-sponsors the seminar series offered by the Department of Natural Resources and the Environment (NRE), the administrative home for our Institute, instead of holding its own separate series. This year the departmental seminar series has been temporarily postponed due to renovations being performed on the W.B. Young Building which houses the NRE Department and the Auditorium. Building renovations are planned for completion in August 2013 and we expect to continue the seminar series in Fall 2013.

**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.

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

- Presentation entitled "Criteria for Identifying Water Bodies for Potential Dry Hydrant Installation in the Natchaug Watershed Basin CT" at two workshops held by Department of Energy and Environmental Protection as part of program for water sources for rural fire control.
- The "Connecticut River Watershed Study" workshops organized by The Nature Conservancy

**Special Meetings.** This past January 2013, CT IWR hosted a meeting of the New England Institute Directors. The daylong meeting focused on the discussion of regional collaboration for water resources issues. The facilitation for the discussion was provided by Gene Likens, Special Advisor to Environmental Affairs at the University of Connecticut. Several project ideas were

discussed among the attendees, and all were supportive of developing a collaborative project. Of highest priority is to look at ways to enhance groundwater sustainability in a rapidly urbanizing environment, and providing training opportunities for undergraduate and graduate students. The group will work to identify potential funding sources to support a regional project involving the New England Institutes.

# USGS Summer Intern Program

None.

<b>Student Support</b>					
<b>Category</b>	<b>Section 104 Base Grant</b>	<b>Section 104 NCGP Award</b>	<b>NIWR-USGS Internship</b>	<b>Supplemental Awards</b>	<b>Total</b>
<b>Undergraduate</b>	3	0	0	0	3
<b>Masters</b>	2	0	0	0	2
<b>Ph.D.</b>	2	0	0	0	2
<b>Post-Doc.</b>	0	0	0	0	0
<b>Total</b>	7	0	0	0	7

## **Notable Awards and Achievements**

None to report.