

**Water Resources Center  
Annual Technical Report  
FY 2016**

# Introduction

During FY 2016 the Rhode Island Water Resources Center has supported two research grants and one information transfer project. The research project entitled, “Modeling and Simulation of Groundwater Contamination,” by Angelo Lucia utilized the numerical reservoir simulator AD-GPRS to investigate (1) the response of a real groundwater model system to 5 days of continuous pumping at various pumping rates, and (2) the migration contaminant transport. The second research grant, “Disinfectant Byproducts Precursors and Formation Potentials in Source Waters of Rhode Island,” by Soni M Pradhanang and Thomas B. Boving. The researchers discovered that a spatial and temporal analysis of TOCs in the source water showed that certain reservoirs in the north of RI have relatively high TOC levels compared to the ones that are located in the southern area of Rhode Island. The Scituate Reservoir, which is the primary reservoir that supplies drinking water to vast majority of the population in RI has the lowest concentration of TOCs indicating that the formation potential of harmful DBPs could be low. The information transfer project supported a summer Water Academy for high school students.

In addition to these activities, the Rhode Island Water Resources Center continued to support graduate and undergraduate students in research. The RI Water Resources Center published a newsletter. This year, the Center added content to the Center’s website ([www.wrc.uri.edu](http://www.wrc.uri.edu)) to include a video of the complete Clean Water Conference as well as a video of a special Earth Day lecture by Professor Jay Famiglietti entitled "21st Century Global Freshwater Security: Can it Exist and can scientists Communicate the Challenge?"

## Research Program Introduction

The Rhode Island Water Resources Center supported two research projects. The first project was a groundwater modeling project entitled, "Modeling and Simulation of Groundwater Contamination" by Angelo Lucia. The second project investigated the formation of disinfection by-products in Rhode Island waters and was entitled, "Disinfectant Byproducts Precursors and Formation Potentials in Source Waters of Rhode Island," by Soni Pradhanang and Tom Boving.

Lucia's research utilized the numerical reservoir simulator AD-GPRS to investigate (1) the response of a real groundwater model system to 5 days of continuous pumping at various pumping rates, and (2) the migration of contaminants. The examples studied in his work highlight the applicability of the AD-GPRS/GFLASH reservoir modeling and simulation framework to groundwater flow systems. In this work, for example, an equation of state model was used for determining the variation of density with pressure. An example in which the contaminant concentration introduced into the source is greater than the solubility of the contaminant in the water phase was presented to illustrate the capability of modeling multi-phase flow in groundwater applications.

The results from Pradhanand's research found that all the water samples that were tested for this study showed low concentrations of total trihalomethanes. The total organic carbon (TOC) concentration measured in a water sample can be used as a precursor for the DBPs formation potential. The spatial and temporal analysis of TOCs in the source water showed that certain reservoirs in the north of Rhode Island have relatively high TOC concentrations compared to the ones that are in the southern area of Rhode Island. The Scituate Reservoir, which is the primary reservoir that supplies drinking water to the vast majority of the population in Rhode Island has the lowest concentration of TOCs indicating that the formation potential of harmful DBPs could be low.

# Modeling and Simulation of Groundwater Contamination

## Basic Information

<b>Title:</b>	Modeling and Simulation of Groundwater Contamination
<b>Project Number:</b>	2016RI123B
<b>Start Date:</b>	3/1/2016
<b>End Date:</b>	2/28/2017
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	2nd
<b>Research Category:</b>	Ground-water Flow and Transport
<b>Focus Categories:</b>	Groundwater, Models, Solute Transport
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Angelo Lucia

## Publications

There are no publications.

# Modeling and Simulation of Groundwater Contamination

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## **Abstract**

Automatic Differentiation General Purpose Research Simulator (AD-GPRS) is a numerical reservoir modeling and simulation tool developed by the SUPRI-B group at Stanford University. It has been used to simulate a wide variety of industrial processes, including enhanced oil recovery and carbon dioxide sequestration processes. Some of the basic features of AD-GPRS are (1) a fully compositional treatment of the fluid mixture in the reservoir, (2) the ability to use rigorous EOS-based phase equilibrium calculations, and (3) the choice of a wide range of cubic equations in the van der Waals family for the determining fluid density as a function composition, pressure, and temperature. While some of these features are usually not needed in the state-of-the-art groundwater simulators, there are cases in which their inclusion would better represent the physics of the system. In this work, a contaminated groundwater flow example for a reservoir in central Rhode Island is presented to highlight the utility of AD-GPRS for groundwater simulation problems. Our numerical results provide an excellent match of numerical simulations generated using MODFLOW and also show how contaminants in watershed can be easily tracked using AD-GPRS. Finally, some of the remaining challenges for the application of AD-GPRS are also discussed.

## **Keywords**

AD-GPRS; Numerical reservoir simulation; Gibbs-Helmholtz constrained EOS; Groundwater flow modeling; Contaminants

## Introduction

Understanding the flow of pure fluids and their mixtures in porous media is of interest a wide variety of practical applications including oil and gas exploration/recovery, carbon dioxide sequestration, and ground water flow. Several software tools exist that allow one to solve the set of partial differential equations governing fluid flow in porous media numerically. However, despite some of the underlying similarities in the physics of model development, most of these tools are specific to the application problem. The two software packages that are of interest in this work are Automatic Differentiation General Purpose Research Simulator (AD-GPRS) (Voskov & Zhou, 2012) and MODFLOW-2005 (Harbaugh, 2005), developed by the SUPRI-B group at Stanford University and US Geological Survey (USGS), respectively.

AD-GPRS is a numerical reservoir simulator built around Automatic Differentiation (AD) technology. Originally developed as a hydrocarbon reservoir simulator, AD-GPRS currently has advanced features which allow the user to model complex physical phenomena and represents the state-of-the-art in reservoir simulation. Recently, AD-GPRS has been adapted for modeling CO<sub>2</sub> sequestration application (Voskov et al., 2017) such as CO<sub>2</sub> injection into a deep saline aquifer, where mineralization of CO<sub>2</sub> can impact the dissolution rate of CO<sub>2</sub> and hence effect the storage capacity of the formation.

MODFLOW is a mature open source numerical groundwater simulation program developed by USGS. It has been used to study the interaction between ground and surface water, the long and short term effects of pumping, and the change in the water table as a function of variations in seasonal inflow and outflow. MODFLOW has a wide user base, and many extensions have been developed to add features to the basic MODFLOW package, including the ability to adjust for variable density fluid flow (a posteriori), track particles originating in some point source for a given system, and many different boundary conditions representing surface features such as rivers and streams.

The tools and extensions developed for MODFLOW are very useful for studying groundwater systems. However, the main MODFLOW package makes several major assumptions about the composition of the fluid and its physical properties which limit its applicability. The specific assumptions include that (1) the fluid is a single component (water), (2) the density of the fluid is independent of pressure, temperature or composition, and (3) the fluid is stable in a single phase (liquid) state. For many causes, these assumption are completely reasonable. However, in systems where pressure change is expected to be large, or additional phases may be present in the system, these assumptions are not adequate to represent the physics of the system such as in the carbon sequestration example recently presented in Voskov et al. (2017) using AD-GPRS in which the variation in density with composition and pressure strongly effects the dissolution rate CO<sub>2</sub> from a supercritical carbon dioxide phase into a brine phase. In contrast, the advanced features implemented in AD-GPRS allow the study of groundwater systems in which density variation due to pressure or fluid composition may strongly effect the results, multiple phases may be present, and/or the distribution of the fluid composition at a given time step is of interest to the user.

Due to differences in the formulation of the model equations, implementation, and availability of various boundary conditions, a direct comparison between MODFLOW and AD-GPRS is not feasible. Therefore, the purpose of this study is to demonstrate the efficacy of using AD-GPRS to model groundwater flow in a realistic groundwater system, to highlight the advantages gained from using AD-GPRS in these systems, and to identify the weaknesses and/or challenges that should be overcome to apply AD-GPRS to these systems more efficiently. To accomplish these goals, a simulation model for the AD-GPRS simulator was developed using a previously developed MODFLOW model as a guide. The reservoir model used in this study is the Big River Management area in central Rhode Island, published in the USGS report of Masterson and Granato (2012).

## **Procedure**

The AD-GPRS reservoir simulator (Voskov and Zhou, 2012) developed by the SUPRI-B group at Stanford University was used in the work. AD-GPRS is a state-of-the-art, multi-phase, fully thermal and compositional reservoir simulation program. It has been used to simulate many industrial processes including steam injection and steam injection with propane co-injection for enhanced oil recovery (Zaydullin et al. 2014; Voskov et al., 2016), in situ CO<sub>2</sub>-steam co-injection for heavy oil recovery, and plume migration in carbon dioxide sequestration in the presence of convective dissolution and gravity currents (Elenius et al., 2015; Voskov et al., 2017). In this work, AD-GPRS is used to model and simulate fully compositional simulations of groundwater flow. Treating the groundwater flow problem in this way enables one to study problems in which the composition of the formation water is not constant throughout the reservoir and to monitor the concentration of any one species in the mixture can be monitored at any location in the model at any time step.

In this section, we will briefly highlight some of the features of the software used in this work and discuss the development of the simulation model using the published MODFLOW model of the Big River Management area as a guide. Fluid properties were calculated using a program developed by Professor A. Lucia at URI called GFLASH, which has been interfaced with AD-GPRS.

### *AD-GPRS Overview*

The subsurface flow numerical simulation program used in this work is called AD-GPRS. AD-GPRS is a simulation program written primarily in C++ and maintained by the SUPRI-B project at Stanford University. It is used extensively in the reservoir engineering community due to its wide ranging capabilities, which include

1. Flexible treatment of all nonlinear physics.
2. A fully thermal-compositional formulation for any number of phases.
3. Multi-phase CSAT for efficient and robust computation of phase behavior.
4. A variety of spatial and temporal discretization schemes.
5. Thermal geo-mechanical modeling including the effects of fractures.
6. A fully coupled, thermal, multi-segmented well model with drift-flux.
7. An adjoint-based optimization module.

A more detailed overview of the capabilities listed above is given in a previous article by Zaydullin et al., 2014. Additional details regarding the implementation of AD-GPRS can be found in the open literature. For example different options for the choice of independent variables (e.g., natural versus molar formulation) can be found in Voskov and Tchelepi (2012), discretization schemes are described in Zhou et al. (2011), Voskov (2011) gives a description of the methods for solving non-linear and linear systems of equations, and the many approaches for fluid phase behavior computations are presented in the work of Iranshahr et al. (2013).

### *GFLASH Overview*

The GFLASH software developed by Professor A. Lucia was used for all the fluid properties calculations in this work. GFLASH is a FORTRAN program suite which given temperature, pressure, and overall mixture composition calculates the number of equilibrium phases and their compositions, along with their respective densities, fugacities, enthalpies. Several commonly used cubic equations of state (EOS) models are implemented in GFLASH including Soave-Redlich-Kwong (SRK) equation (Soave, 1972), the Peng-Robinson (PR) equation (Peng & Robinson, 1979), and the Gibbs-Helmholtz constrained (GHC) equation of Lucia et al. (2012). For this work, the GHC EOS was used exclusively because it predicts the density of water more accurately than the traditional cubic equations of state (Lucia et al., 2012) and because it is applicable to aqueous electrolyte solutions. Neither the SRK nor PR equations can treat aqueous electrolytes. Additional information about the methodologies in GFLASH for the solution of the classical isothermal, isobaric flash problem can found in the literature (Lucia, 2000), as can more information on the GHC EOS model (Lucia et al., 2012).

### *Converting the MODFLOW Model*

The AD-GPRS model used in this work was developed from the input files from a MODFLOW study of the Big River Management area in Rhode Island (Maserson & Granato, 2012). Most of the data from of the original 512 x 232 x 7 MODFLOW was simply converted into the required units for AD-GPRS and re-represented in AD-GPRS input file format. However, because of the additional computational complexity of the AD-GPRS simulator, the size of the original MODFLOW was reduced by a factor of 0.25 in the horizontal dimensions to yield a 128 x 58 x 7 model. The actual dimensions of the entire model were left unchanged. That is, the dimensions of the scaled blocks were increased so that the same volume used in the MODFLOW model was represented by the AD-GPRS model. The number of layers in the vertical dimension remained unchanged. In reducing the size of the model, the properties were averaged accordingly. Finally, the locations of the wells and inflows into the model were taken directly from the MODFLOW input files transformed into the corresponding locations in the AD-GPRS model. The resulting AD-GPRS model locations are indicated in Fig. 1.

## **Results and Discussion**

Simulation results using the model described in the previous section are detailed in this section for three distinct cases. In the first case, the inflows and outflows to/from the active model area represent rivers or streams entering or exiting the model area. There is no other pumping/injection in the model. The second case is a modification of the first in which pumping

is performed at designated locations for a period of 5 days. The effects of pumping at a specified rate for 5 day is analyzed. This type of analysis is important to determine amount of pumping that is acceptable for an aquifer of interest, and in understanding the effects of pumping on the water level in the surrounding areas. Finally, the third example illustrates the capability of AD-GPRS to run a fully compositional simulation by introducing a contaminant into one of the inflows. The composition distribution can then be analyzed over time to understand the spread of contaminant, the potential size of the contaminated area, and possible remediation strategies.

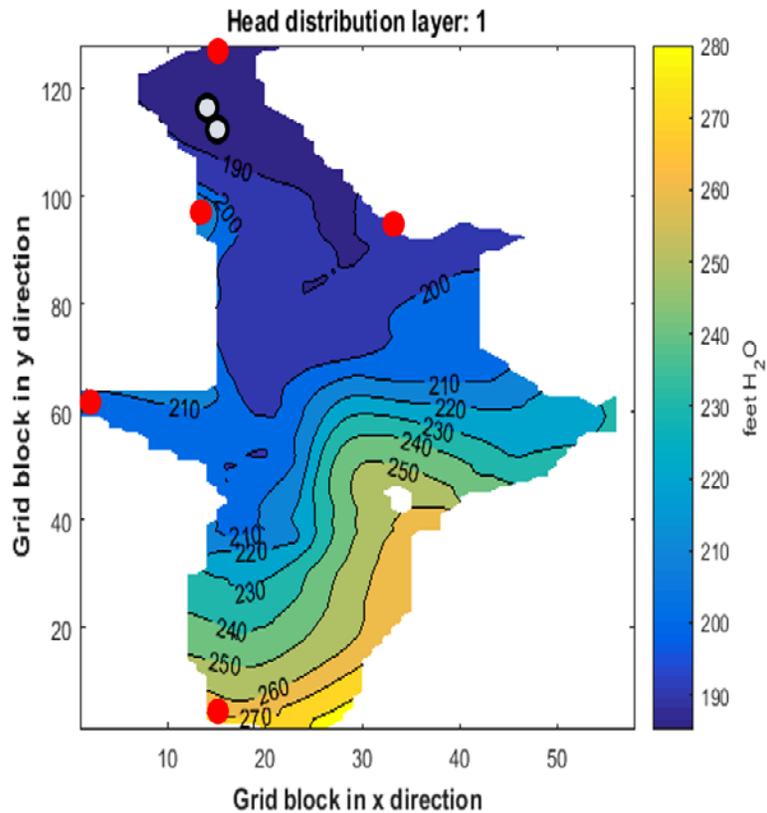
*Example 1: Simple case with no pumping*

This case was initialized using the same initial pressure distribution as the MODFLOW model. Locations of inflows and outflows across the boundary of the model area were also adapted from the MODFLOW model. The simulation was run for 1000 days in AD-GPRS to allow it come to steady state and for hydrostatic equilibrium to be reached. The composition of the fluid in the reservoir is given in Table 1. The GHC EOS was used to calculate the fluid density as a function of pressure and the necessary derivatives.

**Table 1 - Fluid Mixture Mole Fraction**

Species	Mole Fraction
n-Octane	1.00000e-10
Water	0.999984e0
Na <sup>+</sup>	4.60000e-06
Ca <sup>2+</sup>	1.70000e-06
Mg <sup>2+</sup>	7.40000e-07
Cl <sup>-</sup>	4.24000e-06
HCO <sub>3</sub> <sup>-</sup>	3.40000e-06
SO <sub>4</sub> <sup>2-</sup>	9.20000e-07

Figure 1 shows the equilibrated pressure distribution after 1000 days, the approximate inflow (red circles) and outflow (grey circles) locations are marked on the figure for reference. Note that in the first case, there was no pumping from the wells, all inflow and outflow sources were located on the top model layer, and the pumping wells were located in the fifth layer as in the MODFLOW model.

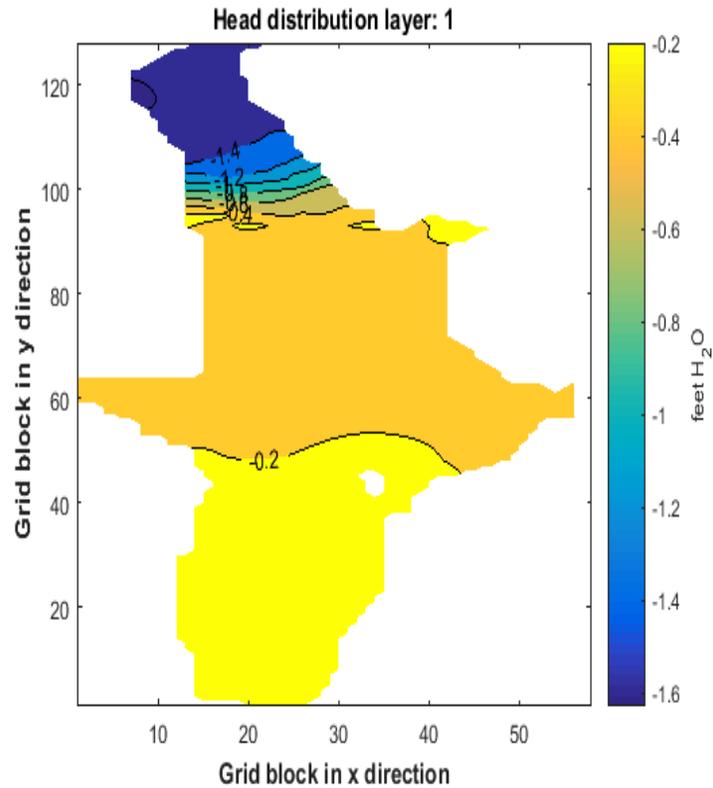


**Figure 1: Equilibrated Head (no pumping)**

The results from the 1000 day equilibration simulations with no pumping depicted in Fig. 1 were used to initialize a second simulation in which water was pumped out of the system at the two production wells (the gray dots in Fig. 1) for 5 days. Note that the results using AD-GPRS/GFLASH shown in Fig. 1 provide an excellent match of those shown in Fig. 9 of Maserson & Granato (2012).

*Example 2: Pumping response in 5 days*

The model parameters for this example are exactly the same as in the previous example, with the exception that the two production wells were added at the locations indicated in Fig. 1. Figures 2 and 3 show the change in head after pumping for 5 days in layers 1 and 2 respectively.



**Figure 2: Layer 1 head distribution change after 5 days of pumping at an average of 190 gpm**

The well rates were adjusted throughout the simulation to keep a constant bottom hole pressure of 3 bar at each production well. The average rate of production for each well over the time horizon for the simulation was approximately 190 gpm.

It is clear from Figs. 2 and 3 that the areas closest to the wells experience a greater decrease in head due to sustained pumping. The distribution and magnitude of the response of the formation to water production can be an important metric for determining maximum allowable production rates, since it can be used to predict the effects that sustained pumping will have on water level in different areas of the formation. To highlight the effects of pumping on water level, additional simulation runs were carried out with modified average pumping rates. Figures 4 and 5 show results after 5 days of pumping at average rates of 800 gpm and 1000 gpm, respectively.

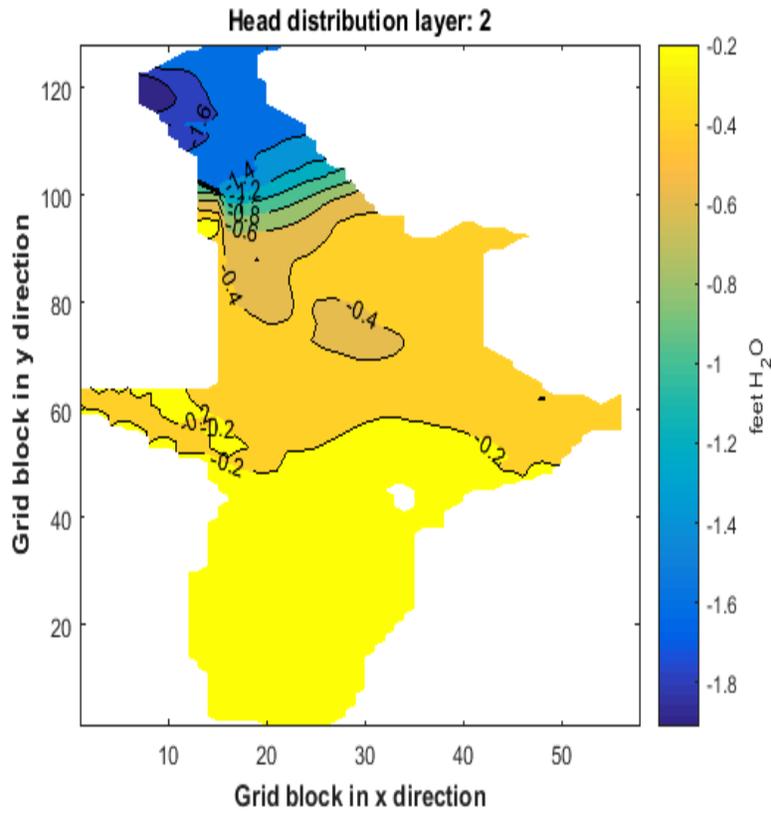


Figure 3: Layer 2 head distribution change after 5 days of pumping at average rate of 190 gpm

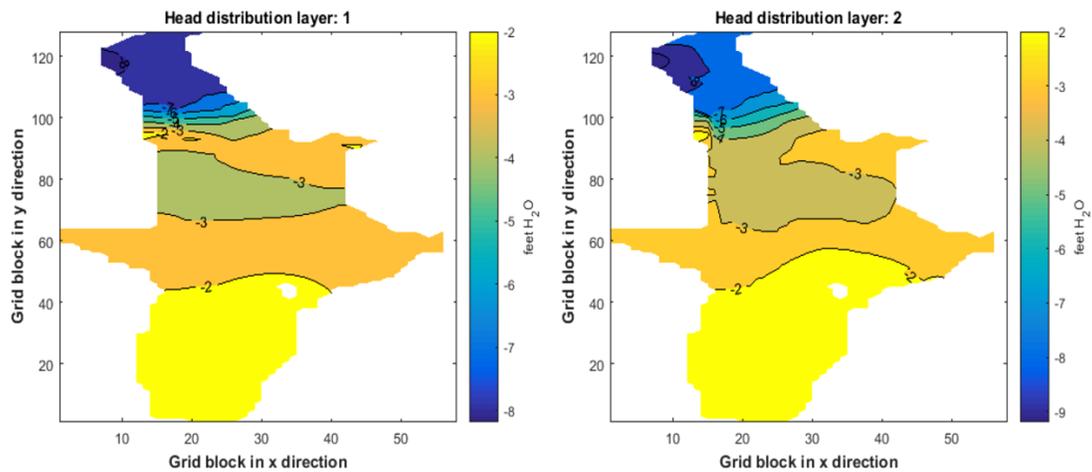
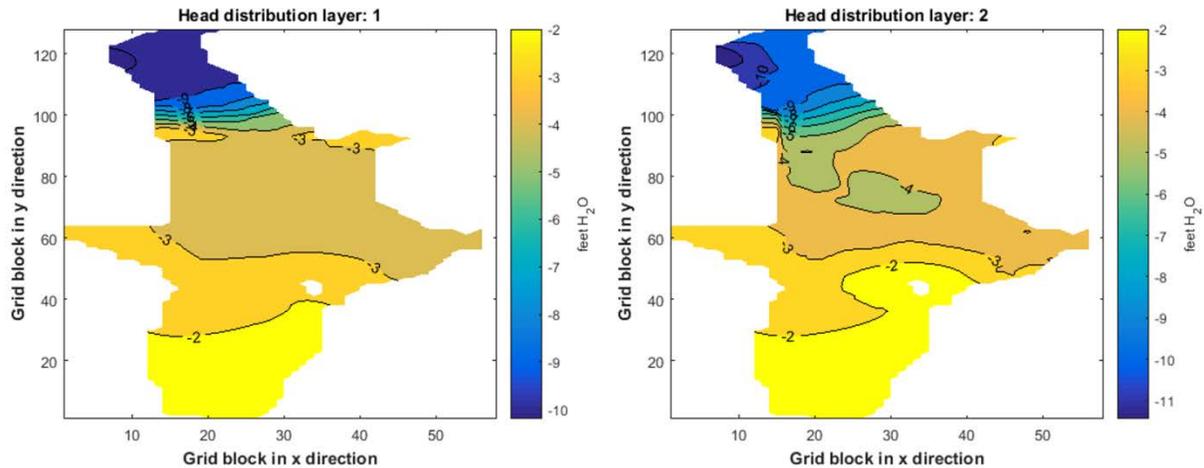


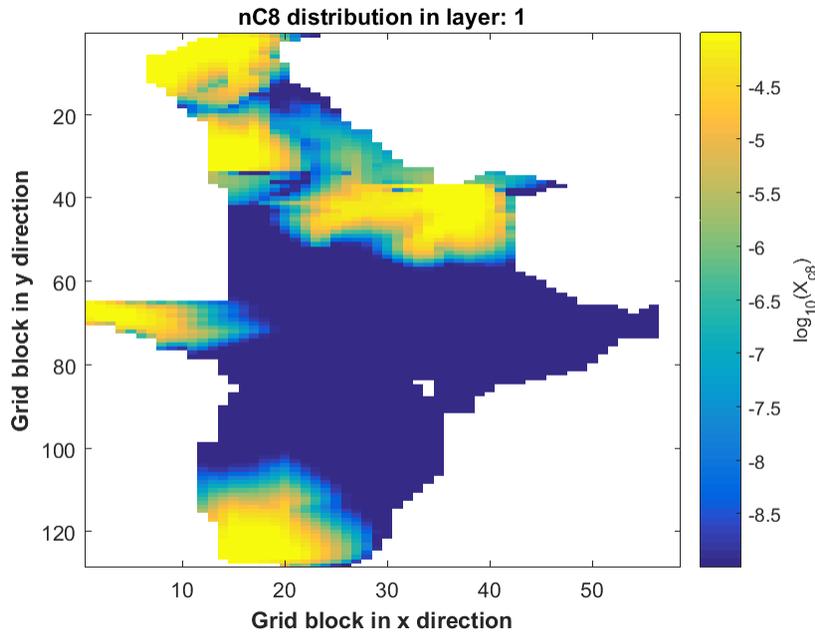
Figure 4: Change in head after pumping for 5 days at 800 gpm: layer 1 (left); layer 2 (right)



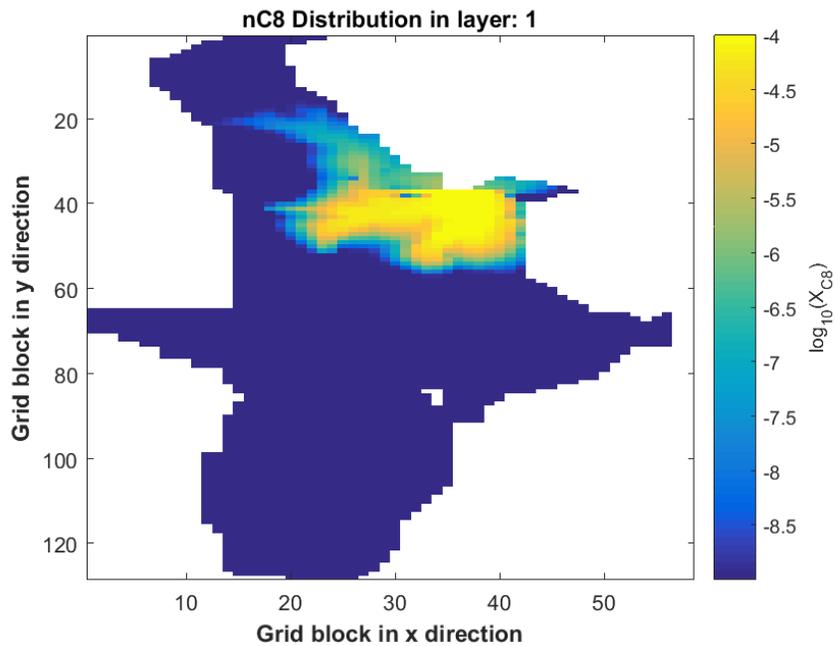
**Figure 5: Change in head after pumping for 5 days at 1000 gpm: layer 1 (left); layer 2 (right)**

*Example 3: Contaminant flow*

Compositional simulation capabilities implemented in AD-GPRS facilitate the study of the spatial distribution of contaminant as a function of time. As an illustration of this functionality, two example cases are presented. In the first case, a small amount of n-octane is introduced into all the source blocks while in the second case, contaminant is introduced into only one source block. Both examples use the same model and initialization as the previous examples, with exception of the concentration of contaminant in the injection stream. Figure 6 shows the contaminant distribution after 5000 days of simulation in the case in which all sources to the model contain contaminant, while Fig. 7, on the other hand, shows the case in which only one source is contaminated.



**Figure 6: Contaminant Distribution After 5000 Days**

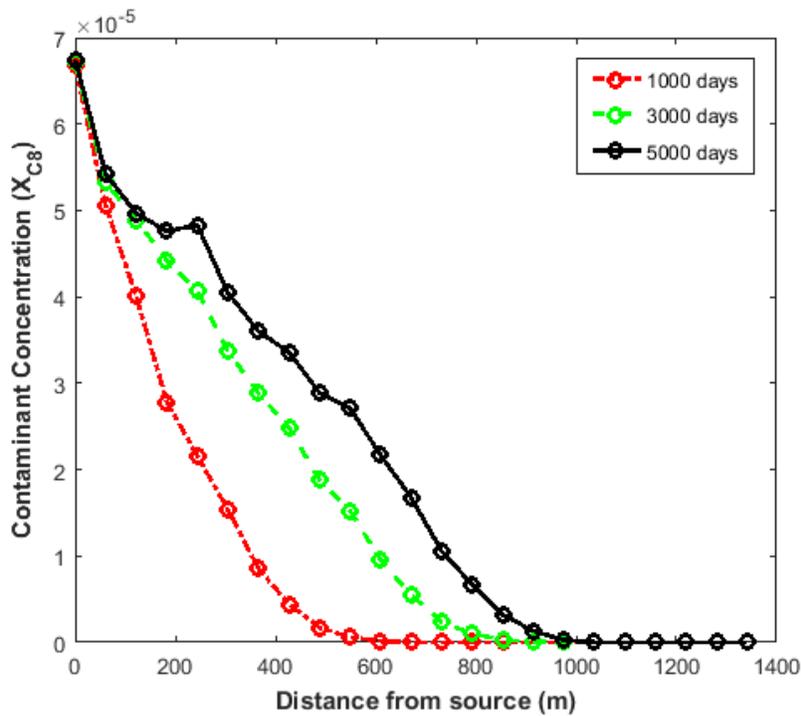


**Figure 7: Contaminant Distribution After 5000 Days**

Contaminant concentration as function of distance from the source is depicted in Fig. 8, for 1000, 3000, and 5000 days. Clearly, the contaminant concentration decreases as distance from the source increases, as expected.

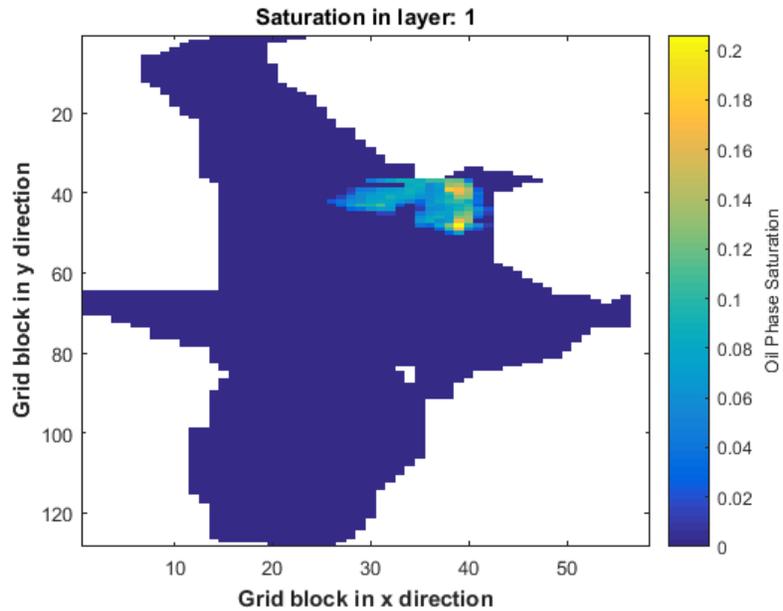
Examples such as the previous two can also be used to predict the concentration of contaminant at any point within the model at any given time. This type of analysis could prove useful in

evaluating different contamination scenarios by varying the location and concentration of contaminant introduced into the reservoir. In addition, the AD-GPRS/GFLASH modeling framework makes it possible to introduce contaminant levels greater than the corresponding solubility limits of those contaminant in water, which in turn could result in the formation of a second fluid phase. In addition, the migration of multiple fluid phases throughout the reservoir is easily modeled in the AD-GPRS/GFLASH framework by including a model of the relative permeability as function of saturation. Figure 9 shows the saturation of the octane-rich phase in the two-phase example described previously. The octane concentration introduced into the source block is greater than the solubility of octane in water and a second liquid phase forms and propagates through the reservoir model.



**Figure 8: Contaminant Concentration as a Function of Distance from Source**

These last examples clearly illustrate the capability of AD-GPRS/GFLASH to model fluid mixtures in the aquifer with variable density, the formation of a second liquid phase, and multi-phase flow through porous media. These features are useful for the development of a model for investigating the migration of contaminant 'spills' which enter the model area a variety of inflows.



**Figure 9: n-Octane Phase Saturation after 5000 Days**

## Conclusion

The numerical reservoir simulator AD-GPRS was used to investigate (1) the response of a real groundwater model system to 5 days of continuous pumping at various pumping rates, and (2) the migration contaminant. The examples studied in this work highlight the applicability of the AD-GPRS/GFLASH reservoir modeling and simulation framework to groundwater flow systems. Fully compositional treatment of the reservoir fluids allows mixtures to be easily incorporated into the model and many methods for the evaluation of fluid properties are available in AD-GPRS/GFLASH. In this work, for example, an equation of state model was used for determining the variation of density with pressure. An example in which the contaminant concentration introduced into the source is greater than the solubility of the contaminant in the water phase was presented to illustrate the capability of modeling multi-phase flow in groundwater applications.

Currently, the boundary conditions that are required to model constant inflow rates over an area of the model such as non-point sources due to rain fall or runoff and the presence of ponds and streams within the model are not explicitly implemented in AD-GPRS. However, these features could easily be added.

Future work may include the implementation of boundary conditions and features into AD-GPRS that allow the study of groundwater/surface water interactions in groundwater systems.

## **Acknowledgement**

The authors would like to express our gratitude to Professor Denis Voskov of TU Delft for his guidance and to Professor Hamdi Tchelepi and the SUPRI-B project at Stanford University for permission to use AD-GPRS for this study. We would also like to thank the Rhode Island Water Resources Center and USGS for providing financial support of this work.

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# Bench-top simulation of water treatment system to assess disinfectant byproducts precursors and formation potentials in source waters of Rhode Island

## Basic Information

<b>Title:</b>	Bench-top simulation of water treatment system to assess disinfectant byproducts precursors and formation potentials in source waters of Rhode Island
<b>Project Number:</b>	2016RI124B
<b>Start Date:</b>	3/15/2016
<b>End Date:</b>	2/14/2017
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	2
<b>Research Category:</b>	Water Quality
<b>Focus Categories:</b>	Water Quality, Water Supply, Surface Water
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Soni M Pradhanang, Tom Boving

## Publication

1. Pradhanang, S. M., and Pokharel, H., 2016. Disinfectant Byproducts in Drinking Water. World Environmental Water Resource Congress, EWRI, ASCE, May 22-26, 2016 West Palm Beach, FL

# **Disinfectant byproducts precursors and formation potentials in source waters of Rhode Island**

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## **Introduction**

Public water systems in Rhode Island range in size from large city systems that serve nearly 300,000 residents to small, rural, non-community transient systems, such as restaurants or convenience stores that utilize wells as their drinking water source. According to the Rhode Island Department of Health Report prepared by Tetrattech, Rhode Island's public drinking water systems face many challenges in meeting the public health protection standards to ensure safe drinking water (Tetrattech, 2012).

In many cases, source water from a lake, river, reservoir or ground water aquifer needs to be disinfected to inactivate (or kill) microbial pathogens. A major challenge for water suppliers in Rhode Island is how to balance the risks from microbial pathogens and disinfection by products. According to Environmental Working Group's (EWG)'s analysis of water quality data supplied by state water agencies, 40 water utilities reported detecting Total Trihalomethanes (TTHMs) in tap water since 2004. The concentration ranged from 28.69 ppb in Kent County Water Authority water to 100.95 ppb at the Naval Station, Newport. Formation of regulated and non-regulated disinfection by-products (DBPs) is an issue at both potable water and wastewater treatment plants. In 2010 there were 28 water systems regulated by this rule (EWG, 2016). There were also 16 systems that purchase and distribute water that has been treated with disinfectants such as chlorine and ozone. These systems currently monitor the residual chlorine levels throughout their distribution systems. The monitoring of DBPs began in 2012. In Rhode Island there are 10 water

systems that are covered by these rules. All of these 10 water systems provide filtration and disinfection as part of their treatment processes. The Surface Water Treatment Rules requires an additional 15 suppliers that are secondary sellers of surface water to maintain chlorine residual throughout their distribution system.

Disinfection is an important process in water treatment targeted mainly at removing disease-causing microorganisms from water supplies. Chlorine is the most widely used disinfectant in the U.S. because of its efficiency in killing certain harmful pathogens and its ability to provide residual disinfection in the distribution system (USEPA, 1995). However, there is a growing concern regarding the use of chlorine due to the formation of numerous DBPs. DBPs are formed when chlorine reacts with chemical species in water, referred to as DBP precursors. DBP precursors can be organic in nature, such as natural organic matters (NOMs), or inorganic, such as bromide and iodide ions (IPCS, 2000). Disinfection via chlorination or chloramination has been critical processes for controlling pathogens in both drinking and treated wastewaters. However, both chlorination and chloramination may result in variety of carcinogenic disinfection by-products that are of concern to human health and ecosystem.

Natural organic materials (NOMs) e.g., humic substances, which are present at various degrees in all RI water supplies, constitute the major component of the total organic carbon (TOC) concentration in most waters. Total organic carbon identified as the main precursors in the formation of THMs and HAAs (Stevens et al., 1976; Christman et al, 1983) Reckhow et al. (1990) have shown that activated aromatic content of NOMs increase formation of halogenated DBP. Substantial research is therefore necessary to advance our understanding of the potential impacts of factors that are responsible in formation of THMs and HAAs in source waters. We propose to conduct DBP formation potential (DBFPs) experiments to study the reactions between the

precursors and disinfectant. With knowledge of trends between precursors and DBPFP, unit processes capable of reducing more important precursors can be employed to reduce overall DBP levels in treated water, which would benefit RI public water consumers.

This report presents the results of

1. TTHM analysis in the distribution system within the State of RI.
2. Analysis of the important formation potential operational parameters of TTHMs and HAAs.

## **Methods**

Traditionally, the most effective route of control has been the removal of precursors before disinfection with chlorine; however, treatment processes have limited effectiveness for precursor removal. For this reason, more recently researchers have emphasized exploring the origin and nature of the precursors that would form DBPs.

Based on the objectives of this research we,

1. Analyzed available data for TTHMs and HAAs in the reservoirs and distribution system
2. Synoptically sampled public water system including wells to collect information on DBPs.

Water samples were collected from several locations within RI. All field samples were collected in acid washed 100ml amber bottles with Teflon caps in three replicates. These samples were kept in a cooler packed with ice until sample collection was complete. All samples were analyzed for TTHMs using a Shimadzu Gas Chromatography Mass Spectrometry using EPA method 524.2 (USEPA, 1995). Samples were then transported to the Hydrology and Water Quality Lab, URI, where they were kept in a 4°C cold storage prior to analysis. Each sample was measured for pH and Turbidity using HACH. We systematically evaluated the relationship between chlorite (synoptic samples), Organic Carbon, THMs and HAAs formation. A simple descriptive statistical analysis was done.

Bench-top experiments (Figure 1) were set up to further evaluate precursors of formation potential. Solutions of each compound at relevant concentrations were prepared; pH and alkalinity of the solution to suggested values were adjusted respectively, followed by chlorination; aliquot samples at frequent time intervals were collected. Proper dilutions, extractions, and analysis were then performed based on the guidelines and EPA methods.

Figure 1.

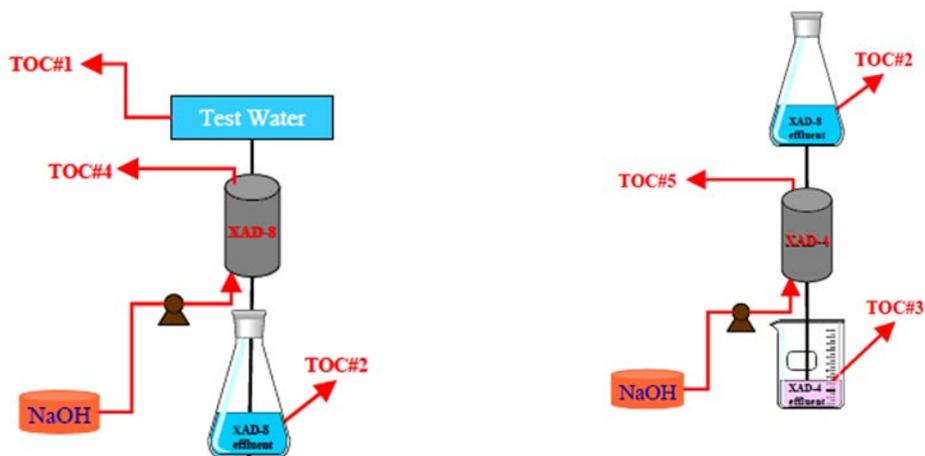


Figure 1. XADs set up to determine hydrophilic and hydrophobic organic carbon

## Results and Discussions

The results presented in this report pertain to the TTHMs and THAAs data analysis from RIDOH data and laboratory analysis conducted in Hydrology and Water Quality Lab at the University of Rhode Island. We conducted descriptive statistical analysis of water quality parameters for several sites within RI. Descriptive analysis of available data for RI reservoirs and distribution systems showed that TTHMs and HAAs show high variability by month. The average monthly concentration of TTHMs and HAAs were well below the threshold limit of 80  $\mu\text{g}/\text{l}$  (Figure 2). Carbon in surface water is known to be the primary precursors of DBPs formation (REF). Figure 3 shows the analysis of Total Organic Carbon from several reservoirs in RI. TOC concentration ranged from 3.0 mg/l to less than 6.8 mg/l. Crook Fall Brook showed

a consistently high TOC concentration compared to other reservoirs in RI, while TOC concentration in Scituate Reservoir was the lowest of all the studied reservoirs. The spatial distribution of TOC concentration varied from month to month and from location to location (Figure 4), although no distinct pattern was observed. TOC used to measure DBPs is now a major part of regulations for large and small water suppliers across the United States. TOC is one of the two parameters used as a substitute and indicator of precursors (Fuji, 1998). Organic matter derived from sources such as forest, agricultural land, wetlands and affected by processes such as decomposition lead to distinctive chemical characteristics in organic carbon. Hydrophobicity and hydrophilicity of organic carbon play an important role in formation potential of TTHMs and HAAs in waters (Reckhow, 1990).

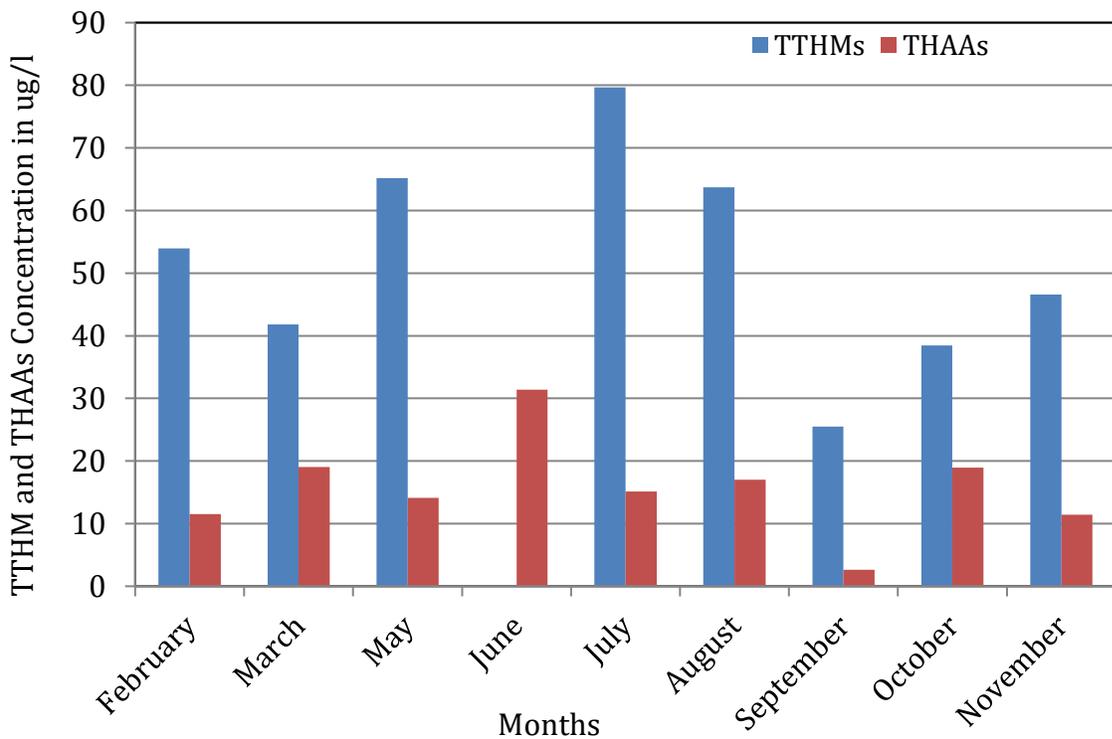


Figure 2 TTHMs and THAAs concentration in the distribution system for 2016 (Data Source: RIDOH)

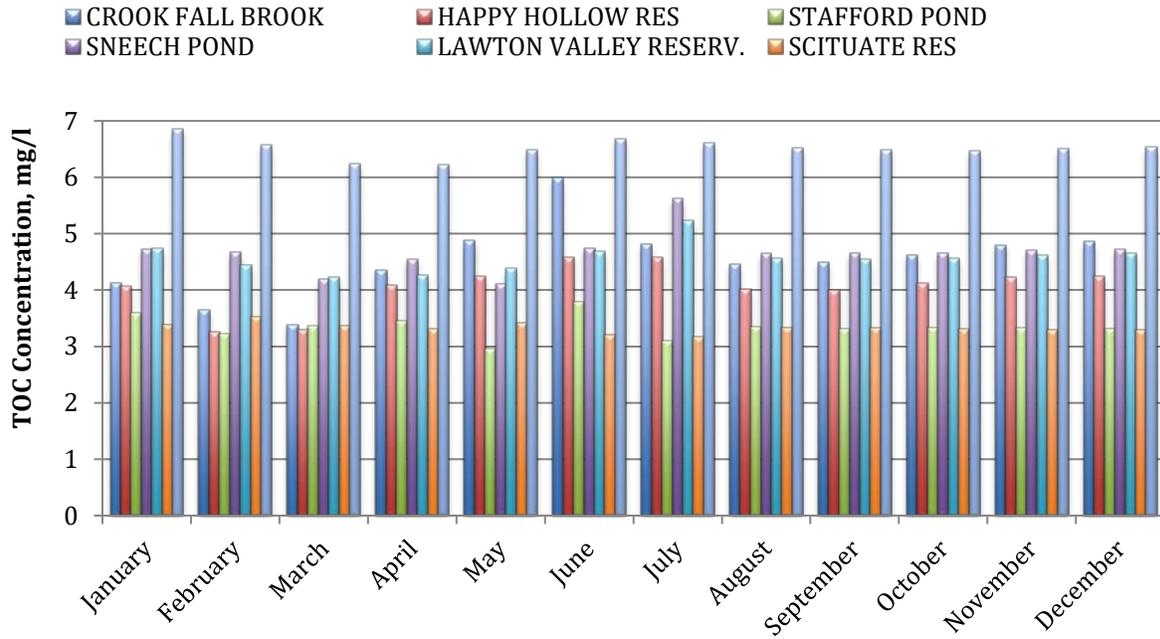


Figure 3 Monthly Total Organic Carbon Concentrations at Different Reservoirs in RI

Treatment techniques with variable removal requirements should be in place when source or treated water TOC > 2 mg/L. Stage 1 Disinfectants/Disinfection By Products Rule therefore are applied to treat these waters if used for drinking water purposes. According to the USEPA (2002), the Stage 1 Disinfectants and Disinfection Byproducts Rule (DBPR) reduces drinking water exposure to disinfection byproducts. The purpose of DBPR is to improve public health protection by reducing exposure to DBPs. Some disinfectants and DBPs have been shown to cause cancer and reproductive effects in lab animals and are suspected to cause bladder cancer and harm reproductive health in humans. All the community water systems and non-transient non-community systems, including those serving fewer than 10,000 people that add a

disinfectant to the drinking water during any part of the treatment process must adhere to this Rule (USPEA, 2002).

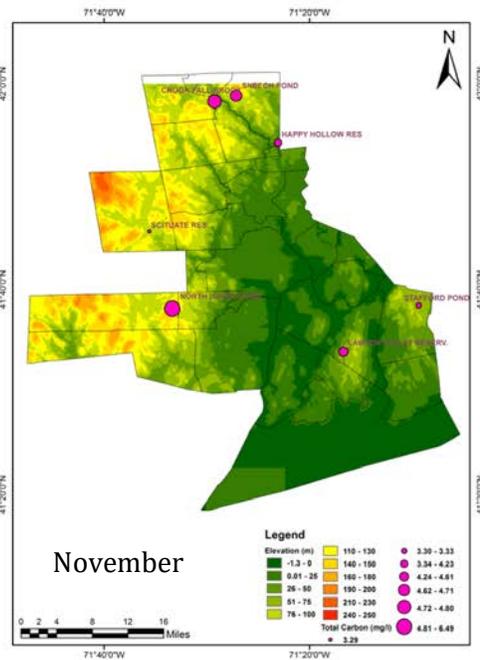
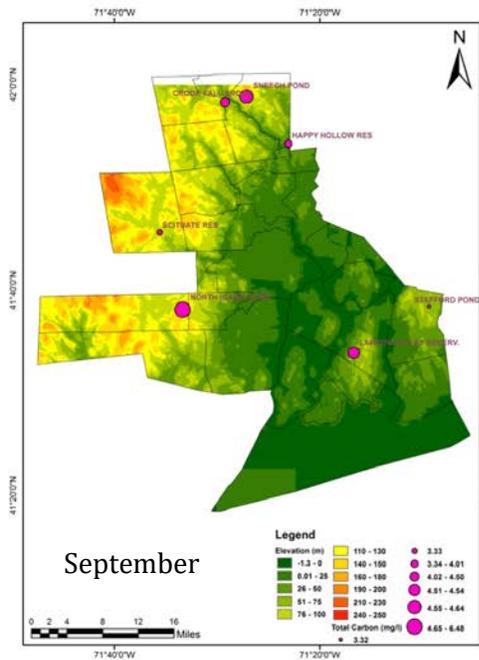
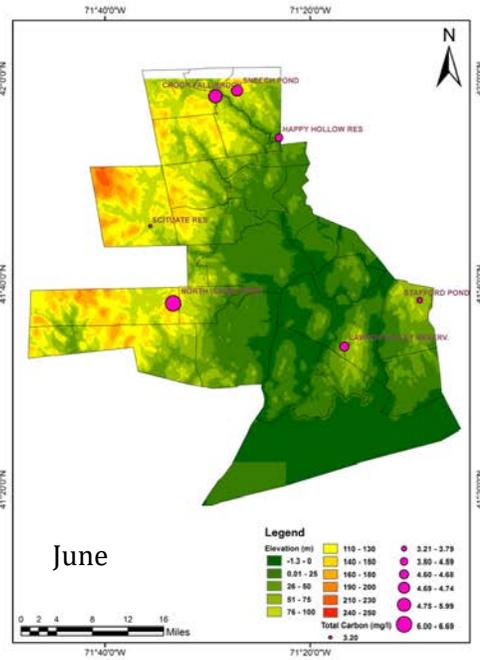
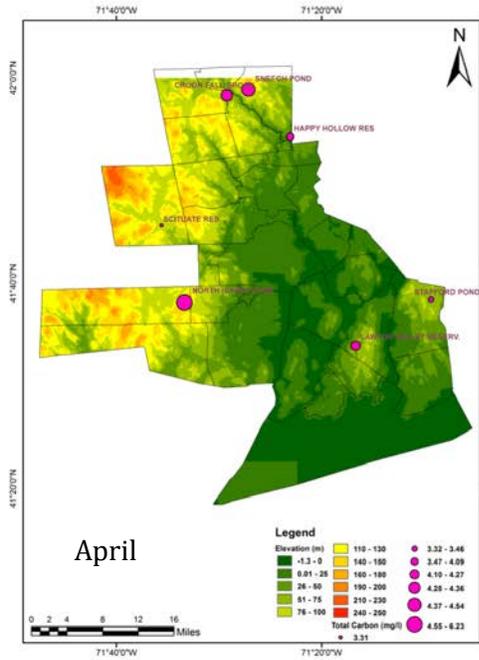


Figure 4 Total carbon concentration in reservoirs in RI for selected months.

We analyzed three replicates of water samples from various locations within Rhode Island for TTHMs using EPA 524.2 method (USEPA, 1995) as a part of synoptic sampling done in May 2016. The tap water from several locations consisted of both public water and well water systems. The results indicated that TTHMs concentration in the tap waters (with no on-site treatment) were well below the threshold concentration. The distribution of TTHM showed a distinct pattern exhibiting a high proportion of chloroform in most of the water samples, followed by the bromodichloromethane concentration (Figure 5). The well water site within North Kingstown showed the lowest concentration of TTHM as expected, since well water does not go through the treatment processes as the tap water that is from the public water system goes through. However, there was a visibly higher proportion of dibromochloromethane and bromoform. Similar observation could be made in the sample from Pascoag although the water sample is not well water. The proportionately high concentration of bromoform and dibromochloromethane is different from what Icanhenko and Zogorski (2006) have reported. They reported that THM detection frequencies in domestic well samples show a decreasing pattern from chloroform to bromoform. Our studies show similar pattern for the tap waters only. Although the concentrations of TTHMs analyzed in this study were far below the threshold set by EPA Stage 1 Rule, it is important to notice that the TOC concentration in source water are high enough to require water being treated before distributed for public drinking purpose. Rhode Island Public Drinking water is treated before being used for human consumption. The sources of TOC in various reservoirs should be identified and managed in order to reduce TOC concentrations at the source. This could tremendously reduce the cost that would otherwise be incurred to treat TOC at the treatment plants. The ongoing research in our lab will explore all the

potential ways to reduce organic carbon or natural organic matter by separating it to its hydrophilic and hydrophobic component and treating them accordingly using combination of methods.

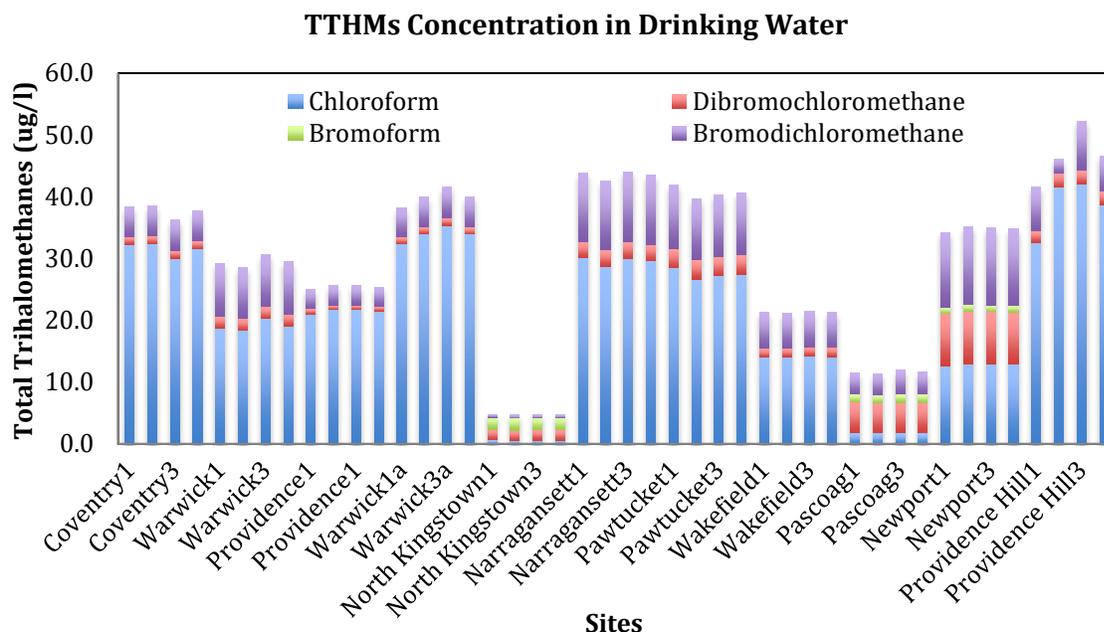


Figure 5. TTHMs concentration in drinking water in RI

Conclusions:

All the samples that were tested for this study showed low concentrations of TTHMs. The total carbon concentration which is used as a precursor for DBPs formation is widely used as a surrogate to assess DBPs formation potential. The spatial and temporal analysis of TOCs in the source water showed that certain reservoirs in the north of RI have relatively high TOC concentrations compared to the ones that are in the southern RI. The Scituate Reservoir, which is the primary reservoir that supplies drinking water to vast majority of population in Rhode Island has the lowest concentration of TOCs indicating that the formation potential of harmful DBPs could be low.

Reference:

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### **Students that were supported from this research**

This project supported two graduates and one undergraduate student. Hem K. Pokharel and Hichem Hadjeres are graduate students and were supported funding for a semester each from this grant and were involved in conducting laboratory experiments of the water samples and setting up the bench-top water treatment column experiment to track and test precursors.

Jordanne Feldman, an undergraduate has benefitted from this research project tremendously. She primarily worked in the lab to analyze organic carbon using UV-vis Spectrophotometer and assisted the graduate students to build a column experiment.

### **Publication:**

Pradhanang, S. M., and Pokharel, H., 2016. Disinfectant Byproducts in Drinking Water. World Environmental Water Resource Congress, EWRI, ASCE, May 22-26, 2016 West Palm Beach, FL

## **Information Transfer Program Introduction**

From July 11 through July 15, 2016, 15 high school students participated in the URI Water Summer Clean Water Science and Engineering Academy. The students were from the Times2 STEM Academy High School in Providence, Rhode island. Students were involved with activities from approximately 9:00AM to 3:30PM each day. The academy was free for the students, and it included a light breakfast, lunch, and snacks.

The week began with a presentation on the impact of water and then the water cycle. Activities for the students involved numerous presentations, various laboratory exercises, field data capture, software applications, and two major field trips. Among the presentations were those on the water cycle, chemistry of water, water quality and treatment, sewage treatment utilizing biological technology, runoff and storm water and pollution prevention.

# Clean Drinking Water in Rhode Island

## Basic Information

<b>Title:</b>	Clean Drinking Water in Rhode Island
<b>Project Number:</b>	2016RI126B
<b>Start Date:</b>	3/1/2016
<b>End Date:</b>	2/28/2017
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	2
<b>Research Category:</b>	Water Quality
<b>Focus Categories:</b>	Water Quality, None, None
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Christopher Dickerson Hunter

## Publications

There are no publications.

## **The 2016 University of Rhode Island (URI) Clean Water Science and Engineering Academy**

### **Christopher Hunter**

From July 11 through July 15, 2016, 15 high school students participated in the URI Water Summer Clean Water Science and Engineering Academy. The students were from Times<sup>2</sup> STEM Academy High School in Providence, and sessions were held there for three days and at URI for two of the days. Students were involved with activities from approximately 9:00AM to 3:30PM each day. The academy was free for the students, and it included a light breakfast, lunch, and snacks.

The week began with a presentation on the impact of water and then the water cycle. This led us into a general discussion session with the students and into the first major activity for the students, "Pop Quiz". Figure 1 gives you an indication of what happens during this game. Students are presented with an answer and a dollar amount, and they must answer in the form of a question.

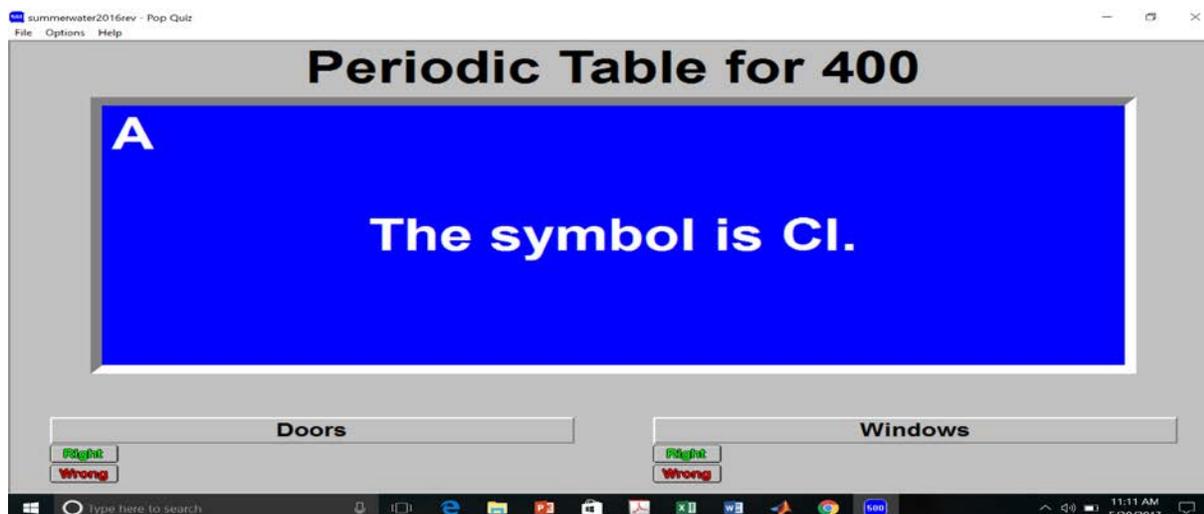
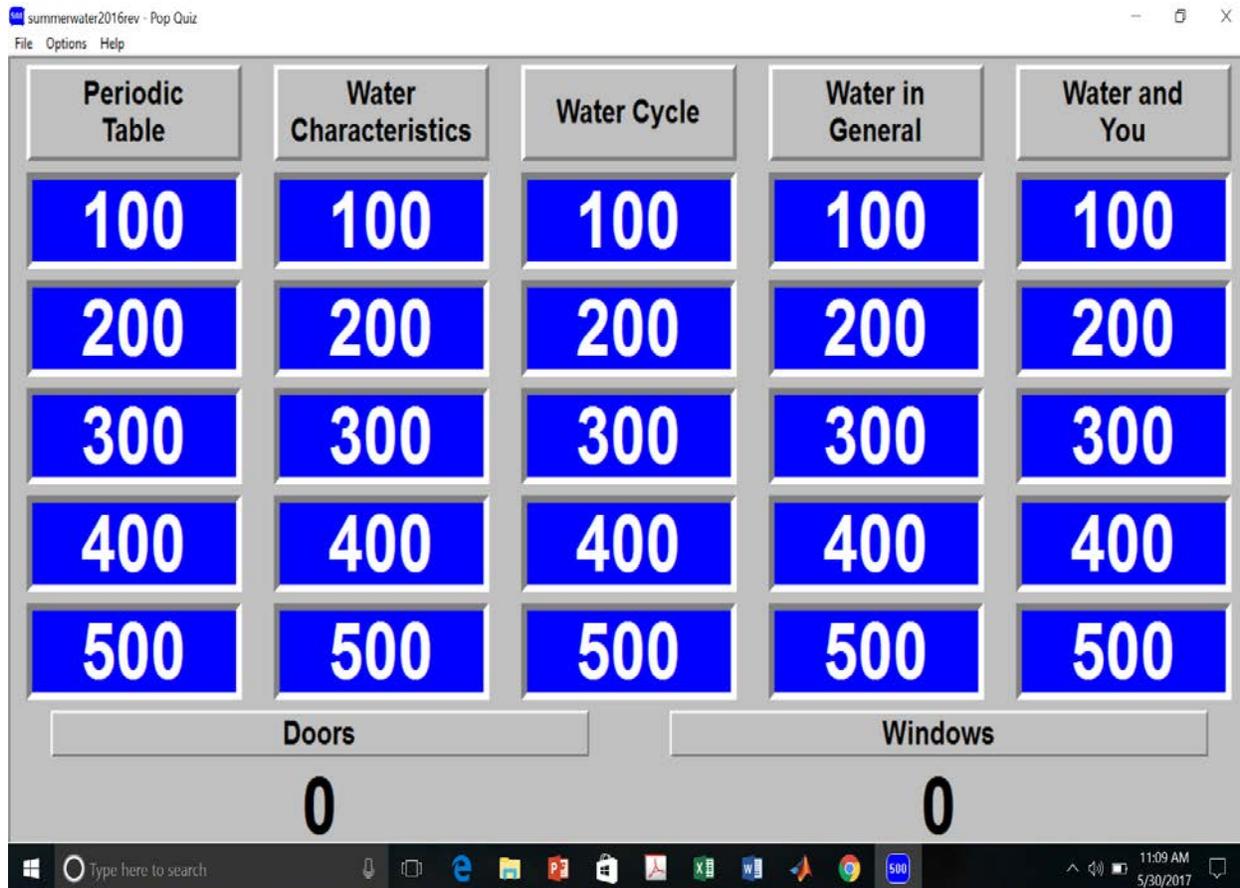


Figure 1. Pop Quiz Activity Example

Overall, activities for the students involved numerous presentations, various laboratory exercises, field data capture, software applications, and two major field trips. Among the presentations were those on of the water cycle, chemistry of water, water quality and treatment, sewage treatment and biological technology, runoff and storm water, pollution prevention, etc.

Laboratory exercises included water quality sampling and testing, pH and dissolved oxygen measurement, filtration, and settling experiments. Field work included the collection of samples from various locations, including 30 Acre Pond at URI, where students were allowed, with guidance and observation, to enter into the shallow areas of the pond to sample for macro-invertebrate life in the pond. Some just stood on the bank and captured what they could with a net or a bucket. This was one of their favorite activities. Field trips were taken to the Holton Water Purification Facility at the Scituate Reservoir and the Warwick Advanced Wastewater Treatment Facility.

Dr. Hunter, from URI, was responsible for most of the presentations and establishing the activities. Helping throughout the process was Dr. Fontaine, a science teacher from Times<sup>2</sup> STEM Academy. He was involved in the recruitment process and in assisting with labs and activities throughout the week. Two guest presenters helped provide different perspectives: (1) Ms. Frances Vazquez, a URI student with the National Society of Black Engineers; and (2) Mr. Sean Osborne, a registered Professional Engineer, who is the Principal at OSD, LLC, a company specializing in environmental engineering and water resource engineering. Ms. Vasquez provided some background on environmental science and water resources, and she led an investigation on water quality. She brought water samples from Narragansett Bay and from a freshwater pond and students used a water test kit to check for such characteristics as pH, nitrates, phosphates, dissolved oxygen, as well as turbidity. Mr. Osborne shared about experiences as a practicing water resources and environmental engineer and used an interactive presentation style and took students through some basic mathematics and science to answer different situations that he faced. He also shared how he was using Apps to help better monitor systems and real-time updates.

Teams were established in groups of 3 to 4 persons for each laboratory exercise. The students were responsible for writing laboratory reports and reporting out their results on the major activities.

One other activity that changed from the 2015 Summer academy was to expose them to some coding and working on an exercise using MATLAB to solve a water runoff scenario.



Figure 2. Ms. Vazquez in her presentation with the students about water quality.



Figure 3. A team engaged in the water quality analysis.

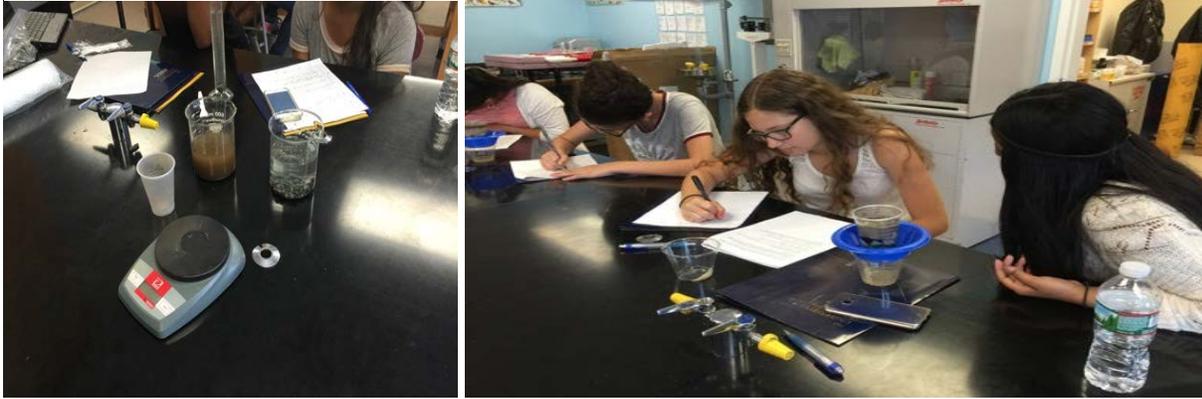


Figure 4. General Pictures Involving Filter System Set-Up and Settling at Times 2 Lab





Figure 5. The Advanced Wastewater Treatment Plant



Figure 6. Pictures from the Holton Water Purification Facility, including a view of one of their labs.



Figure 7. Sampling from 30 Acre Pond at URI for MacroInvertebrates and Investigating the Health of the Pond.

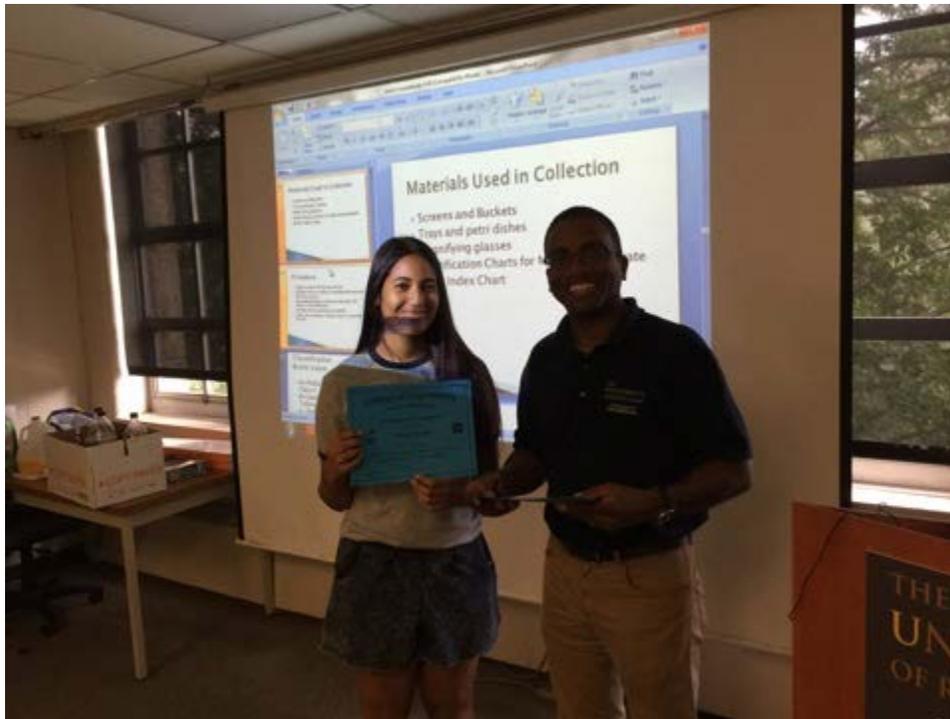


Figure 8. Student Receiving Summer Academy Certificate from Dr. Hunter

# 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>	2	0	0	0	2
<b>Masters</b>	3	0	0	0	3
<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**

The RI Water Resources Center sponsored a presentation by Jay Famiglietti, Professor and Senior Water Specialist on the topic "21st Century Global Freshwater Security: Can it Exist and Can Scientists Communicate the Challenge?"