Water Resources Center
Annual Technical Report
FY 2011

Introduction

This is a report on the projects of the Rhode Island Water Resources Center(RIWRC) during the period between March 1st 2011 to February 28th 2011. The RIWRC is currently under the direction of Dr. Leon Thiem, Associate Professor of Civil and Environmental Engineering, and has been granted permanent approval as a University Center. One graduate research assistant, Hui Chen, and two undergraduate students, Emily Serman and Monica Castellanos, are supported by the RIWRC.

Dr. Vinka Craver, Assistant Professor in the Department of Civil and Environmental Engineering at the University of Rhode Island was funded by a USGS grant through a RIWRC grant to complete her research entitled "Increasing Sources of Water Supply: Advanced Treatment of Stormwater Runoff." Dr. Craver went on to publish an assessment of soil modifications designed to enhance the containment of polycyclic aromatic hydrocarbons. When used in conjunction with porous pavements her findings point towards the potential of harvesting clean water from contaminated roadway runoff.

Dr. Geoffrey Bothun, and Associate Professor in the Department of Chemical Engineering was funded by a USGS grant through a RIWRC grant to complete his research entitled "Stimuli-Responsive nanocomposite Coatings for Mitigating Fouling of Water Treatment Membranes." Funding from this proposal allowed this PI to support an MS graduate student who received his MS degree and is continuing as a Ph.D. Candidate.

Dr. Harry Knickle succeeded in hosting the Fifth Annual Clean Water Conference and the fourth Clean Water Engineering and Science Academy for high school students. Students were recruited from the inner schools in Providence and given the opportunity to participate in water related laboratory experiments using URI's state-of-the-art laboratory facilities. All of the conference presentations have been recorded and can be accessed on the RIWRC's website.

Research Program Introduction

The primary goal of this year's supported research projects was to explore different techniques to increase the supply of purified water. Two research projects were funded.

Dr. Craver's study investigated techniques to modify glacial outwash soils using two different approaches involving soil blending and chemical modification. Both techniques succeeded in enhancing the removal of PAH from roadway runoff. Ultimately, soil modifications such as were studied in this project, in conjunction with a porous roadway pavement could, by purifying contaminated roadway runoff, create a source of treated water.

Dr. Bothun's study was designed to investigate methods of minimizing membrane fouling which could occur in membranes designed to purify water due to the presence of NOMs. The goal of his research was to develop a temperature sensitive membrane surface treatment which could be cycled through a hydrophilic state which would act to prevent foulants from reaching the membrane surface.

Stimuli-Responsive Nanocomposite Coatings for Mitigating Fouling of Water Treatment Membranes

Basic Information

Title:	Stimuli-Responsive Nanocomposite Coatings for Mitigating Fouling of Water Treatment Membranes
Project Number:	2011RI100B
Start Date:	3/1/2011
End Date:	2/28/2012
Funding Source:	104B
Congressional District:	RI-002
Research Category:	Engineering
Focus Category:	Treatment, Water Supply, None
Descriptors:	
Principal Investigators:	Geoffrey Bothun

Publications

1. Sneha Chede, Geoffrey D. Bothun and Isabel C. Escobar, 2012, Responsive Ultrafiltration Membranes Composed of N-Isopropylacrylamide, Superparamagnetic Iron Oxide Nanoparticles and Cellulose Acetate, to be presented at 2012 Annual Meeting of the American Institute of Chemical Engineers, Pittsburg, PA.
2. Hilfer, Thomas, Solute and Solvent Transport Through Nanoporous Ceramic Membranes, MS Thesis, Department of Chemical Engineering,University of Rhode Island, Kingston, RI 02881, 73 pages.

Stimuli-Responsive Nanocomposite Coatings for Mitigating Fouling of Water Treatment Membranes

Dr. Geoffrey D. Bothun
Department of Chemical Engineering
University of Rhode Island
203 Crawford Hall
Kingston, RI 02881
bothun@egr.uri.edu

PROBLEM STATEMENT AND RESEARCH OBJECTIVES

Polymeric membranes typically consist of a porous support layer that provides mechanical strength and stability, and which is covered by a thin selective layer or film responsible for providing the membrane with separation capabilities [1]. The thin selective layer, or skin, may contain surface functional groups such as carboxylic acid (anionic) or amine (cationic) that affect separation properties and can be used for further modification [2, 3].

Membrane replacement due to fouling is the single largest operating cost when membranes are used in water treatment applications [4, 5] and, thus, the greatest hindrance to the local, regional, and global use of membranes. Fouling, which is irreversible (adhesive) macromolecular adsorption, is due to specific intermolecular interactions between macroscale solutes present in the feed water and the membrane that occur even in the absence of filtration. These materials on the membrane surface, which cannot be removed by cross-flow operation, backflushing, or backpulsing, result in permanent flux decline and lead to fouling. Chemical cleaning can be effective, but it leads to downtime and the chemical agents (many toxic) must be thoroughly washed from the system and may be required to meet disposal guidelines. Many researchers agree that natural organic matter (NOM) is considered a major contributor to abiotic membrane fouling in water separation applications [2, 6-13]. NOM is composed of a variety of compounds that can be hydrophobic or hydrophilic. Thus, either hydrophobic or hydrophilic static membranes have been observed to foul. The underlying problem, which affects all current or future membrane-based water treatment processes, is to design a membrane or membrane coating that can prevent the adsorption of hydrophilic or hydrophobic foulants such as NOM, proteins, and microbes. This is daunting and requires the design of novel materials that can adapt to different operating conditions or respond to external stimuli.

Stimuli-sensitive polymers have been gaining attention in recent years due to the interest in the unique property that the polymer changes its conformation from a coiled state to a globular one in the presence of a stimulus [14]. The stimulus can be pH, temperature, ionic strength or electric or magnetic fields [15]. Which stimulus works best depends on the polymer. Some polymers are sensitive to multiple stimuli. The ability to control the expansion and collapse of polymer chains using external stimuli has led to the concept of using stimuli-sensitive polymer films as “gateways” to controlling the release of entrapped molecules, such as drugs, or particles [15]. When temperature is the stimulus, a temperature decrease in most polymer films causes them to expand into a hydrophilic state while a temperature increase causes them collapse into a hydrophobic state. The phase change arises from the existence of a lower critical solution

temperature (LCST) such that the polymer precipitates from aqueous solution as the temperature is increased. This behavior provides an advantageous approach for reducing fouling. Organic matter fouling is reduced in the expanded, hydrophilic state relative to the collapsed, hydrophobic state. By continuously activating the film, it is contended that a dynamic stimuli-responsive surface will prevent foulants from reaching the membrane surface, both to reject it from the feed water and to minimize fouling.

While they have shown significant promise, temperature-stimulated membranes or membrane films will suffer from two foreseen problems. First, using thermal heating to control separation is energy intensive and requires that the entire membrane housing and feed streams be heated. Second, the response time within the membrane is hindered during heating or cooling by the heat transfer resistances in the housing. These scenarios could both be eliminated if membrane heating was localized and intensified within the matrix or surface coating. *The ultimate goal of this is work is to develop a temperature sensitive membrane surface treatment that exhibits changes in adhesion properties (cycling between hydrophilic to hydrophobic) and mechanical structure (cycled thickness changes) in response to temperature changes. Heating within the treatment is sought by induction via AC electromagnetic fields (EMFs) using small superparamagnetic iron oxide (SPIO) nanoparticles (NPs) embedded within the treatment (**Figure 1**).*

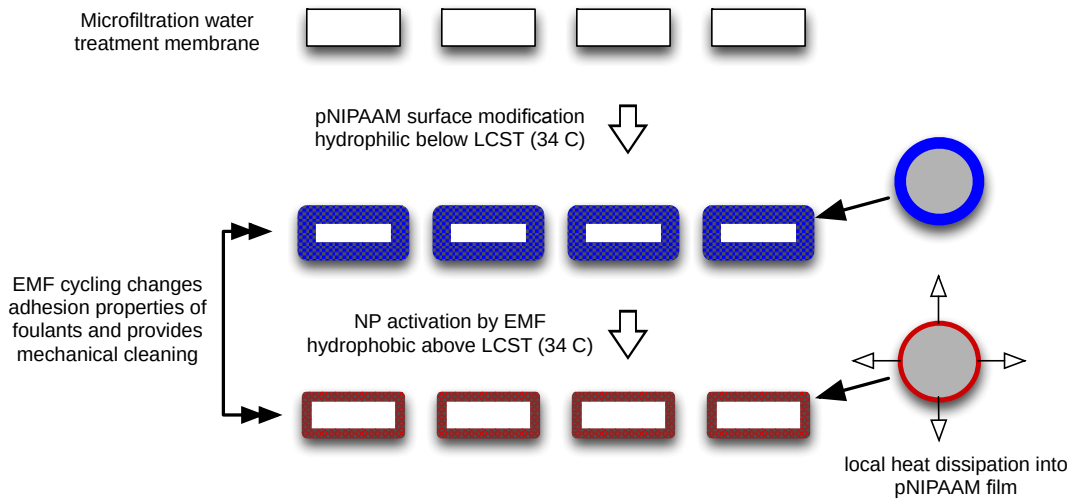


Figure 1. Proposed pNIPAAM membrane surface treatment containing embedded pNIPAAM-functionalized iron oxide nanoparticles.

This work is based on using poly(n-isopropylacrylamide) (pNIPAAM) as the surface treatment. pNIPAAM is a temperature sensitive polymer with an LCST of 34°C in water [15]. The unusual thermal behavior of NIPAAM is the abrupt transition (coil to globule) from a hydrophilic to a hydrophobic peripheral structure at the LCST with increasing temperature. A gel of pNIPAAM expels a large volume of free water as the balance between the hydrophilic (–CONH–) and hydrophobic ($–CH(CH_3)_2$) moieties is shifted. Below the LCST water is a good solvent for the polymer because the polymer-solvent interactions are stronger than the polymer-polymer interactions. Hydrogen bonds are bound to the hydrophilic moieties and the hydrophobic moieties are such that the polymer is in an extended coil conformation. The H-bonds between

water molecules and the amide groups make water molecules orient neatly around isopropyl groups. These structured water molecules act cooperatively to form a cage-like structure, which results in the pNIPAAM chains being hydrated and solublized in surrounding water. Above the LCST, the polymer-polymer interactions increase due to hydrophobic interactions, and at this point water is a poor solvent for the polymer. The pNIPAAM chains precipitate from water due to the dissociation of the hydrating water molecules [16]. The result is the aggregation and formation of compact globules as the hydrogen bonds are broken and water is expelled from the coils. A driving hypothesis of this work is that an AC EMF can be used to selectively heat the nanoparticles to manipulate pNIPAAM film thickness, roughness, and surface hydrophobicity as a means to reduce fouling (**Figure 1**).

METHODOLOGY AND MATERIALS

Successful preparation of NP-embedded pNIPAAM films requires that the NPs contain compatible surface chemistries with pNIPAAM. Hence, work conducted during this grant period focused on NP functionalization and characterization. The functionalization process is depicted in **Figure 2**.

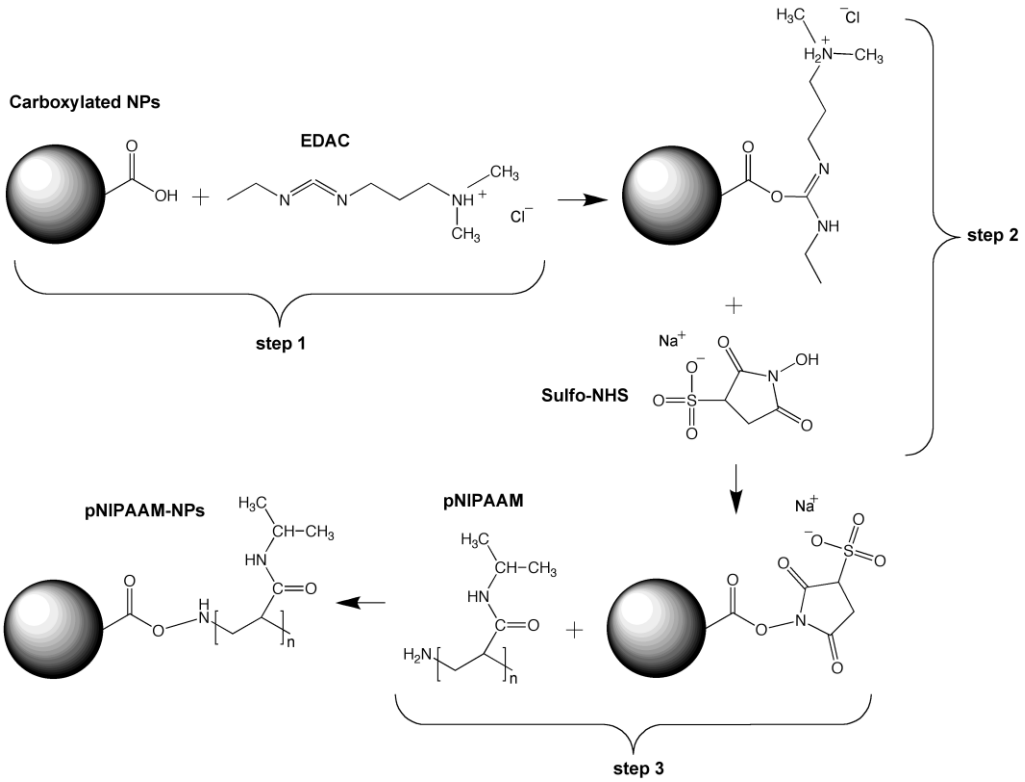


Figure 2. Reaction pathway for functionalizing SPIO NPs with pNIPAAM. Reaction conditions are provided in the text and summarized in **Table 1**.

A solution of 1-ethyl-3-(3- dimethylaminopropyl)carbodiimide (EDAC) + sulfo-N-hydroxysuccinimide was added to the nanoparticles to initiate surface activation (**Figure 2**, steps 1 and 2). The reaction occurred at room temperature for 10 minutes with continuous mixing. Coupling buffer and amine-terminated pNIPAAM was added to the solution allowed to react at

room temperature for 2 hours with continuous mixing (**Figure 2**, step 3). To stop the reaction, quenching solution mixed within the solution and the solution was incubated for 10 minutes at room temperature. pNIPAAM-NPs were collected from the solution via magnetic separation over 24 h at 4°C. After separation the liquid was aspirated from the tube using a pipette and the pNIPAAM-NPs were washed with buffer and then resuspend by mixing. Multiple separation/wash cycles were performed to remove unreacted compounds from the pNIPAAM-NPs. Preparation conditions are summarized below.

Table 1. Samples and sample preparation conditions.

Samples	**Condition/properties**
pNIPAAM	2.5 kDa, amine terminated
NPs	40 nm hydrodynamic diameter, carboxylic acid terminated
Sample A: pNIPAAM-NPs	Standard condition (0.5 mg/ml EDAC, 0.25 mg/ml NHS, 2 h reaction time)
Sample B: pNIPAAM-NPs	2x EDAC concentration from standard condition
Sample C: pNIPAAM-NPs	2x reaction time from standard condition

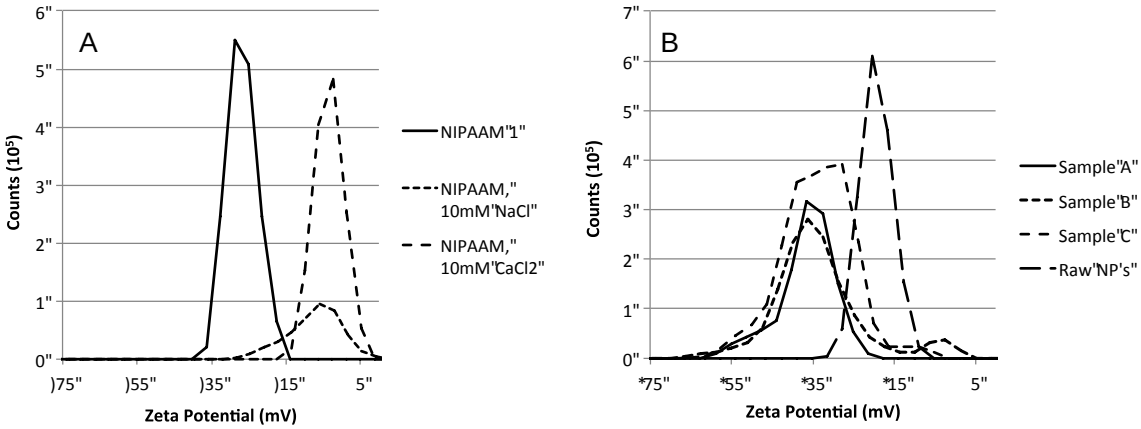
RESULTS

pNIPAAM, bare NPs, and pNIPAAM-NP samples were characterized by zeta potential and dynamic light scattering (DLS) measurements (**Figure 3**). Zeta potential relates to the surface charge of a macromolecule or NP in solution, and changes when molecules with a different charge adsorb or desorb from their surface. DLS was used to measure hydrodynamic diameter of macromolecules or NPs, which is also affected by the adsorption or desorption of molecules. These properties were used to assess pNIPAAM functionalization.

Zeta potential measurements for pNIPAAM alone (no NPs) indicate that the polymer was negatively charged in DI water (~ -30 mV) and the magnitude of the charge decreased in the presence of salts due to charge screening and ion binding. Comparatively, for NPs alone (no pNIPAAM) the zeta potential was also negative, but of a lesser magnitude than pNIPAAM in DI water (~ -18 mV). After pNIPAAM functionalization, the pNIPAAM-NP samples (Samples A, B, and C) exhibit a zeta potential close to that of pNIPAAM.

DLS results further confirm pNIPAAM grafting. NPs alone had a hydrodynamic diameter near 40 nm that was unaffected by temperature from 25°C to 45°C. In contrast, the hydrodynamic diameter of pNIPAAM-NPs was between 48 nm and 54 nm at 25°C, and decreased by roughly 8% as temperature was increased to 45°C. Comparing bare and functionalized NPs indicates that the pNIPAAM coating thickness was between 8 nm and 14 nm below the LCST (34°C) and between 5 and 10 nm above the LCST. This change is due to pNIPAAM collapse when transitioning from hydrophilic to hydrophobic. The fact that the pNIPAAM-NPs did not precipitate after going through the LCST suggests that the pNIPAAM packing on the NP surface is not tight enough to undergo a cooperative transition.

Based on DLS, pNIPAAM thickness was dependent upon reaction conditions. Doubling the EDAC or “activator” concentration (Sample B) led to the thickest pNIPAAM coating, followed by doubling the reaction time (Sample C), and then the standard condition.



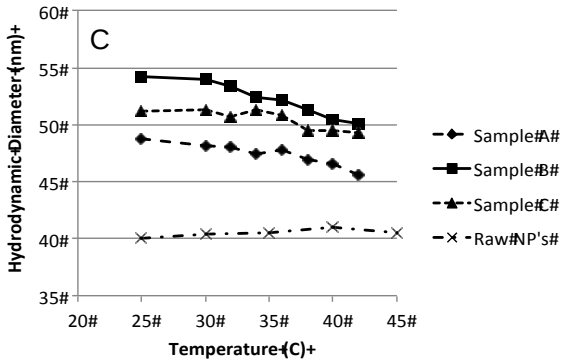


Figure 3. Surface modification of iron oxide nanoparticles with pNIPAAM. (A) Zeta potential, which depicts charge, of pNIPAAM in DI water and in the presence of Na and Ca salts. (B) Zeta potential of NPs and pNIPAAM-NPs. (C) Dynamic light scattering results for hydrodynamic diameter of NPs and pNIPAAM-NPs in DI water. Zeta potential and light scattering results confirmed pNIPAAM grafting on the NPs.

The ability to form pNIPAAM hydrogels with embedded pNIPAAM-NPs was examined. Without pNIPAAM-NPs, the hydrogels are clear and transparent. With pNIPAAM-NPs at 5, 10, and 15wt% (dry basis) the hydrogels are still transparent, but yellow in color due to the presence of iron oxide NPs (**Figure 4**).

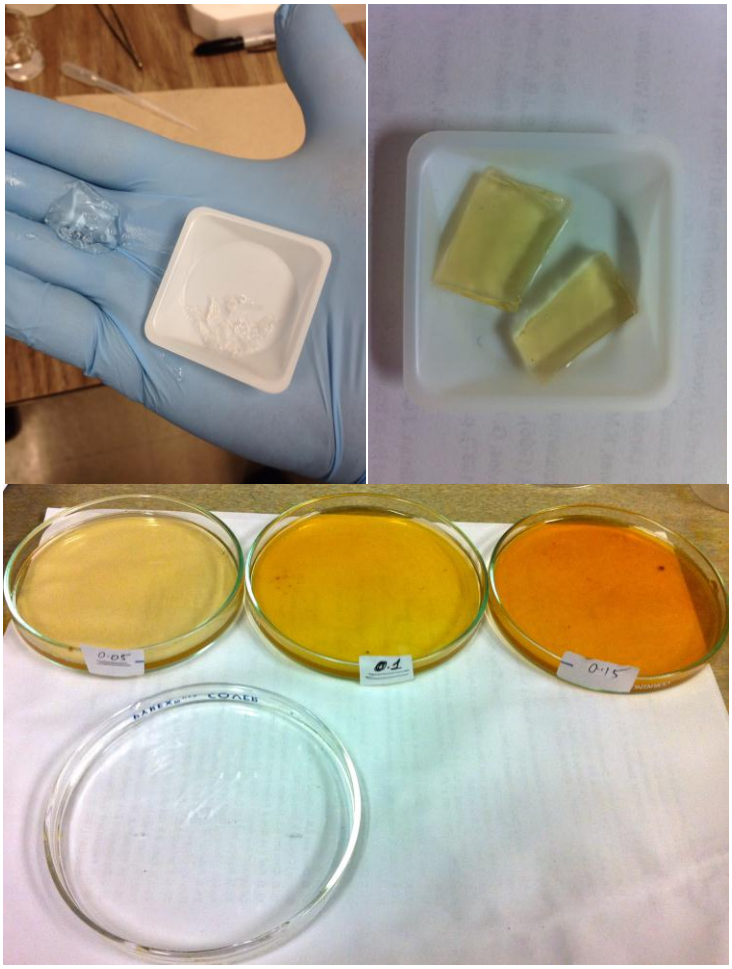


Figure 4. pNIPAAM hydrogels prepared without (top left) and with (top right, bottom) pNIPAAM-NPs at 5, 10, and 15 wt% NPs. Prepared in collaboration with Professor Isabel Escobar at the University of Toledo.

With the successful demonstration of pNIPAAM-NP embedment in pNIPAAM hydrogels, the next step is to prepare hydrogel surface treatments on commercial microfiltration membranes.

Additional Outcomes

- This work supported Mr. Thomas Hilfer during his M.S. work, which he successfully completed and defended in November 2011, and during the first semester of his PhD work (spring 2012).
- Results will be presented at the 2012 annual meeting of the American Institute of Chemical Engineers in Pittsburg, PA:
  Sneha Chede, Geoffrey D. Bothun, and Isabel C. Escobar, Responsive Ultrafiltration Membranes Composed of N-Isopropylacrylamide (NIPAAM), Superparamagnetic Iron Oxide (SPIO) Nanoparticles and Cellulose Acetate.

REFERENCES

1. Mallevialle, J., et al., *Membrane filtration in drinking-water treatment - a case story*. Influence and Removal of Organics in Drinking Water, ed. J. Mallevialle, I.H. Suffet, and U.S. Chan1992. 299-310.
2. Childress, A.E. and M. Elimelech, *Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes.* Journal of Membrane Science, 1996. **119**(2): p. 253-268.
3. Elimelech, M., W.H. Chen, and J.J. Waypa, *Measuring the zeta (electrokinetic) potential of reverse-osmosis membranes by a streaming potential analyzer.* Desalination, 1994. **95**(3): p. 269-286.
4. Wiesner, M.R., et al., *Cost estimates for membrane filtration and conventional treatment.* Journal american water works association, 1994. **86**(12): p. 33-41.
5. Escobar, I.C., et al., *Committee Report: Recent advances and research needs in membrane fouling.* Journal American Water Works Association, 2005. **97**(8): p. 79-89.
6. Hong, S.K. and M. Elimelech, *Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes.* Journal of Membrane Science, 1997. **132**(2): p. 159-181.
7. Nilson, J.A. and F.A. Digiano, *Influence of NOM composition on nanofiltration.* American Water Works Association Journal, 1996. **88**(5): p. 53-66.
8. Vrijenhoek, E.M., S. Hong, and M. Elimelech, *Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes.* Journal of Membrane Science, 2001. **188**(1): p. 115-128.
9. Escobar, I.C., S.K. Hong, and A.A. Randall, *Removal of assimilable organic carbon and biodegradable dissolved organic carbon by reverse osmosis and nanofiltration membranes.* Journal of Membrane Science, 2000. **175**(1): p. 1-17.
10. Escobar, I.C., et al., *Effect of solution chemistry on assimilable organic carbon removal by nanofiltration: full and bench scale evaluation.* Journal of Water Supply Research and Technology-Aqua, 2002. **51**(2): p. 67-76.
11. Hong, S.K., et al., *Biostability characterization in a full-scale hybrid NF/RO treatment system.* Journal American Water Works Association, 2005. **97**(5): p. 101-110.
12. Peng, W. and I.C. Escobar, *Rejection efficiency of water quality parameters by reverse osmosis and nanofiltration membranes.* Environmental Science & Technology, 2003. **37**(19): p. 4435-4441.
13. Peng, W.H. and I.C. Escobar, *Evaluation of factors influencing membrane performance.* Environmental Progress, 2005. **24**(4): p. 392-399.
14. Masci, G., L. Giacomelli, and V. Crescenzi, *Atom transfer radical polymerization of N-isopropylacrylamide.* Macromolecular Rapid Communications, 2004. **25**(4): p. 559-564.
15. Chen, H. and Y.L. Hsieh, *Dual temperature- and pH-sensitive hydrogels from interpenetrating networks and copolymerization of N-isopropylacrylamide and sodium acrylate.* Journal of Polymer Science Part A-Polymer Chemistry, 2004. **42**(13): p. 3293-3301.
16. Zhang, J.T., et al., *Preparation and properties of poly(N-isoproplyacrylamide)/poly(N-isopropylacrylamide) interpenetrating polymer networks for drug delivery.* Journal of Polymer Science Part A-Polymer Chemistry, 2004. **42**(5): p. 1249-1254.

Increasing sources of water supply: advanced treatment of stormwater runoff

Basic Information

Title:	Increasing sources of water supply: advanced treatment of stormwater runoff
Project Number:	2011RI97B
Start Date:	3/1/2011
End Date:	2/28/2012
Funding Source:	104B
Congressional District:	02
Research Category:	Engineering
Focus Category:	Water Quality, Water Quantity, Water Use
Descriptors:	
Principal Investigators:	Vinka Oyanedel-Craver, Vinka Craver

Publications

1. Kasaraneni, V., Boving,T., Eberle, D., and Oyanedel-Craver, V. (2012) Enhancement of stromwater runoff treatment through the amendment of natural soils. Environmental Progress and Sustainable Energy (in preparation)
2. Varun Kasaraneni, Vinka Craver. Porous Concrete Research Facility: Winter Performance and Enhancement of Pollutants Removal. 24th RI Transportation Forum, University of Rhode Island, Kingston, RI, October 28 2011.
3. Tom Boving, Vinka Craver, Leon Thiem, Varun Kasaraneni, Hui Chen, Laura Schifman. Rhode Island Storm Water Demonstration Facility. Discovery@URI. University of Rhode Island, RI. April 13, 2011.
4. Schifman, L.A., T.B Boving, V. Craver, V. Kasaraneni. Fate and Remediation of PAHs in Receiving Soils and Stormwater throughout the State of Rhode Island. Northeast Private Well Symposium. Southbury, CT. November 13-14 201.
5. Shifman, L.A.and T.B. Boving. 2012, Sorption Capacity of PAHs in Rhode Island Soils Along An Urban To Rural Gradient. Northeastern Geological Society of America meeting, Hartford, CT, March 18-20.

Increasing sources of water supply: advanced treatment of stormwater runoff

Vinka Craver
Department of Civil and Environmental Engineering.
University of Rhode Island
Bliss Hall 213
Kingston, RI 02881

ABSTRACT

A technique for enhancing the containment of polycyclic aromatic hydrocarbons (PAHs) in pervious pavement systems was developed through the chemical modification of a typical Rhode Island glacial outwash soil using two different approaches. The first method was direct modification of the soil using quaternary ammonium cations (QAC) through ion exchange process. The second method of modification was blending Rhode Island glacial outwash soil with a commercial organoclay. These modifications successfully increased the fraction of organic carbon (F_{OC}) in the Rhode Island glacial outwash soil by at least 70%. To quantify the capabilities of these amended soils to sorb PAHs, a series of batch isotherms and column experiments were conducted on unmodified and modified soils. The isotherm coefficients K_d, α, K_f , N calculated from batch studies were higher when compared to column experiments. Batch and column studies demonstrated that increasing soils F_{OC} using the synthetic modification enhanced soils ability to sorb PAH up to 20 folds depending of the modification used. The organoclay-glacial outwash blend exhibited the greatest K_f value of 114.2. Break Through Curves (BTCs) obtained using HYDRUS 1D were compared with measured BTCs. The column experiments conducted on concrete and aggregate showed that there was very little contribution to the containment of PAH in pervious pavement systems. The results of this study provide evidence that the advance treatment of stormwater water runoff is feasible and therefore the treated water could be used to recharge groundwater sources of drinking water

KEYWORDS: stormwater runoff, advance treatment, PAH

INTRODUCTION

Better integrated management of the urban water cycle (supply, wastewater and stormwater) is needed if the water needs of the expected population are to be met without further deterioration of the environment. A focal point of proposed national water conservation programs is the recycling urban stormwater for residential use.

Previous water recycling studies have considered different sources, such as roof runoff (Gardner et al., 2001), wastewater (Davison, 2001), and combined sewer systems (Field et al., 2000), have focused on geographically small areas (Argue and Pezzaniti, 1999), or on a single type of recycling such as for irrigation or infiltration purposes only (Al-Hoti and Abdullah, 1989). While there is plenty of literature relevant to both wastewater and rainwater recycling, at this stage there is little on the subject of general urban runoff recycling (such as parking lots). Most readily accessible literature is specific to particular stormwater recycling schemes (Dallmer, 2002) most of them oriented to industrial water consumption.

Due to the growing needs for storm water harvesting, some novel concepts are emerging that may enhance the potential for application of storm water harvesting systems across a greater range of situations. One such technology is based on the proven concept of porous pavement, which has been used for decades in storm water flow and pollution management. Traditional design

of a porous pavement system consists of a porous surface overlaying a filter layer that is placed on top of a sub-base. The porous surface can be modular (unbound individual and nonporous blocks, laid down with gaps in between) or monolithic (asphalt or concrete without fine aggregate). The sub-base may contain a collection pipe for drainage. The systems are usually installed in car parks and sections of streets with low traffic volume.

In some countries, porous pavements have been widely used for control of storm water (Newton et al., 2003). They have infiltration capacities usually upward of 4500 mm h^{-1} when new. Reductions in annual runoff coefficients from around 0.95 for normal pavement to around 0.4 for porous pavement are typical, with many authors reporting even greater reductions (Pratt et al., 1995). Consistent water quality performance has been observed from porous pavers, with reductions in total suspended solids, total P, and total N of around 80, 65, and 60%, respectively, and hydrocarbon and metal reductions commonly around 85 and 75%, respectively (Pratt et al., 1995; Pagotto et al., 2000). Early perceptions of clogging and structural problems have hindered the adoption of porous pavement. It has been shown that most systems are not very prone to clogging, with localized problems being relatively easy to fix. Studies show after 15 to 20 yr of operation, they provide high infiltration rates (100–1000 mm h^{-1}) (Pratt et al., 1995; Davies et al., 2002; Pratt et al., 1981). These systems are rather inexpensive and suitable for densely populated areas where other storm water treatment systems are usually not applicable.

This research will study a series of advance treatment technologies to enhance the removal of contaminant of concerns in pervious pavement facilities to reuse the effluent in residential settings. We propose to improve sorption/biodegradation of polyaromatic hydrocarbons using a two-stage approach: (1) amending the porous matrix of the pervious systems and (2) advance post treatment

2. Methods and Materials

Naphthalene, Fluorene and Acenapthene (purity grade of 98% or higher) were obtained from Aldrich Inc. Dichloromethane and methanol were analytical grade obtained from Fisher Scientific. All solutions were prepared using deionized water free of detectable traces of PAHs and pH near neutral. Two gas chromatograph equipments were used: a Shimadzu GC-17A Gas Chromatograph with Flame Ionized detector and a Shimadzu GC-MS QP2010. Only glass vessels were used for all experimentation containing PAH. Care has been taken to prevent any photo degradation during all the experiments.

The PAH saturated solutions were prepared following a method described by Wang et al. (2005). In brief, PAHs were dissolved in 1 mL of dichloromethane in 4 L Erlenmeyer flask. As the solvent volatilized a thin crust of PAH was left securely attached to the glass bottom. The flask was filled to the top with deionized water and allowed to saturate for one week.

2.1 Materials

A bulk sample of typical Rhode Island glacial outwash soil was collected at URI's soil sampling pits at Peckham farm. The soil is fully dried and sieved through a number 10 sieve (2.0 mm) and was autoclaved for 30 minutes to prevent the bacterial degradation of any compounds being studied. The aggregates used were ASTM C 33, Size No. 67 (3⁄4 in. to No. 4)obtained from Cherenzia excavation in Rhode Island. In addition, Portland type II cement was used. Pervious concrete mix typically used in parking lots was prepared following techniques mentioned in Bradley J. Putman et al (2011). The pervious concrete prepared had a void content of 15%-18% which is typical for this type of systems (Tennis, 2004).

2.2 Material Characterization

The cation exchange capacity (CEC) of the soil was determined by the Soil, Water, and Plant Testing Laboratory at Colorado State University. A characterization of the soil particle size distribution was conducted on all modified and unmodified soils by sieve and hydrometer analysis using ASTM 136 and 152 H methods (Das, 2009).

Hydraulic conductivity of the concrete, aggregate and soils was determined using falling head permeameter method. To obtain the permeability rate of the Aggregate, Pervious concrete, soil blend, HDTMA, and BHDH, the equation for falling head method.

2.2 Soil Modification

Hexadecyltrimethyl ammonium chloride (HDTMA) and Benzyldimethylhexadecyl ammonium chloride (BHDH) were the cations chosen for direct modification because longer alkyl chains contain more carbon therefore enhancing organic carbon in soil. Equation developed by Boyd was used to determine the mass of QAC with respect to mass of soil and CEC (Boyd et al., 1988). The wet method used by Breakwell et al. (1995) has been followed for soil modification. To summarize, a known amount of QAC obtained from Boyd's equation for 100 grams of 100% modified soil was dissolved into 400 mL of deionized water using a stir bar and glass beaker. Soil was mixed into the QAC solution and placed on a shake plate for 3 days at 150 rpm in an incubator at 20 °C. Contents of the glass beaker carefully decanted after settling and soil was placed into the oven for 6 hours at 100° C to dry the soil without burning off any organic carbon. The residual chloride ions were removed through a thoroughly rinsing process. The effluent decantation samples were measured with an electrical conductivity meter to be certain the chloride anions were thoroughly washed away. Once dried the modified soils and PM-199 were analyzed with a Carlo Erba EA1108 Carbon Hydrogen and Nitrogen analyzer to quantify the amount of carbon

The second approach for enhancing the soils natural carbon was to amended the soil by adding the commercial organoclay PM-199 produced by CETCO Oil Field Services. To keep a point of reference in isotherm and column experiments, the commercial organoclay was blended with the glacial outwash to match the total mass of organic carbon in BHDH which resulted in 1:18 ratio of commercial organoclay and RI glacial outwash.

2.3 Sorption Isotherms

A series of batch isotherms were run for all sorbent media. To study the static interaction between soil and aqueous naphthalene, a constant mass of the particular sorbent media being studied was exposed at increasing concentrations of aqueous naphthalene solution. Kinetic investigation showed an equilibrium time of 30 hours therefore to ensure equilibrium conditions the isotherms tests were carried out for 48 hours the samples were continuously mixed at 20 °C. After the 48 hours, all samples were centrifuged for 10 minutes at 2500 rpm to remove any particulate sorbent so the aqueous naphthalene concentrations could be extracted and analyzed. EPA 610 method of PAH protocol analysis was followed for liquid-liquid extraction. Langmuir linearization was applied for unmodified glacial outwash. The Langmuir equation (equation 1) was used to model sorption data for glacial outwash and Freundlich equation (equation 2) was used to model the sorption data with nonlinear regression for modified soils.

$$\frac{Cs}{Ce} = \frac{1}{\alpha\beta} + \frac{Cs}{\beta} \qquad [1]$$

$$C_s = K_f C_e^n \qquad [2]$$

C_e is the concentration of naphthalene in solution in equilibrium with the mass of solute sorbed to onto the sorbent [mg/L]; C_s is the mass of naphthalene sorbed per dry unit weight of sorbent [µg/g]. α is a Langmuir adsorption constant related to the binding energy; and β is the Langmuir maximum amount of naphthalene that can be absorbed by the sorbent; n is the unitless Freundlich linearity exponent; and K_f is the Freundlich sorption coefficient.

2.4 Column Experiments

Column experiments were conducted to study the sorption and desorption of PAHs. For concrete and aggregate glass columns (length: 15.0 cm, ID: 8.5 cm) were used. Glass columns (length: 5.0 cm, ID: 2.5cm) were used for soil. Concrete and aggregate columns were connected to Masterflex L/S pump with Teflon tubing. The columns packed with soil was connected to an Accuject Series I injector pump with Teflon tubing. Conservative tracer tests with sodium chloride NaCl were performed to determine column parameters including pore velocity and dispersion coefficient. After determining column intrinsic parameters, an aqueous solution saturated with PAHs was pumped through the columns, samples were collected until break through. Once fully broken through the influent pumping port was switched to pump deionized water to observe desorption. The pumping of deionized water continued until at least 90% of the PAH pumped in was recovered. This same procedure was repited for concrete, aggregate and all soil media. This allowed for the comparison of PAH breakthroughs for all tests. The flow velocities were held constant at 2 mL/min for soil columns and 20 mL/min for concrete and aggregate columns.

2.5 HYDRUS 1D

The HYDRUS-1D, version 4.14 software was used to stimulate solute transport through unmodified and modified soils. Parameters obtained from sorption Isotherms, soil characterization and column experiments were used to predict the BTCs for naphthalene in unmodified and modified soils. (Jaehoon Lee et al 2002). HYDRUS-1D was also used to estimate the adsorption coefficient from column experiments using inverse solution. The inverse procedure uses the Levenberg–Marquardt nonlinear parameter optimization method. The data obtained from column breakthrough experiments were used for estimation of adsorption isotherm coefficients.

2.6 Experimental methodology

The experimental methodology followed was divided in two phases. First phase was the evaluation of the effectiveness of the organic modification in RI soil which involves batch isotherms and column experiments using naphthalene. Naphthalene is chosen as it is found in higher concentrations in storm runoff and its aqueous solubility is higher when compared to other PAHs. The best amendment outcome among the modified soils was selected based on the retardation factor and ability o retain naphthalene. The second part was the assessment of PAHs retaining capabilities of a model pervious pavement with and without the modified soil media. This was done performing column experiments on concrete, aggregate, RI glacial outwash and glacial outwash-organoclay blend. Acenaphthene and Fluorene which are higher molecular weight (3-ring) PAHs and commonly found in storm runoff were used as model PAHs for this experimental phase

.

3. Results and Discussion

3.1 Evaluation of the effectiveness of the organic modification in RI soil.

3.1.1 Soil Characterization and Modification

A CEC of 5.6 milli-equivalents of exchangeable cations per 100 grams of glacial outwash soil (meq/100g) was measured and reported by Colorado State University. These results were consistent with the CEC values determined in a previous study by Wright et al (1998) for Rhode Island soils. The results from the soil modification, the particle size analysis and hydraulic conductivity are shown in Table 1.

Table 1 Soil Organic Carbon, Particle Size, and Hydraulic Conductivity Properties

Soil Type	F_{oc} *[%]*	F_{oc} Increase *[%]*	D_{10} *[mm]*	Uniformity (U)	Porosity (n)	Hydraulic Conductivity (K) *[cm/s]*
Unmodified Glacial outwash	1.70	--	0.070	9.286	0.54	1.93E-03
HDTMA	2.90	70.6	0.030	13.333	0.504	6.73E-04
BHDH	2.94	72.9	0.040	12.500	0.56	8.33E-04
Blend	2.94	72.9	0.090	6.667	0.52	2.93E-03

F_{OC}= Fraction of Organic Carbon; D_{10} =effective size;

Quaternary ammonium cations successfully increased the fraction of organic carbon in a Rhode Island glacial outwash soil. The modifications increased the fraction of organic carbon for both HDTMA and BHDH direct modifications by 70.6% and 72.9% respectively. The magnitudes of the hydraulic conductivities for all soils studied concurred with previous characterization of glacial outwash by Wright and Sautter, (1988). The chemical modification reduced the hydraulic conductivity of the soil media in all cases. This occurred as a function of the decreasing effective size (D10) and porosity. Oppositely, adding the PM-199 sorbent to the unmodified soil increased the effective size of the blend while decreasing the uniformity coefficient. A material with increased hydraulic conductivity, such as the organoclay-glacial outwash blend will be best suited for application below permeable pavement because it will aid in faster drainage of stormwater.

3.1.2 Sorption Isotherms

Kinetic investigation revealed an equilibrium time of 30 hours (data not shown). These kinetic equilibrium results were consistent with prior research (Bayard et al., 2000; Reible *et al*., 2010). To be certain equilibrium between sorbed and aqueous naphthalene concentration was reached the isotherms were carried out for 48 hours. The isotherms results for the glacial outwash seemed to better fit the Langmuir model in which limited number of sorption sites are available and can be fully saturated during isotherm experimentation. This was a result of the glacial outwash's small fraction of organic carbon and the large amounts of naphthalene in solution. The Langmuir fit for glacial outwash is consistent for with what others have found for porous media with limited organic matter and naphthalene concentrations exceeding 10% of aqueous solubility (Appert-Collin *et al*., 1999). Correlation coefficients values, R^2, of the glacial outwash Langmuir fit were 0.997 compared to the Freundlich fit of 0.886. Therefore, the Langmuir fit was adopted for the glacial outwash data series. Figure 1a shows the result of the naphthalene-soil isotherm experiments for glacial outwash.

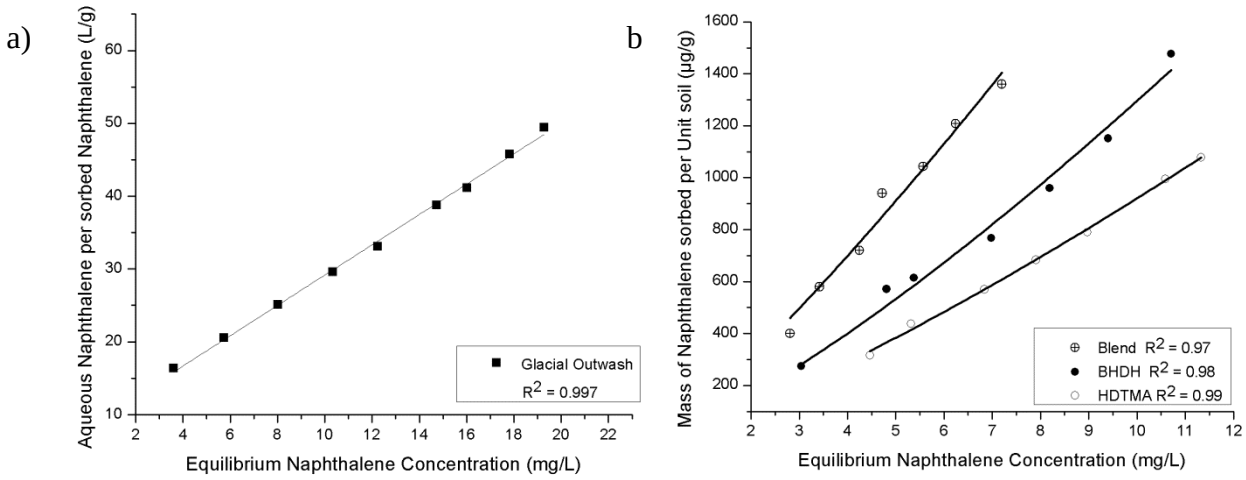


Figure 1: Isotherms for the sorption of naphthalene. a) Langmuir Isotherm Linearization for Glacial Outwash Soil b) Nonlinear fit Freundlich Isotherm for Modified Soils. Origin data analysis software was used for fitting. Freundlich Model power fit was used to obtain

Freundlich Isotherm constants.

The maximum amount of naphthalene that can be sorbed by the glacial outwash, β, was determined to be 0.48 mg naphthalene / g soil. The adsorption constant related to binding energy α was 0.24 L/g. The predicted α from column experiments is 0.18 L/g. Increasing soils F_{oc} enhanced soils ability to sorb naphthalene in all cases.

Figure 1b shows the Nonlinear Freundlich isotherms for modified soils. All modified soils were fit with Non-linear Freundlich model, indicating that during isotherms experiments the potential naphthalene sorption sites were not exhausted. The Freundlich power trendline fit the data with an R^2 higher than 0.98 for all cases. Freundlich Constants of modified soils are displayed in Table 2. The K_f value increased with increased organic carbon in soils. This means for all modified soils the increased fraction of organic carbon led to increased naphthalene sorption.

Table 2: Freundlich sorption parameters from batch and column studies of modified Soils

	Batch Isotherm			Column study	
Soil	**K_f**	**N**	**R^2***	**K_f**	**N**
HDTMA	36.9	1.23	0.99	5.5	1.58
BHDH	54.3	1.28	0.98	19.3	1.04
Blend	114.2	1.18	0.97	89.9	1.12

*R^2 is coefficient of determination for Freundlich power trendline fit

Out of the modified soils the organoclay-glacial outwash blend (1:18 ratio) exhibited the greatest K_f value of 114.2. A Freundlich fit suggested that there was no upper limit for sorption in the range that the experiments were performed. In reality there will be an upper limit of naphthalene sorption however; this limit was not reached for modified soils during at the experimental conditions used in this study. This means for all modified carbon enhanced soils the increased fraction of organic carbon led to increased naphthalene sorption

3.1.3 Column Experiments with unmodified, organically modified and blended RI glacial outwash soils

Conservative tracer experiments performed for each column using sodium allowed for the determination of intrinsic column parameters including pore volume, pore water velocity, and dispersion coefficients. These parameters are shown in Table 3.

Table 3 Column Intrinsic Parameters and Naphthalene Retardation

Soil	Pore Volume *[cm3]*	Bulk Density *[g/cm3]*	Velocity *[cm/min]*	Dispersion *[cm2/min]*	Retardation factor *graphical*	Retardation factor *CXT fit*
G. O*	13.23	1.43	0.75	0.6	52	54.3
HDTMA	12.37	1.58	0.96	0.77	70	76
BHDH	12.75	1.45	0.82	0.73	319	304
Blend	13.75	1.15	0.76	0.26	438	408

Retardation factor obtained from breakthrough curve plotted in the unitless terms of relative concentration (C/Co) and pore volumes (PV). * G.O Glacial outwash. **

Observed and predicted Naphthalene BTCs are plotted in the dimensionless term of relative concentration (C/Co) and time (min) are shown in Figure 2.

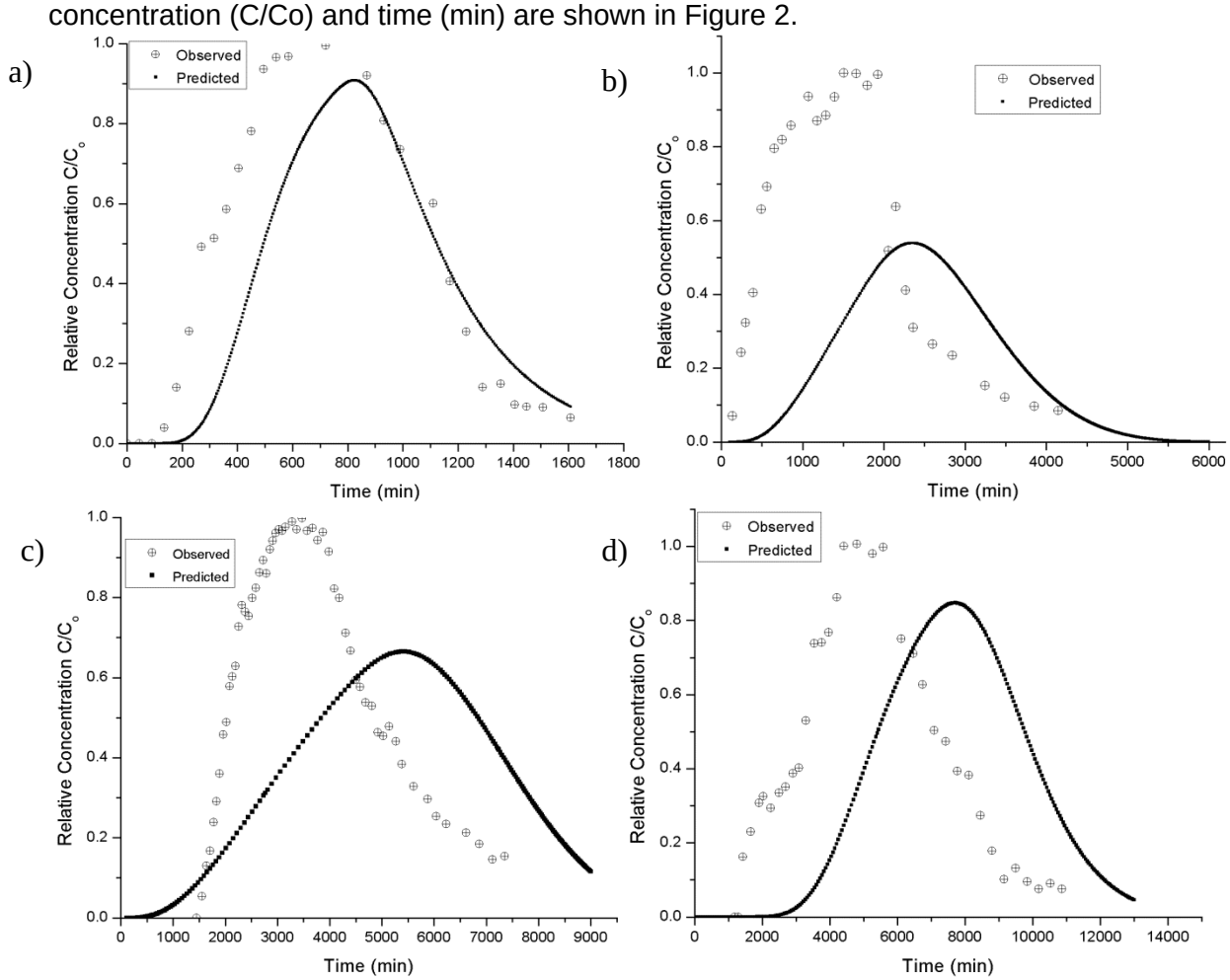


Figure 2: Observed and Predicted BTCs of Naphthalene for a) RI Glacial Outwash b) HDTMA modified soil c) BHDH modified soil d) Blended modified Soil. The injected naphthalene concentrations were 30±2mg/l and flow rates were maintained at 2ml/min. Desorption experiment started once the relative concentration reached 1.

Column experiments supported the results obtained from the batch isotherms. Naphthalene was

retarded when pumped at solubility through a column of sorbent. Unmodified glacial outwash soil had the fastest breakthrough and lowest retardation factor of 52. These results are consistent with the outwash having the lowest F_{oc} and being fitted with the finite sorption site Langmuir model. Out of the modified soils fitted with Freundlich isotherm model the HDTMA soil had the lowest retardation factor 70. This retardation correlates with HDTMA also having the lowest K_f of the modified 36.9. The breakthrough of BHDH modified soil showed a significant reduction of the naphthalene's movement through the column therefore increasing its retardation to 319. HDTMA and BHDH had very similar FOC values at 2.90% and 2.94% respectively. However, the Freundlich sorption constant for the BHDH was higher than the HDTMA value. One explanation for the difference in batch and column sorption between these two sorbents is the presence of the benzyl group in the BHDH. These results are consistent with what other studies have found regarding organic contaminants sorbing to QAC modified sorbents containing benzyl groups (Smith et al., 1990). The column that exhibited the greatest retardation of naphthalene was the blended commercial organoclay-glacial outwash material. This sorbent retarded naphthalene by R = 438. This correlates with the blended material having the largest K_f of 114.2.

The HYDRUS predicted BTCs using Isotherm coefficients compared poorly with the measured BTCs. The adsorption isotherm coefficients predicted (Table 2) using HYDRUS inverse solution for column experiment data are also lower than the values from batch experiments. Maraqa et al. (1998) also reported that their batch study overestimated coefficients of benzene and dimethylphthalate compared with the results from column study. The Langmuir coefficients predicted from column experiments for glacial outwash are in close agreement with isotherm coefficients. The *f* (fraction of type 1 adsorption sites at which sorption is assumed to be instantaneous was set to 1 and α (first order rate constant) was set to 0 for the calculation of BTCs and inverse solution. The chemical non equilibrium (adsorption-desorption process) and physical non equilibrium (possible heterogeneity of soil) were not accounted an this could be one of the reasons for the poor prediction of BTCs. Lee et al (2002) encountered similar problems as their predicted BTCs did not match with measure BTC for naphthalene. The batch isotherm determined parameters representing equilibrium conditions while the column determined parameters represent dynamic and non-equilibrium sorption and transport conditions.

3.2 Efficacy of organically modified soils in pervious pavement system

The contributions of the various components of pervious pavement systems retaining different molecular weight PAHs were determined through the column experiments. The sorption and desorption results for acenaphthene and flourene from column experiments on concrete and aggregate are shown in Figure 3a, b. Both acenaphthene and flourene has retardation factor of R_f =1 for concrete indicating that there was no retardation which implies that pervious concrete has very little sorption capacity for PAH containment. For the aggregate, acenaphthene had a retardation factor of R_f = 11 and flourene the retardation factor was R_f = 7. The aggregate showed higher sorption capacity for PAH than concrete but when compared to soil its performance was lower. As expected these results indicated that concrete and aggregate have very little sorption capacity of PAHs. The high porosity and hydraulic conductivity rerults in low residence time preventing adsorption to happen. In addition, concrete and aggregate contain very low organic matter in their composition then PAH partitioning to organic carbon can not occur (Brändli et al., 2008; Cornelissen et al., 2006; Jonker and Koelmans, 2002). The results of the column experiments are shown in Table 4.

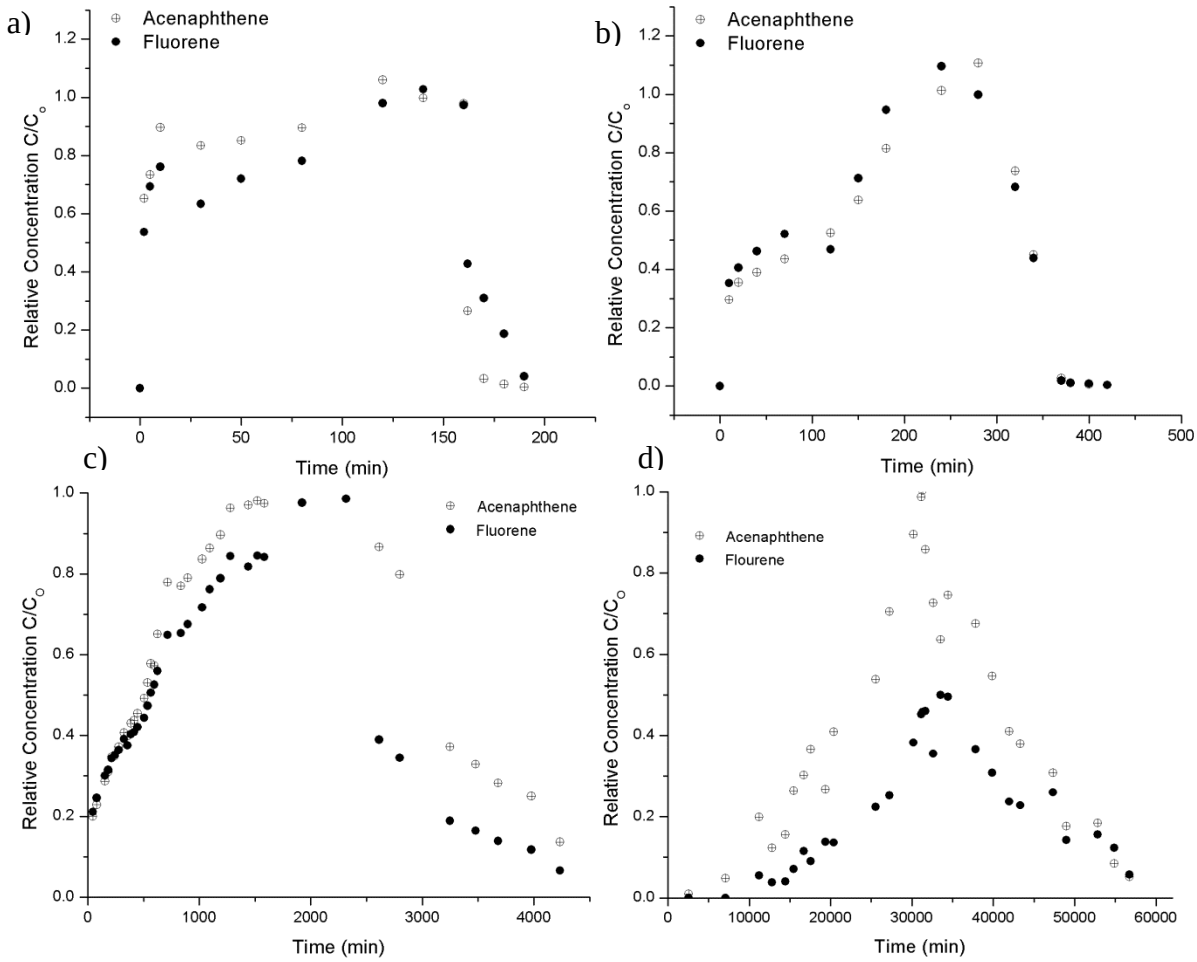


Figure 3: BTCs of Acenaphthene and flourene in Column Experiments for a) Concrete b) Aggregate c) RI glacial outwash.d)Blend of organo clay-glacial outwash Desorption experiment started once the relative concentration reached 1. The influent concentrations of Acenaphthene and fluorene were 1.6±0.2mg/l and 0.6±0.2mg/l respectively.

The glacial outwash has shown very little retardation for PAHs. The results show there is a very little retention of PAHs in pervious concrete pavement systems. The column experiment on the Blend of organoclay-glacial outwash with higher molecular weight PAHs also reiterated that increasing fraction of organic carbon increases the PAH sorption capacity of the soil which was supported by retardation factors of 4,985 for acenaphthene when compared to 16.5 for glacial outwash soil. Retardation of fluorene was not calculated, as during the breakthrough experiment for organo clay-glacial outwash blend column acenaphthene first broke through.

Table 4: Column Intrinsic Parameters and Retardation factors

	ρ [g/cm3]	P.V [cm^3]	Porosity	Dispersion *[cm2/min]*	Acenaphthene R_f	Flourene R_f	K *[cm/s]*
Concrete*	2.4	190	0.17	47.6	1	1	9 E-02
Aggregate*	1.8	380	0.45	10.3	11	7	11.7 E-02
Glacial** outwash	1.82	11.43	0.46	0.72	16.5	18.2	1.93E-03
Blend**	1.86	10.18	0.41	0.31	4125.6	-	2.87E-03

ρ is bulk density, P.V is pore volume, R_f is Retardation factor * The volume of concrete and aggregate columns were 850 cm^3 ** Column volume is 24.5 cm^3

After flushing several hundred pore volumes of PAH saturated water, the modified soil media removed a considerable fraction of PAH. Thus, modified soil media such as blend of organoclay and glacial outwash could have great potential applications BMPs for rthe eduction of contamination in roadway runoff, thereby reducing contaminant flux into surface or ground water. Incorporating a modified layer of organo clay-glacial outwash blend in pervious pavements could contain PAH from entering in to surface and ground water with the additional advantage of increasing the hydraulic conductivity if the soil. However, cost is an important factor when incorporating an additional layer of this amendment into permeable pavement design. Commercial organoclay is also expensive with costs ranging between one to two dollars per pound.

5. Conclusions

The adverse effects of contaminants commonly present in storm runoff water can be minimized using BMPs, such as pervious pavement systems. However, the results of this study demonstrated that pervious pavement systems with concrete, aggregate and unmodified soil have little capacity to retain PAHs from the aqueous phase. Modification of glacial outwash using QAC increased the fraction of organic carbon in the soil. The modification also enhanced the sorption capacity of the soils. The use of pervious pavement systems enhanced with modified media could increase the PAH containment in storm runoff up to 20 folds. The modified media may also have the potential to retain other contaminants in storm runoff.

References

Kadurupokune, N., and N. Jayasuriya (2009). Pollutant load removal efficiency of pervious pavements: is clogging an issue? Water science and technology., 60, 1787–1794.

Luck, J. D.,. Workman S. R., Coyne M. S., Higgins S. F., (2008). Solid material retention and nutrient reduction properties of pervious concrete mixtures. Biosystems Engineering., 100, 401–408.

Luck, J. D., Workman S. R., Coyne M. S., Higgins S. F., (2009). Consequences of manure filtration through pervious concrete during simulated rainfall events., Biosystems Engineering.,102, 417–423.

Abbate, C., Arena, M., Baglieri, A., Gennari, M. (2009). Effects of organoclays on soil eubacterial community assessed by molecular approaches., Journal of Hazardous Materials., 168, 466–472.

Ronald, M. Atlas., (1981). Microbial Degradation of Hydrocarbons: An Environmental Perspective., *Water Science and Technology*., 32, 49-56.

Lucilene, Betega de Paiva, Morales A. R., and Díaz F. R. V., (2008). Organoclays: Properties, preparation and applications., Applied Clay Science., 42, 8-24.

Boving, T. B., and Zhang, W., (2004). Removal of aqueous-phase polynuclear aromatic hydrocarbons using aspen wood fibers. Chemosphere. 54, 831-839.

Boyd, S.A., Mortland M.M., and Chiou C.T., (1988). Sorption characteristics of organic

compounds on hexadecyltrimethylammonium-smectite. Soil Science Society of America Journal 52, 652-657.
Brattebo B. O., Booth, B. D.,(2003). Long-term stormwater quantity and quality performance of permeable pavement systems. Water Research 18, 4369–4376.
Brändli, R.C., Hartnik, T., Henriksen, T., and Cornelissen G., (2008). Sorption of native polyaromatic hydrocarbons (PAH) to black carbon and amended activated carbon in soil. Chemosphere. 73, 1805-1810.
Gobel P., Dierkes C., Coldewey W.G., (2007). Storm Water Runoff Concentration Matrix for Urban Areas. Journal of Contaminant Hydrology 91, 26-42.
Hoffman, E. J., Mills G. L., Latimer J. S., and Quinn J. G., (1984). Urban Runoff as a Source of Polycyclic Aromatic Hydrocarbons to Coastal Waters. Environ. Sci. Technol.. 18, 580-587.
Breakwell, Iain K., John Homer, Monique Lawrence, and McWhinnie. "Studies of Organophilic Clays: The Distribution of Quaternary Ammonium Compounds on Clay Surfaces and the Role of Impurities." *Polyhedron*. 14.17 (1995): 2511-2518.
Bureau of Transportation Statistics, BTS, (2007) "Number of U.S. Aircraft, Vehicles, Vessels, and Other Conveyances." *Bureau of Transportation Statistics*. May 8, 2010.
Cornelissen, Gerard , Gijs D. Breedveld, Stavros Kalaitzidis, Kimon Christanis, and Anne Kibsgaard. "Strong Sorption of Native PAHs to Pyrogenic and Unburned Carbonaceous Geosorbents in Sediments." Environmental Science and Technology. 40.4 (2006): 1197–1203
Das, Braja M. Soil Mechanics Laboratory Manual. 7th. New York: Oxford University Press, 2009. 17-36.
Eisler, Ronald. "Polcyclic Aromatic Hydrocarbon Hazard to Fish, Wildlife, and Invertabrates: A Synoptic Review." Patuxent Wildlife Research Center Contaminant Hazard Reviews. 1.11 (1987): 1-55.
Jonker, Michiel T. O., and Albert A. Koelmans. "Sorption of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls to Soot and Soot-like Materials in the Aqueous Environment: Mechanistic Considerations." *Environmental Science and Technology*. 36.17 (2002): 3725–3734.
Joneck, M., Prinz, R., 1996. Organische und anorganische Schadstoffe in straßennahen befahrener Verkehrswege in Bayern. Wasser und Boden 48, 49–54 (Berlin).
Jaehoon Lee, Lakhwinder S. Hundal, Robert Horton, and Michael L. 2002 Thompson Sorption and Transport Behavior of Naphthalene in an Aggregated Soil Journal of Environmental Quality 31:1716–1721 (2002).
Mittal, Menka , and Karl J. Rockne. "Naphthalene and phenanthrene sorption to very low organic content diatomaceous earth: Modeling implications for microbial bioavailability ." *Chemosphere*. 74.8 (2008): 1134-1144.
Mumtaz, M., George, J. "Toxilogical Profile of Polycyclic Aromatic Hydrocarbons." *Public Health Service Report*. Atlanta, GA: U.S. Department of Health and Human Services, 1995.
Newman, A.P., Pratt, C.J. Coupe, S.J. and Cresswell, N. (2001), *Oil Bio-Degradation in Permeable Pavements by Inoculated and indigenous Microbial Communities*, NOVATECH 2001, School of Science and the Environment, Coventry University, UK.
Odong, Justine. "Evaluation of Empirical Formulae for Determination of Hydraulic Conductivity based on Grain-Size Analysis." *Journal of American Science*. 3.3 (2007).
Oros, Daniel R, John R.M. Ross, Robert B. Spies, and . "Polycyclic Aromatic Hydrocarbon (PAH) Contamination in San Francisco Bay: A 10-year Retrospective of Monitoring in an Urbanized Estuary." *Environmental Research*. 105.1 (2007): 101-118.
Pratt, C.J., A.P. Newman, and P.C. Bond, (1999), “Mineral Oil Bio-degradation within a permeable pavement: long term observations,” *Water Science and Technology* , v. 39, p. 103-109.
Smith, James A. "Effect of Ten Quaternary Ammonium Cations on Tetrachloromethane Sorption to Clay from Water." *Environmental Science and Technology*. 24.8 (1990): 1167-1171.
Spark, D.L., (ed). 1996. Methods of Soil Analysis: Part 3. Chemical Methods Ref. 2, pp. 1201-12302. Soil Science Society of America, Inc., Madison, Wisconsin.
Wang, Jiann-Ming, Raina M Maier, and Mark L. Brusseau. "Influence of hydroxypropyl-b-cyclodextrin (HPCD) on the bioavailability and biodegradation of pyrene." *Chemosphere*. 60.5 (2005): 725-728.
Witthuhn, Barbara, Peter Klauth, Erwin Klumpp, Hans Narres, and Holger Martinus. "Sorption

and biodegradation of 2,4-dichlorophenol in." *Applied Clay Science*. 28.1 (2005): 55-66.
Wong, Eva. (2005). "Cool Pavements." *Reducing Urban Heat Islands: Compendium of Strategies*. EPA. Washington D.C
Zhu, Runliang, and Lizhong Zhu. "Thermodynamics of Naphthalene Sorption to Organoclays: Role of Surfactant Packing Density." *Journal of Colloid and Interface Science*. 322.1 (2008): 27-32. Comparison of test specimen preparation techniques for pervious concrete pavements
Bradley J. Putman, Andrew I. Neptune
Maraqa, M.A. 1998. Retardation coefficients of nonionic organic compounds determined by batch and column techniques. Soil. Sci. Soc. Am. J. 62:142–152
Eisler, Ronald. "Polcyclic Aromatic Hydrocarbon Hazard to Fish, Wildlife, and Invertabrates: A Synoptic Review." *Patuxent Wildlife Research Center Contaminant Hazard Reviews*. 1.11 (1987): 1-55.
Unites States Environmental Protection Agency. *Technical Fact Sheet on Polycyclic Aromatic Hydrocarbons*. EPA Safewater, 2009.

Information Transfer Program Introduction

The information transfer project is entitled "Drinking Water Outreach in Rhode Island." This project organized a conference for professionals in the clean water field as well as graduate and undergraduate students to present recent developments in drinking water technology. In addition, a summer camp/workshop for high school students attracted 30 and participant numbers are expected to grow next year. The Clean Water Conference will continue to be held annually.

The goals of the RIWRC information transfer program was to encourage students to pursue careers in fields relevant to water resources and encourage continuing education for professionals as well as promoting an exchange of ideas and research between water professionals. Dr. Harry Knickle worked to promote the awareness of clean water issues in Rhode Island in the minds of the state's high school students and water resources professionals.

Drinking Water Outreach in Rhode Island

Basic Information

Title:	Drinking Water Outreach in Rhode Island
Project Number:	2011RI99B
Start Date:	3/1/2011
End Date:	2/28/2012
Funding Source:	104B
Congressional District:	Two
Research Category:	Not Applicable
Focus Category:	Education, Water Quality, Treatment
Descriptors:	
Principal Investigators:	Harold Knickle, Geoffrey Bothun

Publications

There are no publications.

Clean Drinking Water in Rhode Island

Harold N. Knickle
Professor of Chemical Engineering
University of Rhode Island
knickleh@egr.uri.edu

Geoffrey Bothun
Associate Professor of Chemical Engineering
University of Rhode Island
bothun@egr.uri.edu

Abstract

There were two goals for this project. The first goal was to host a conference to provide background and knowledge for working professionals in the clean water fields as well as to educate graduate and undergraduate students on research and practices in the clean water field. To accomplish this goal, an ongoing Rhode Island Water Resources Center Clean Water Conference on clean drinking water was promoted and held at the University of Rhode Island (URI). This conference focused on the technical aspects associated with providing clean water in the state of Rhode Island as well as providing a forum for current clean water research. The second major activity of this project was the hosting of a summer workshop (camp) at the University of Rhode Island for middle and high school students to introduce them to clean water concepts using lectures, laboratories, and field trips to promote interest in clean water careers.

INTRODUCTION

The project focused on information technology and education by two major outreach activities, a comprehensive conference for the clean water community and a summer camp for middle and high school students to promote interest in clean water careers.

OBJECTIVES

Two major objectives were set for this project.

1. The first was to advance the awareness and knowledge of the importance of clean water in Rhode Island and to provide insight into the various factors affecting the ability to obtain clean water for multiple uses in Rhode Island by hosting a Rhode Island Water Resources Center Clean Water Conference. The hosting of the conference provided background and knowledge of the work of professionals in the clean water fields. The conference has become an annual event. Through their attendance at the conference, graduate students were encouraged to take courses in clean water environmental areas and undergraduates were encouraged

to consider pursuing degrees related to the clean water profession. In addition the conference provided a forum for presentation of research on clean water topics.

2. The second major activity was the hosting of a summer camp at the University of Rhode Island which was sponsored by the Departments of Civil and Environmental Engineering as well as the Department of Chemical Engineering for middle and high school students to introduce students to technical and scientific clean water concepts with a goal of promoting interest in clean water careers.

KNOWLEDGE TRANSFER

Dissemination was an important part of this project. Results of this project were shared with all participants. A web page was added to the Rhode Island Water Resources web site on Clean Water. The webpage contains important information on the conference and information presented at the conference including a video of each of the presentations as well as their powerpoint presentations. The webpage also contains a description of the summer camp. The audiences included clean water professionals such as water utility managers, graduate, undergraduate, and middle and high school students, faculty and administrators. The WEB page can be found at www.wrc.uri.edu.

LEADERSHIP

The conference effort was guided by a steering committee. The steering committee provided guidance in choosing key speakers and presenters and hosting special break-out sessions. The steering committee consisted of students, faculty and administrators at the University of Rhode Island and representation from government and industry. Specific representation on the committee included a representative from the Providence Water Supply Board, Dr. Rose, member of the Kingston Water District Board of Commissioners, Dr. Thiem, Director of the RI Water Resources Center, Dr. Barnett, director of the RI Pollution Prevention Center, Dr. Gray, Chemical Engineering Department Professor with research interests in green solvents for cleaning, Dr. Bothun Chemical Engineering Professor and co-PI with interests in student learning and Dr. Knickle Chemical Engineering Professor and PI with research interests in clean water.

TIMELINE

June 27, 2011 to July 1, 2011: Clean Water Summer Camp for High School Students held.

November 10, 2011: Rhode Island Clean Water Conference was presented

SUMMER CAMP FOR MIDDLE AND HIGH SCHOOL STUDENTS ON CLEAN WATER

High school students were recruited from high schools in Providence, Rhode Island to participate in the 2011 Clean Water Summer Camp. Recruitment took place by visiting

the schools and meeting with the science teachers at each school. With the teacher's help appropriate students (academic and emotional development) were recruited that have an interest in this clean water program. The schedule for the camp was from Monday to Friday and from June 27 to July 1. Students arrived by bus at 9:00 am and left at 3:30 pm. Lunch was provided by an LSAMP grant. There were no fees for this summer camp and both lunch and buses were provided without charge.

Activities included presentations of the water cycle, chemistry of water, water quality and treatment, sewage treatment and biological technology, runoff and storm water, industrial water pollution, pollution prevention, and investigation of macro-invertebrate in the URI pond. Laboratory exercises included water quality sampling and testing, pH and dissolved oxygen measurement, bacteria pollution testing, conductivity testing, acid rain testing, aeration, adsorption and health effects. Field work included the collection of samples from various locations such as treatment facilities and water bodies. Field trips were made to a drinking water treatment facility, a sewage treatment plant as well as to the URI drinking water well and the water distribution building on the URI campus.

A measure of the effectiveness of the summer camp was determined by two surveys, one at the beginning and one at the end of the camp. Each student also wrote a brief laboratory report for each laboratory exercise and an essay indicating the activities of most interest to each individual student.

Excellent laboratory facilities were used at URI for the summer camp middle and high school students. These were held in both Bliss Hall, where the environmental engineering laboratories are located, and in Crawford Hall which houses the chemical engineering laboratories. Glassware, scales, pH and conductivity meters, chemicals and other equipment was available in these laboratories for use in the summer camp activities. Classrooms and computer labs were available in both building with appropriate audio-visual devices.

Training Potential.

Summer Camp on Clean Water

The number of high school students attending was 28, 9th, 10th and 11th grade students. These students were screened for having potential interest in pursuing a career in clean water professions as well as an interest in the STEM disciplines

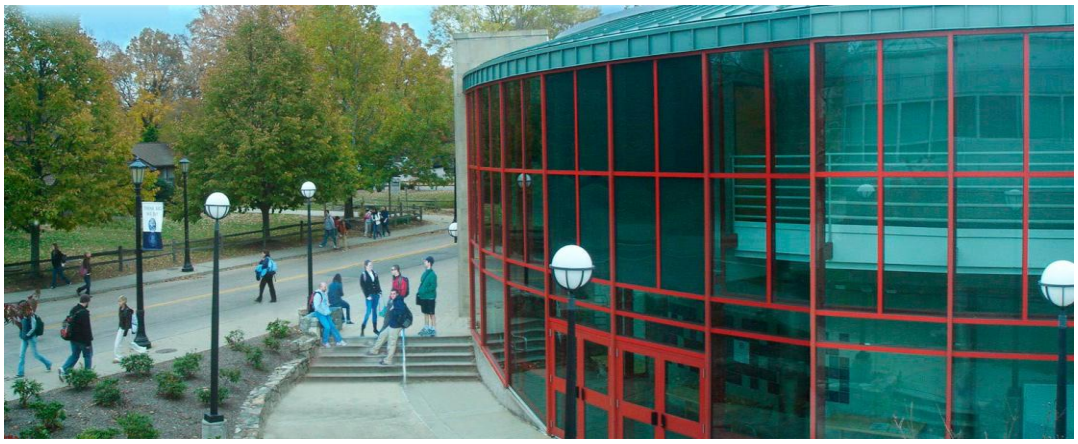
Rhode Island Clean Water Conference

The RI Clean Water Conference was held at URI in Cherry Auditorium. Invited speakers provided presentations on two areas including managing clean water and new technology related to clean water in Rhode Island. The program is included on the next page. The presentations are on the RI Water Resources web site: www.wrc.uri.edu

The audience consisted of 35 graduate students and 60 undergraduates. These students were primarily from Civil and Environmental Engineering and from Chemical Engineering.

About 20 others attended including clean water professionals from industry as well as faculty. Most of the undergraduates were juniors or seniors. This attendance exceeded expectations.

The Cherry Auditorium was used for the conference along with the attached gallery for displays and exhibits. Coffee breaks were held within the hallways surrounding the auditorium.



Final program

Clean Drinking water CONFERENCE

12:45 to 1:00pm Registration

1:00 Welcome Remarks
Dean Wright,
Dr. Thiem, Dr. Knickle

Session 1: 1:10pm to 2:00 pm

- **Chlorine Dioxide: Nitrification Control**
  Michal Trottier,
  Dupont Engineering and Technology Manager

COFFEE BREAK

Session 2: 2:15 to 3:00 pm

- **Ceramic Water Filter Bacterial Removal**
  Vinka Craver
  Dept. Civil & Environmental Engineering, URI

Session 3: 3:00 to 3:45 pm

- **Biological Health of a Pond- Measurements**

Leon Thiem, Harold Knickle,
Dept. Civil & Chemical Engr.

Questions and Discussion

3:45 to 4:00 pm

4:00 pm ADJOURN

Planning Committee Members
From the College of Engineering
Dr. Stanley Barnett, Dr. Donald Gray, Dr. Harold Knickle, Dr. Vincent Rose, Dr. Leon Thiem, Dr. Geoff Bothun

Sponsored by

RI Water Resources Center

www.wrc.uri.edu

Department of Chemical Engineering

www.egr.uri.edu/che

Department of Civil and Environmental Engineering

www.egr.uri.edu/cve

Conference is Free All Welcome

Refreshments Courtesy of Amgen, W Greenwich RI

RESULTS AND BENEFITS.

The conference provided insight into the various factors affecting the ability to obtain clean water for multiple uses in Rhode Island. The breadth and depth in this project on water quality provided both awareness and knowledge to the clean water community in Rhode Island and to graduate and undergraduate students. This conference raised awareness of conservation and new technologies.

The hosting of a summer camp at the University of Rhode Island for high school students brought 28 students to the URI campus and provided lectures and labs on to clean water concepts with a goal of promoting interest in clean water careers.

A paper was presented at the conference on the results of two years of testing for macro vertebrate in Rhode Island's Thirty Acre Pond. The results of the two years of monitoring were presented by Professors Knickle and Thiem.

Collecting Macro-invertebrate at the URI Campus Pond Summer Camp

Collecting Macro-invertebrate at the URI Campus Pond Summer Camp

Water Testing Summer Camp

Visit to Scituate Reservoir and Clean Water Plant Summer Camp

Water Testing Summer Camp

Program/Flyer for the Summer Camp on Clean Water 2011

Clean water ACTIVITIES BUS LEAVES AT 8:15 AM

ALL SESSIONS 9:00 TO 3:30

Breakfast Snack and Lunch Included

Session 1: Monday June 27

- Introduction and Survey
- Intro to Water Cycle
- Settling LAB
- Introduction to Water Chemistry
- Drinking Water Quality inWarwick, RI
- Water Quality Testing
- Water Sample Collection
- Immediate and 3 minute
- Water Test LAB Report

Session 2: Tuesday June 28

- Introduction to Health Effects Associated With Water Quality
- Introduction to and Theory of Adsorption
- Adsorption LAB
- Intro to Scituate Reservoir
- Field Trip to Water Treatment Plant Arriving at 1 pm

Session 3: Wednesday June 29

- pH LAB
- Introduction to Water
  Runoff and Storm Water
- Introduction to Pollution Prevention.
- Oil Spills Laboratory and Graphs
- Alternate LAB
- Video: Ponds & Rivers
- Laboratory and Report Writing

Session 4: Thursday June 30

- Reaction Time & Temperature
- Introduction to Sewage Treatment
- Introduction to Biology Technology
- Introduction to COD and BOD
- Bacteria Check for microbes Using Google
- Field Trip to Sewage Treatment Plant at East Greenwich, RI Arrive 12:30
- Laboratory Report

Session 5: Friday July 1

- 30 Acre Pond Sampling
- Dissolved Oxygen, pH, and Hardness Testing, RO
- Filtration and Settling
- Filtration Laboratory
- Salt Water Conductivity
- Post Assessment Survey
- Certificates

Sponsored by LSAMP & URI Water Resources Center Leon Thiem, Director

College of Engineering **No person shall be denied membership because of race, color, sex, handicap, nationality, religious affiliation or belief**

Dr H. Knickle and LSAMP

UNIVERSITY OF
Rhode Island

URI

Summer 2011

Clean Water Engineering & Science Academy

June 27 July 1

9:00 AM to 3:30 PM

College of Engineering
Dr. H. Knickle, Professor
(knickle@egr.uri.edu)

Application to Clean Water Academy 2011

June 27 to July 1

CIRCLE YOUR INTEREST

Math Science Engineering

Name: _____

Address: _____

Telephone: _____

Email: _____

School Name:_____

_____

Grade: _____

PARENTS' APPROVAL SIGNATURE

_____

Return to: Dr H. Knickle, College of Engineering 874-2678, knickle@egr.uri.edu

122 Crawford Hall, Kingston, RI 02881

Clean Water Academy Summer 2011
June 27-July 1

Sponsored by URI Water Resources Center and the College of Engineering

Are you a high school student interested in math and science?

Are you interested in understanding how math and science are a key part of being an engineer?

Do you want to experience some of the fun of doing experiments?

Then you should participate in our own Clean Water Academy.

The Academy Coordinators want to help you to see just how exciting your future can be.

These **hands on** sessions will show you how interesting science and engineering can be, while you explore the options in engineering and learn valuable tools for success.

The University of Rhode Island's College of Engineering has eight undergraduate programs

There are also many physical, chemical, and biological science programs at URI.

If you decide to participate, other students will join you in the following activities:

- *Interactive workshops.*
- *Participate in real hands-on experimental activities.*
- *Interact with teachers and students from the University of Rhode Island.*

H. Knickle, PI

USGS Summer Intern Program

None.

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	6	0	0	0	6
Masters	3	0	0	0	3
Ph.D.	1	0	0	0	1
Post-Doc.	0	0	0	0	0
Total	10	0	0	0	10

Notable Awards and Achievements

The Clean Water Science Academy program is similar to and modeled after the LSAMP program which is funded by NSF. The Academy focuses on the water cycle and clean water. The program runs for five consecutive days and includes three field trips.

The academic programs funded by the RIWRC (camp and forum) are very helpful in recruiting students to our URI STEM (Science, Technology, engineering and Mathematics) programs. Our minority enrollment of students in the URI College of Engineering has increased from approximately 3% eight years ago to 13% this year. Total minority enrollment has more than doubled at URI during this same time period. By recruiting students from targeted schools over a four year period, the number of applications has increased to 24 students. The College of Engineering has hired a counselor to advise undergraduate minority students.

Publications from Prior Years

1. 2010RI86B ("Use of Manometric Techniques to Evaluate the Disinfection Properties of Nanomaterials for the Treatment of Different Sources of Drinking Water") - Book Chapters - J. Rayner, H. Zhang and V. Oyanedel-Craver (2012) Sections 2.4 and 4 in Investigation into the effects of Manufacturing Variables on the Microbiological Efficacy of Ceramic Pot Filter Material, Ed.1 Seattle, WA, USA, PATH.
2. 2008RI75B ("Utilization of Silver Nanoparticles as Chlorine-free Biocide for Water Treatment") - Articles in Refereed Scientific Journals - V. Oyanedel-Craver, and J. A. Smith (2008) A sustainable colloidal-silver-impregnated ceramic filter for point-of-use water treatment. Environmental Science and Technology 42 (3), 927-933
3. 2010RI86B ("Use of Manometric Techniques to Evaluate the Disinfection Properties of Nanomaterials for the Treatment of Different Sources of Drinking Water") - Articles in Refereed Scientific Journals - E. Kallman, V. Oyanedel-Craver, and J.A. Smith (2011) Ceramic Filters Impregnated with Silver Nanoparticles for Point-of-Use Water Treatment in Rural Guatemala. ASCE-Journal of Environmental Engineering, 136 (6) 407 – 415.