Introduction

This is a report on the projects of the Rhode Island Water Resources Center (RIWRC) during the period between March 1st 2009 to February 28th 2010. The Rhode Island Water Resources Center is currently under the direction of Dr. Leon Thiem, Associate professor of Civil and Environmental Engineering, and is in the process of gaining permanent approval as a University center. One graduate research assistant, Hui Chen, and one undergraduate student, Ashlee Bettencourt is supported by the Center.

Dr. Vinka Craver, professor in the department of Civil and Environmental Engineering at the University of Rhode Island, was funded by a USGS grant to complete her research entitled Nanosilver-clay Composite Material as a Reactive Permeable Barrier to Control Microbiological and Chemical Contamination in Groundwater. Dr. Craver went on to publish a rigorous assessment of the success of nanosilver used in ceramic water filters for point-of-use treatment for drinking water.

Dr. Kelly G. Pennell of Brown University, a professor in the Division of Engineering, was granted funding by the USGS to explore the topic of Sequential Inactivation of Microorganisms in Drinking Water using Ultraviolet (UV) Radiation and Residual Chlorine. Dr. Pennell previously published a paper in the Journal of Engineering Science, Sequential Inactivation of Bacillus subtilis Spores with UV Radiation and Iodine, and a publication in connection with her current research is expected in the near future.

Dr. Harry Knickle, assisted by Dr. Geoffrey Bothun, succeeded in hosting the third annual Clean Water conference and the second Clean Water Engineering and Science Academy for high school students. Students were recruited from the county of Providence and given the opportunity to participate in water related laboratory experiments using URI's state of the art facilities. Conference material will be made available on the RIWRC website and the conference will be held again next year.
Research Program Introduction

The primary goal of this year's supported research projects was to explore two different water disinfection techniques. Dr. Craver's project developed and evaluated a water filter made up of composite material produced by combining local clay materials and silver nanoparticles. This water filter was designed to treat microbiological contaminants and will also be tested for removing inorganic and organic compounds such as iron and petroleum hydrocarbons. Such a treatment process could serve to increase the amount of potable water available. Dr. Craver's Nanosilver-clay composite water filters can be have potential for application by Rhode Island well owners as well as poverty stricken individuals without access to clean water.

Dr. Pennell's project expands upon her previous research on the subject of sequential disinfection. Her work with ultraviolet radiation and chlorination is an evaluation of how the damage that occurs during UV exposure can subsequently enhance the sensitivity of spores to other disinfectants. This process has the potential to target a wider range of microorganisms in relation to percent and range of inactivation.
Nanosilver-clay composite material as a reactive permeable barrier to control microbiological and chemical contamination in groundwater

Basic Information

| Title: | Nanosilver-clay composite material as a reactive permeable barrier to control microbiological and chemical contamination in groundwater |
| Project Number: | 2009RI80B |
| Start Date: | 3/1/2009 |
| End Date: | 2/28/2010 |
| Funding Source: | 104B |
| Congressional District: | 02 |
| Research Category: | Water Quality |
| Focus Category: | Water Supply, Water Quality, Groundwater |
| Descriptors: | |
| Principal Investigators: | Vinka Oyanedel-Craver |

Publications

There are no publications.
Nanosilver-clay composite material as a reactive permeable barrier to control microbiological and chemical contamination in groundwater

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ABSTRACT

As are most natural resources, Rhode Island’s ground water is both valuable and limited. Rhode Island’s ground water resources supply drinking water to approximately 25% of the statewide population and as much as 100% of the local population in the southern and western portions of the state.

This one-year water quality project builds on the expertise of its team members and will directly benefit the people of Rhode Island by safely enhancing water supply from contaminated ground water resources.

This project will develop and evaluate a water filter made of a composite material. The composite material referred to herein is produced by combining local clay materials and silver nanoparticles. This filter will be designed primarily to treat microbiological contaminants such as \textit{E. coli}, but will also be tested for its removal efficiency for inorganic and organic compounds. Iron and petroleum hydrocarbons present a current pollution quandary in Rhode Island and have been detected in many private wells in the state. The results of these tests will be used to design a water filter application suitable for use in private homes. This project builds on the previous work of this research team and carries the promise for future funding of subsequent extensions of this project.

KEYWORDS: silver nanoparticles, ionic strength, organic matter

PROBLEM STATEMENT AND RESEARCH OBJECTIVES

Rhode Island’s population is supplied solely by ground water in approximately 25% of the state. In the southern and western portions of the Rhode Island as much as 100% of local populations are dependent on groundwater resources (Figure 1).
Groundwater is typically accessed via well and private well owners are responsible for the maintenance of their drinking water supply. Well owners need to ensure that the quality of their well water is fit for human consumption. Well water can be contaminated by biological, inorganic and organic compounds. The most common sources of well contamination are malfunctioning septic systems within the well catchment area, agricultural liquid waste infiltration, and inundation or infiltration of the well by floodwater.

If a private well becomes contaminated, households have several treatment options. However, current point-of-use technologies (e.g. reverse osmosis) tend to be expensive, difficult to operate and maintain, and/or may not be effective for removing the wide variety of pollutants potentially present in the groundwater. For instance, activated carbon filters very efficiently remove organic and inorganic compounds, but basically fail at the removal of bacteria.

To address this problem, we propose to develop a simple, cheap and locally manufactured water filter technology to be used as a point-of-use drinking water treatment alternative.

**METHODOLOGY**

**Pathogenic microorganism quantification**

*Escherichia coli* HCB 137 was used to create bacterial suspensions. This organism has been selected because it is a specific indicator of fecal contamination of water. The HCB 137 strain is non-pathogenic, i.e. its infective properties have been repressed. Bacterial-buffer solutions have been prepared as described by Oyanedel-Craver and Smith (2008), and aliquots have been added to synthetic water samples to obtain the desired bacterial concentration of approximately $10^8$ cfu/mL.

**Silver nanoparticles**

Due to the current application of a commercial formulation of Ag-NP in some low-tech water treatments (i.e., ceramic filters by Potters for Peace), we have characterized and used Collargol™ (a silver nanoparticle product developed by Argenol Laboratories in Spain). Dynamic light scattering (DLS) was used to characterize the particle-size distribution of synthesized Ag-NP.

**Column Tests**

The following summarizes how the column systems have been characterized prior to amendment with Ag-NP. All column experiments have been carried out with water-saturated porous media. A known quantity of one of the three porous media was packed into a glass column (Kontex® or similar, volume: 25 to 75 cm³). Teflon tubing and fittings were connected the columns to a precision piston pump (Acuflow Series I or similar). The porosity, pore volume (PV), and dispersion coefficient of each column was determined from the breakthrough curve of a conservative tracer, titrated water (Fetter, 1998) and the transport model CXTFIT 2.0. The flow velocity was held constant during each column experiment.

Column effluent samples were collected frequently and immediately analyzed using the analytical methods described previously. Effluent concentrations were reported as relative
concentrations, \( C/Co \), where \( Co \) is the concentration of the solute entering the column and \( C \) is its effluent concentration at time \( t_n \).

**RESULTS**

**Characterization of nanoparticles at different water chemistry**

Since several dissolved compounds are commonly found in natural waters, monovalent and divalent ions were used as background ions to test the effect of different water chemistries on the physical characteristics of silver nanoparticles.

Table 1 presents a summary of the values of average particles’ size for silver nanoparticles. It can be observed that at the concentration tested in this study the average size of the particles does not change considerably. Silver nanoparticles can be synthesized using a variety of techniques, including electric spark discharging methods (Der-ChiTien et al. 2008), irradiation methods (Long et al. 2007), and chemical reduction methods (Soukupova et al. 2008). The most common manner of synthesis of silver nanoparticles is the chemical reduction of a silver salt solution by a reducing agent, such as borohydride, citrate, ascorbate, or a reducing sugar (Soukupova et al. 2008). The size of the particles can be manipulated using various reducing agents in the reaction. For example, using disaccharides as a reducing agent yields a smaller particle size than using monosaccharides (Soukupova et al. 2008).

The nanoscale sizes of these particles leads to a large surface area per volume ratio, such that a large percentage of atoms are in immediate contact with the solution and thus are readily available for reaction. In addition to the different shapes and sizes that can be manufactured, the surface of the nanoparticles can be modified using different agents; this process is called functionalization or capping. Capping agents are used in the synthesis process to prevent nanoparticles from aggregating and to obtain a range of small particle sizes. Olenin et al. (2008) determined that agglomeration was caused by high surface energy and thermodynamic instability of the nanoparticle surface. Capping agents interact with the surface of nanoparticles through electrostatic repulsion forces caused by surface charge, steric stabilization, or both (Sun et al. 2005; Guo et al. 2008). The most common capping agent used for the manufacture of silver nanoparticles is citrate (50%), followed by polyvinylpyrrolidon (20%), amines (10%), amides (5%), cetyltrimethylammonium bromide (5%), and others (10%) (Tolaymat et al. 2010).

Polyelectrolytes, surfactants, amines, and sugars are used to functionalize the surface of nanoparticles (Sen et al. 2006). These compounds increase the surface charge of the particles and provide electrostatic repulsions between particles to minimize aggregation and prevent the attachment of particles to surfaces (Sun et al. 2005). In addition to the electrostatic repulsion forces, high molecular weight organic compounds adsorbed to the nanoparticles surface can induce steric repulsion. To be effective, a thick and dense layer of adsorbed organic compound is employed to overcome the van der Waals attraction between the particles. The combination of electrostatic and steric repulsion (electrosteric repulsion) tends to be quite strong and long-ranged, and is known to be robust even at high ionic strengths.
Table 1. Effect of different ions dissolved on the average size of the silver nanoparticles

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>NaCl</th>
<th>Ca(NO3)2</th>
<th>KNO3</th>
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<td>50</td>
<td>101</td>
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<tr>
<td>250</td>
<td>80</td>
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Some change, although not significant, was observed on the average particle distribution of the silver nanoparticles in the range of dissolved salt concentrations used. Figure 1 relates the particle size distribution of silver nanoparticles suspended at different concentration of salts. It can be observed that bigger particles are formed at higher concentrations, however, it seems that the number of these particles is not high enough to increase the overall average particle size distribution of the nanoparticles suspension. Below, Figure 2 quantifies the effect that different concentrations of dissolved compounds has on the particle size distribution of silver nanoparticles.

![Figure 2 (a)](image)

![Figure 2 (b)](image)
Figure 2. Effect of different concentration of dissolved compounds of the particle size distribution of silver nanoparticles (A) NaCl, (B) Ca(NO3)2 and (C) KNO3.

The storage time of silver nanoparticles in a liquid solution did not seem to have a significant effect either in the particle size distribution or the overall average particles size as it is presented in Figure 3.

Figure 3. Effect of storage time on the particle size distribution of silver nanoparticles

The disinfectant performance of silver nanoparticles was also determined as a function of time. Figure 4 shows the summary of the different tests performed within the scope of this project. The figure shows that after a week of storage in liquid solution silver nanoparticles lost less than 2% of their original disinfectant properties.
Column experiments
The column tests were performed using Ottawa sand to determine the bacteria and nanoparticle retention in porous media. The retention of bacteria cells in the sand matrix have been extensively studied by other researchers. Figure 5a presents the breakthrough curve of the tracer (NaCl) and E. coli. Approximately 50% of the bacteria were retained inside the column. This result agrees with other studies found elsewhere. Figure 5b shows the breakthrough curves of the tracer (NaCl) and silver nanoparticles. Silver nanoparticles are proven to be slightly retained (about 2%), most likely because of their small particles size and low charge. Since Ottawa sand has a low charge, surface to surface interaction was expected in a low rate.
Figure 5 (b)

Figure 5. Breakthrough curves (A) Tracer and bacteria and (B) Tracer and silver nanoparticles.

CONCLUSIONS

The effect of various dissolved compounds as well as the storage time did not have a significant negative impact either on the physical properties or antibacterial performance of the silver nanoparticles. Therefore, silver nanoparticles are a potential suitable amendment to enhance antibacterial properties in porous media.

Sand type materials are not appropriate for the immobilization of silver nanoparticles due to their low surface charge reducing the possible interactions with the nanoparticles.

FUTURE WORK

Future research is necessary to determine the effectiveness of other types of porous media for filter technology. Materials with different characteristics such as higher cationic exchange capacity and higher organic matter content should be explored for this use.

Additionally, the implementation of different surface modifications to alter the silver nanoparticles surface must be studied in order to increase surface interactions with porous media.

REFERENCES


Sequential Inactivation of Microorganisms in Drinking Water using Ultraviolet Radiation and Residual Chlorine

Basic Information

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<td>Principal Investigators:</td>
<td>Kelly G. Pennell</td>
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Publications

There are no publications.
Sequential Inactivation of Microorganisms in Drinking Water using Ultraviolet (UV) Radiation and Residual Chlorine

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ABSTRACT

Sequential disinfection processes use two or more disinfectants with fundamentally different mechanisms of inactivation to target a wider range of microorganisms and to eradicate a greater percent. Combining methods of disinfection is more effective than administering either separately. Sequential disinfection processes are often considered when the primary disinfectant is not capable of providing a long-lasting residual (such as the case with UV radiation), or when a synergistic response is developed through the combined application of disinfectants. Sequential disinfection may also be employed as a means of broadening the potential application of antimicrobials in a treatment setting, relative to the application of a single disinfectant.

The sequential disinfection research presented herein focused on evaluating the effectiveness of UV radiation followed by chlorination. This application is appropriate for not only large water treatment systems that may have lengthy distribution times, thereby requiring a residual disinfectant, but also for smaller scale systems where UV treatment can be practiced on a routine basis and augmented with residual chlorine as needed.

Disinfection experiments with Bacillus subtilis (ATCC# 6633) spores were conducted using UV (254 nm) and free chlorine. The results suggest that spores are susceptible (at some level) to both UV and free chlorine. Sequential disinfection experiments confirmed that the combined effects of UV and chlorine were additive (not synergistic), regardless of pre-irradiation dose (for the doses investigated). This research represents one of the first attempts to quantify the effect of pre-irradiation dose on sequential UV and chlorine exposure.

KEYWORDS: disinfection, microbial contamination, UV radiation, chlorination

PROBLEM STATEMENT AND RESEARCH OBJECTIVES

Microbial contamination of drinking water is an ongoing challenge. This is especially true for areas where water sources are not routinely disinfected (including groundwater-supplied drinking water systems). The Center for Disease Control (CDC) reports that between 1991 and 2000 groundwater-supplied drinking water systems were responsible for 68 waterborne disease outbreaks, which accounted for 51 percent of all waterborne disease outbreaks in the United States (USEPA 2006a).
Currently, in the United States, the most common approach to treating microbial contamination in drinking water is through the addition of chlorine. Free chlorine (HOCl and OCl-) is the active form of chlorine that is actually available to kill bacteria and algae, and this is the form that is commonly referenced in regards to drinking water disinfection. However, free chlorine is non-selective and therefore reacts not only with microorganisms, but also with naturally-occurring organic matter (NOM). The reaction between NOM and chlorine can form a variety of disinfection by-products (DBPs) and reduce the efficiency of the substance as a disinfectant. Some DBPs can also cause adverse health effects, reducing the overall safety of the treated water.

In the 1970s, the detection of chloroform, a suspected carcinogen, in chlorinated drinking water supplies heightened awareness of disinfection byproducts. Since then, chloroform, other trihalomethanes (THMs), and haloacetic acids (HAAs) have been regulated by the United States Environmental Protection Agency (USEPA) under the Safe Drinking Water Act (Means and Krasner, 1993). The Federal Drinking Water Maximum Contaminant Level (MCL) for total THMs (TTHMs) is 0.08mg/L. It should be noted, however, that the TTHM MCL only monitors a total of four THMs; chloroform, bromodichloromethane, dibromochloromethane, and bromoform. Due to the toxic nature of DBPs, and since studies have indicated that some viruses and protozoa, such as Cryptosporidium parvum, are highly resistant to conventional chlorine-based disinfectants (USEPA 2006b), alternatives to chlorine disinfection, such as ultraviolet radiation (UV), are being considered.

UV treatment is appealing because it has less potential for DBP formation. This water disinfection treatment also typically goes undetected by the consumer because UV does not alter the taste or odor of the drinking water. Over 400 UV disinfection facilities exist worldwide, including several large UV installations being constructed and/or designed for municipalities such as Seattle, WA (180-mgd) and New York City (2,200 mgd) (USEPA 2006b). While UV radiation has many advantages over chlorine disinfection there are concerns, such as the lack of a residual disinfectant. This research project investigated the sequential application of UV as a primary disinfectant and free chlorine as a residual disinfectant. Chlorine was selected as the residual disinfectant because it is the most commonly used disinfectant for water treatment in the United States. Therefore, it was of interest how pre-treatment with UV might affect the efficacy of chlorination.

Several investigators have conducted sequential disinfection research, including the use of various disinfectants (UV, ozone, hydrogen peroxide, silver, iodine, chlorine, etc.). With few exceptions, most sequential disinfection experiments are conducted by selecting individual doses of disinfectants and applying them sequentially with little regard for the disinfectant’s dose-response curve (examples: Ballaster and Malley 2004; Butkus et al. 2004; Cho et al., 2006; Kashinkunti et al. 2004; and Koivunen and Heinonen-Tanski 2005). This project took into consideration the missing link in prior research of disinfectant dose-response curves.

It is well-known that for most disinfectants, the reduction in the concentration of viable microorganisms occurs in three distinct stages: a lag period (or shoulder) where disinfection is slow, until a “threshold dose” is reached, followed by a first-order decrease in the viable
population, then a transition to the tailing regime. The subject research investigated different pre-irradiation doses along the UV dose-response curve. This rationale was based on sequential disinfection experiments performed previously by Pennell et al (2008). Figure 1 illustrates a “typical” dose response curve of B. subtilis spores, which includes a threshold (or lag) region, a region corresponding to a log-linear dose-response relationship, and a tailing region. Figure 2 communicates the results of the sequential inactivation experiments for UV254 followed by iodination, which was previously reported.

As illustrated in Figure 2, there was an increase in synergism when UV exposure was increased from shoulder region doses to first-order region doses. However, when UV exposure was increased to near-tailing UV doses, synergism decreased. Tailing occurs when a (small) subpopulation of a microbial population is not effectively inactivated as a result of disinfectant exposure. In a general sense, it is not clear why subpopulations of microorganisms persist. The results reported in Figure 2 suggest that a limiting factor may be responsible for reducing the synergism of spores exposed to sequential disinfection with near-tailing doses of UV. Pennell et al (2008) showed for sequential disinfection processes that incorporate UV and molecular iodine, the UV dose-response behavior affects the observed disinfectant synergism. The focus of the subject research was to investigate this finding for UV/chlorine systems. Chlorine and iodine inactivate microorganisms by different mechanisms, so it was not obvious how the results from Pennell et al (2008) applied to chlorine systems.

METHODOLOGY

Experiments were performed to investigate the independent and combined effects of UV and free chlorine using Bacillus subtilis spores as the challenge microorganism. Spore forming bacteria have been recognized as one of the “hardest” forms of life on Earth. B. subtilis have been widely studied as a surrogate for other spore-formers in laboratory settings because they are nonpathogenic to humans and their resistance to many forms of external stress, including disinfectants, has been well documented in literature (Nicholson et al. 2000). B. subtilis spores
have been identified by the USEPA as a challenge microorganism suitable for validation of UV disinfection systems used for drinking water production (USEPA 2006). Further, *B. subtilis* spores are used internationally for validation of UV reactors used for drinking water treatment (Österreichisches Normungsinstitut (ÖNORM), 2001, 2003; Deutsche Vereinigung des Gas- und Wasserfaches (DVGW), 2003). For all of these reasons, *B. subtilis* spores were selected as a suitable challenge organism for evaluating the use of UV and chlorine as sequential disinfectants.

**Spore Preparation**

*B. subtilis* ATCC #6633 was propagated by inoculation of nutrient agar plates (DIFCO) followed by incubation at 30°C for 24 hours. The vegetative cells were harvested and resuspended in sterile nanopure water. The resulting suspension was centrifuged for three minutes to separate free bacteria from bacterial debris, which remained at the bottom of the centrifuge tube. Approximately 250 µL of the supernatant free cell suspension was transferred to Schaeffer sporulation agar plates (Schaeffer et al. 1965). The inoculated sporulation agar plates were incubated for 6 days at 37°C. After 6 days, spores from the sporulation agar plates were harvested and resuspended in sterile nanopure water. Purification of spores was performed following recommended methods (Nicholson and Setlow 1990).

**UV Irradiation**

Aqueous suspensions of *B. subtilis* spores (10⁶-10⁷ cfu/mL) were generated using sterile nanopure water as the base matrix. For each UV dose investigated, the spore suspensions were added to sterile 47 mm or 100 mm Petri dishes and subjected to UV irradiation a (quasi-) collimated, nearly monochromatic UV254 device. The UV device, a conventional low-pressure Hg lamp, housed in a flat-plate collimating device, yields UV radiation with a characteristic wavelength of 254 nm. The collimating device was custom built for this research by Ernest R. Blatchley III (Purdue University).

During UV exposure, suspensions were mixed using a small magnetic stir bar. Liquid depth below the collimating device will be maintained at less than 1 cm. Collectively, these attributes of the stem promoted dose uniformity within the exposed spore population subsamples. Irradiance was measured using an International Light radiometer calibrated for 254 nm. The reported UV doses have not been corrected for reflection/refraction or beam divergence.

**Chlorine Experiments**

Aqueous suspensions of *B. subtilis* spores (10⁶-10⁷ cfu/mL) were added to sterile glass reactors. The reactors were positioned on magnetic stir plates and continuously stirred using magnetic stir bars. All materials that came in contact with the spore suspension were sterilized prior to the experiment.

At the beginning of each experiment, the reactor containing the spore suspension was dosed with a stock (standardized) chlorine solution. The stock solution was standardized using diethyl-p-phenylene diamine/ferrous ammonium sulfate (DPD-FAS) titration. The analysis of samples by DPD-FAS was performed in accordance with Standard Method 4500-Cl F *Standard Methods* (1998). After the reactor had been dosed with chlorine, subsamples were collected for filtration
at predetermined time intervals. At each of these intervals, the chlorine concentration in the reactor was monitored using the DPD-FAS method. Throughout all of the experiments, the chlorine concentration was stable.

**Sequential Disinfection Experiments**
Experiments designed to investigate the effect of UV radiation followed by chlorine were performed using the same methods discussed above. Samples were subjected to UV irradiation under a collimated beam. For each UV dose, multiple volumes were irradiated to allow accumulation of sufficient volume for chlorination. Once adequate volume had been obtained, a subsample was collected and plated. This subsample serves as a benchmark for the comparison of sequential disinfection experimental results. The remaining sample was then chlorinated according to the methods discussed previously.

**Spore Viability Counts**
Aliquots of treated spores were diluted in triplicate using sterile nanopure water. In the case of chlorine treatment sterile Na₂S₂O₃ solution was added prior to dilution in order to chemically reduce the chlorine and terminate disinfection. Each dilution was subjected to membrane filtration using a 0.45 μm filter (Millipore). The filter was placed on a DIFCO Nutrient Agar plate and incubated for 18-24 hours at 37°C, or until no new colonies were observed. Visible colonies were counted and recorded. Only plates that developed 10-200 cfu/plate were included in data analysis. All data points are shown on the figures. Typically plate count data for identical doses agreed within 0.5 logs.

**PRINCIPLE FINDINGS**

The subject research investigated whether or not spore inactivation via chlorine would depend on UV pre-irradiation doses by conducting experiments using UV (254 nm) and free chlorine. Figure 3 shows the results for *B. subtilis* spore inactivation by UV alone. These experiments were conducted to establish the dose-response behavior of the spores prepared as part of this research. The results are similar to those previously published by Pennell et al (2008) Figure 2. However, the spores included this research were slightly more resistant to UV radiation. In general, the sensitivity of the spores prepared for this research was similar to the results reported by USEPA (2006).
The results of the free chlorine (alone) experiments are related in Figure 4. The dose-response behaviors shown in Figures 3 and 4 include a shoulder and a first-order region. A tailing region was not investigated.

![Graph showing dose-response behavior](image)

**Figure 3.** UV (254 nm) and *B. subtilis* spores Dose-Response Behavior (this research)

The results of the free chlorine (alone) experiments are related in Figure 4. The dose-response behaviors shown in Figures 3 and 4 include a shoulder and a first-order region. A tailing region was not investigated.

![Graph showing dose-response behavior](image)

**Figure 4.** Free Chlorine (pH=7.2) and *B. subtilis* spores Dose-Response Behavior
Given the presence of two regions (shoulder and first-order), the data were fitted to the series-event model (Severin et al. 1983). The model parameters are shown in Table 1 (and the curve fits are shown on Figures 3 and 4).

**Series-Event Inactivation Kinetic Model**

\[
\frac{N(t)}{N_0} = \exp(-k_A \cdot I \cdot t) \cdot \sum_{i=0}^{n-1} \frac{(k_A \cdot I \cdot t)^i}{i!}
\]

Where:
\(N_0\) = The concentration of microorganisms (susceptible and persistent);
\(t\) = The time of disinfectant exposure;
\(N(t)\) = The concentration of microorganisms (susceptible and persistent) at exposure time, \(t\);
\(k_A\) = Inactivation constant for the microbial population (cm\(^2\)/mJ or L/(mg-min));
\(I\) = UV intensity (mW/cm\(^2\));
\(I \cdot t\) = UV dose (mJ/cm\(^2\) or Einstein/cm\(^2\));
\(n\) = Threshold event level when inactivation occurs.

Table 1. Series-Event Model Fitted Parameters for Dose Response Behavior.

<table>
<thead>
<tr>
<th>Disinfectant</th>
<th>(k_A)</th>
<th>(n)</th>
<th>(R^2)</th>
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<tbody>
<tr>
<td>UV (254 nm)</td>
<td>0.301</td>
<td>3</td>
<td>0.969</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.094</td>
<td>8</td>
<td>0.989</td>
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Figure 5 shows the results for sequential experiments. Spore solutions were exposed to UV at pre-determined doses (0 mJ/cm\(^2\), 19 mJ/cm\(^2\), and 38 mJ/cm\(^2\)). Then, they were exposed to free chlorine (pH=7.2).

**Figure 5. Dose-Response Behavior for B. subtilis spores and Sequential Exposure (UV followed by Free Chlorine (pH=7.2))**
The dashed line represents the fitted curve for the chlorine-only experiments. This line fits the sequential experimental data well, suggesting that UV and chlorine result in additive inactivation. Table 2 gives the R² values for each sequential data set using the chlorine only kinetic model parameters (Table 1).

### Table 2. Comparison of Series-Event Model Parameters for Chlorine-only Experiments and Sequential Experiments.

<table>
<thead>
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<th>UV Exposure</th>
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<td>No pre-irradiation</td>
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<tr>
<td>19 mJ/cm²</td>
<td>0.923</td>
</tr>
<tr>
<td>38 mJ/cm²</td>
<td>0.962</td>
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Note: The “No pre-irradiation” data was collecting independently of the data presented in Figure 4. The R² value (0.990) indicates laboratory methods resulted in reproducible data collection.

The data presented in Figure 5 and Table 2 indicate synergism was not observed for the UV pre-irradiation doses investigated. It should be noted that both pre-irradiation doses investigated were within the first-order region of the UV dose-response curve (Figure 3). It is possible that doses outside of this region may result in different effects. However, Cho et al. 2006 reported little or no synergism occurred when *B. subtilis* spores were exposed to UV doses that corresponded to 1 log₁₀ unit of inactivation (near-shoulder region). The lack of synergism is likely a result of the mechanism for chlorine inactivation of *B. subtilis* spores, in which the spore coat provides considerable protection.

Another important implication of Figure 5 is how the results of this project compare to the results reported in Figure 2. Figure 2 includes the results for sequential disinfection experiments that involved the exposure of *B. subtilis* spores to UV and iodine. Unlike chlorine, iodine inactivates spores primarily by damage to the spore cortex and in some cases the spore coat (Tennen et al. 2000). The results shown in Figure 5 suggest that UV exposure does not increase susceptibility of the spore to subsequent exposure to chlorine, which implies that the UV does not substantially damage the spore coat. Therefore the observed synergism between UV and iodine is more likely a result of UV causing damage to the spore inner membrane, and not a result of spore coat damage.

**SIGNIFICANCE**

More research is needed to fully understand how damage that occurs during UV exposure can subsequently enhance the sensitivity of spores to other disinfectants. Additional research
proposals are being prepared to investigate the nature of non-lethal damage caused by UV radiation. Once non-lethal damage is more understood, better sequential disinfection systems can be designed. For instance, if UV is used as the primary disinfectant, than a residual disinfectant could be chosen that targets the same portion of the microorganism that is damaged (either lethally, or non-lethally) by pre-irradiation. By a more systematic pairing of sequential disinfectants, chemical use could be reduced, and disinfection efficacy could be improved.

FUTURE WORK

Research is also needed to investigate the tailing region of the dose-response curves. Sequential disinfection experiments that extend into the tailing region should be conducted. These experiments are difficult because of the low number of viable microorganisms that are present in the tailing region (which makes data collection via conventional plating techniques extremely challenging). Developing non-direct viability assays to assist in better characterization of antimicrobial experiments holds much promise and will be the focus of future research proposals.

REFERENCES


Dr. Harry Knickle and co-PI Geoffrey Bothun worked together 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. The intention of Rhode Island's Water Resource Center's information transfer program was to encourage students to pursue careers in fields relevant to water resources and encourage continuing education for professionals.

The information transfer project is entitled "Clean Drinking Water in Rhode Island." This project organized a conference to introduce professionals in the clean water field as well as graduate and undergraduate students to recent developments in drinking water technology. In addition, a summer-camp/workshop for high school students utilizing lectures, field trips, and laboratory experiments was held. The summer-camp/workshop for high school students attracted 16, and participation numbers are expected to grow next year. The Clean Water conference will be held annually and promotion for the November 2010 conference will be more expansive than this year.
Rhode Island Clean Drinking Water

Basic Information

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Publications

There are no publications.
Clean Drinking Water in Rhode Island

H. Knickle and G. Bothun
Department of Chemical Engineering
University of Rhode Island
122 Crawford Hall
Kingstown, RI 02881

ABSTRACT

This project focused on information transfer and education. A summer camp for high school students and a comprehensive conference for the clean water community were organized as outreach activities to promote interest in clean water careers.

There were two components to this project. The first major activity was the hosting of a week long summer day-camp/workshop at the University of Rhode Island for high school students. The purpose of this camp was to introduce students to clean water concepts through the use of lectures, laboratories, and field trips and also to promote interest in clean water careers. The second element of this project was the creation of a conference to provide both background and working knowledge for water resource professionals as well as to educate graduate and undergraduate students in the scope of the clean water field. This ongoing Rhode Island conference series on clean drinking water is promoted and held at the University of Rhode Island. The goal of this conference series is to enhance student interest in professions associated with clean water while simultaneously meeting the continuing education needs of current water professionals in Rhode Island. The subject of this year’s conference pertained to the technical aspects associated with providing clean water in the state of Rhode Island.

KEYWORDS: clean drinking water, information transfer, education

INTRODUCTION

Two primary objectives were set for this project. The first goal was to increase awareness of the importance of clean water to the state of Rhode Island and the second was the provision of insight into the various factors affecting the ability to obtain clean water for multiple uses in Rhode Island. It is hoped that as a result of an increased awareness of Rhode Island’s clean water issues students will choose to enter into the fields of chemistry, civil engineering, geosciences and other related majors.

These objectives were achieved through the hosting of a summer camp at the University of Rhode Island (URI) for high school students and a valuable Clean Water Conference held on URI’s Kingstown campus. The camp’s aim was to introduce students to clean water concepts with a goal of promoting interest in clean water careers. On a separate note, the conference provided an opportunity for working professionals to share their background and experience in
the clean water field with peers and students. This year’s conference will be used as a model to make the conference an annual event. The conference targeted the interest of graduate students and encouraged them to take courses in environmental areas. Undergraduate students were also encouraged to consider pursuing degrees related to the clean water profession.

Information dissemination was also an important part of this project. Results of this project are intended to be shared with all participants as well as with the public through a webpage on clean water which will be added to the Rhode Island Water Resources Center web site. The webpage will contain both a description of the summer camp held from June 28th through July 3rd and the important details and material presented during the Clean Water conference that was held November 12th 2009. The targeted audiences of the summer camp and conference included high school students, undergraduate and graduate students, clean water professionals, faculty and administrators. The webpage is www.wrc.uri.edu.

The conference effort was guided by a steering committee. The committee provided guidance in the choice of key speakers, presentation topics, and the hosting of special break-out sessions. The steering committee consisted of students, faculty and administrators at the University of Rhode Island and representation from the state’s government and industry. Committee members included a representative from the Providence Water Board, Dr. Rose, on the board of the Kingston Water Supply, Dr. Thiem, Director of the RI Water Resources Center, Dr. Barnett, leader of the RI Pollution Prevention Center, Dr. Gray, a man with research interests in the replacement of solvents for cleaning, Dr. Bothun, with interests in student learning and Dr. Knickle, with research interests in Clean Water.

**METHODOLOGY**

The actual schedule for the summer program follows as does the program for the Clean Water conference.
Session 1: Monday June 29
- Introduction and Survey
- Drops on a Penny
- Intro to Water Cycle
- Intro to Water Chemistry
- Water Sample Collection
- Water Quality Testing
- Drinking Water Testing
- Laboratory Report

Session 2: Tuesday June 30
- Rxn Time & Temperature
- Intro to Sewage Treatment
- Introduction to Biology Technology
- Introduction to COD and BOD, Bacteria Check.
- www.norweco.com
- Field Trip to Sewage Treatment Plant East Greenwich
- Laboratory Report

Session 3: Wednesday July 1
- Pond Water Lab
- Introduction to Water Runoff and Storm Water
- Macro Invertebrates & Micro Slides at URI pond
- Video: Ponds & Rivers
- Laboratory and Report

Session 4: Thursday July 2
- Introduction to Health Effects Associated With Water Quality
- Introduction to Pollution Prevention. Oil Spills Lab
- Intro to Adsorption
- Intro to Scituate Reservoir
- Field Trip to Water Treatment Plant

Session 5: Friday July 3
- Filtration and Settling
- Filtration Laboratory
- Turbidity Measurements
- Dissolved Oxygen, pH, and Hardness Testing
- Lab Report
- Theory of Adsorption
- Adsorption Experiments
- Laboratory Report
- Post Assessment Survey
- Certificates

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

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

Dr H. Knickle, Dr. G. Bothun and Kerri Krawczyk, Coordinators
Clean Water Conference  
University of Rhode Island, Cherry Auditorium  
November 12th, 12:45 PM- 4:00 PM

12:45 to 1:00 pm Registration

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

Session 1:  1:10 pm to 2:00 pm  
• Chlorine Dioxide:  
Nitrification Control  
Michal Trottier,  
Dupont Engineering and  
Technology Manager

2:00 pm COFFEE BREAK

Session 2: 2:15 pm to 3:00 pm  
• Ceramic Water Filter  
Bacterial Removal  
Vinka Craver,  
Dept. Civil & Environmental  
Engineering, URI

Session 3: 3:00 pm to 3:45 pm  
• Biological Health of a Pond-  
Measurements  
Leon Thiem, Harold Knickle,  
Dept. Civil & Chemical Engr.

3:45 pm to 4:00 pm  
• Questions and Discussion

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

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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,  
West Greenwich,
SUMMER CAMP DETAILS

High school students were recruited from schools in Providence, Rhode Island to participate in the 2009 summer camp. Recruitment took place by visiting the schools and meeting with several science teachers. With these teachers’ help, students with an interest in this clean water program were recommended for participation in the summer camp. These students were screened for having potential interest in entering into clean water professions and their interest in the STEM disciplines. The number of high school students in grades 9, 10 and 11 in attendance was 16. The camp’s schedule was between the hours of 9:00 am and 3:30 pm during the week of June 28th through July 3rd. Lunch and transportation via bus were provided by a LSAMP grant and therefore were offered free of charge to students.

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 the 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 the exploration of the health effects of various pollutants. Field work included the collection of samples from various locations and water bodies. Field trips were made to a fresh water treatment facility, a sewage treatment plant and to the well water and distribution source on the URI campus.

Success of the summer camp was determined by two surveys. An initial survey was taken in the morning of the first day of camp and the second at the conclusion of the week. Each student also wrote a brief laboratory report for each laboratory exercise and a final essay indicating the activities that they found most interesting.

The University of Rhode Island’s excellent laboratory facilities were used for the Clean Water Engineering and Science Academy for high school students. Laboratory exercises were held in Bliss Hall, where the environmental laboratories reside, and in Crawford Hall, which houses the chemical engineering laboratories. Glassware, scales, pH and conductivity meters, chemicals and other equipment were made available in these laboratories for use in summer camp activities. Classrooms and computer labs equipped with appropriate audio-visual devices were also made available in both buildings.

CLEAN WATER CONFERENCE DETAILS

The Clean Water conference was held at the University of Rhode Island in Cherry Auditorium. The auditorium was used as lecture space, the attached gallery for displays and exhibits, and coffee breaks were held in the ample hallway space surrounding the auditorium.

Invited speakers provided focus in the areas of the availability of clean water and new technology related to clean water in Rhode Island. The conference’s program is included above. The presentations will be made available on the RI Water Resources website: www.wrc.uri.edu.
Approximately 30 graduate students attended as well as 50 undergraduates. The undergraduate students were mostly juniors and senior. These students were from the University of Rhode Island and primarily consisted of students from the departments of Civil and Environmental Engineering and Chemical Engineering. About 20 others attended. This attendance exceeded expectations.

RESULTS

16 students participated in the summer-camp on the University of Rhode Island campus hosted by the University and funded by the Rhode Island Water Resources Center. The summer-camp provided lectures and labs dedicated to clean water concepts. The goal of promoting interest in clean water careers was pursued.

The Clean Water conference provided insight into the various factors affecting the state’s 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, graduate and undergraduate students, and faculty members in attendance. This conference met its goal of raising awareness of water conservation and new clean water technologies.

The following photos are from the Clean Water Engineering and Science Academy held from June 28th to July 3rd.

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 Filtration Experiment, Summer Camp
USGS Summer Intern Program

None.
## Student Support

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Notable Awards and Achievements

The Information Transfer Project headed by Professor Knickle was responsible for introducing high school students into the area of Water Resources. Professor Knickle was able to use this grant seed money to obtain an LSAMP grant from the National Science Foundation. Professor Craver's Research Project allowed her to continue to develop a mechanically simple, cost effective treatment method for biologically contaminated waters. She has implemented this research by field testing in Central American countries and has obtained an NSF grant to advance her research.
## Publications from Prior Years


4. 2007RI60B ("Clean Drinking Water in Rhode Island") - Water Resources Research Institute Reports - Knickle, Harold. "Clean Drinking Water in Rhode Island"

5. 2007RI60B ("Clean Drinking Water in Rhode Island") - Other Publications - Power Point Presentations, available on RIWRC website.


8. 2006RI50B ("Incorporating Latest Technologies in a Cost-Effective Design of Rainfall Catchment and Filtration Systems for Coastal Rhode Island Communities") - Water Resources Research Institute Reports - Incorporating Latest Technologies in a Cost-Effective Design of Rainfall Catchment and Filtration System for Coastal Rhode Island Communities


14. 2005RI32B ("Development of a Statewide Public Water-Supply GIS Coverage for Rhode Island") - Articles in Refereed Scientific Journals - Logan, Patricia; Veeger, Anne, and Boving, Thomas,


26. 2004RI26B ("Mitigating Runoff Contamination Due to Delicing and Anti-Icing Operations at T.F.Green Airport") - Water Resources Research Institute Reports - Hunter, Chris D. Mitigating Runoff Contamination Due to Deicing and Anti-Icing Operations at T. F. Green Airport
29. 2004RI23B ("Stream Stability and Scour Potential for Rhode Island Bridges") - Water Resources Research Institute Reports - Tsiatas, George, Stream Stability and Scour Potential for Rhode Island Bridges
31. 2003RI21B ("Electronic Dissemination of Institute Related Research") - Water Resources Research Institute Reports - Tsiatas, George. Electronic Dissemination of Institute Related Research
34. 2003RI14B ("URI Water Conservation Program Development") - Water Resources Research Institute Reports - Rose, Vincent C. URI Water Conservation Program Development