

**Water Resources Center
Annual Technical Report
FY 2010**

Introduction

This is a report on the projects of the Rhode Island Water Resources Center (RIWRC) during the period between March 1st 2010 to February 28th 2011. The Rhode Island Water Resources Center 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 one undergraduate student, Ashlee Bettencourt is supported by the Center.

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 RI Water Resources Center Grant to complete her research entitled “Use of Manometric Techniques to Evaluate the Disinfection Properties of Nanomaterials for the Treatment of Different Sources of Drinking Water.” 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 in a previously funded project in addition to applying the results of this research to water treatment in developing countries.

Dr. Thomas Boving, an associate professor in the College of the Environment and Life Sciences, was funded by the USGS through a RI Water Resources Center Grant to complete his research entitled “Influx of Petroleum Hydrocarbons to Impermeable Surfaces and Surface Water.” Funding from this grant allowed him to develop stormwater contaminant sampling techniques. Knowledge gained allowed him to apply for and receive a RI Department of Transportation grant to create a Stormwater Demonstration Center at URI.

Dr. Harry Knickle succeeded in hosting the Fourth Annual Clean Water Conference and The Third 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. 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 a water disinfection measurement procedure and to develop techniques to sample and measure roadway runoff hydrocarbons. Two research projects were funded.

Dr. Craver's study aimed to determine the effect of different water chemistry conditions on the bactericidal properties of silver nanoparticles. Her conclusions were that there was a correlation between the survival rate of *E. coli* and the average size of silver nanoparticles. Her findings can be applied to the design of mechanically simple filters which can not only remove particulates but can also have disinfection properties.

Dr. Boving's study was designed to measure the influx of hydrocarbons such as PAHs from the atmosphere to infrastructure surfaces such as parking lots. These adsorbed hydrocarbons can be released to the aquatic environment during precipitation events. His goal was to develop sampling techniques which would be simple but efficient. These results could be used to develop strategies for purifying stormwater runoff.

Use of Manometric Techniques to Evaluate the Disinfection Properties of Nanomaterials for the Treatment of Different Sources of Drinking Water

Basic Information

Title:	Use of Manometric Techniques to Evaluate the Disinfection Properties of Nanomaterials for the Treatment of Different Sources of Drinking Water
Project Number:	2010RI86B
Start Date:	3/10/2010
End Date:	12/31/2010
Funding Source:	104B
Congressional District:	02
Research Category:	Water Quality
Focus Category:	Water Quality, Groundwater, Treatment
Descriptors:	
Principal Investigators:	Vinka Craver

Publications

1. Submitted and currently in review: Oyanedel-Craver, Vinka; Hongyin Zhang, 2011, Evaluation of the Disinfectant Performance of Silver Nanoparticles in Different Water Chemistry Conditions, Journal of Environmental Engineering.
2. Conference Presentation: Zhang, Hongyin; Vinka Oyanedel- Craver, 2010, Effect of Water Chemistry on Disinfection Performance of Silver Nanoparticles (Abstract), "in" Abstracts of Papers of the American Chemical Society, ENVIR-260.
3. Conference Presentation: Oyanedel-Craver, Vinka; H. Zhang, S. Narckiewicz, 2011, Evaluation of Different Silver Compounds Applied to Point-of-Use Ceramic Water Filter, "in" Ceramic Water Filter Workshop, WEF Disinfection 2011, Cincinnati, Ohio.
4. Conference Presentation: Oyanedel-Craver, Vinka; C. F. H. Krause, J. A. Smith, 2011, A Characterization of Bacterial Disinfection Kinetics Using Silver Nanoparticles, "in" Conference Proceedings WEF Disinfection 2011, Cincinnati, Ohio.
5. Conference Presentation: Oyanedel-Craver, Vinka; E. Fauss, N. Swami, H. Yu, C. Krause, J. A. Smith, 2011, Impact of Silver Nanoparticle Concentration and Size in Colloidal-Silver-Impregnated Ceramic Filters for Point-of-Use Removal of E. coli and MS-2 Phage, "in" Conference Proceedings WEF Disinfection 2011, Cincinnati, Ohio.

Use of Manometric Techniques to Evaluate the Disinfection Properties of Nanomaterials for the Treatment of Different Sources of Drinking Water

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ABSTRACT

This study aimed to determine the effect of different water chemistry conditions on the bactericidal properties of silver nanoparticles (AgNPs). Lower disinfection performance of AgNPs was obtained in divalent cationic solutions in comparison with monovalent solutions with the same concentration. Average particle size of AgNPs increased with increasing electrolyte concentration as divalent cat-ions (Ca^{2+} and Mg^{2+}) produced larger AgNPs aggregates than those formed with monovalent solutions. ξ -potential measurements showed that AgNPs in divalent cat-ionic solutions had low absolute ξ -potential values (-9.8- -23.2 mV) while the values obtained in monovalent solutions were considerable higher. The measurements of the concentration of ionic silver released indicated that the fraction of dissolved Ag^+ (5.9-18.8 ppb) was around 0.1% of the total mass of Ag^0 added. The contribution of Ag^+ to the overall disinfection performance was negligible at the conditions tested. In this study, we have analyzed different physico-chemical properties of silver nanoparticles and the survival rate of *Escherichia coli* (*E. coli*) in different AgNPs solutions. The data we collected lead to a correlation between the survival rate of *E. coli* and average the size of AgNPs. We found a strong correlation between these two parameters that can be fitted to a saturation type curve, reaching a survival plateau around 20% survival at an average particle size of 200 nm for all the water chemistry conditions tested.

KEYWORDS: silver nanoparticles, ionic strength, organic matter

PROBLEM STATEMENT AND RESEARCH OBJECTIVES

Groundwater resources supply drinking water to approximately a quarter of the statewide population and in some southern and western part of the state communities are fully dependent on this valuable resource. Large water treatment plants commonly use chlorination to disinfect the water and also to prevent the re-growth of potentially pathogenic bacteria in the distribution

system [3]. The low concentration of organic matter in groundwater in these areas and the production of disinfection by-products are at a minimum, however, since chlorine-based disinfection processes were introduced in Rhode Island less than 10 years Rhode Island residents have been dissatisfied with the taste and smell of chlorinated water. Even more challenging is problem that more than 100,000 private well owners have to keep up a high water quality in their homes and therefore must turn to less favorable methods of treatment, such as chlorine. Point-of-consumption technologies (e.g. reverse osmosis, filtration) are currently available for well owners, but they tend to be expensive, difficult to operate and maintain 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 removing bacteria. Previous research performed by the principal investigator on this project with silver nanoparticles suggested that this nanomaterial could be use as an alternative to chlorine in small point-of-of use technologies- such as ceramic filters and sand filters. This research proposes an innovative approach to evaluate the use of three new metal-based nanomaterials using manometric respirometry techniques. Respirometry has been used extensively for wastewater toxicity monitoring for decades. The principle of the method relies on the inhibition of the respiration of the bacteria in the presence of toxicants. Hence, microbial respirometry is a more direct indication of toxicity for this environment. Bacterial respiration is usually monitored by the oxygen uptake rate of the bacteria and standardized respirometric tests have been established for this use. In manometric respirometry techniques bacterial respiration is monitored by means of the pressure drop, due to oxygen uptake by the microorganisms, in the headspace of a closed container where the bacteria/sample mixture is placed.

METHODOLOGY

Synthetic water solutions

Synthetic water solutions were prepared using eight different solutions, four mono-valent and three divalent salts in addition to one solution containing humic acids (HA). These different solutions were prepared using cations concentrations ranging from 10 to 1000 mg/L (ionic strength range 0.25-167) and HA concentrations ranging from 0.2-20 mg/L. These ranges of concentrations were selected to mimic the ionic strength and dissolved organic carbon (DOC) content in natural waters (seawater conditions were not included). Table 1 presents the complete list of solutions tested. The effect of cations with different valence and anions on the disinfection performance and average particle size of AgNPs was evaluated using a statistical test using a general linear model in PASW SPSS 18.0. All salts and other reagents were ACS reagent grade and used as received.

Preparation and characterization of AgNPs

AgNPs (70.37% w/w Ag⁰) stabilized with casein were obtained from Argenol laboratories. The nanoparticles are proposed to bind to casein polymers surface via complexation with the carboxylate or amino group of casein (Liu & Guo, 2009). A fresh AgNPs stock solution of 4 mM was prepared immediately before testing using deionized (DI) water and the respective electrolyte as presented in Table 1. Transmission Electron Microscopy (TEM) observations of AgNPs were performed with a JEM-2100 TEM transmission electron microscope (Jeol) (Figure 1). The surface charge and average size distribution were determined by zeta potential and dynamic light scattering (DLS) using a Zetasizer (Nano ZS, ZEN 3600, Malvern) at 25 °C. Silver

nitrate (ACS reagent grade) was used to compare the antimicrobial activity between AgNPs and Ag⁺ ion. Silver ions released in each batch test concentrations were measured by passing a sample through an 10,000 nominal molecular weight cut-off (NMWCO) ultrafiltration membrane (Millipore, NMWCO: 10,000) using a stirred ultrafiltration cell (Millipore, Model 8200) in dark condition. Concentrations of silver ion were analyzed using ICP-MS (X series, Thermo Elemental).

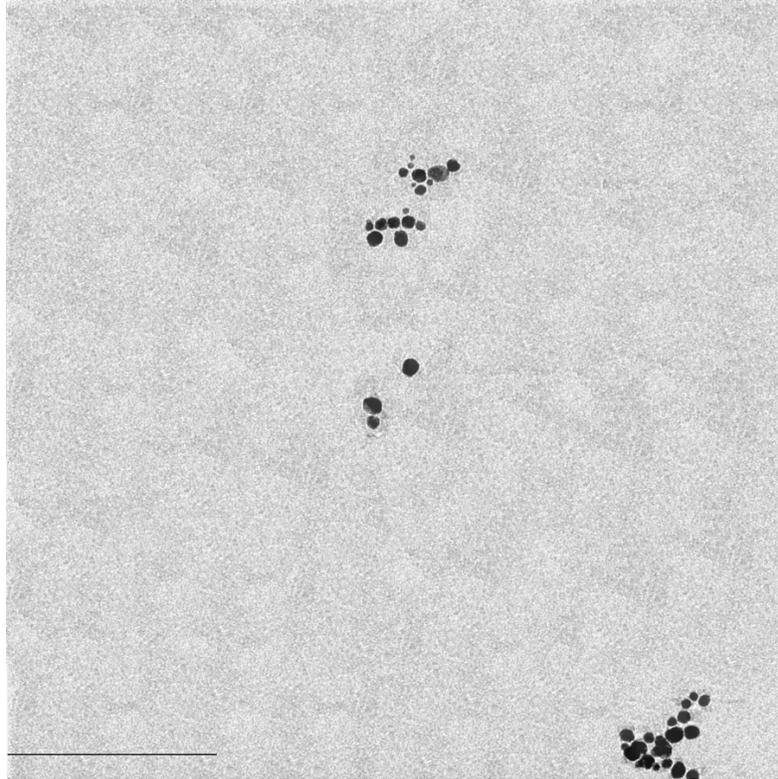


Figure 2. TEM image of AgNPs.

Microbial cultures

A non-pathogenic wild strain of *E.coli* provided by IDEXX laboratories was used for bacteria transport experiments. This organism was selected because of its use as a specific indicator of fecal contamination in drinking water and its extensive use in several studies on AgNPs, which will allow us to compare our results with previously published work. Bacteria were grown as described by Vigeant et al. (2002). Cells were re-suspended in a sterilized solution prepared with the respective electrolyte solution (Table 1) to a concentration of $(1\pm 4) \times 10^{10}$ CFU/ml. Determination of the *E. coli* concentration was performed using the membrane filtration technique, applying m-FC with Rosolic Acid Broth (Millipore) and incubation at 44.5 °C for 24 h. Blue colonies were counted and recorded as individual *E. coli*.

Table 1. Ion composition and pH across various water chemistry conditions

	Cation	Anion		
Ca²⁺(Cl)	Conc.(mg/L)	Conc.(mg/L)	Ionic strength	pH
	1000	1775	75	5.84
	500	887.5	37.5	6.11
	250	443.8	18.8	6.43
	50	88.8	3.8	6.76
	10	17.8	0.8	6.81
Ca²⁺(NO₃⁻)	1000	1550	75	6.13
	500	775	37.5	6.16
	250	387.5	18.8	6.27
	50	77.5	3.8	6.38
	10	15.5	0.8	6.6
Na⁺(Cl)	648	1000	28.2	6.76
	324	500	14.1	6.76
	162	250	7.05	6.77
	32.4	50	1.41	6.79
	6.5	10	0.3	6.79
Na⁺(HCO₃⁻)	377	1000	24.4	9.26
	188.5	500	12.2	9.16
	94.3	250	6.1	8.78
	18.9	50	1.22	7.5
	3.77	10	0.24	7
K⁺(NO₃⁻)	629	1000	16.1	6.92
	314.5	500	8.05	6.92
	157.3	250	4	6.92
	31.5	50	0.81	6.91
	6.3	10	0.16	6.91
K⁺(SO₄²⁻)	812.5	1000	31.2	7
	406.3	500	15.6	6.99
	203	250	7.8	6.98
	40.6	50	1.56	6.9
	8.1	10	0.3	6.9
Mg²⁺(SO₄²⁻)	1000	4000	166.8	6.25
	500	2000	83.4	6.34
	250	1000	41.7	6.39
	50	200	8.34	6.42
	10	40	1.7	6.54

Humic acid	20	n/a	n/a	6.5
	10	n/a	n/a	6.65
	2	n/a	n/a	6.66
	1	n/a	n/a	6.66
	0.2	n/a	n/a	6.65

n/a: not applicable

Antibacterial assay

Different solutions were prepared with mono-valent and divalent salt and organic matter compounds to mimic different natural water chemistries. Bacteria deactivation batch tests were performed using manometric respirometric equipment (OxiTop control system, WTW Weilheim, Germany). An OxiTop control system includes a sample bottle sealed with a measuring head, a small container for CO₂ absorbent fixed at the neck of the bottle, and an OxiTop controller for data recording. The test is based on automated pressure measurements conducted via piezoresistive electronic pressure sensors in a closed bottle under constant temperature. Different amount of salts, DI water, and 10 ml *E. coli* (total 100 ml mixture, *E. coli* concentration: 10⁹ CFU/ml) were inoculated into sample bottles. The sample bottles were sealed with the measuring heads and placed in the incubator at 25 °C. The endogenous respiration was determined by measuring the pressure drop within 2-3 h without adding carbon source or nanoparticles. Then, 0.5 ml glucose of a 70 g/L was injected to determine the oxygen uptake rate (OUR) without AgNPs. Finally, after about 2-3 h, 0.25 ml AgNPs stock solution was injected into the bottles to determine the alteration of the OUR due to the reduction of bacteria. The total duration of the experiments was 20 h. The percentage of the bacteria reduction using a modified equation from Tzoris et al. (2005) was calculated using equation 1:

$$Survival\ rate\ (\%) = \frac{P_t - P}{P_c - P} \times 100 \text{ (eq.1)}$$

Where P_c is the pressure drop after the injection of glucose, P_t is the OUR after the injection of AgNPs, P is the OUR during the endogenous respiration without the addition of carbon source or nanoparticles. Figure 2 presents a typical respiration curve. Compared to the conventional deactivation methods based on microbial growth (such as plate count method), the manometric respirometric method determined the activity of all active bacteria (not only those that are able to grow). Other advantage is that this method is based on the total oxygen uptake rate of all bacteria while the plate count method could miscount colonies grown from bacteria aggregates, considering only individual bacteria.

Data analysis

The data acquired were fitted using the Origin 8 software, minimizing the weighted sum of squared errors of determined parameters between the calculated values and the experimental data. Linear regression analysis with a dummy variable to compare the survival rate of *E. coli* and particle size in the presence of different ions was performed using PASW SPSS 18.0. F statistic values and *p* values were calculated. *p* values of less than 0.05 were considered significant.

RESULTS

The shape and sizes of AgNP in DI water determined by TEM are presented in Figure 1. AgNPs exhibited a spherical shape which is in common with other studies (Liu & Hurt, 2010; Morone et al., 2005). The average size of AgNP was 75.5 ± 2.56 nm using DLS which is larger than sizes determined by TEM (12.6 ± 5.7 nm). This discrepancy is likely due to the formation of AgNP aggregates. In addition, DLS measurement takes into account volume-squared weighted distributions and it can be more significantly influenced by small numbers of large aggregates in comparison to TEM size measurement.

Figure 3 shows that the survival rate of *E. coli* (0-20%) increased with increasing ion concentration across all conditions tested. The survival rates of *E. coli* were 18.3% and 20.2% at 1000 mg/L for Mg^{2+} and Ca^{2+} , respectively, while survival rate for most mono-valent cations and anions at 1000 mg/L was below 10% (with the exception of sulfate mono-valent salts). Humic acid (HA) was used as natural organic matter in this antimicrobial assay. The survival rate of *E. coli* in HA was between 4 and 5%. Similarly, Gao et al. (2009) showed that the toxicity of AgNPs of bacteria and microinvertebrate decreased with increasing concentration of natural organic matter as total organic carbon (10^{-4} -10 mg/L).

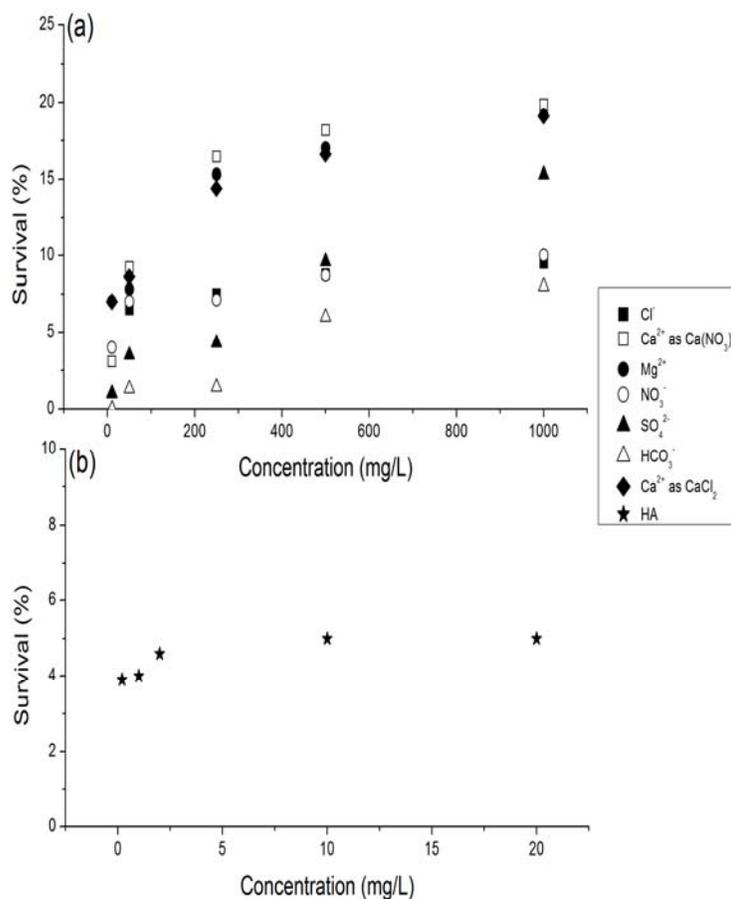


Figure 2. Plot of viability of *E. coli* cells in the presence of AgNPs in (a) salts solutions, (b) HA solutions. Incubation time: 20h, temperature: 25 °C, AgNPs concentration in each sample: 11.5 mg/L. The concentrations of the ions are listed in Table 1. It is clear that Ca^{2+}

and Mg^{2+} increase the survival rate of *E. coli*.

Figure 4 presents the sizes of AgNPs across different water chemistry conditions. The average size of AgNPs increased when the concentration of salts increased. Our result showed that Mg^{2+} and Ca^{2+} cations produce a large aggregation of AgNPs. At 1000 mg/L, sizes of AgNPs reached over 1000 nm for Mg^{2+} and Ca^{2+} cations while aggregates produced by mono-valent cations at the same concentration were about ten times smaller. These observations agree with the Schulze-Hardy rule, which indicates that the critical coagulation concentration of a typical colloidal system is extremely sensitive to the valence of the counter-ions. Sizes of AgNPs in HA solutions decreased with increasing HA concentration except at the point of 1 mg/L (32.5 nm). At 10 mg/L, AgNPs sizes in HA solution reached 31.3 nm, which was similar to the sizes for mono-valent cations at the same concentration. The aggregates produced by mono-valent cations at 10 mg/L were below 40 nm.

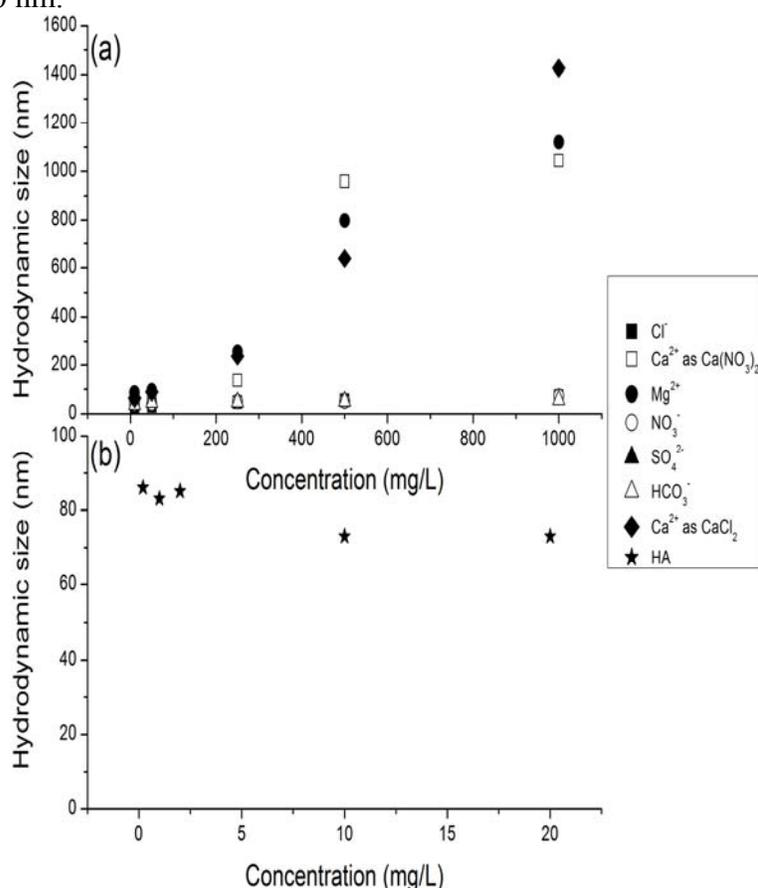


Figure 3. Plot of hydrodynamic particle sizes of AgNPs in different water chemistry conditions. (a) Hydrodynamic particle sizes in salts solutions. (b) Hydrodynamic particle sizes in HA solutions. Incubation time: 20h, temperature: 25 °C, AgNPs concentration in each sample: 11.5 mg/L. The concentrations of the ions are listed in Table 1.

ξ -potential is related to the stability of the colloidal systems. Its value (negative or positive) indicates the degree of repulsion between adjacent or charged particles in a colloidal system. As Figure 5 shows, AgNPs had negative ξ -potentials across all water chemistry conditions, which is attributed to the adsorption of various anions onto the AgNPs surface. The data also showed that

ζ -potential of AgNPs solutions became less negative as the salt concentration increased. However, AgNPs in divalent cationic solution exhibited lower absolute ζ -potential values (-9.8 mV to -23.2 mV) in comparison with mono-valent cations (-15.6 mV to -39.8 mV). Our values are smaller than those obtained by Jin et al., (2010) who found that the ζ -potentials of AgNPs at different fixed ionic strength solutions (5.6 mM) ranged from -10mV to -60 mV and with the addition of divalent cationic to the solutions (7 mg/L Mg^{2+} and 40 mg/L Ca^{2+}), the range decreased to between -10 mV to -40 mV. A different surface modification of the nanoparticle and, in our case, higher concentration of electrolyte can explain the difference in the results. However, both studies showed that the attractive interaction between divalent cations and negative charged AgNPs increased led to higher aggregation and large particles. For AgNPs in HA solutions, ζ -potentials decreased (-29.1- -35.2 mV) with increasing concentration. At 10 ppm, ζ -potentials of AgNPs in HA solution exhibited similar values to those in the mono-valent cationic solutions, except NaCl solution.

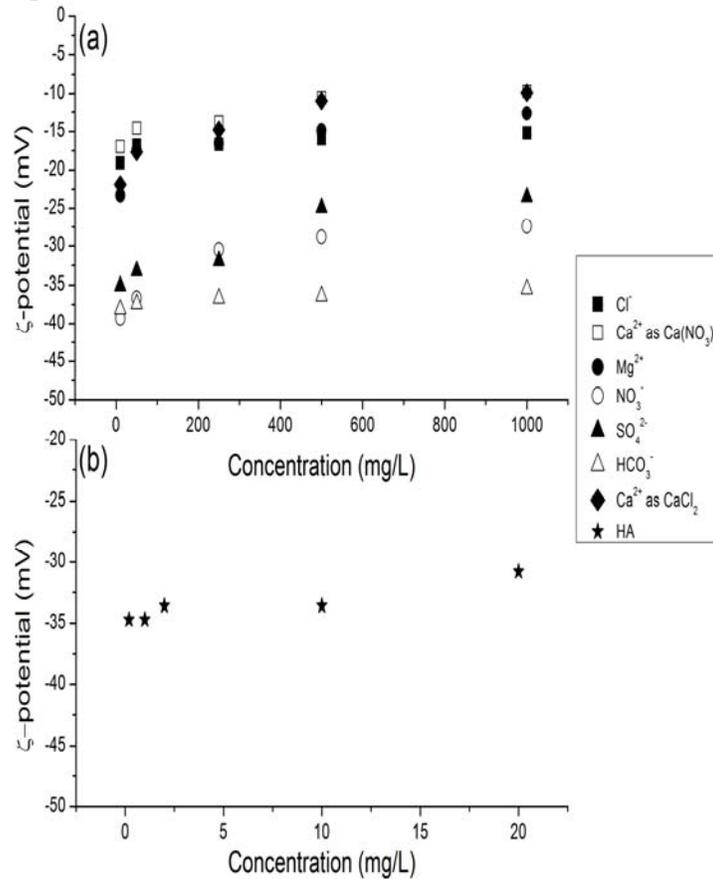


Figure 4. Plot of ζ -potential of AgNPs in (a) salts solutions, (b) HA solutions. Incubation time: 20hr, temperature: 25 °C, AgNPs concentration in each sample: 11.5 mg/L. The concentrations of the ions are listed in Table 1.

Figure 6 shows that the absolute ζ -potential values for *E. coli* solutions were lower compared to those for AgNPs solutions at the same electrolyte concentration. Similarly to the AgNPs, *E. coli* in divalent cationic solutions had less negative values, ranging from -0.71 mV to -5.44 mV, while in NaHCO₃ solutions, the most negative values were obtained (-7.7 mV to -11.6 mV). Divalent cations were more likely to be adsorbed to the *E. coli* membrane, reducing the absolute

ζ -potential values. Consequently, less electrostatic repulsion was produced when AgNPs were mixed with the bacteria in solutions containing divalent cations, making the AgNPs-bacteria interaction easier to happen; thus, decreasing the survival rate of *E. coli*.

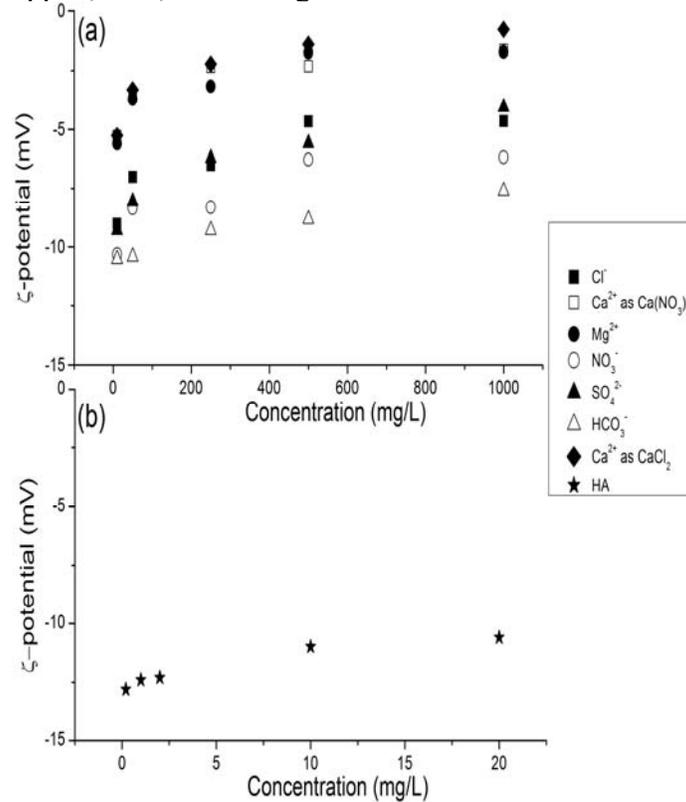


Figure 5. Plot of ζ -potential of *E. coli* in (a) salts solutions, (b) HA solutions. Incubation time: 20h, temperature: 25 °C, *E. coli* concentration: 10⁹ CFU. The concentrations of the ions are listed in Table 1.

The silver ionic release (Figure 7) measured during these tests was about 0.1% of the total mass of silver added as AgNPs (5.9-18.8 ppb). Discrepancies in the silver ionic release have been found in previous studies. Liu & Hurt, (2009) reported that the silver ionic release of AgNPs (initial concentration: 0.05 mg/L) in seawater (ionic strength: 0.7 M) and deionized (DI) water after 24 h were 20 wt% and 50 wt%, respectively. However, percentages below 1% have been also obtained under conditions similar to the ones used in this study (Suresh et al., 2010; Jin et al., 2010). To determine the contribution of the silver ions released to the overall disinfection performance of the AgNPs, several AgNO₃ solutions were prepared ranging from 1 to 20 ppb (as Ag⁺), and the survival rate of *E. coli* was determined following the same abovementioned manometric respirometric method. At all the concentrations tested, 100% *E. coli* survival was obtained, which indicated that silver ions in solution have a negligible effect on the disinfection performance of AgNPs.

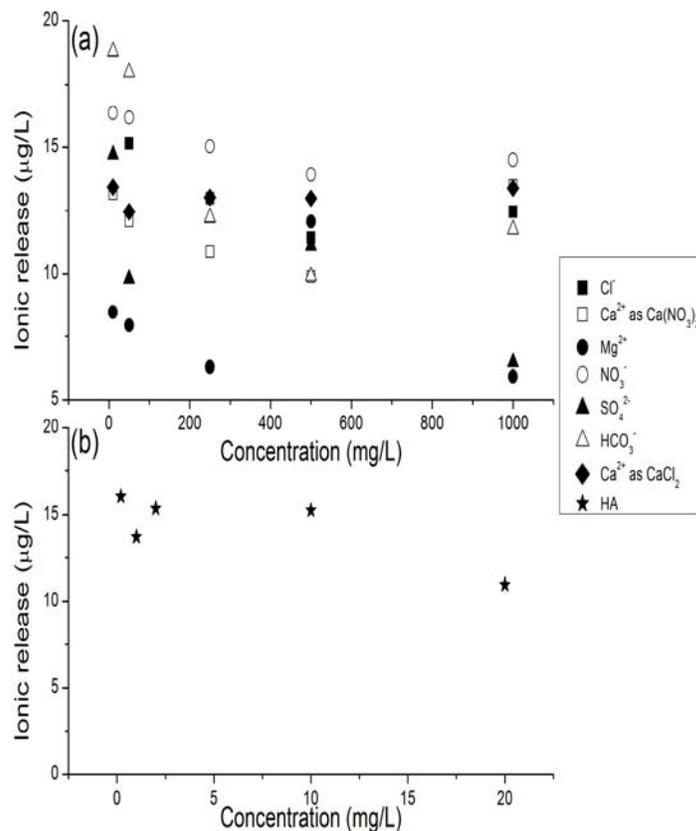


Figure 6. Silver ionic release in (a) salts solutions, (b) HA solutions. Incubation time: 20h, temperature: 25 °C, AgNPs concentration in each sample: 11.5 mg/L. The concentrations of the ions are listed in Table 1.

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Influx of Petroleum Hydrocarbons to Impermeable Surfaces and Surface Water

Basic Information

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Focus Category:	Water Quality, Surface Water, Non Point Pollution
Descriptors:	
Principal Investigators:	Tom Boving

Publications

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2. Boving, T.B.; B.S. Choudri, P. Cady, A. Davis, K. Patil, V. Reddy, 2011, Acceptance of a Riverbank Filtration System in Rural India- Special Issue on Bank Filtration, J. Indian Water Works Association. (accepted).
3. Boving, T.B.; R. Rowell, 2010, Environmental Applications of Lignocellulosic Filter Materials, Sustainable Development in the Forest Products Industry. (Editor: R. Rowell). Chapter 9, UFP Editions, Lisbon, Portugal.
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Influx of Petroleum Hydrocarbons to Impermeable Surfaces and Surface Water

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ABSTRACT

Storm water runoff around the United States and most other developed countries contains elevated concentrations of a variety of contaminants, including petroleum hydrocarbons. An important, but little investigated source of these contaminants is influx from atmospheric sources. These hydrocarbons accumulate on impermeable surfaces, such as parking lots, and together with “conventional”, automotive derived hydrocarbon contamination, eventually wash off into surface and ground water. To aid in a better understanding of the potential significance of this atmospheric influx, a time-integrated atmospheric bulk-deposition sampler network was installed in Rhode Island. The principal goal of this sampler network is to quantify the bulk deposition rates of a particularly important class of petroleum hydrocarbons, i.e. PAH (polycyclic aromatic hydrocarbons). Relying on a sampler system developed in Germany, where this system is the accepted national standard for quantifying atmospheric bulk deposition rates, we installed four samplers in a (1) rural, (2) urban, (3) sub-urban, and (4) coastal land use area during the summer and fall of 2010. A first sampling round was conducted in the fall of 2010 which yielded no results. Difficulties in extraction of the sampler cartridges together with a sampling period that proved to be too short (60 days) to accumulate sufficient PAH mass for analysis were the reasons attributed to this lack of results. Due to freezing and breakage of the sampler cartridges during the winter, no samples could be collected between January and March 2011. Since April 2011, four samplers have been collecting PAH atmospheric deposits. Based on our earlier findings, the sample period was extended to 90 days, which means that at the time this report was prepared, no new data was available for discussion.

PROBLEM STATEMENT AND RESEARCH OBJECTIVES

Pollution of air, soil, and water is a global problem and because contaminants can persist in the environment for long periods, they pose a threat to human health and marine environments (Tuhackova et al., 2001). Even in remote areas, such as the arctic, airborne contaminants that settle out of the atmosphere have poisoned local food chains and caused adverse effects on local wildlife. The fate of Polar bears (Cone, 2003) is one well-known example for how even supposedly pristine regions have already been impacted by global pollution. Sources of airborne pollutants are manifold: combustion of petroleum hydrocarbons, forest fires, accidental and diffusive releases of toxic compounds, or windblown soil particles laced with anthropogenic chemicals, such as pesticides or fertilizers. Typically, pollutants associate with airborne particles (“dust”) or aerosols or are part of the gaseous phase. Much of the atmospheric dust is locally derived and consists of materials such as loess, pollen, or soot. Some atmospheric deposits, however, are exotic and have traveled thousands of kilometers from their source, e.g. major dust storms or volcanic eruptions (NADP 2004).

When these contaminants finally settle out (dry deposition) or wash out of the atmosphere (wet deposition), their deposition is diffuse and deposition rates vary over time and space (Leister and Baker, 1994; Bühler et al., 1998; Brun et al., 2004). This is why atmospheric bulk deposition (sum of wet and dry deposition) is a classical non-point source pollution problem. Wet deposition typically exceeds dry deposition in deposition rates (Franz et al., 1998) and deposition rates are typically higher in winter than in summer (Gocht, 2005). For both types of deposition, several processes such as washout of vapours or particles, particle sedimentation, gas absorption (air to water), and volatilization contribute to the flux rates. Thus, the deposition process of a certain compound strongly depends on its partitioning between gaseous and particle phases in the atmosphere (Gocht et al., 2006).

Although the scientific community is well aware of the pollution problem associated with airborne toxins, we have only a limited understanding of the fate and transport of these pollutants once they settle out of the atmosphere. Knowledge gaps exist in the understanding of spatial and temporal variations and the magnitude of contaminant bulk flux rates in urban, rural, and coastal areas. Also, it is largely unknown if the receiving soil(s) have a finite contaminant storage capacity, that – once exhausted – permits the partitioning of contaminants into water resources.

Leister and Baker (1994) identified atmospheric deposition as an important pathway of diffuse soil contamination with persistent organic pollutants (POPs) in rural areas. Since then several studies on passive air sampling for measuring air concentrations were published (Jaward et al., 2004; Farrar et al., 2005; Paschke and Popp, 2005; Söderström et al., 2005). But investigations using passive samplers for the determination of the atmospheric bulk deposition are scarce. For instance, Gocht et al. (2006) used the same sampler system employed in this study to quantify atmospheric bulk deposition rates in a rural area in southwestern Germany. Their results demonstrated that polycyclic aromatic

hydrocarbons (PAH) compounds can accumulate at annual deposition rates around $200 \mu\text{g m}^{-2} \text{a}^{-1}$. The mean wet PAH-deposition rates (i.e. the sum of 16 PAH species per cm of precipitation) in the New England region are described in Golomb et al. (2001), who determined deposition rates between $720 \text{ ng m}^{-2} \text{cm}^{-1}$ and $831 \text{ ng m}^{-2} \text{cm}^{-1}$. Sheu et al. (1996) measured dry deposition flux of total-PAHs near urban and industrial sites in South Korea. Their PAH flux averaged 166 and $211 \mu\text{g/m}^2\cdot\text{d}$, respectively.

Of particular interest is the transport and fate of pollutants associated with storm water runoff. The runoff from roadways and parking lots contains elevated concentrations of a variety of organic and inorganic contaminants, including polycyclic aromatic hydrocarbons (PAH) (Gooble et al. 2007). Most of these PAH compounds are toxic or even mutagenic and originate from many, predominantly anthropogenic, sources, such as automobile traffic or combustion processes. PAHs generally occur as complex mixtures and not as single compounds. Members of the PAH class include benzo(a)pyrene, naphthalene, and pyrene. Benzo(a)pyrene along with other PAHs are suspected of causing cancer in humans and are considered by the U.S. Environmental Protection Agency as “persistent, bioaccumulative toxic pollutants” (www.epa.gov/opptintr/pbt/fact.htm). PAH can travel in the atmosphere in association with dust particles, aerosols, and in gas phase over long distances. According to Söderström et al. (2005), PAHs with two or three rings are mainly associated with the vapor phase, 4-ring PAHs occur in both the gas and particle phases, whereas PAHs with five rings or more, are mostly bound to particles. Their eventual deposition is diffuse and varies over time and space (Söderström et al., 2005).

At this time, very little is known about the magnitude of PAH bulk flux rates in Rhode Island, i.e. the mass influx from the atmosphere to aquatic systems and soils. Quantifying this mass flux will permit a comparison with other contaminant inputs, such as automotive derived pollution that tends to accumulate on impermeable surfaces, such as parking lots or roadways.

The measurement and quantification of atmospheric PAH fluxes is important because it provides the data for a better understanding and management of non-point source pollution problems in Rhode Island and beyond. There are several different designs of bulk deposition sampling devices described in the literature (Winegar, 1993). In general, atmospheric deposition rates are best measured with a network of well calibrated and validated sample devices. The number of existing networks, however, is comparably small. Examples include the *Integrated Atmospheric Deposition Network* (IADN) that was established in 1990 to determine the magnitude and trends of atmospheric loadings of toxic contaminants to the Great Lakes (Cussion 1996). Also, EPA’s *Clean Air Status and Trends Network* (CASTNET) provides a nationwide, long-term monitoring platform designed to estimate dry deposition since 1991. A number of studies have determined wet or dry PAH deposition rates (Golomb et al., 2001; Sheu et al. 1996). Only very few investigations used passive samplers for the determination of the atmospheric bulk deposition of PAH (e.g. Gocht et al., 2006).

In this study we relied on a time-integrated bulk atmospheric deposition sampler device that was developed and field tested in Germany and other European countries. Because

this system is comparably low-tech and low-cost (ca. \$1500 a piece), it is now the national standard measurement device for determining atmospheric PAH bulk deposition rates in Germany (German Industrial Standard DIN 19739-2, 2003). Differences in measurement methods unnecessarily complicate the comparison of atmospheric deposition data and it is therefore sensible that scientists on both sides of the Atlantic use the same devices. Hence, the main benefits of employing this German sampler system are (1) using a field-tested and accepted sampler system that requires no additional investments in method development and analytical techniques and (2) generation of data that is directly comparable with data from overseas.

Obtaining a better understanding of the relative contribution of atmospheric pollution sources of PAH contaminants is the overarching, long-term goal of this project. We expect that our data will help scientists and environmental managers to assess and, if necessary, respond to the emerging environmental problem of atmospheric contaminant deposition. The immediate project objective was to set-up a time-integrated atmospheric PAH bulk-deposition sampler network in Rhode Island and start collecting data of PAH deposition rates in different land use areas. Further, this project permits testing of the sample collection protocol and chemical extraction procedures developed in Germany and, if necessary, the adjustment of these to the environmental conditions prevalent in Rhode Island.

METHODOLOGY AND MATERIALS

Passive sampler and extraction methods: A schematic drawing of the PAH bulk atmospheric deposition sampler is shown in Figure 1. The system was developed at the *Center for Applied Geosciences*, University of Tübingen (Martin, 2000; Holger, 2000). The system was extensively tested at the bench scale as well as in the field (e.g., Gocht, 2005; Gocht et al., 2006) and is now validated as a national standard in Germany after DIN 19739-2, 2003.

The passive sampling system consists of a borosilicate glass funnel and an adsorption cartridge packed with Amberlite® IRA-743 (Figure 1). The cartridges trap both the wet and dry deposition, either by adsorption and/or filtration of particles, respectively. Each cartridge contains about 15 g of the adsorber material, which was fixed on top and at the bottom with glass wool plugs. In the field, the funnels were placed inside a stainless steel container (open at top and bottom), which was connected to an 1 1/4 galvanized steel pipe vertically anchored in 2 feet of concrete. The container shields the sampler from direct sunlight exposure that could cause degradation of UV-sensitive PAHs (Orazio et al., 2002). After sampling periods of initially 60 days, later extended to 90 days, the cartridges were replaced by fresh ones and the funnels were cleaned with 200 ml acetone to avoid cross contamination. For QA/QC purposes, blanks (cartridges containing the adsorber material) accompanied the field cartridges from the sample site to the lab. Meteorological observations (temperature, precipitation and other data) were obtained from the nearest NOAA stations.

The cartridges underwent sequential solvent extraction four times with 50 ml acetone. An internal standard (fluoro-biphenyl) was added to determine recoveries. A liquid-

liquid extraction with cyclohexane transferred the PAHs into the cyclohexane phase followed by purification using column chromatography with coupled polar (Al_2O_3 , 5% deactivated) and non-polar (SiO_2 , 5% deactivated) adsorbents. Any litterfall that was collected in the samplers would have been sequentially extracted with an Accelerated Solvent Extractor (ASE 300, Dionex or similar), two times with acetone at 100°C and then with toluene at 150°C . However, no litterfall accumulated during the sampling period. The PAH (EPA 16-PAH) was quantified with a Shimadzu gas chromatograph/mass spectrometer (carrier gas: Helium; column: 30 m, 0.25 mm I.D.).

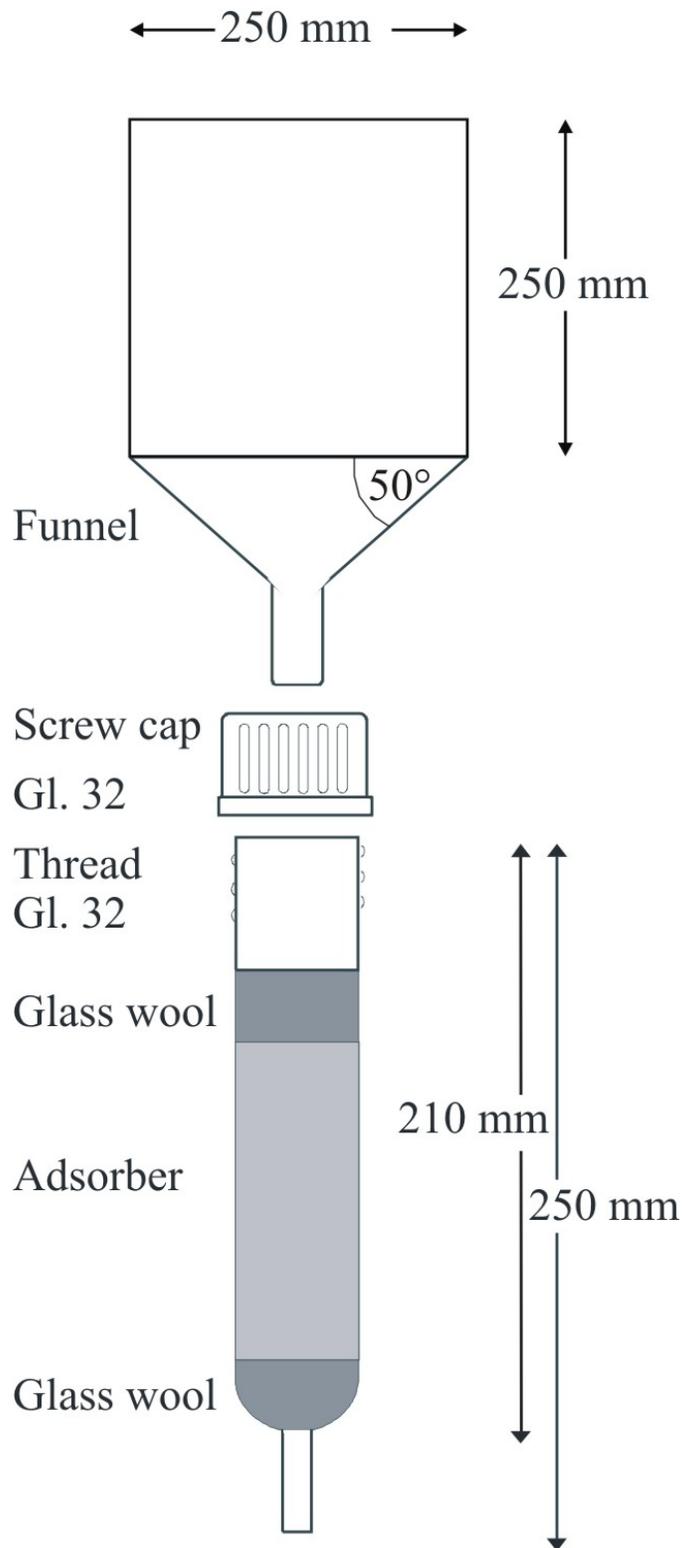


Figure 1: The bulk atmospheric deposition sampler for PAHs was developed at the *Center for Applied Geosciences, University of Tübingen* (After Gocht et al., 2006)

RESULTS

Study Area: Four PAH deposition samplers were installed during the summer and fall of 2010 (Figure 2). The principal site selection criterion was to cover different land uses, i.e. rural, urban, sub-urban and coastal areas. The sampler installed near Pascoag is placed in a low population density, forested watershed in a predominantly rural part of northern RI. Another sampler was installed on the grounds of the Brown University athletic complex in downtown Providence with the intent to capture atmospheric deposition in a densely populated urban area. A third sampler was installed on the grounds of the URI Weather Station on the Kingston campus in a sub-urban setting in southern RI. This sampler will be moved in the summer of 2011 to the newly completed Rhode Island Stormwater Treatment Demonstration Facility, which is located about 1/2 mile to the east of the current site. The re-location will permit direct PAH deposition measurements next to a parking lot/roadway from which the runoff quality/quantity (including PAH concentrations) will be extensively monitored. Finally, a fourth sampler was installed about a quarter mile inland from Rhode Island's south coast, near Indigo Point, South Kingstown. The GPS coordinates of all four sample stations were recorded.

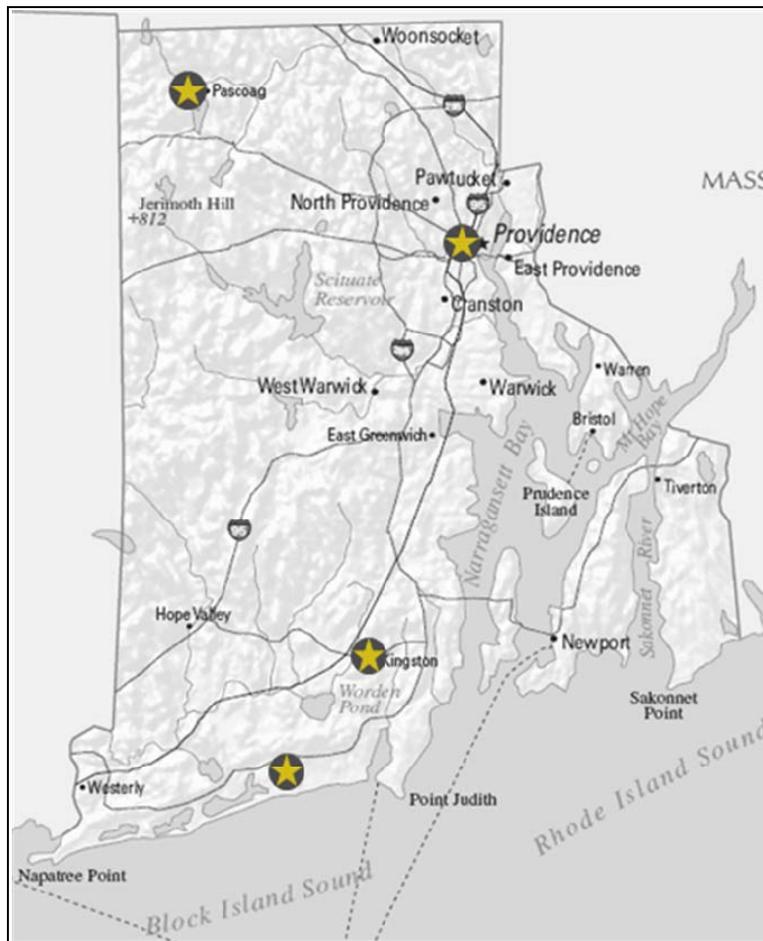


Figure 2: Map of the bulk deposition network installed at four Rhode Island locations (Stars).

Each site was vetted for safety of the field personal maintaining the sample stations as well as to prevent unauthorized access and tampering with the samplers. All samplers were installed 1.5 m above ground and permanently fixed to a 1 1/4 galvanized steel pipe that was cemented approximately 2 feet into the ground. Sample sites with no tree cover were selected to minimize blow-in of leaves and other debris.

The sampler at the URI weather station, Kingston campus, was selected in order to reliably test the sampling protocol and laboratory methods. The first deposition measurement period lasted 60 days, i.e. mid October to mid December. Extraction of the sampler sorbent material provided inconclusive results. That is, responses were detected in the GC/MS spectrum, but the PAH concentrations were below detection limit. The reason for the lower than expected detection of PAH were (1) short length of field sampling time (60 days) and (2) incomplete recovery of PAH sorbed to the sampler matrix. Based on these observations, it was decided to extend the sample exposure time to 90 days and to refine the sorbent extraction procedures by pre-purifying the Amberlite sorbent and the Al₂O₃ and SiO₂ used in purifying the extract before injection into the gas-chromatograph.

During a preliminary test of the PAH sampler device it was found that the glass cartridge that contains the Amberlite sorbent is prone to cracking at temperatures below freezing. Under those circumstances, any water co-sorbed to the Amberlite or simply caught inside the glass cartridge freezes and expands, resulting in the destruction of the cartridge and loss of the sorbent. For this reason, no samples were collected between January and March 2011. To circumvent this problem in the future, we researched solar heating devices which, if wrapped around the glass cartridge, would prevent freeze-cracking and therefore enable continued sampling year-round. However, the cost of these warming devices are currently beyond the available funding for this project.

Sampling resumed in April 2011 and is still continuing at this time. Hence, until the end of the currently ongoing sampling period (end of June) no PAH deposition results are available for discussion.

In anticipation of future funding, we have negotiated additional sampling locations outside the United States. During a visit to India and Oman in May 2011, we obtained permission to set up samplers on the campus of the Sultan Quaboos University in Muscat, Oman, and on the grounds of The Energy Research Institute (TERI) in Goa, India. We are currently negotiating with the University of Cape Verde Islands and the University of Puerto Rico, Mayaguez to set up two more samplers. These potential sampling sites were selected because they would permit tracking of atmospheric PAH fluxes to and from the United States, depending on the predominant wind directions.

This project supported one female PhD student, Miss Laura Schifman. Also, this project was leveraged to obtain funding for installing the Rhode Island Stormwater Treatment Demonstration Facility, which is intended to quantify the flux of organic (incl. PAH) and inorganic as well as pathogenic contaminants resulting from roadway and parking lot surfaces and demonstrate best management practices for their treatment. On this

background, the knowledge of the magnitude of the PAH atmospheric influx will enable us to discern this pathway from directly automotive derived inflows.

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Information Transfer Program Introduction

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. The goals of the Rhode Island's Water Resource Center 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.

The information transfer project is entitled "Clean Drinking Water 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 utilizing lectures, field trips and laboratory experiments was held. The summer-camp/workshop for high school students attracted 24, and participation numbers are expected to grow next year. The Clean Water conference will be held annually and promotion for the November 2011 conference will be more ambitious than this year.

Clean Water in Rhode Island

Basic Information

Title:	Clean Water in Rhode Island
Project Number:	2010RI89B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	2
Research Category:	Water Quality
Focus Category:	Education, Water Quality, Treatment
Descriptors:	None
Principal Investigators:	Harold Knickle, Geoffrey Bothun

Publications

There are no publications.

Clean Drinking Water in Rhode Island

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ABSTRACT

“Clean Drinking Water in Rhode Island” was a project focused on spreading information, sharing technology and the advancement of education by means of two major outreach activities: a hands-on summer workshop, centered on the topic of clean water, for middle and high school students to promote interest in clean water careers and a “Clean Water Technology Conference” for college students and clean water professionals.

Objectives

1. Run a summer workshop for middle and high school students on clean water
2. Host a technology conference on clean water

KEYWORDS: clean drinking water, information transfer, education

INTRODUCTION

Middle and high school students were recruited with the help of school teachers’ encouragement to participate in a week of lectures, lab activities and field trips that focused on clean water. The schedule for the workshop was Monday thru Friday during the week of June 28th-July 2nd, 2010. Students arrived at 9:00 am and left at 3:30 pm each day.

The Clean Drinking Water Conference is in its third year running. Lecturers were booked and students, professors and clean water professionals were invited to learn the recent happenings of the clean water industry.

METHODOLOGY

Campers predominately congregated in the University of Rhode Island Engineering Labs in Crawford and Bliss Halls on the URI Campus. Field trips to the East Greenwich Sewage Treatment Plant, URI 30 Acre Pond and associated wells, Scituate Reservoir and the Providence Water Supply Board Water Treatment Plant were also conducted during the week long summer camp.

Activities included presentations of the water cycle, the exploration of the chemistry of water, drinking water quality and treatment, sewage treatment and biological technology, runoff and storm water, industrial water pollution, pollution prevention, filtration and adsorption, the health effects of unclean drinking water and a discussion of the major sources of drinking water in

Rhode Island. Laboratory exercises included water quality sampling and testing, pH and dissolved oxygen measurement, bacteria pollution testing, conductivity testing, acid rain testing, aeration, as well as adsorption and filtration activities. Laboratory experience also included the use of some of the major equipment in the Environmental Laboratory.

Field work consisted of the collection of water samples from various locations and water bodies. Field trips were made to multiple fresh water treatment facilities and a sewage treatment plant. Students wrote a brief laboratory report for each laboratory exercise.

SUMMER CAMP DETAILS

**University of Rhode Island
Clean Water Engineering and Science Academy
Summer 2010: June 28th – July 2nd**

Session 1: Monday June 28

- Introduction and Survey
- Drops on a Penny Surface Tension
- Intro to Water Cycle
- Settling LAB
- Turbidity Measurements
- Intro to Water Chemistry
- Water Quality Testing
- Water Sample Collection
- Water Test LAB
- Laboratory Report 1

Session 2: Tuesday June 29

- Rxn Time & Temperature
- Intro to Sewage Treatment
- Introduction to Biology Technology
- Introduction to COD,BOD
- Bacteria check 4 microbes www.google.com
- Field Trip to Sewage Treatment Plant East Greenwich Arrive 12:30
- Laboratory Report 2

Session 3: Wednesday June 30

- Macro Invertebrates
- Introduction to Water
- Runoff and Storm Water
- Introduction to Pollution Prevention.
- Oil Spills Lab and graphs
- Alternate Lab
- Video: Ponds & Rivers
- Laboratory Report 3

Session 4: Thursday July 1

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

Session 5: Friday July 2

- 30 Acre Pond Sampling
- Dissolved Oxygen, pH, and Hardness Testing
- Filtration and Settling
- Filtration Laboratory
- Laboratory Report 4
- Post Assessment Survey
- Certificates

Example of a laboratory assignment: Oil Spill Laboratory

What is a **surfactant**? (soap) grabs water and grabs oil with weak bonds

Work in Teams

Procedure

Part 1

1. Fill aluminum pans to about one inch
2. Fill small ketchup cup half way with light oil (SAE10W30)
3. Pour oil carefully in corner of aluminum pan (Weigh Oil)
4. Measure the distance the oil spreads with time using a ruler at predetermined intervals
5. Measure the longest distance the oil travels from the corner of the pan

Part 2

1. Fill an eye dropper with liquid soap (**surfactant**)
Dishwashing soap is OK
2. Place a drop from the eye dropper in the pan near the edge of the spread
What happens?
3. Repeat with more drops
Describe in words what has happened.

Part 3

1. Use EXCEL to graph the experimental spread of oil in the aluminum pan
Use the computers in the Engineering Computer LAB
2. Use the proper procedures in making the graph as follows-
Title: include information about the experiment
X Axis: This is time and include the units of time
Y Axis: This is distance and include the units of distance

Part 4

1. Calculate the spread of oil with time from a theoretical equation
Graph this calculation on the same graph as the experimental data
2. Describe the differences in the results
3. Any explanations?

CLEAN WATER CONFERENCE DETAILS

URI

Cherry Auditorium

Upper College Road across from the University Club

Clean Drinking Water Conference

Thursday, November 4, 2010

1:00 PM to 4:00 PM

Clean Drinking Water Conference Final Program

Session 1: 1:15pm to 2:00 pm

- **Dr. Michael Sullivan, DEM Director**
Clean Water Challenges in Rhode Island

COFFEE BREAK

Session 2: 2:15 pm to 2:45 pm

- **June Swallow, Department of Health**
New Regulations for Clean Water

Session 3: 2:45 pm to 3:05 pm

- **Yasah Vezele, Dr. Thiem and Dr. Knickle**
Expanding Water Supply in Rhode Island

Session 4: 3:05 pm to 3:35 pm

- **Henry Meyer, District Manager, Kingston Water District**
Clean Water from Wells

Session 5: 3:35 pm to 4:00 pm

- **Hongyin Zhang, URI PhD Student,**
Effect of Different Water Qualities on the Disinfection Performance of
Silver Nanoparticles Zhang

ADJOURN

These presentations have been posted to www.wrc.uri.edu.

SUMMER CAMP RESULTS

Twenty-three students, from three different communities in Rhode Island, enrolled in the clean water summer workshop. Three undergraduate College of Engineering students acted as student-to-student mentors for this academy. These URI undergraduates provided organization and encouragement to the high school students to complete the four laboratory assignments. The high school students were highly motivated and their performance enabled each to complete the various laboratory assignments. Campers made comments of especially liking the hands-on laboratory assignments.

The water treatment plant visits were well received by both the visiting students and the plant employees. One such facility was a modern wastewater treatment plant in East Greenwich, Rhode Island. This plant is typical of wastewater treatment plants in its primary treatment methods; however its secondary treatment is unique due to the use of rotary filters. It is important to note that before discharging into Narragansett Bay this East Greenwich plant uses ultraviolet lamps to kill any bacteria left in the discharge stream.

Another significant field trip was the visit of the University of Rhode Island's fresh water system. This visit included students taking the trek down to Thirty Acre Pond which supplies the aquifer from which water is pumped for the entire campus. Lime is added to neutralize the water which is then pumped up to a large storage tank that is gravity feed to the academic buildings.

On Thursday, campers were bused to the Scituate Reservoir and the Providence Water Supply Board Water Treatment Plant. This plant provides water to more than 60% of the residents of the State of Rhode Island. The Providence Water Supply Board Water Treatment Plant also exhibits a number of important drinking water treatment steps including settling, aeration and chlorination which were fully explained to the students by plant personnel. The plant visits were enhanced with lecture and laboratory experiences outlined in the schedule for this week long academy.

CLEAN WATER CONFERENCE RESULTS

The Clean Drinking Water Conference was a success in that attendance was up from last year. This conference's success can be attributed to the excellent selection of speakers and the fact that this is its third year running. The Director of DEM gave an eye opening lecture concerning Rhode Island's Clean Water Challenges, which touched base with the Rhode Island Water Resources Center's mission of researching solutions to these challenges. Later that same day, RIDEM Director Michael Sullivan sat for an interview with the RIWRC, going into more depth about his earlier lecture. This interview was posted on RIWRC's website for those who could not make the conference and other interested public to view.

The following pictures are from the Scituate Reservoir and Providence Water Supply Treatment Plant.





Academy Students in front of the water aeration system at the Scituate Clean Water Plant

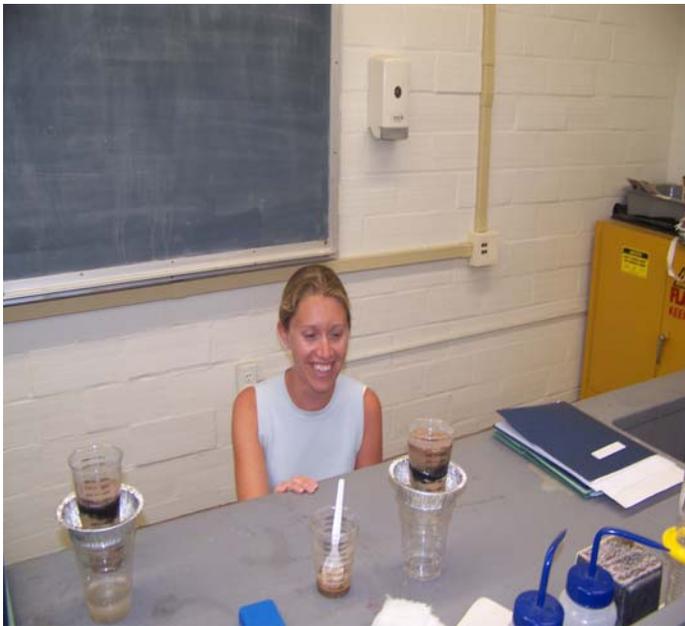


Rotary Filters at the East Greenwich Sewage Treatment Plant



Hands-on Experiments:

The filter consists by layer, from the bottom to the top of aquarium gravel: fine white sand, a layer of cotton, powdered charcoal, another layer of cotton, followed by a final layer of sand. A mixture of clay water was passed through the filter to determine both the filter's effectiveness and the time for accumulation of clean water.



Students constructing the filters for experimentation



Academy Students Performing Tests on URI Drinking Water with Mentor Jonathon Suero in Background

Water Quality Lab



The following pictures depict the URI Fresh Water System



Pump Building



30 Acre Pond

USGS Summer Intern Program

None.

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	1	0	0	0	1
Masters	3	0	0	0	3
Ph.D.	2	0	0	0	2
Post-Doc.	0	0	0	0	0
Total	6	0	0	0	6

Notable Awards and Achievements

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

We have found these academic projects to be 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 9.4% this year. Also, total minority enrollment has more than doubled at the University during this same time period. By working with the same school over a three year period, the number of applications in these three years has increased from zero, to 4 and then 19. Admission during these same three years went from zero, to 4 to 13. Another major positive result of this program was the hiring of a full time counselor at the University to help advise undergraduate minority students.

Forming high school and junior high school partnerships can lead to success because of the focus given to a school, to students, to teachers and to the principal. It can also lead to the dispersion of follow-up grants which help to emphasize mathematics and science and their importance to the engineering curriculum. Grant money can also be used in the expansion of the busing program to get students from their hometowns to URI's campus in Kingston, RI. The RIWRC intends to hold this summer program again next year, and hopefully in the years to follow.

The project entitled the "Influx of Petroleum Hydrocarbons to Impermeable Surfaces and Surface Water" was leveraged to obtain funding for installing the Rhode Island Stormwater Treatment Demonstration Facility, which is intended to quantify the flux of organic (incl. PAH) and inorganic as well as pathogenic contaminants resulting from roadway and parking lot surfaces and demonstrate best management practices for their treatment. On this background, the knowledge of the magnitude of the PAH atmospheric influx will enable us to discern this pathway from directly automotive derived inflows.

In anticipation of future funding, we have also negotiated additional sampling locations outside the United States. During a visit to India and Oman in May 2011, we obtained permission to set up samplers on the campus of the Sultan Quaboos University in Muscat, Oman, and on the grounds of The Energy Research Institute (TERI) in Goa, India. We are currently negotiating with the University of Cape Verde Islands and the University of Puerto Rico, Mayaguez to set up two more samplers. These potential sampling sites were selected because they would permit tracking of atmospheric PAH fluxes to and from the United States, depending on the predominant wind directions.

Publications from Prior Years