University of Rhode Island

DigitalCommons@URI

2014

NONPOINT SOURCE POLLUTION ASSESSMENT AND MANAGEMENT OF AIR, SURFACE- AND GROUNDWATER IN RHODE ISLAND

Laura A. Schifman
University of Rhode Island, laura.schifman@gmail.com

Follow this and additional works at: https://digitalcommons.uri.edu/oa_diss

NONPOINT SOURCE POLLUTION ASSESSMENT AND MANAGEMENT OF

AIR, SURFACE- AND GROUNDWATER IN RHODE ISLAND

BY

LAURA A. SCHIFMAN

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

ENVIRONMENTAL SCIENCE

UNIVERSITY OF RHODE ISLAND

2014

DOCTOR OF PHILOSOPHY IN ENVIRONMENTAL SCIENCE
OF

LAURA A. SCHIFMAN

APPROVED:

Thesis Committee:

Major Professor   Thomas Boving

Dawn Cardace

Vinka Craver

Nasser H. Zawia
DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND
2014

ABSTRACT

Nonpoint source (NPS) pollution is one of the major sources of environmental contamination in the United States. Depending on the contaminant and its origin, NPS pollution can be introduced through atmospheric deposition or in the aqueous phase, for example through stormwater runoff. Here, both the atmospheric deposition of 16 EPA priority polycyclic aromatic hydrocarbons (PAHs) was measured at six different sites in Rhode Island as well as their removal, including other contaminants, from stormwater runoff. For the first part of this study seasonal and spatial variation in atmospheric PAH deposition rates were quantified along with investigating the source of the PAHs. The atmospheric deposition of PAHs followed an urban-to-rural gradient with deposition rates significantly higher in urban areas (up to 2261 $\mu g\ m^{-2}\ yr^{-1}$ $\sum PAH_{16}$) compared to rural areas (as low as 73.6 $\mu g\ m^{-2}\ yr^{-1}$ $\sum PAH_{16}$). In fall and winter, PAH deposition was up to 10 times higher compared to summer/spring. In part two of this study a stormwater best management practice (BMP) was evaluated for its contaminant treatment efficiency, with specific attention paid to PAH removal and microbial load reduction. Because many BMPs are not designed to treat bacteria specifically, a novel engineered material, amended red cedar wood chips with different loadings of two antimicrobial compounds: 3-(trihydroxysilyl)propyldimethyloctadecyl ammonium chloride (TPA) and silver nanoparticles (AgNP), was developed and tested in the laboratory to target microbial load reduction and removal of stormwater co-contaminants, including PAH. Laboratory tests showed that *E. coli* inactivation, at 25°C, can be achieved with $\log_{10}$ removal values (LRV) up to 3.71 ± 0.38 (mean ±

standard error) for TPA-red cedar and 2.25 ± 1.00 for AgNP-red cedar, while

unmodified red cedar only achieved 0.45 $\log_{10}$. Similarly, PAH removal from the

aqueous phase was 68.9 times higher using TPA modified red cedar compared to the

conventional shale used in the tree filter BMP. After the screening under laboratory

conditions, bioactive TPA amended red cedar wood chips were tested in a pilot-scale

field project using a tree filter BMP. The performance of the amended wood chips was

compared to a commercially available tree filter BMP that contains a mixed sand/shale

filtration matrix. Under pilot test conditions, the two filters performed similarly with

regards to bacteria removal. But, the tree filter containing amended red cedar was

significantly more effective at removing PAH. As demonstrated in the first part of this

study, PAH influxes to stormwater are not limited to local sources, e.g. automobiles,

but also have an atmospheric deposition component. Also, because PAH are just one

of many contaminant classes present in stormwater runoff, it is therefore important

that innovative BMP technologies have multi-contaminant treatment capabilities that

can effectively prevent contaminants like PAHs, heavy metals, and/or bacteria from

entering the environment. While this study has shown that tree filters can be modified

to meet that expectation, more work is necessary to develop, improve and demonstrate

a full-scale BMP device.

ACKNOWLEDGMENTS

First and foremost, I would like to thank my major professor Dr. Thomas Boving. Tom was instrumental in guiding me through the process of obtaining a PhD; from sharing his passion for concrete mixing to expanding my knowledge in the field of hydrology and giving me the chance to present at various conferences in the field. Tom's support was unconstrained and was only enhanced through our common mother tongue, German. I would also like to thank two very powerful women on my committee, Dr. Dawn Cardace and Dr. Vinka Craver, for all their invaluable input on scientific advice and mentoring and proving that success in the science and engineering world is not tied to a gender. My thanks also go to Jose Amador and Rainer Lohmann, both of whom have played important roles as mentors and teachers. Overall, the combined knowledge of my committee has been encouraging and fruitful for my professional advancement and academic growth.

Without Kevin Broccolo's help in constructing research equipment and his wide creativity, several portions of this project would have been nearly impossible to carry out.

I want to recognize the ongoing support I received from the faculty and students of the URI Geoscience department from the day I stepped foot in Rhode Island. All of you have made me feel at home for the past five years and I could not have asked for a better support network. Simple encounters at URI, such as being classmates (E.

Migneault, J. Scott,), roommates (A. Parmenter, J. Cooper, K. Osienski), officemates (D. Carnevale, D. Ciccalone), research partners (V. Kasaraneni, N. Anaya) and field/ laboratory assistants (B. Spirito, R. Sullivan), have all blended into one – a wonderful set of noteworthy friends that have helped me stay motivated throughout this whole time. I want to especially thank B. Spirito who has been extremely caring and supportive for the last year, motivating me to stay focused and making sure everything got done in time.

Last but not least, my family, and in particular my mother, deserve more than a written thank you could ever express. Even though I was asked jokingly for how long I would avoid the real world, the never fading love and support from my family have helped me accomplish my goal of obtaining this degree.

PREFACE

This dissertation is written and organized in manuscript format in accordance with the University of Rhode Island Graduate School guidelines. The dissertation is divided into five sections, which correspond to a brief introduction and manuscripts either submitted to or in preparation for submission to scientific journals. Chapter 1 is a manuscript entitled "*Spatial and Seasonal Variation in PAH Sources and Atmospheric Deposition Patterns in a Small Northeastern State in the United States*" with the authors L. Schifman and T. Boving and has been submitted to the journal Environmental Pollution. Chapter 2 is a manuscript entitled "*Selecting an antimicrobial filter media for improved stormwater best management practices*" with the authors L. Schifman, V. Kasaraneni, R. Sullivan, V. Craver, and T. Boving and is in preparation for submission to the journal Water Research. This chapter builds on a previous publication entitled "*Enhancement of Surface Runoff Quality Using Modified Sorbents*", which has been published in ACS Sustainable Chemistry and Engineering in 2014. This publication is in Appendix I. Chapter 3 and 4 focus on pilot field studies of tree filters. Chapter 3 is a manuscript entitled "*Evaluation of Stormwater Runoff Treatment using a Tree Filter BMP*", and Chapter 4 is a manuscript entitled "*Field Performance of one conventional and one innovative tree filter BMP: A pilot study*". The chapters will be combined into one manuscript with the authors L. Schifman, V. Kasaraneni, R. Sullivan, V. Craver, and T. Boving that is being prepared for submission in the Journal of Environmental Engineering.

TABLE OF CONTENTS

ix

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Nonpoint source (NPS) pollution is a type of contamination that is introduced

into the environment from a non-traceable or several sources, i.e. not a single spill or

leak. Therefore, NPS pollution is neither limited spatially nor temporally. It is also not

restricted to one type of contamination and contaminant phase (e.g. soil, water, or air).

Any location ranging from urban areas to coastal regions and mountainous terrain may

be impacted by one or more types of NPS pollution (Carrera et al., 2001; Neary and

Boving, 2011; Zehetner et al., 2009; Stewart et al., 2008; Golomb et al., 2001). This

can include, but is not limited to atmospheric deposition of pollutants and runoff from

agricultural, industrial areas, or roadways (Gocht et al., 2007; Göbel et al., 2007;

Kaushal et al., 2011). Because NPS pollution impacts all environmental

compartments it is important to understand contaminant fluxes so that managing and

prevention of NPS pollution results in improved water and air quality as well as

ecosystem health.

Even though NPS pollution encompasses a wide range of contaminants, such

as nutrients, heavy metals, suspended solids, organic contaminants, and pathogens, the

emphasis of this study lies in one type of organic contaminants, namely polycyclic

aromatic hydrocarbons (PAH), and one type of indicator bacteria that is commonly

used to monitor water quality, specifically *Escherichia coli* (*E. coli*).

As one of the major groups of persistent organic pollutants, PAHs are typically

not produced at large quantities for any specific industrial uses. Rather, PAHs are by-

products of many combustion processes from which they get released into the

atmosphere (Jacob, 2008; Baek et al., 1991; Lima et al., 2005). PAHs are suspected

carcinogens and their presence in the environment poses a health risk to humans

(Harvey, 1991); however, PAHs are part of the human lifestyle. Common combustion

processes that produce PAHs can include wood burning, residential heating,

automobile combustion, just to name a few (Ravindra et al., 2008;Rogge et al.,

1997;Simcik et al., 1999). Once emitted through combustion processes, atmospheric

transport of PAHs causes diffuse pollution of whole landscapes as PAHs settle out of

the atmosphere via dry particle deposition, gaseous deposition, and wet deposition

(Bidleman 1988). This can result in the contamination of surface waters, soils, and

eventually groundwater, even in rural areas (Golomb et al., 2001; Gocht et al., 2007;

Lohmann et al., 2000).

As discussed in Manuscript 1, the exact emission source of PAHs in the

atmosphere can rarely be identified, but general emission source types can be

fingerprinted when atmospheric PAH samples are collected. Several studies have

identified PAH profiles that correspond to specific emission sources, such as wood,

gasoline, diesel, and oil combustion (Ravindra et al., 2008; Rogge et al., 1997; Simcik

et al., 1999; Yunker et al., 2002; Rogge et al., 1993; Motelay-Massei et al., 2007;

Khalili et al., 1995). Using these fingerprints and statistical source attribution models

allows for identification of emission sources that contribute to PAH contamination in a

specific region.

In addition, PAHs can also be found in roadway runoff, one of the major non-

point sources within the United States (Göbel et al., 2007; Lau et al., 2009; Brown and

Peake, 2006). When present in runoff, PAHs commonly stem from gas and oil

drippings, leaks, spills, or coal-tar sealed impervious structures such as parking lots

(Göbel et al., 2007; Van Metre et al., 2000; Van Metre et al., 2012). Stormwater runoff containing contaminants including PAHs introduces high loads of contaminants into soils along road sides or nearby surface water bodies and estuaries during the first flush of rain events (Göbel et al., 2007). The physicochemical properties of PAHs lead to accumulation of these compounds in soils and sediments, significantly impacting the ecosystem (Zehetner et al., 2009; Krein and Schorer, 2000).

Besides PAHs, pathogens are another prevalent contaminant class in stormwater runoff. Within that contaminant class, *E. coli* and fecal coliforms are typically monitored in watersheds, as their presence is considered an indicator of pathogenic microbial contamination (EPA, 2012). Microbial contamination is often traced back to stormwater runoff and its uncontrolled release into the environment can cause public health concerns. For instance, shell fishing bans or precautionary beach closures are often implemented in the interest of public health (Stewart et al., 2008; Soller et al., 2014; Dorfman and Rosselot, 2012). Hence, bacteria contamination can have significant economic repercussions in areas like Rhode Island that rely strongly on fisheries and the tourism industry (Dorfman and Rosselot, 2012; Mallin et al., 2000; Ahn et al., 2005).

Manuscripts 2 through 4 focus on bacteriological contamination of stormwater runoff and how it, together with other pollutants (mainly PAH) can be possibly attenuated by innovative structural best management practices (BMP). While stormwater runoff itself cannot be prevented, the contaminant flux associated with it can be remediated through the use of structural BMP. Several states in the U.S. have started implementing structural BMPs to improve the quality of stormwater runoff in

addition to other benefits like flood mitigation (Bakeman et al., 2012; MDE, 2009; PA DEP, 2006; VT ANR, 2002; RIDEM, 2010). Rhode Island has gone further and set minimum contaminant removal standards that structural BMPs should comply with (RIDEM, 2010). However, many BMPs are not designed to treat bacteria. Building on research focused on point-of-use drinking water filtration methods that rely on bioactive compounds, such as nano-silver or quaternary ammonium compounds, this research investigated if these bioactive compounds can find use in the enhanced treatment of pathogens in stormwater runoff. This project was undertaken with the goal to identify an improved filtration matrix that can be implemented in stormwater BMPs (Zhang and Oyanedel-Craver, 2013; Oyanedel-Craver and Smith, 2007; Boving and Neary, 2007; Boving and Zhang, 2004).

As this and related research shows, the contaminant influx through atmospheric deposition of PAHs can be orders of magnitude lower than that of stormwater. Hence, ATM deposition of PAH can be detected everywhere and anytime, even in remote areas and during times of little rainfall. Conversely, stormwater runoff impacts areas like New England more significantly because frequent precipitation events result in the quick spreading of locally derived contaminants. Therefore, the deposition of atmospheric pollutants along with the management of locally derived pollutants associated with stormwater runoff must be incorporated in the design of sustainable management strategies for nonpoint pollution sources.

MANUSCRIPT 1: SPATIAL AND SEASONAL VARIATION IN PAH SOURCES AND ATMOSPHERIC DEPOSITION PATTERNS IN A SMALL NORTHEASTERN STATE IN THE UNITED STATES

Submitted to Environmental Pollution

Laura A. Schifman [1*], and Thomas B. Boving [1,2]

[1]Department of Geosciences, University of Rhode Island, Kingston, RI 02881

[2]Department of Civil Engineering, University of Rhode Island, Kingston, RI 02281

*Corresponding Author: Laura A. Schifman

Department of Geosciences

330 Woodward Hall

University of Rhode Island

Kingston, RI 02881

Email: laura.schifman@gmail.com

5

ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) enter the environment through combustion processes and can travel long distances via atmospheric transport. Here, atmospheric PAH deposition was measured in six locations throughout Rhode Island using passive atmospheric bulk-deposition samplers for 3 years. The measurements were evaluated using two source-specific PAH isomer signatures and an innovative contamination index. An urban–to-rural gradient was observed with deposition rates significantly higher in urban areas (up to 2261 $\mu g \ m^{-2} \ yr^{-1}$ $\sum PAH_{16}$) compared to rural areas (as low as 73.6 $\mu g \ m^{-2} \ yr^{-1}$ $\sum PAH_{16}$). In fall and winter, PAH deposition was up to 10 times higher compared to summer/spring. A statistical analysis of the results with positive matrix factorization identified gasoline, diesel, and oil combustion sources in all samples year-round. Wood combustion associated PAH deposition was highest during the cold season.

CAPSULE

Atmospheric PAH deposition from gasoline, diesel, oil, and wood combustion sources is up to 10-fold higher in winter than in summer in RI with wood combustion only occurring in winter.

6

GRAPHICAL ABSTRACT
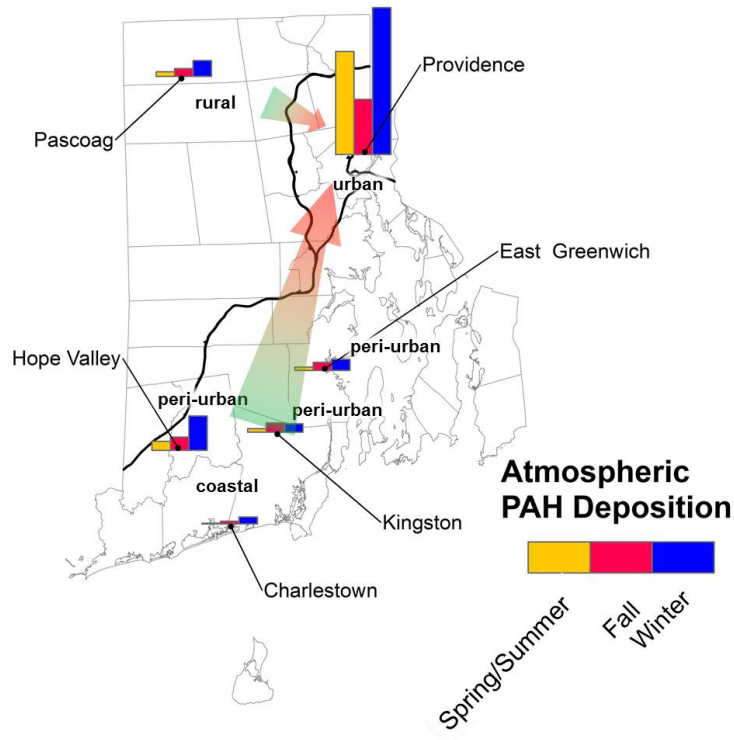
HIGHLIGHTS:

- Passive bulk atmospheric samplers collected atmospheric deposition of PAHs
- Annual PAH deposition in urban areas was up to 30 times higher than in coastal areas
- Atmospheric deposition in winter was up to 10 times higher than in spring/summer
- PAH Sources were gasoline, diesel, oil and, wood combustion
- Wood combustion was only prevalent in the winter months

KEYWORDS:

passive bulk sampling, diffuse pollution, polycyclic aromatic hydrocarbons, PMF

analysis, source attribution

INTRODUCTION:

Atmospheric non-point sources, such as automobile exhaust and by-products of other combustion processes, introduce gaseous and particulate contamination to both urban and rural areas. Even though contamination is highest in regions closest to emission sources, often urban and industrial areas, atmospheric deposition can take place far away from the original emitting source(s) and can lead to diffuse contamination of whole landscapes (Lohmann et al., 2000; Garban et al., 2002; Lima et al., 2005; Gocht et al., 2007a; Schwarz et al., 2011). With fossil fuel consumption increasing in response to a growing population and vehicle density, urban areas experience increased loadings of atmospheric contaminants, especially polycyclic aromatic hydrocarbons (PAH) (Van Metre et al., 2000). Many of the fossil fuel derived contaminants introduced into the atmosphere, including PAHs, are toxic and suspected carcinogens (Harvey, 1991; Jacob, 2008). Thus, increasing levels of PAHs in the environment result in health and safety concerns of the general public (Schoonover and Lockaby, 2006).

There are local and regional sources of PAH. A prominent local contamination source is linked to traffic. Although stricter environmental regulations over the past years decreased the emissions from individual cars, much of the gain is outweighed by the increase in the number of registered automobiles as well as urban sprawl, an increased number of roadways, and the construction of parking lots and other (coal tar) sealed surfaces that volatilize petroleum hydrocarbons to the atmosphere (Van Metre et al., 2000; Lima et al., 2005; Anderson et al., 2011). Another prevalent local source of PAH in winter results from wood combustion (Freeman and Cattell, 1990;

8

Khalili et al., 1995; Lohmann et al., 2000). In New England where wood burning is a very popular means of heating homes during the cold season, this source can locally contribute upwards of 70% to atmospheric PAH contamination (Skog and Watterson, 1984; Freeman and Cattell, 1990; Kroetz and Friedland, 2008).

These regional inputs from combustion and burning processes are linked to atmospheric deposition and include dry particle and gaseous deposition, as well as wet deposition (Gigliotti et al., 2005; Gocht et al., 2007a). The combined contribution of gaseous and particulate phase deposition, including precipitation derived compounds is referred to as bulk deposition.

Besides reflecting actual differences in the deposition rates over space and time, the influence of different PAH deposition sampling techniques cannot be ignored. Liu et al. (2007) reviewed sample collection, pretreatment and analytical methods for quantifying PAH in airborne particulates and the gaseous phase and concluded that even though passive and active sampling techniques are available, neither technique is optimal for bulk (gaseous + particle bound) sampling of PAHs. This is because active sampling techniques employ high volume air filters that trap particle bound, mostly heavy molecular weight PAHs on a filter that is later extracted. Passive sampling systems rely on sorptive processes; therefore trapping mostly more volatile, low molecular weight compounds (Liu et al., 2007). In Europe, researchers have tested and verified a passive sampling technique that can capture the time-integrated long term atmospheric bulk deposition rates of PAH and other compounds (German Industrial Standard DIN 19739-2, 2003).

Studies in Europe and the eastern United States quantified deposition rates of PAH to land surfaces using both, passive and active sampling systems, often report 2-6 times higher deposition rates for particulate and gaseous phase samples in proximity to urban areas relative to rural sites that are considered distant from potential PAH sources (Gigliotti et al., 2000; Garban et al., 2002; Gigliotti et al., 2005; Gocht et al., 2007a; Schwarz et al., 2011). For instance, Gigliotti et al. (2000) investigated the atmospheric PAH concentration in the particulate and gas phase using an active sampling system in the metropolitan area of New Jersey. In the urban area of New Brunswick gas phase $\sum PAH_{36}$ concentrations were on the order of 3.5 to 84 ng m^{-3} while particulate $\sum PAH_{36}$ concentrations were 0.38 to 11.6 ng m^{-3} compared to 2.8 to 42 ng m^{-3} and 0.15 to 4.0 ng m^{-3} for particulate and gas phase $\sum PAH_{36}$ concentrations at a coastal site in Sandy Hook, NJ, respectively. This resulted in bulk annual deposition rates of up to 34.8 µg m^{-2} yr^{-1} for the urban area and 16.8 µg m^{-2} yr^{-1} for the coastal area (Gigliotti et al., 2000). Gocht et al. (2007a) used a passive sampling system to quantify bulk atmospheric PAH deposition at three rural sites in Germany from 2001 to 2002 and found an average annual deposition of 134.2 µg m^{-2} yr^{-1} to 222.2 µg m^{-2} yr^{-1}. A similar study from Germany in 2005 reported bulk PAH deposition rates ranging from 68.78 µg m^{-2} yr^{-1} in a rural open field area to 256.6 µg m^{-2} yr^{-1} in a rural village (Schwarz et al., 2011). Overall, the PAH deposition rates from studies on both sides of the Atlantic differ by an order of magnitude.

Deposition of PAHs does not only vary spatially, but also temporally. For instance, in study areas in Europe and the eastern United States, 2-3 times higher deposition rates were observed during the cold season and attributed to increased

residential heating with fossil fuels (Gigliotti et al., 2000; Garban et al., 2002; Guo et al., 2003; Motelay-Massei et al., 2003; Gocht et al., 2007b). In addition, particle bound PAH concentrations are often elevated during the cold months compared to the warmer months because of the association of PAH with atmospheric soot particles with combustion origins (Baek et al., 1991; Gigliotti et al., 2000).

The advantage of using a passive sampling system is that natural, seasonal bulk deposition rates can be easily determined because no maintenance or electrical power is required to operate the sampler. Also, while active sampling techniques can capture atmospheric deposition over shorter periods of time by pumping air through a filter at a specific rate (Hayward et al., 2010), they may produce artificially high deposition rates due to temporarily high or low emissions sources in the vicinity of the measuring station. This can possibly lead to misrepresenting longer term depositional patterns (Hayward et al., 2010).

Another important factor in comparing PAH studies lies in the reporting of results. Many studies, including this one, use the sum of the 16 priority PAHs identified by the U.S. EPA ($\sum PAH_{16}$; EPA, 2006) to quantify PAH deposition rates (Liu et al., 2007). However, some studies report the sum of 30 or more PAH (Gigliotti et al., 2000; Okuda et al., 2002; Naumova et al., 2003; Gigliotti et al., 2005) further complicating a comparison of field studies. Aside from comparing atmospheric deposition of PAHs using $\sum PAH_{16}$ as a marker, contamination indices (van den Elshout et al., 2008; Li et al., 2014) were found practical because PAHs, along with other organic contaminant classes, such as poly chlorinated biphenyls or dioxins, are made up of a variable number of chemically similar compounds that originate from a

11

source with no fixed composition. Environmental studies of these contaminant classes are often presented with the problem of not detecting the same analytes all the time. Thus, reporting a contaminant sum may not be a representative means of displaying and comparing data from different sites. A benefit of a contaminant index is that it normalizes the data for each sample and weights them by both the concentration and the number of analytes detected. Hence, higher values indicate a greater degree of contamination and number of compounds detected. Using a contamination index allows researchers to communicate findings more easily to the public instead of using conventional concentrations of atmospheric contamination (Liu et al., 2007); however, the sources of contamination origins cannot be specified in this manner.

To identify individual combustion sources in atmospheric PAH samples, ratios of environmentally stable PAH isomers that are characteristic in source combustion PAH signatures can be employed (Simcik et al., 1999; Yunker et al., 2002; Ravindra et al., 2008; Tobiszewski and Namieśnik, 2012). These isomer ratios are beneficial for assigning general emission sources, however their use has been criticized because differential reactivities of the PAH isomers may skew the emission source signature (Kavouras et al., 2001; Galarneau, 2008; Katsoyiannis et al., 2011). A multivariate factor analysis, such as Positive Matrix Factorization (PMF) (Kavouras et al., 2001; Larsen and Baker, 2003; Lee et al., 2004; Galarneau, 2008) circumvents this problem when apportioning sources of airborne particulate matter in the atmosphere (Hopke, 1991; Paatero and Tapper, 1994; Larsen and Baker, 2003; Ravindra et al., 2008).

Herein, PMF was adopted to evaluate PAH sources and receptor locations in addition to the IP/(IP+BgP) and Fla/(Fla+Pyr) isomer ratios. The goal of this study

12

was to identify sources that contribute to PAH deposition in urban, peri-urban, and rural areas in Rhode Island (RI), a small coastal state on the east coast of the United States and determine whether state recommendations for atmospheric PAH load reductions are required for wood burning stoves, which introduce a high concentration of PAHs to New England (Skog and Watterson, 1984; Freeman and Cattell, 1990). More specifically, the aim was to 1) quantify the seasonal atmospheric deposition of PAH rates at six different locations in RI using a contamination index, 2) trace and fingerprint the PAH sources using two methods: isomer ratios and PMF analysis, and 3) compare atmospheric deposition patterns in RI to similar latitudes in Europe where PAH bulk deposition rates were quantified with the same passive bulk deposition sampling method. By evaluating bulk PAH deposition rates and patterns in their spatial and temporal context, the basis is provided for determining the potential effects of PAH contamination in Rhode Island.

METHODS:

Site Descriptions

All study sites were located in Rhode Island (RI), which is a coastal state in New England that has 2710 km² of land mass and has just over one million residents with a population density of 388/ km². RI is the smallest state in the United States and more than one hundred times smaller than Germany. Like many Northeastern states, RI is characterized by densely developed urban and peri-urban areas concentrated along major transportation arteries, while large parts of the state are covered by forest interspersed with small rural settlements. The study sites were chosen to reflect this

rural-to-urban gradient (Figure 1.1). The urban site is located in Providence, the
capital of RI, which has >100,000 inhabitants. The peri-urban sites are located in East
Greenwich and Hope Valley. The rural sites are located over a kilometer away from
main roads in a forested area in the north (Pascoag) and a coastal area in the south
(Charlestown). The latter site is located approximately 350 meters from the Atlantic
Ocean. The actual sampling spots were chosen to minimize the influence of trees or
any other obstructions.

Atmospheric Deposition Sampling

Atmospheric deposition of PAH was measured using a passive sampling system
that was tested and validated in previous studies (Figure S1.1) (Martin, 2000; Gocht et
al., 2007a; Gocht et al., 2007b; Schwarz et al., 2011). Sampling collection and
processing is described in the supplemental information. All samples were analyzed
for the 16 EPA priority PAH with a Shimadzu Gas Chromatograph/Mass Spectrometer
QP2010 and following a modified EPA method (Method 610; Manoli and Samara,
1999).

The PAH fluxes detected here were converted into ambient air concentrations
through

$$Atmospheric\ Concentration\ \left[\frac{ng}{m^3}\right] = \frac{Deposition\ Flux\ \left[\frac{ug}{m^2 d}\right] * 0.864}{V_{dep}\ \left[\frac{cm}{s}\right]}$$

where V_{dep} is the deposition velocity, which is approximated to be 0.5 cm/s as
reported in the literature (Franz et al., 1998; Gigliotti et al., 2005; Esen et al., 2008;
Castro-Jiménez et al., 2012). This value describes the dry deposition of particle

distributions that are dominated in size by particles less than 1 μm of mass median diameter, as is appropriate for urbanized and industrialized regions (Franz et al., 1998; Zufall et al., 1998; Gigliotti et al. 2002; Gigliotti et al., 2005).

Contamination Index, Source Assignment, and Source Apportionment

To quantify the PAH deposition based on both, concentration and the number of compounds detected, a contaminant index for a specific sample i was defined as:

$$Contaminant\ Index_i = \log\left(\sum(PAH) * \frac{n}{N}\right)$$

where $\sum$PAH is the sum of PAH concentrations detected in a sample in ng/m^{2}d, n is the number of compounds detected in the sample, and N is the number of analytes, in this case 16 PAH, excluding extraction standards or spikes. In this study, contaminant index values that are below 1 or close to 0 indicate very low or no contamination, whereas values >2 signify high contamination.

Two isomer ratios, IP/(IP+BgP) and Fla/(Fla+Pyr), were used to distinguish between petroleum and biomass combustion sources and to assign sources to seasonal PAH deposition. Biomass combustion sources have IP/(IP+BgP) ratios >0.5, whereas liquid fossil fuel combustion sources fall below 0.5. Further, IP/(IP+BgP) values above 0.35 are indicative of diesel combustion, whereas values below 0.35 point to gasoline combustion sources. It is not possible to discern between diesel and heating fuel sources using this method due to chemical similarities in combustion products of the two fossil fuels. In case of Fla/(Fla+Pyr), typical biomass combustion indices are

15

greater than 0.5 and petroleum combustion ratios are less than 0.5 (Yunker et al., 2002; Ravindra et al., 2008).

To further identify sources of PAH contamination and link them to their spatial distribution in RI, positive matrix factorization (PMF) was carried out (further details on PMF in supplemental information). For that, the PAH deposition datasets were split up to represent a warm and a cold season: spring/summer and fall/winter. Four combustion source factors were defined (gasoline, diesel, oil, wood; Table 1.1) and analyzed with PMF 5.0 software (EPA, 2014). Oil describes PAHs originating from heating oil, ship, and aviation fuel combustion. These "oil" sources have similar PAH signatures and their separation by the 16 EPA PAH compounds analyzed in this study is not possible (Larsen and Baker, 2003; Lee et al., 2004). The PMF model was run 100 times to achieve a final solution for each data set. Afterward, the results were optimized by running the model with an fpeak value of -0.5. Results from the base model and fpeak model were compared to determine the robustness of the model.

RESULTS AND DISCUSSION

Variation in Spatial and Seasonal Deposition Patterns.

As expected, the annual sum of the 16 priority PAH ($\sum PAH_{16}$) deposition throughout RI followed a rural-to-urban gradient. The sites in Charlestown (coastal) and Kingston (peri-urban) had the lowest annual deposition rates ($\sum PAH_{16}$ 73.64 $\pm$ 9.88 $\mu g\ yr^{-1}\ m^{-2}$ and $\sum PAH_{16}$ 92.0 $\pm$ 4.07 $\mu g\ yr^{-1}\ m^{-2}$, respectively), followed by the peri-urban and rural sites in East Greenwich and Pascoag ($\sum PAH_{16}$ 154.8 $\pm$ 28.8 $\mu g\ yr^{-1}\ m^{-2}$ and $\sum PAH_{16}$ 175.7 $\pm$ 114.2 $\mu g\ yr^{-1}\ m^{-2}$, respectively). Hope Valley, categorized

as a peri-urban site, because even though it is located in a more rural area of RI, it is in close proximity to I-95, has a 4.6 to 2.7 times higher annual PAH deposition rate ($\sum PAH_{16}$ 428.3 ± 106.2 µg yr^{-1} m^{-2}) compared to Kingston and East Greenwich, the two peri-urban sites (Figure 2). The sampling site with the highest annual PAH deposition rate is located in the center of urban Providence ($\sum PAH_{16}$ 2261.3 ± 1050.8 µg yr^{-1} m^{-2}).

Over the survey duration and when compared by seasons, the highest PAH deposition rates in RI usually occur in the winter season followed by fall, while the lowest seasonal deposition rates occur in spring and summer (Figures 1.2&1.3). This pattern is consistent with other studies (Baek et al., 1991; Gigliotti et al., 2000; Lee et al., 2004; Schwarz et al., 2011) and can be attributed to more heating fossil fuels and wood biomass burning during the heating season (Garban et al., 2002; Guo et al., 2003). In addition, shorter daylight hours as well as lower temperatures reduce the photo-oxidation and chemical destruction of PAHs, potentially leading to higher concentrations of PAHs relative to the summer months (Freeman and Cattell, 1990; Baek et al., 1991; Motelay-Massei et al., 2003).

Even though no PAH specific air quality standard exists for Rhode Island, these data can be evaluated against regional air quality standards. For instance, in Vermont the annual Benzo(a)pyrene (BaP) concentrations should not exceed the hazardous ambient air standard of 480 pg/m^3 (VT ANR, 2007). In this study, the average VT ambient air standard was never exceeded when atmospheric BaP concentrations were calculated for time frames covering one year or individual sampling seasons (Table 1.3). However, on an average daily basis the Providence and Hope Valley sites

exhibited BaP air concentrations that exceeded the Vermont ambient air standard for 20.7% and 16.1% of the three year sampling period. Similar results have been document in a study conducted in the United Kingdom where ambient air standards were exceeded due to wood burning in the winter time (Lohmann et al. 2000 and 2006).

Comparing the results from this study to studies conducted in rural southwestern Germany during 2001 and 2002 (Gocht et al., 2007a; Schwarz et al., 2011), the deposition rates in RI's peri-urban sites are similar in magnitude. Differences exist between the rural German sites, which has a deposition of $\sum PAH_{16}$ 222 µg yr^{-1} m^{-2} and the RI coastal site, which has a slightly lower deposition rate of 73.6 ± 9.9 µg m^{-2} yr^{-1}. Also, the deposition rate at the RI urban site (2261 ± 1020 µg m^{-2} yr^{-1}) is ~10 times higher than at the German rural sites. (Figure 1.3).

Both study areas are at similar latitudes, i.e. RI at 41°N and southern Germany at 48°N, and fall within comparable climatic patterns. However, differences exist in the predominant wind directions and quality of air masses. Air mass trajectories can have a significant impact on depositional patterns in the study area. For instance, at a site in Massachusetts, Golomb et al. (2001) found that higher PAH deposition occurred when air masses originated in the Great Lakes area before passing over Pennsylvania, New Jersey, and New York before moving into the New England coastal area compared to air masses originating in the Great Lakes area, then passing over Canada, Maine, and the Atlantic and into New England.

An analysis of RI's predominant wind directions (Figure S1.2) indicates that the air masses moving into the state are a mix of continental and oceanic air. As shown

18

by others (Driscoll et al., 2001; DeBell et al., 2004), continental air masses moving in from the interior of the United States and Canada are more polluted with natural and anthropogenic PAH relative to the air masses coming off the Atlantic Ocean. On-shore southerly wind directions are more dominant during the RI summer, while continental northwestern winds are typical for the winter season. The mixing of these air masses over RI contributes to diffusing and diluting the atmospheric pollutant loads at the coastal site in the summer. During winter, the northwesterly winds may contribute to increased contamination loads in the southern part of the state, such as Hope Valley and Charlestown. In comparison, the predominant winds at the landlocked German study sites are from the west-southwest (Figure S1.3), which is where several of Germany's coal power plants and other heavy industry is situated (De Ridder et al., 2008). The origin of the prevailing air masses evidently is a factor that must be considered when explaining observed differences in PAH deposition rates at different localities, such as rural Germany and the northeastern United States.

Assessing PAH deposition based on the Contaminant Index

Of all six sites investigated, the urban Providence site has the highest contaminant index during all seasons (annual average 2.66 ± 0.09), indicating that PAH contamination there is highest (Figure 1.3, Table 1.2). The lowest seasonal contaminant index was calculated for the most rural site, Pascoag (annual average 1.02 ± 0.19). Listed from highest to lowest average annual contamination index, the order is: Providence> Hope Valley> East Greenwich> Charlestown> Kingston> Pascoag.

Compared to the sites sampled in Germany by Gocht et al. 2007a, the average annual contaminant indices for Providence and Hope Valley are similar to those in Germany, while the contaminant indices for the other sites are up to 2.5 times lower than the ones computed for Germany. As the contaminant index weights the sample based on the number of compounds detected, this difference can be attributed to the detected compounds in the samples and highlights the importance of using a weighted contaminant index when comparing sampling sites (Table 1.2).

Source Identification and Source Contribution Assessment

Source Identification using Isomer Ratios

The IP/(IP+BgP) isomer ratio was applied to distinguish between biomass, diesel, and gasoline combustion, while Fla/(Fla+Pyr) distinguishes between biomass and petroleum combustion (Yunker et al., 2002; Ravindra et al., 2008). Correlated against each other, the distribution of data points can be used to identify the predominant sources of PAH deposition at a specific site and season (Figure 1.4).

Spring/Summer. The Fla/(Fla+Pyr) isomer ratios at all sites indicate that petroleum combustion sources dominate during the warmer season. Based on the IP/(IP+BgP) ratios, the site data from Pascoag suggests a dominant gasoline combustion source (Figure 1.4). All other sites are dominated by diesel combustion rather than gasoline. Because these ratios were measured during the time of year when heating fuels are not widely used, it is likely that these combustion sources represent fuels used in transportation, i.e. diesel or marine fuels.

Fall. The isomeric signatures at all sites point to an increasing amount of biomass burning in the fall season (Figure 1.4). This shift coincides with the beginning of the heating season in Rhode Island when many households start burning wood and/or use other heating fuels.

Winter. The PAH signature derived from the two PAH isomer ratios is almost exclusively that of biomass burning, which is explicable by the number of homes in this region that are heated with wood stoves or fireplaces during the cold season (Skog and Watterson, 1984). In New England, wood combustion is and has been a major source of heating, especially in rural areas, where up to 50 % of households use wood burning stoves (Skog and Watterson, 1984). Thus, an increase in biomass combustion markers during the cold period points to PAH emissions resulting from wood combustion sources (Lohmann et al., 2000). The results from the two most rural areas, Pascoag and Charlestown confirm this trend, whereas the more urban sites have a slightly lesser biomass fingerprint and maintain a gasoline and diesel PAH signature (Figure 1.4). Only the peri-urban site in Hope Valley continues to carry a IP/(IP+BgP) diesel fuel signature, albeit with a greater Fla/(Fla+Pyr) ratio, which indicates additional contributions from biomass burning during winter. The continued prominence of diesel fuel combustion derived PAH is likely attributed to the site's proximity to the busy interstate highway I-95 (about 3 km to the west) (Figure S4). The problem of identifying unique sources of PAH emission showcases the limitations of PAH isomer ratios.

Positive Matrix Factorization

To further elucidate the contribution of specific combustion sources to the PAH profile, a PMF analysis was carried out using the spring/summer data sets and the combined winter/fall data sets. The datasets for each period and site were analyzed based on four factors: combustion of gasoline, diesel, oil, and wood (Table 1.1). Again, oil denotes emissions from heating oil and marine and aviation fuel combustion, which carry a different combustion signature than diesel fuel emissions from automotive sources.

Spring/Summer. According to the PMF analysis the East Greenwich site is dominated by a high percentage of diesel emissions (62%) (Figure 1.5a). This finding correlates with the site's PAH isomer ratio results (Figure 1.4). The sites with the highest gasoline source percentages were Pascoag (73%) and Providence (66%) (Figure 1.5a). In Pascoag, the PMF signature is in line with the PAH isomer fingerprints. In Providence, the PAH isomer source ratios indicate that the main PAH source was diesel, rather than gasoline combustion (Figure 1.4&1.5a).

The PMF gasoline and diesel source percentages at the Hope Valley site were 43% and 33%, respectively. The dominance of both of these automotive fuel combustion fingerprints correlates with the site's proximity to an interstate highway (Figure S1.4).

The summer PMF profiles of the Charlestown and Kingston sites are both dominated by oil combustion (73% and 64%, respectively). In both cases, the PMF analysis does not agree fully with PAH isomer ratios, which indicated that diesel combustion was the main PAH source (Figure 1.4). The locality of the Kingston and

22

Charlestown sites, however, support the link to oil combustion sources. At the coastal

site in Charlestown, the deposition of oil combustion products is likely related to

marine fuel oil (Cooper, 2001; Lee et al., 2004) and possibly originated from the

nearby Point Judith harbor and the general boat traffic along the coast (Figure S1.4).

The source of oil combustion at the Kingston site is not as obvious, but could be at

least partially related to heavy fuel oil burning freight trains that run on the Amtrak

line, which is located less than 1 km to the northwest of the sampling site (Melymuk et

al., 2013) (Figure S1.4). Or, the oil signature could reflect the heating oil combustion

emissions from the University of Rhode Island power plant that is located less than 1

km to the east of the sampling site.

These problems identifying the exact source of those oil combustion products

illustrate the limitations of using PAH signatures in combination with a PMF analysis.

This is because disseminating oil combustion signatures can be complicated by

differences in the properties and composition of oils (density, aromaticity), the nature

and effectiveness of the combustion processes, ranging from oil burning in home

heating boilers compared to marine and aviation engines, and the combustion

temperature together with the oxygen percentage in the burner's intake air (Rogge et

al., 1997).

During summer, but not during winter, the PMF analysis of the sites in

Providence, Hope Valley, and Pascoag had residual PAH signatures that could not be

attributed to any of the four combustion sources or other PAH signatures reported in

the literature (Table 1.1). The residual for the three sites was 9.2% for Providence,

11.1% for Hope Valley, and 17.5% for Pascoag (Figure S1.5). These residual

percentages were not included in Figure 1.5a. The reason for the presence of residuals during summer only could be related to the longer, more intense daylight in combination with higher temperatures that can cause the photolytic degradation of low molecular PAH compounds. This can alter the PAH signature of emission sources (Motelay-Massei et al., 2007). However, this degradation effect and a possible shift of the PAH signature was not investigated herein.

Fall/Winter. All sites across the rural to urban gradient show a significant shift of their PAH profiles toward wood combustion emissions (Figure 1.5b). A very similar shift was observed by analyzing the PAH isomer ratios. At the urban Providence and peri-urban Hope Valley sites, the relative contribution of wood combustion sources are the lowest, 22.5% and 20%, respectively. The remaining source attribution percentages at these two sites are about equally distributed between diesel and gasoline combustion sources.

The highest wood combustion contributions were measured at the Kingston (38%) and Charlestown (36%) sites. It is noteworthy that the Kingston site also has a significant oil combustion signature (38%) (Figure 1.5b), likely from a nearby heating oil power plant operating at capacity in the winter time (Rogge et al., 1997).

The influence of wood combustion at the East Greenwich and Pascoag sites was similar; 28% and 29%, respectively. During the winter, the East Greenwich site still had a high diesel combustion source PMF profile (31%). The relative high percentage of diesel related deposits at the sampling station cannot be readily explained without further investigations of major emission sources in this area, including diesel-like fuels

from transportation sources, such as kerosene emissions from two nearby airports (Figure 1.5b &S1.5).

During winter in rural Pascoag, a strong oil and wood combustion source is prevalent (28% and 29%, respectively) and can be attributed to residential heating with heating oil along with wood burning (Rogge et al., 1997; Kroetz and Friedland, 2008).

CONCLUSIONS

A passive atmospheric bulk deposition sampling system developed and tested in Europe (Martin, 2000; Gocht et al., 2007a; Gocht et al., 2007b) was successfully employed to measure the bulk atmospheric deposition of PAH in RI. The results show that the PAH deposition follows an urban-to-rural trend with higher deposition rates closer to urban area. These results confirmed deposition trends in other studies, several of which used the same passive sampling technique as was used in this study (Martin, 2000; Gocht et al., 2007a; Gocht et al., 2007b; Schwarz et al., 2011) and others, which used active sampling devices (Gigliotti et al., 2000; Garban et al., 2002; Gigliotti et al., 2005). Even though results obtained using different sampling techniques cannot be compared directly, the spatial and temporal trends observed can be used as a basis for comparison (Liu et al., 2007; He and Balasubramanian, 2010). In addition, seasonal trends in PAH deposition patterns were identified, i.e. higher deposition rates in winter and fall contrasts with lower rates during spring/summer. These findings corroborated bulk PAH atmospheric deposition measurements in France (Garban et al., 2002; Motelay-Massei et al., 2003; Gigliotti et al., 2005; Motelay-Massei et al., 2007), and

Germany (Gocht et al., 2007a; Schwarz et al., 2011), and studies that took measurements of gaseous and particle phase PAH deposition in the United States (Gigliotti et al., 2000; Lee et al., 2004; Gigliotti et al., 2005) and China (Guo et al., 2003).

Because the bulk atmospheric PAH deposition sampler used in this study was identical to that of samplers used in studies at German locales, the findings between the two studies were compared (Martin, 2000; Gocht et al., 2007a; Gocht et al., 2007b; Schwarz et al., 2011). Relative to German sites, the PAH deposition in RI was comparable to the peri-urban sites; however, the coastal sites received up to 3 times less atmospheric PAH deposition, whereas the urban site received up to 50 times higher PAH deposition. A major difference between RI and Germany appears to be related to the prevailing wind directions that transport the PAH from their sources to the sampling station. RI is influenced to a greater extent by cleaner oceanic air masses during the summer, whereas more continental and thus more polluted air masses prevail in Germany (Figure S1.2&S1.3). This explanation is consistent with previous measurements of PAH deposition in the Northeastern United States.

Overall, the comparably large temporal and spatial differences between the rural, peri-urban, and urban study sites clearly demonstrate that even within a small state like RI, there are strong local differences in the PAH deposition magnitude and the origin of the contamination. It is important to note that a large emitter of PAHs in the fall and winter time is wood and oil combustion. Even though Rhode Island Department of Environmental Management does not have ambient air quality

standards for PAHs, these high seasonal emissions resulting from wood burning and oil heating should be assessed further.

REFERENCES

Anderson, S.T., Parry, I.W.H., Sallee, J.M., Fischer, C., 2011. Automobile Fuel Economy Standards: Impacts, Efficiency, and Alternatives. Review of Environmental Economics and Policy 5, 89-108 doi: 10.1093/reep/req021.

Baek, S., Field, R., Goldstone, M., Kirk, P., Lester, J., Perry, R., 1991. A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior. Water Air Soil Pollut. 60, 279-300.

Bidleman, T.F., 1988. Atmospheric processes. Environ. Sci. Technol. 22, 361-367.

Castro-Jiménez, J., Berrojalbiz, N., Wollgast, J., Dachs, J., 2012. Polycyclic aromatic hydrocarbons (PAHs) in the Mediterranean Sea: Atmospheric occurrence, deposition and decoupling with settling fluxes in the water column. Environmental Pollution 166, 40-47.

Comero, S., Capitani, L., Gawlik, B., 2009. Positive Matrix Factorisation (PMF)–An introduction to the chemometric evaluation of environmental monitoring data using PMF. Office for Official Publications of the European Communities, Luxembourg .

Cooper, D., 2001. Exhaust emissions from high speed passenger ferries. Atmos. Environ. 35, 4189-4200.

De Ridder, K., Lefebre, F., Adriaensen, S., Arnold, U., Beckroege, W., Bronner, C., Damsgaard, O., Dostal, I., Dufek, J., Hirsch, J., 2008. Simulating the impact of urban sprawl on air quality and population exposure in the German Ruhr area. Part II: Development and evaluation of an urban growth scenario. Atmos. Environ. 42, 7070-7077.

DeBell, L.J., Talbot, R.W., Dibb, J.E., Munger, J.W., Fischer, E.V., Frolking, S.E., 2004. A major regional air pollution event in the northeastern United States caused by extensive forest fires in Quebec, Canada. Journal of Geophysical Research: Atmospheres (1984–2012) 109.

Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L., Weathers, K.C., 2001. Acidic Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management Strategies: The effects of acidic deposition in the northeastern United States include the acidification of soil and water, which stresses terrestrial and aquatic biota. Bioscience 51, 180-198.

EPA, 2014. EPA Positive Matrix Factorization (PMF) 5.0 model. Research Triangle Park, NC 5.0 doi: http://www.epa.gov/heasd/products/pmf/pmf.html.

EPA, 2006. Current national recommended water quality criteria.

Esen, F., Sıddık Cindoruk, S., Tasdemir, Y., 2008. Bulk deposition of polycyclic aromatic hydrocarbons (PAHs) in an industrial site of Turkey. Environmental pollution 152, 461-467.

Franz, T.P., Eisenreich, S.J., Holsen, T.M., 1998. Dry deposition of particulate polychlorinated biphenyls and polycyclic aromatic hydrocarbons to Lake Michigan. Environ. Sci. Technol. 32, 3681-3688.

Freeman, D.J., Cattell, F.C., 1990. Woodburning as a source of atmospheric polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 24, 1581-1585.

Galarneau, E., 2008. Source specificity and atmospheric processing of airborne PAHs: implications for source apportionment. Atmos. Environ. 42, 8139-8149.

Garban, B., Blanchoud, H., Motelay-Massei, A., Chevreuil, M., Ollivon, D., 2002. Atmospheric bulk deposition of PAHs onto France: trends from urban to remote sites. Atmos. Environ. 36, 5395-5403.

German Industrial Standard DIN 19739-2, 2003.
Air and soil quality - Measurement of atmospheric deposition of organic trace substances; Funnel adsorber method - Part 2: Determination of polynuclear aromatic hydrocarbons. 1-17.

Gigliotti, C.L., Totten, L.A., Offenberg, J.H., Dachs, J., Reinfelder, J.R., Nelson, E.D., Glenn IV, T.R., Eisenreich, S.J., 2005. Atmospheric concentrations and deposition of polycyclic aromatic hydrocarbons to the Mid-Atlantic East Coast Region. Environ. Sci. Technol. 39, 5550-5559.

Gigliotti, C.L., Brunciak, P.A., Dachs, J., Glenn, T.R., Nelson, E.D., Totten, L.A., Eisenreich, S.J., 2002. Air—water exchange of polycyclic aromatic hydrocarbons in the New York—New Jersey, USA, Harbor Estuary. Environmental Toxicology and Chemistry 21, 235-244.

Gigliotti, C.L., Dachs, J., Nelson, E.D., Brunciak, P.A., Eisenreich, S.J., 2000. Polycyclic aromatic hydrocarbons in the New Jersey coastal atmosphere. Environ. Sci. Technol. 34, 3547-3554.

Göbel, P., Dierkes, C., Coldewey, W.G., 2007. Storm water runoff concentration matrix for urban areas. J. Contam. Hydrol. 91, 26-42 doi: 10.1016/j.jconhyd.2006.08.008.

Gocht, T., Klemm, O., Grathwohl, P., 2007a. Long-term atmospheric bulk deposition of polycyclic aromatic hydrocarbons (PAHs) in rural areas of Southern Germany. Atmos. Environ. 41, 1315-1327.

Gocht, T., Moeckel, C., Chaemfa, C., Thomas, G.O., Jones, K.C., 2007b. Validation of an passive atmospheric deposition sampler for polybrominated diphenyl ethers. J. Environ. Monit. 9, 1176-1182.

Golomb, D., Barry, E., Fisher, G., Varanusupakul, P., Koleda, M., Rooney, T., 2001. Atmospheric deposition of polycyclic aromatic hydrocarbons near New England coastal waters. Atmos. Environ. 35, 6245-6258.

Guo, H., Lee, S., Ho, K., Wang, X., Zou, S., 2003. Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. Atmos. Environ. 37, 5307-5317.

Harrison, R.M., Smith, D., Luhana, L., 1996. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. Environ. Sci. Technol. 30, 825-832.

Harvey, R.G., 1991. Polycyclic Aromatic Hydrocarbons: Chemistry and Carcinogenicity. Cambridge University Press, Cambridge, England.

Hayward, S.J., Gouin, T., Wania, F., 2010. Comparison of four active and passive sampling techniques for pesticides in air. Environ. Sci. Technol. 44, 3410-3416.

He, J., Balasubramanian, R., 2010. A comparative evaluation of passive and active samplers for measurements of gaseous semi-volatile organic compounds in the tropical atmosphere. Atmos. Environ. 44, 884-891.

Hopke, P.K., 1991. Receptor Modeling for Air Quality Management. Elsevier.

Jacob, J., 2008. The significance of polycyclic aromatic hydrocarbons as environmental carcinogens. 35 years research on PAH—a retrospective. Polycyclic Aromatic Compounds 28, 242-272.

Katsoyiannis, A., Sweetman, A.J., Jones, K.C., 2011. PAH molecular diagnostic ratios applied to atmospheric sources: a critical evaluation using two decades of source inventory and air concentration data from the UK. Environ. Sci. Technol. 45, 8897-8906.

Kavouras, I.G., Koutrakis, P., Tsapakis, M., Lagoudaki, E., Stephanou, E.G., Von Baer, D., Oyola, P., 2001. Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHs) using multivariate methods. Environ. Sci. Technol. 35, 2288-2294.

Khalili, N.R., Scheff, P.A., Holsen, T.M., 1995. PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions. Atmos. Environ. 29, 533-542.

Krein, A., Schorer, M., 2000. Road runoff pollution by polycyclic aromatic hydrocarbons and its contribution to river sediments. Water Res. 34, 4110-4115 doi: 10.1016/S0043-1354(00)00156-1.

Kroetz, K.M., Friedland, A.J., 2008. Comparing costs and emissions of northern New England space heating fuel options. Biomass Bioenergy 32, 1359-1366.

Larsen, R.K., Baker, J.E., 2003. Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. Environ. Sci. Technol. 37, 1873-1881.

Lee, J.H., Gigliotti, C.L., Offenberg, J.H., Eisenreich, S.J., Turpin, B.J., 2004. Sources of polycyclic aromatic hydrocarbons to the Hudson River Airshed. Atmos. Environ. 38, 5971-5981.

Li, L., Qian, J., Ou, C., Zhou, Y., Guo, C., Guo, Y., 2014. Spatial and temporal analysis of Air Pollution Index and its timescale-dependent relationship with meteorological factors in Guangzhou, China, 2001–2011. Environmental Pollution 190, 75-81.

Lima, A.L.C., Farrington, J.W., Reddy, C.M., 2005. Combustion-derived polycyclic aromatic hydrocarbons in the environment—a review. Environmental Forensics 6, 109-131.

Liu, L., Liu, Y., Lin, J., Tang, N., Hayakawa, K., Maeda, T., 2007. Development of analytical methods for polycyclic aromatic hydrocarbons (PAHs) in airborne particulates: A review. Journal of Environmental Sciences 19, 1-11.

Lohmann, R., Northcott, G.L., Jones, K.C., 2000. Assessing the contribution of diffuse domestic burning as a source of PCDD/Fs, PCBs, and PAHs to the UK atmosphere. Environ. Sci. Technol. 34, 2892-2899.

Lohmann, R., Lee, R.G., Abbott, J., Coleman, P., Jones, K.C., 2006. Verifying emission factors and national POPs emission inventories for the UK using measurements and modelling at two rural locations. Journal of Environmental Monitoring 8, 79-88.

Mahler, B.J., Van Metre, P.C., Bashara, T.J., Wilson, J.T., Johns, D.A., 2005. Parking lot sealcoat: an unrecognized source of urban polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 39, 5560-5566.

Manoli, E., Samara, C., 1999. Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis. TrAC Trends in Analytical Chemistry 18, 417-428.

Martin, H., 2000. Development of passive samplers for time-integrated deposition and groundwater monitoring: adsorption cartridges and ceramic dosimeters. Thesis, bound.

May, W.E., Wise, S.A., 1984. Liquid chromatographic determination of polycyclic aromatic hydrocarbons in air particulate extracts. Anal. Chem. 56, 225-232.

Melymuk, L., Robson, M., Helm, P.A., Diamond, M.L., 2013. Application of land use regression to identify sources and assess spatial variation in urban SVOC concentrations. Environ. Sci. Technol. 47, 1887-1895.

Miguel, A.H., Pereira, P.A., 1989. Benzo (k) fluoranthene, benzo (ghi) perylene, and indeno (1, 2, 3-cd) pyrene: new tracers of automotive emissions in receptor modeling. Aerosol Science and Technology 10, 292-295.

Motelay-Massei, A., Ollivon, D., Garban, B., Chevreuil, M., 2003. Polycyclic aromatic hydrocarbons in bulk deposition at a suburban site: assessment by principal component analysis of the influence of meteorological parameters. Atmos. Environ. 37, 3135-3146.

Motelay-Massei, A., Ollivon, D., Garban, B., Tiphagne-Larcher, K., Zimmerlin, I., Chevreuil, M., 2007. PAHs in the bulk atmospheric deposition of the Seine river basin: source identification and apportionment by ratios, multivariate statistical techniques and scanning electron microscopy. Chemosphere 67, 312-321.

Naumova, Y.Y., Offenberg, J.H., Eisenreich, S.J., Meng, Q., Polidori, A., Turpin, B.J., Weisel, C.P., Morandi, M.T., Colome, S.D., Stock, T.H., 2003. Gas/particle distribution of polycyclic aromatic hydrocarbons in coupled outdoor/indoor atmospheres. Atmos. Environ. 37, 703-719.

Okuda, T., Kumata, H., Naraoka, H., Takada, H., 2002. Origin of atmospheric polycyclic aromatic hydrocarbons (PAHs) in Chinese cities solved by compound-specific stable carbon isotopic analyses. Org. Geochem. 33, 1737-1745.

Paatero, P., Tapper, U., 1994. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. Environmetrics 5, 111-126.

Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos. Environ. 42, 2895-2921.

Ravindra, K., Bencs, L., Wauters, E., De Hoog, J., Deutsch, F., Roekens, E., Bleux, N., Berghmans, P., Van Grieken, R., 2006. Seasonal and site-specific variation in vapour and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities. Atmos. Environ. 40, 771-785.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R., 1997. Sources of fine organic aerosol. 8. Boilers burning No. 2 distillate fuel oil. Environ. Sci. Technol. 31, 2731-2737.

Schoonover, J.E., Lockaby, B.G., 2006. Land cover impacts on stream nutrients and fecal coliform in the lower Piedmont of West Georgia. Journal of Hydrology 331, 371-382.

Schwarz, K., Gocht, T., Grathwohl, P., 2011. Transport of polycyclic aromatic hydrocarbons in highly vulnerable karst systems. Environmental Pollution 159, 133-139.

Simcik, M.F., Eisenreich, S.J., Lioy, P.J., 1999. Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. Atmos. Environ. 33, 5071-5079.

Skog, K.E., Watterson, I.A., 1984. Residential fuelwood use in the United States. J. For. 82, 742-747.

Tobiszewski, M., Namieśnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environmental Pollution 162, 110-119.

van den Elshout, S., Léger, K., Nussio, F., 2008. Comparing urban air quality in Europe in real time: A review of existing air quality indices and the proposal of a common alternative. Environ. Int. 34, 720-726.

Van Metre, P.C., Majewski, M.S., Mahler, B.J., Foreman, W.T., Braun, C.L., Wilson, J.T., Burbank, T.L., 2012. PAH volatilization following application of coal-tar-based pavement sealant. Atmos. Environ.

Van Metre, P.C., Mahler, B.J., Furlong, E.T., 2000. Urban Sprawl Leaves Its PAH Signature. Environ. Sci. Technol. 34, 4064-4070 doi: 10.1021/es991007n.

Venkataraman, C., Lyons, J.M., Friedlander, S.K., 1994. Size distributions of polycyclic aromatic hydrocarbons and elemental carbon. 1. Sampling, measurement methods, and source characterization. Environ. Sci. Technol. 28, 555-562.

Vermont Air Pollution Control Regulations. 2001. State of Vermont Agency of Natural Resources. Air Pollution Control Division. Waterbury, VT. 29 November 2001. 187 pp.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org. Geochem. 33, 489-515.

Zufall, M.J., Davidson, C.I., Caffrey, P.F., Ondov, J.M., 1998. Airborne concentrations and dry deposition fluxes of particulate species to surrogate surfaces deployed in southern Lake Michigan. Environ. Sci. Technol. 32, 1623-1628.

TABLES

Table 1.1. Prevalence of the sixteen EPA priority PAH compounds in the four major combustion sources contributing to the PAH deposition pattern investigated in this study.

Constituent^	Nap	Acy	Ace	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	BgP	IP	DBA
Gasoline			*f*				*c*	*c*	*j*	*a*	*a*	*a*	*a, j*	*a, b, c,*	*a, f*	
Diesel			*f*				*c*	*c*	*j*	*a*	*a, c*	*a, c, d*	*a, j*	*a, b, c, j*	*a, f, j*	
Oil*	*a*				*h*		*b, c, h*	*b, c*	*h*				*h*	*j*	*j*	
Wood	*i*	*i*			*a, c k, i*	*c, k, i*	*c, k*	*c, k*						*i*		

35

^PAHs abbreviated as follows: Nap = Naphthalene, Acy = Acynaphthalene, Ace = Acenaphthene, Flu = Fluorene, Phe = Phenanthrene, Ant = Anthracene, Fla = Fluoranthene, Pyr = Pyrene, BaA = Benzo(a)anthracene, Chr = Chrysene, BbF = Benzo(b)fluoranthene, BkF = Benzo(k)fluoranthene, BaP = Benzo(a)pyrene, BgP = Benzo(ghi)perylene, IP = Indeno(123-cd)pyrene, DBA = Dibenz(a,h)anthracene.
*Includes domestic heating oil (Larsen and Baker, 2003) and ship and aviation oil (Lee et al., 2004)
References correspond as follows: a = (Larsen and Baker, 2003); b = (Harrison et al., 1996); c = (Ravindra et al., 2006); d = (Miguel and Pereira, 1989); e = (Venkataraman et al., 1994); f = (May and Wise, 1984); g = (Simcik et al., 1999); h = (Lima et al., 2005); i = (Khalili et al., 1995); j = (Lee et al., 2004); k = (Guo et al., 2003)

Table 1.2. Summary of seasonal and annual contamination indices for RI.
For comparison, the results are shown from a study using identical PAH bulk atmospheric deposition samplers at three sites in Germany (Gocht et al., 2007a).

Study	Site	Spring/Summer Contamination Index	Fall Contamination Index	Winter Contamination Index	Annualized Contamination Index
This study (RI , United States)	Charlestown	0.49 ±0.68	1.23. ±1.01	2.12 ±0.24	1.28 ± 0.82
	Pascoag	0.82 ± 0.95	1.18 ± 0.80	1.07 ± 0.88	1.01 ± 0.19
	Kingston	0.90 ± 0.66	1.47 ± 0.67	1.27 ± 1.31	1.21 ± 0.29
	East Greenwich	0.94 ± 0.86	1.57. ± 0.38	1.43 ± 1.38	1.31 ± 0.33
	Hope Valley	2.11 ± 0.47	2.52 ± 0.79	1.97 ± 1.06	2.20 ± 0.28
	Providence	2.47 ± 0.81	2.57 ± 0.37	2.67 ± 0.32	2.66 ± 0.09
(Gocht et al., 2007a) Germany	Seebach				2.73 ± 0.04
	Schönbuch				2.61 ± 0.09
	Waldstein				2.78 ± 0.01

*Latitude and Longitude for all study sites can be found in Table S1.1.

Table 1.3. Average seasonal atmospheric concentrations of Benzo(a)pyrene.
Rhode Island currently does not have ambient air quality standards for PAHs, however
Vermont ambient air standards require that Benzo(a)pyrene concentrations do not exceed 480
pg/m^3.

	Spring/Summer pg/m^3	**Fall** pg/m^3	**Winter** pg/m^3
Providence	360 ± 132	198 ± 282	346 ± 385
Hope Valley	167 ± 285	225 ± 342	314 ± 466
Kingston	3.1 ± 2.1	11.7 ± 45.9	72.5 ± 70.3
East Greenwich	11.9 ± 15.2	13.8 ± 126	205 ± 191
Charlestown	1.4 ± 1.0	13.2 ± 17.3	2.1 ± 1.6
Pascoag	5.7 ± 8.7	73.0 ± 122	99.7 ± 134

FIGURES
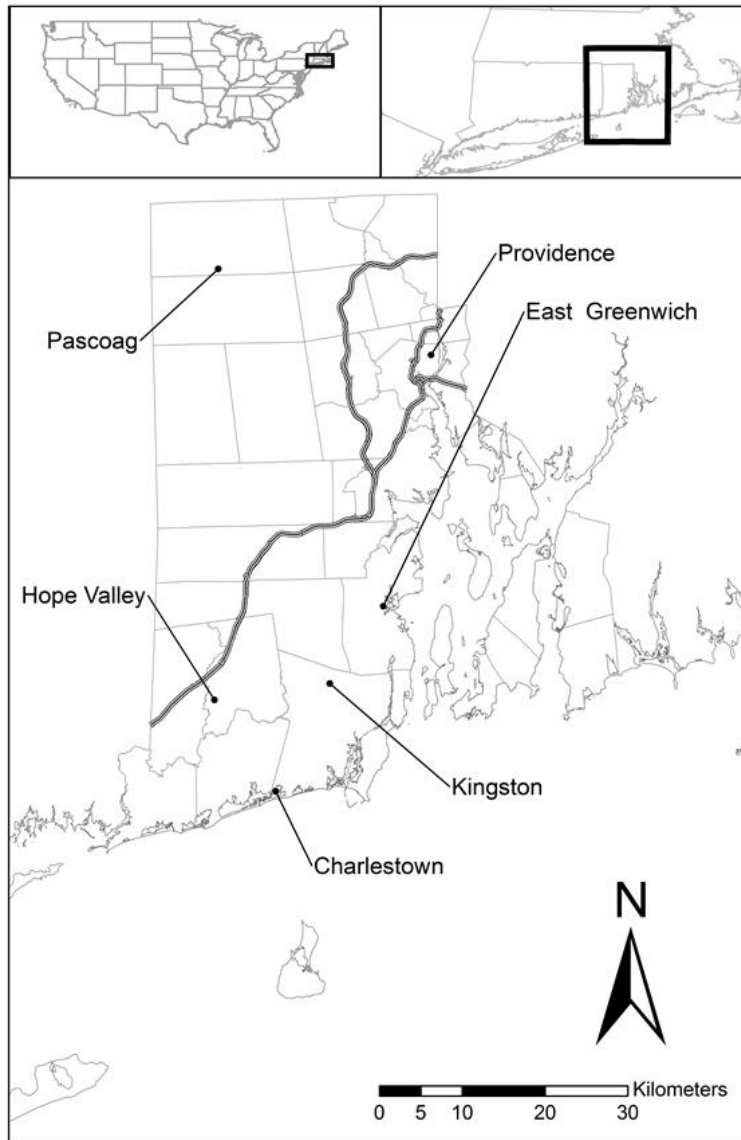
Figure 1.1. Map of sampling locations in RI.
Providence is an urban site, East Greenwich and Hope Valley are peri-urban and Charlestown and Pascoag are rural and coastal sites, respectively. The dark line represents interstate 95 and its auxiliary highways 295 and 195.
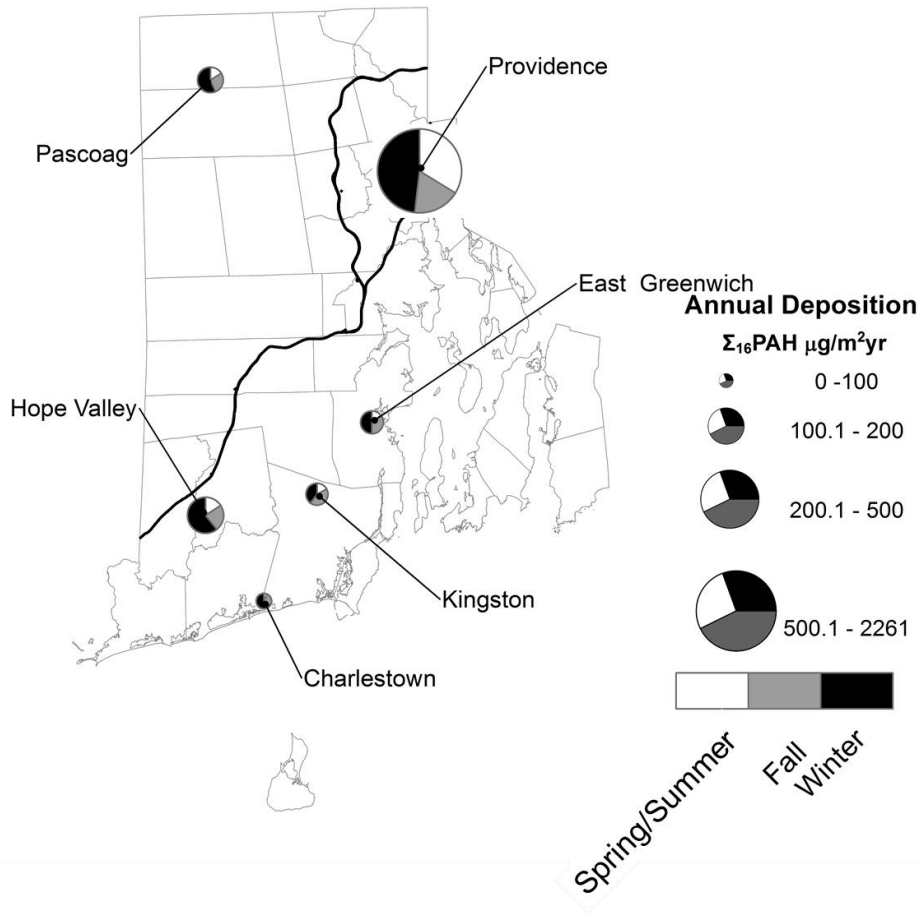
Figure 1.2. Average annual Σ_{16}PAH deposition in µg m^{-2} yr^{-1} for the six sampling sites in RI along with the seasonal breakdown showing the contributions in spring/summer in white, fall in grey, and winter in black. The dark lines dissecting the state are major interstates (I-95 and I-295 near Providence).
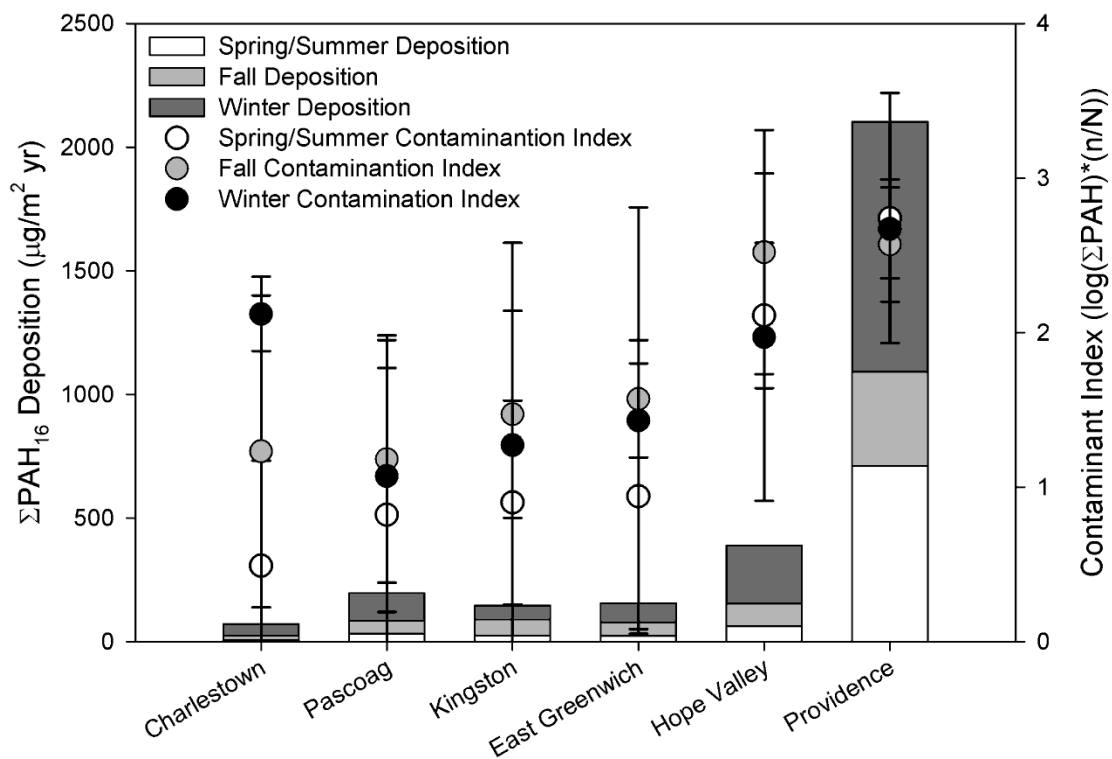
Figure 1.3. Average annual atmospheric deposition of $\sum_{16}$PAHs stacked by season in μg m^{-2} yr^{-1}. Dark grey bars and black circles represent the winter sampling season; medium grey bars and circles represent the fall sampling season, and white bars and circles represent the spring/summer sampling season.
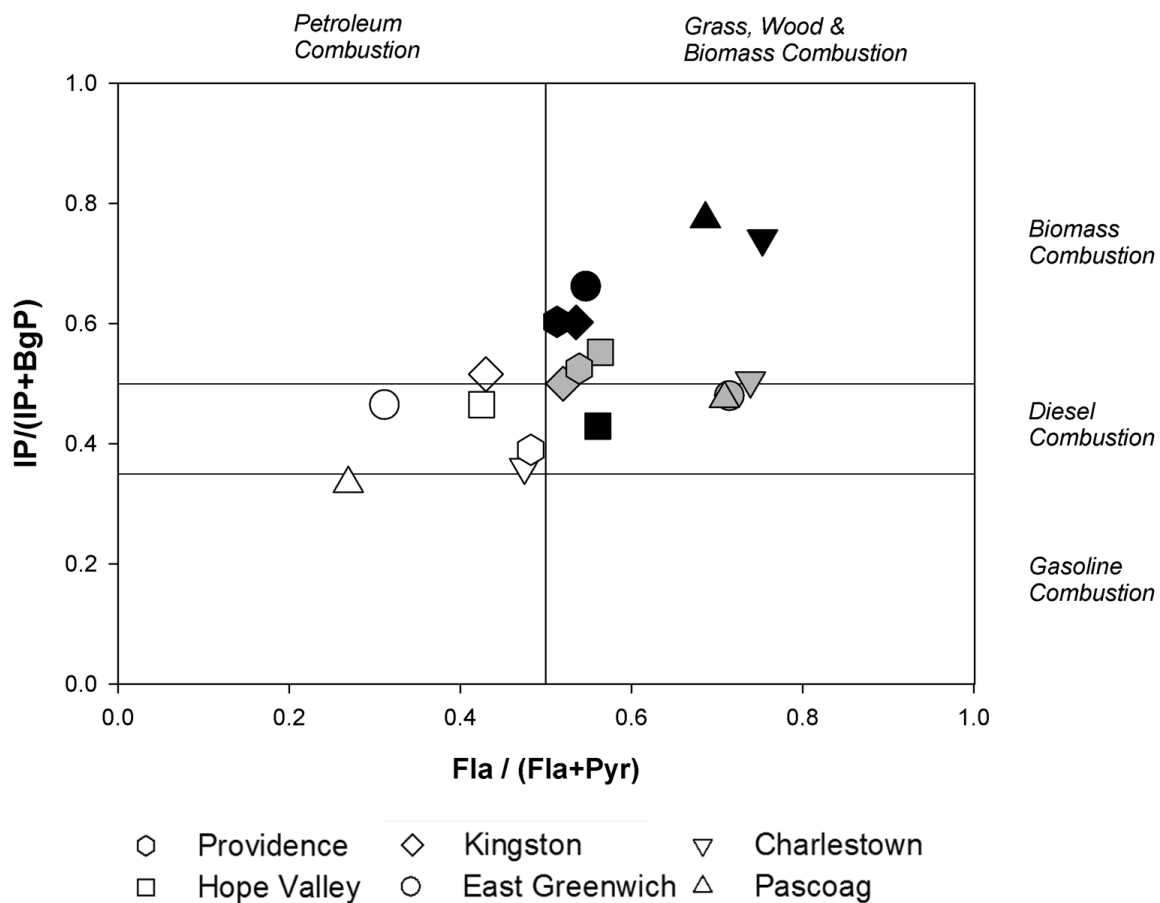
Figure 1.4. Cross plots of PAH ratios of IP/(IP+BgP) vs. Fla/(Fla+Pyr). Symbol colors are indicative of the different sample seasons: white for spring/summer (n=8), grey for fall (n=5), black for winter (n=10). If one of the compounds required for the ratio calculation was not detected, the ratio was not plotted.
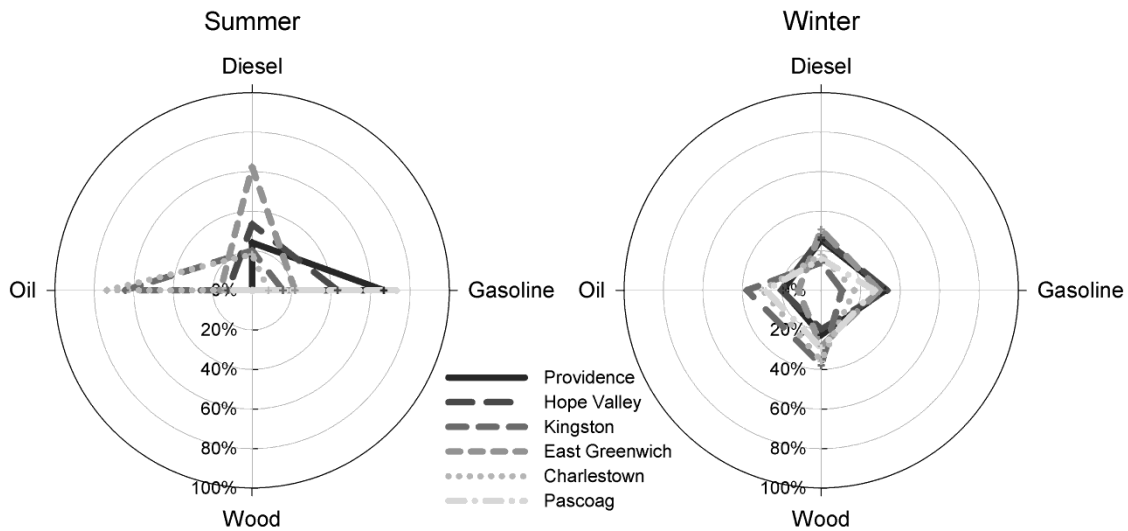
Figure 1.5. Seasonal combustion sources contributing to PAH deposition in the six sampling areas determined by PMF. Each axis represents a percentage contribution for the four defined combustion sources (gasoline, diesel, oil, wood), where fingerprints typical of wood are detected only in the winter time and not in the summer time. Residuals that could not be attributed to any of the four sources were present at three sites during summer (up to 11 %) These residuals are not shown in this figure, but are included in Figure S1.5 in the Supplemental Information.

SUPPORTING INFORMATION

Spatial and Seasonal Variation in PAH Sources and Atmospheric Deposition Patterns

in a small northeastern state in the United States

Laura A. Schifman[1*], Thomas B. Boving[1,2]

[1]Department of Geosciences, University of Rhode Island, Kingston, RI 02881

[2]Department of Civil Engineering, University of Rhode Island, Kingston, RI 02281

Contents

Supplemental Text

Methods – Atmospheric Deposition Sampling

The passive atmospheric sampling system consists of a glass funnel that measures 25 cm in diameter and has an open glass cartridge attached to it. During the winter, the glass funnels and sampling cartridges were replaced with aluminum samplers of the same size because the formation of ice inside the glass funnel and cartridge caused breakage. The sampling cartridge is filled with 15 g of ion-exchange resin (Amberlite-IRA-743 ®, Sigma Aldrich) and plugged at the top and bottom with glass wool that had been cleaned in methanol for 48 hours. The glass funnel and sampling cartridge were protected by stainless steel housing. The sampler was mounted to a steel post 150 cm above the ground (German Industrial Standard DIN 19739-2, 2003). Four samplers were deployed on April 13th, 2011 (Providence - Urban, Pascoag - Rural, Kingston - Rural, and Charlestown - Rural). Additional samplers in peri-urban areas were added on December 31st, 2011 (Hope Valley) and April 25th, 2012 (East Greenwich). All samplers were deployed for approximately four months at a time. The last sampling event was on May 10th, 2014.

After a ~ 120 day collection period in the field (enough time for deposited PAHs to accumulate to detectable ranges; Martin, 2000; Gocht et al., 2007b) the collection cartridges were detached and the funnel was rinsed with 125 ml of acetone (ACS Grade, Fisher Scientific). The acetone was collected in an amber glass bottle and brought back to the laboratory along with the cartridge. The cartridge, including the ion-exchange resin, was washed with 200 ml of acetone to extract PAH from the Amberlite®, allowing at least 15 minute contact time. The solvents containing the extracts from the sampler (funnel and cartridge) were mixed with approximately 800 ml deionized water and extracted following a modified EPA Method 610 using cyclohexane (ACS Grade, Fisher Scientific).

Methods – Quality Control and Quality Assurance

Blank extraction cartridges were prepared for each sampling campaign and handled under the same conditions as the field samples. A recovery standard containing six deuterated PAHs (acenaphthene-d10, benzo[a]pyrene-d12,

benz[a]anthracene-d12, phenanthrene-d10, fluoranthene-d10, dibenz[a,h]anthracene-d14, dibenzo[a,i]pyrene-d14; Ultra Scientific, USA) was added to all acetone extract-DI water mixtures before liquid-liquid extraction. PAH recovery from the extractions was $78.8 \pm 24.4\%$ and results from blank cartridges were subtracted from each field sample.

Methods – Positive Matrix Factorization (PMF)

Also referred to as receptor modeling, PMF uses input data consisting of several analytes and their concentrations to produce two matrices: factor contributions and factor profiles (Paatero and Tapper, 1994). The user specifies the number of factor profiles that describe the sample and then identifies profiles based on known emission source information (Table 1.1). Finally, the model assigns the factor contributions based on the factor profiles and the input dataset. PMF can model compounds occurring at very different concentrations caused, for example, by different source emissions. Because the user includes data uncertainty in the model, PMF can manage and resolve inhomogeneous datasets without prior univariate analysis (Comero et al., 2009).

Supplemental Tables

Table S1.1. Latitudes and Longitudes of locations investigated in this study and the German reference sites investigated by (Gocht et al., 2007a)

Latitude	Longitude	Site
41°22'28.47" N	71°37'04.09" W	Charlestown, RI, U.S.
41°56'24.47" N	71°41'47.32" W	Pascoag, RI, U.S.
41°28'3.26" N	71°42'07.59" W	Hope Valley, RI, U.S.
41°29'26.15" N	71°32'29.22" W	Kingston, RI, U.S.
41° 34'07.48" N	71°27'44.46" W	East Greenwich, RI, U.S.
41°50'29.13" N	71°23'35.59" W	Providence, RI, U.S.
48°34'36.42" N	8°09'49.77" E	Seebach, Germany
48°37'23.96" N	9°03'48.78" E	Schönbuch, Germany
50°09'06.79" N	11°52'21.56" E	Waldstein, Germany

Supplemental Figures
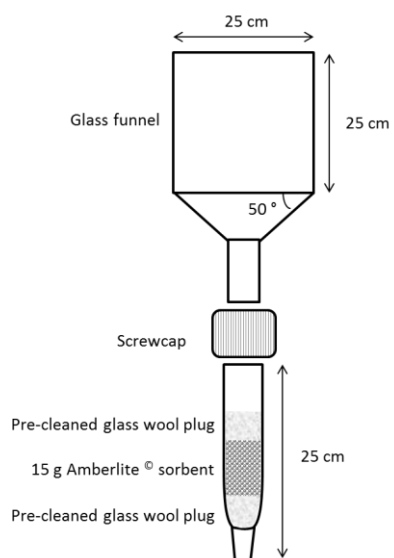
Figure S1.1. Diagram of the atmospheric bulk sampler used in this study.
Image adapted from (Gocht et al., 2007a).
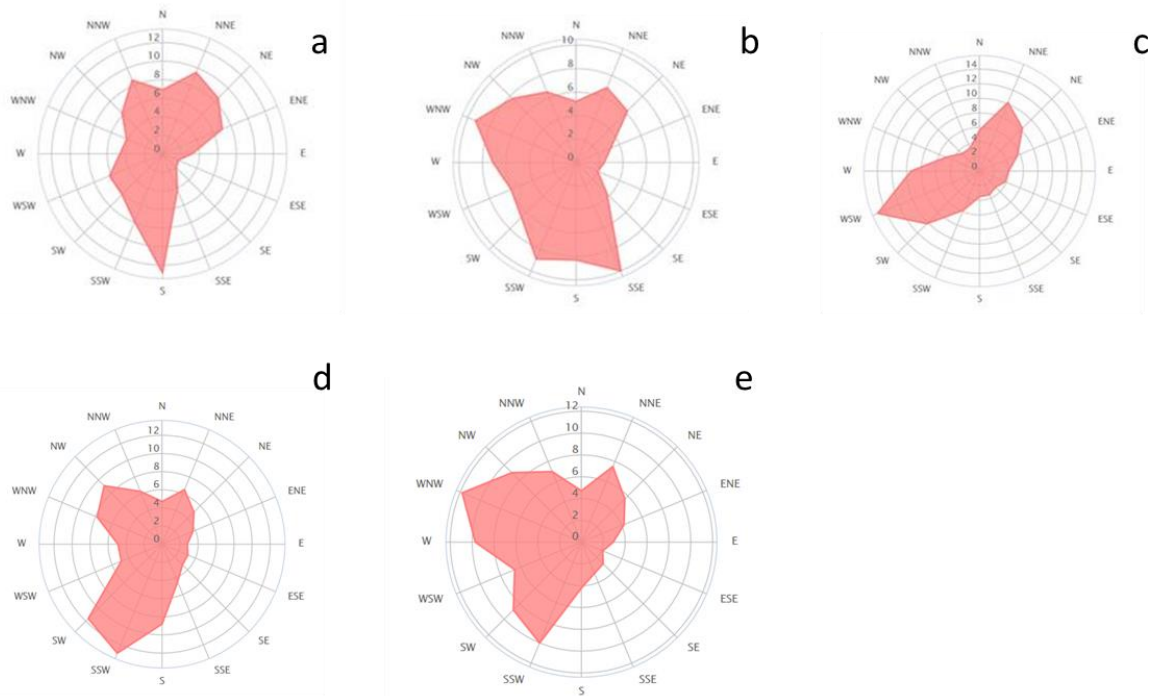
Figure S1.2. Annual wind direction distribution in RI (%).
Insets show a) Providence, b) T.F.Green Airport, close to East Greenwich, c) N. Kingston, close to Kingston, d), Charlestown e), Pawtucket, close to Pascoag, RI. No meteorological station was located near the Hope Valley site. (Source: www.windfinder.com/windstatistics/).
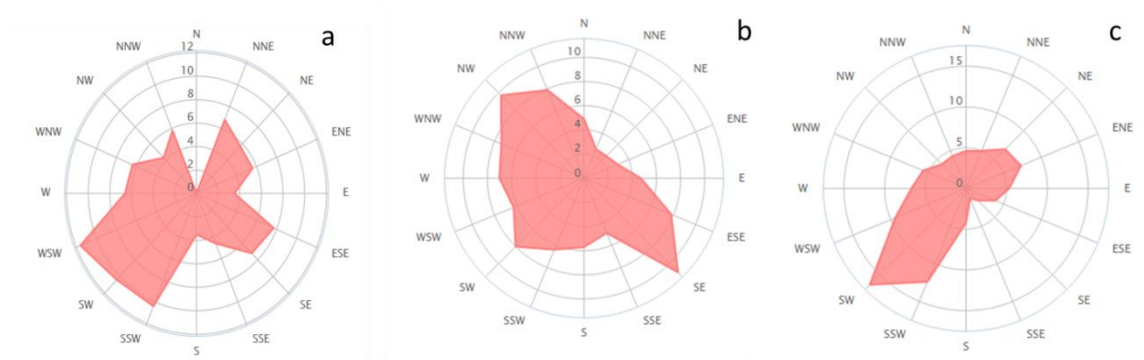
Figure S1.3. Annual wind direction distribution (%) at three German study sites investigated by (Gocht et al., 2007a).
Insets show wind direction for a) Rommelsbach, close to Seebach, b) Böblingen, close to Schönbuch, and c) Wundsiedel in the Fichtelgebirge, close to Waldstein (Source: www.windfinder.com/windstatistics)
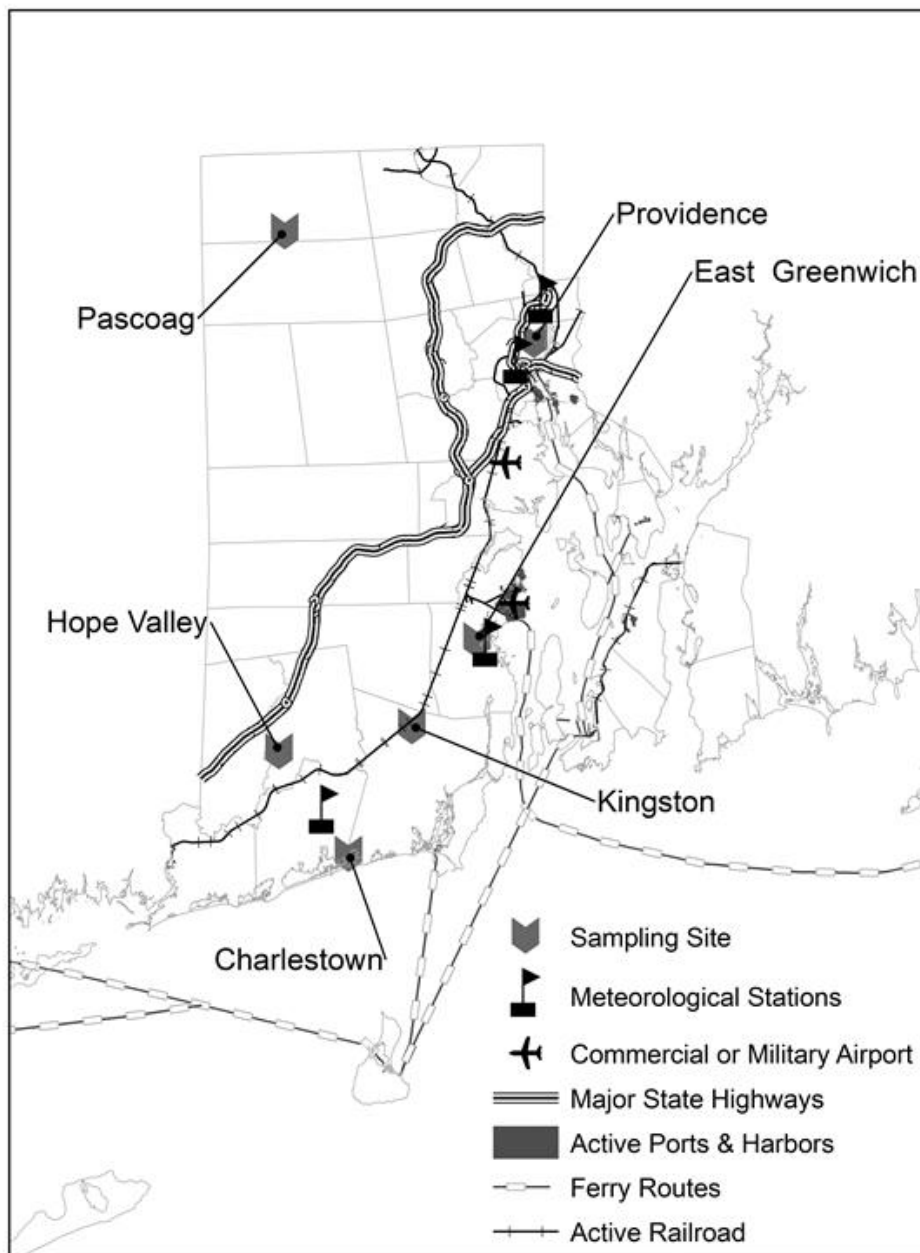
Figure S1.4. Map of RI showing the sampling locations in relation to major potential PAH sources, such as airports, major highways, ports and harbors, as well as ferry routes and railroads.
Also included are the meteorological stations where information about wind directions was obtained (See Figure S1.2).
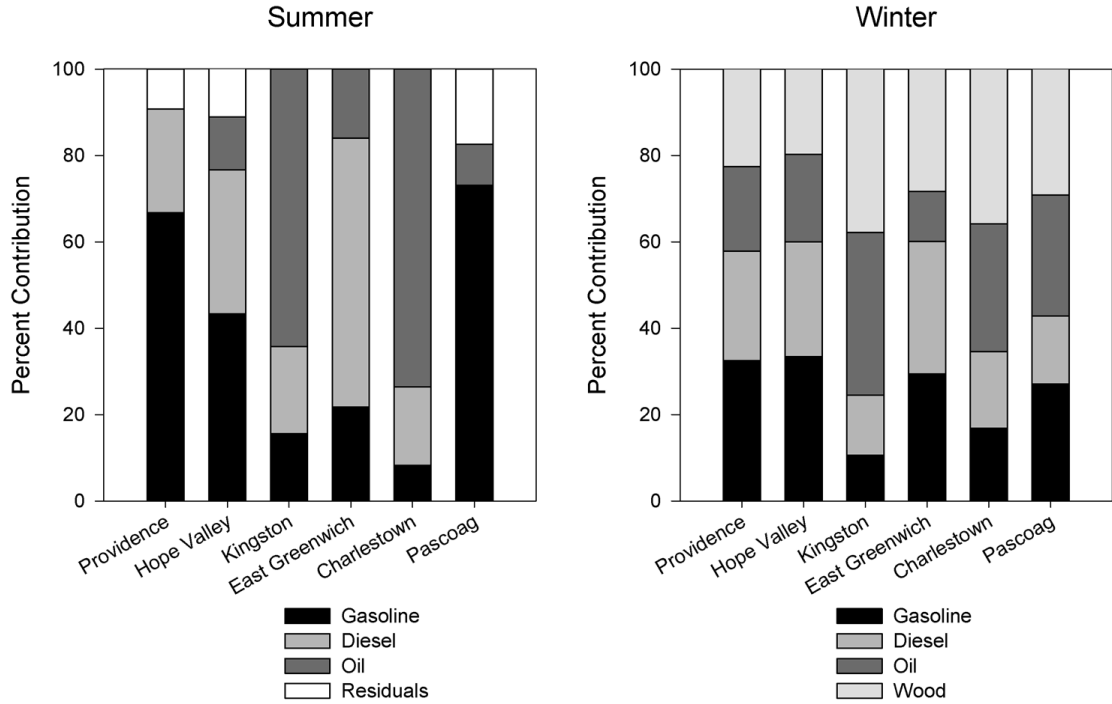
Figure S1.5. Seasonal combustion sources contributing to PAH deposition in the six sampling areas determined by PMF.
The four sources described are gasoline combustion, diesel combustion, oil combustion, and wood combustion, where fingerprints typical of wood combustion are detected only in the winter time, and other unidentifiable sources are detected in the summer time, described by the category "residuals" in the caption.

MANUSCRIPT 2: SELECTING ANTIMICROBIAL FILTER MEDIA FOR IMPROVED STORMWATER BEST MANAGEMENT PRACTICES

In preparation for submission to Water Research

Laura A. Schifman [1*], Varun K. Kasaraneni [2], Ryan K. Sullivan [1], Vinka Oyanedel-Craver [2], Thomas B. Boving [1, 2]

[1] Department of Geosciences, University of Rhode Island, Kingston RI 02881, USA

[2] Department of Civil and Environmental Engineering, University of Rhode Island, Kingston RI 02881, USA

*Corresponding Author: Laura A. Schifman

        Department of Geosciences

        330 Woodward Hall

        University of Rhode Island

        Kingston, RI 02881

        Email: laura.schifman@gmail.com

ABSTRACT

Stormwater runoff can contain high concentrations of pathogens that may impair water bodies used for drinking or recreational purposes. Currently, stormwater best management practices (BMP) are typically not designed to treat bacteria. In this study, we amended red cedar wood chips with different loadings of two antimicrobial compounds: 3-(trihydroxysilyl)propyldimethyloctadecyl ammonium chloride (TPA) and silver nanoparticles (AgNP) for use in stormwater treatment. After exposing *Escherichia coli* (*E. coli*) suspensions to the modified wood for three hours, the culturable bacteria in the aqueous phase and ones attached to the red cedar were determined. Results showed that *E. coli* inactivation, at 25°C, can be achieved with log_{10} removal values (LRV) up to 3.71 ± 0.38 (mean ± standard error) for TPA-red cedar and 2.25 ± 1.00 for AgNP-red cedar, while unmodified red cedar only achieved 0.45 log_{10}. Similar trends were obtained when a temperature of 17.5°C was used. At even lower temperature (10°C) there was no statistically significant difference in the level of bacteria inactivation between modified and unmodified cedar wood. The stability of the amended materials, in terms of efficiency, was also tested through storage under saturated conditions for 120 days, (equivalent to ~4.25 years of projected field use). We found that the level of bacteria inactivation for concentrations of 10^6 CFU/100ml using 6 mg/g TPA modified red cedar was reduced from 2.20 log_{10} to 1.62 log_{10} over the storage period, which was still elevated compared to unmodified red cedar at 0.42 log_{10}. This study demonstrated that cedar wood chips amended with antimicrobial compounds could find application in structural BMP systems, such as tree filters.

Keywords: Antimicrobials, Poly(Trihydroxysilyl)Propyldimethyloctadecyl Ammonium Chloride, Modified Wood, Silver Nanoparticles, Stormwater, Bacteria Treatment, *E. coli*, Chick-Watson Model

INTRODUCTION

Stormwater runoff mobilizes microorganisms into surface and ground water bodies, potentially impairing their quality (Schueler and Holland 2000; Ahn et al. 2005; Göbel et al. 2007; Parker, et al. 2010). Research links microbial inputs from stormwater runoff and other nonpoint sources with elevated prevalence of waterborne diseases (Rose et al. 2000; Curriero et al. 2001). *Escherichia coli* (*E. coli)* and fecal coliforms are typically monitored in watersheds, as their presence is used as an indicator of fecal microbial contamination, suggesting that other pathogens that may pose a human health risk are present (EPA. 2001; EPA 2012). In runoff, *E. coli* concentrations often exceed 10^4 colony-forming units (CFU) per 100 ml (Schueler and Holland 2000; EPA 2001; Ahn et al. 2005). Coastal areas are vulnerable to microbiological contamination, as high bacteria loads are introduced through untreated surface water runoff during storm events, resulting in beach closures and impacting the economic activities of coastal communities (Mallin et al. 2000; McLellan and Salmore 2003; Ahn et al. 2005; Lee et al. 2006; Parker et al. 2010; Dorfman and Rosselot 2012). Despite the potential risks to human health, there are very few regulations pertaining to the removal of pathogens from stormwater runoff. Currently, Rhode Island is the only state in the United States that requires bacteria removal of 60% from stormwater runoff through the use of structural best management practices (BMPs) (RIDEM 2010; EPA 2011). However, 60% removal of fecal indicator bacteria (FIB) at concentrations of 10^4 CFU/100 ml in runoff may not result in acceptable water quality, depending on the level of mixing in the receiving water body. There are currently very few BMP technologies that advertise FIB removal capacities, e.g.

54

BactoLoxx (Filtrexx, Goffstown, NH) or *Bacterra* (Filterra Bioretention Designs, Ashland, VA). The *BactoLoxx* technology relies on proprietary flocculation agents that result in the settling of bacteria (Faucette et al. 2009), and *Bacterra* relies on physical filtration and predation from biomat formation (Coffman, Ruby and Beach 2008). Their stated bacteria removal efficiency reaches up to 99%, however field studies indicated that FIB removal is variable and can range from 0-80%, which is not considered sufficient from a public health perspective when taking into consideration FIB concentrations in runoff (EPA 2012; Schueler and Holland 2000; EPA. 2001; Ahn et al. 2005.) Additionally, recent studies on a wide range of structural BMPs concluded that their removal was less effective, as the removal of pathogens primarily relied on attachment/collection and not inactivation (Stevik et al. 2004; Zhang and Lulla 2006). This is because sorbed pathogens can remain viable and even grow during attachment (Davies and Bavor 2000; Mohanty et al. 2013) and therefore can be remobilized/detached during intermittent flow conditions (Mohanty et al. 2013). This is especially relevant in areas with high water tables because not enough soil depth is present to filter out pathogens effectively, therefore increasing the risk of bacterial contamination (Morales et al. 2014). New approaches are therefore needed to enhance the microbial load reduction in stormwater and possibly implement these technologies in the next generation BMPs.

Materials with antimicrobial properties, such as nanoparticles and polymeric compounds, are widely and successfully used in many applications, ranging from treated fabrics in the medical industry (Li et al. 2006; Song, Kong and Jang 2011) to point of use water filtration (Oyanedel-Craver and Smith 2007; Zhang and Oyanedel-

Craver 2013). Other, chemically less complex compounds suggested for removing bacteria include iron oxide or copper (Mohanty et al. 2013; Ren et al. 2009). Prior studies investigated various media, including wood chips and shale to enhance stormwater treatment of BMPs (Kasaraneni et al. 2014; Li, Deletic and McCarthy 2014). However, these studies focused primarily on the amendment procedures and did not evaluate these modified materials for their antimicrobial properties. Particularly, the use of 3-trihydroxy silylpropyldimethyloctadecyl ammonium chloride solution (TPA) and silver nanoparticles (AgNP) antimicrobials in the reduction of microbial load in stormwater treatment applications has not been documented.

The scope of this research was to develop materials with antimicrobial properties than can effectively treat stormwater runoff contaminants with emphasis on the reduction of microbial load. Red cedar wood was chosen as the base material and AgNP and TPA were the antimicrobial agents. Red cedar has a high affinity for organic contaminants and heavy metals (Kasaraneni et al. 2014) and is resistant to degradation (Grohs et al. 1999). Based on our prior research, both amendments show enhanced removal of organic and inorganic contaminants and are expected to provide antimicrobial properties (Kasaraneni et al. 2014).

The antimicrobial performance of a material in a complex environment, e.g. stormwater BMP, depends on the amount of antimicrobial matter in the filtration matrix, microbial loading, temperature, hydraulic loading (contact time), water chemistry and other factors. Here, we hypothesize that antimicrobial properties of TPA and AgNP can be transferred to cedar wood and that the resulting material can significantly enhance the microbial treatment of stormwater runoff under a range of

56

environmental conditions simulated under laboratory conditions. Using a batch experiment approach, the specific objectives of this study were to 1) perform kinetic studies and model the disinfection performance to achieve a desired bacteria inactivation given a specific disinfectant concentration and exposure time; 2) determine the microbial inactivation efficiency of red cedar modified with varying loadings of AgNPs and TPA, 3) evaluate the bacteria removal efficiency of the three most effective materials at lower, environmentally relevant temperatures, and 4) evaluate the long term saturated storage impacts on the inactivation efficiency of the three most effective materials.

METHODS

Materials

Untreated red cedar (RC) wood, obtained from Liberty Cedar and New England Wood Products (both West Kingston, RI), was chipped, thoroughly mixed, and sieved. Wood chips passing through a 10 mm sieve, but retained on a 3.3 mm sieve were collected and used for the experiments. Wood chips were soaked in deionized water for a minimum of two weeks to leach out soluble matter and remove fines. Biosafe (Pittsburgh, PA) provided a 5% solution of TPA (EPA product Reg.No. 83019-2). The TPA molecule differs from other organosilane quaternary ammonium compounds previously studied (e.g. Torkelson et al. 2012) as the structure is a polymer consisting of a mixture of condensed 3-(trihydroxysilyl) propyldimethyloctadecyl ammonium chloride molecules (Figure S2.1). AgNPs were synthesized in the laboratory via the Tollens method as described by Zhang et al. (2012), using polyvinylpyrrolidone (PVP, average molecular weight: 29,000 g/mol,

Sigma Aldrich) as a stabilizer. To achieve various loadings of TPA and AgNPs, red cedar wood chips were amended following procedures described in Kasaraneni et al. (2014) (Table 2.1). Briefly, wood chips were submerged in TPA or AgNP solutions of 1.3 mmol/L ionic strength (NaCl) and were allowed to equilibrate for four to six days on a shaker to achieve a range of loadings that include the maximum possible loading of each antimicrobial (Table 2.1) (more details on modification and desorption in Kasaraneni et al. (2014) in Appendix I).

A nonpathogenic wild strain of *E. coli* (IDEXX, Westbrook, ME, USA) was used to test the antimicrobial performance of the filter matrix. *E. coli* was chosen because it is commonly used as an indicator bacteria for fecal contamination in drinking water and surface waters and monitoring it is typically required in stormwater regulations (Edberg et al. 2000; Wheeler et al. 2003; Ashbolt 2004; Dorfman and Rosselot 2012). In addition *E. coli* is a widely used reference pathogen when testing filter media for drinking water treatment (Zhang et al. 2012; Zhang and Oyanedel-Craver 2013).

Experimental Methodology

The first part of the study involved batch experiments to test the inactivation kinetics of TPA and AgNP modified red cedar (RC) at 25°C and establish whether exposure time or disinfectant loading were more important in inactivating bacteria. This was followed by testing the disinfection performance of each material at 25°C and establishing bacteria inactivation efficiency at three different temperatures (25°C,

17.5 °C, and 10°C) for the most effective materials. In the last part of the study, the amended materials were submerged in water to test for possible changes in bacteria inactivation efficiency over 120 day period.

During all experiments the experimental solution ratio was 1 g of sorbent to 25 ml of solution containing the desired *E. coli* concentration. This ratio was based on a previous study that tested the performance of contaminant removal from an aqueous solution using the wood chips (Kasaraneni et al. 2014). All experiments were carried out in triplicates. Controls, buffer blanks, and NaCl blanks were analyzed for *E. coli* to establish microbial contamination, quality control, and natural decay of bacteria over the experimental period. All solutions, glassware and other materials used for the experiments were sterilized through autoclaving. All work surfaces were sterilized with a 70% isopropyl alcohol solution.

Bacteria Culturing and Enumeration

Bacteria were cultured in LB broth (10 g/L sodium chloride, 10 g/L tryptone, and 5 g/L yeast extract, Sigma Aldrich) at 37.5 °C for 13 hrs. After culturing, the bacteria were removed from the LB broth, washed and stored in phosphate buffer solution (11.2 g/L K_2HPO_4, 4.8 g/L KH_2PO_4, and 20 mg/L ethylenediaminetetraacetic acid, all Sigma Aldrich; pH: 7.3). *E. coli* concentration was determined using the membrane filtration technique, applying m-FC with Rosalic Acid Broth (Millipore) with subsequent incubation at 44.5 °C for 24-48 hrs.

To enumerate bacteria attached onto the solid phase, samples were carefully sonicated (QSonica, Q125, Newtown, CT, USA) twice at 20% amplitude in 25 ml

phosphate buffer solution for 10 minutes each and filtered following the above procedure. The sonication procedure was previously established by Rayner et al. (2013) (Rayner et al. 2013), further tests were performed to determine the number of cycles required and the effect of sonication on *E. coli* (data not shown). The test results indicated that two cycles for 10 min is sufficient to remove attached *E. coli* from the wood chips and the sonication did not inactivate *E. coli*.

Inactivation Kinetics

The experiments were conducted with solutions containing *E. coli* at 10^6 CFU/100 ml and 10^5 CFU/100 ml in 1.3 mM NaCl solution (comparable to surface water conditions in RI; Zhang and Oyanedel-Craver 2013) at 25°C in a rotisserie incubator set to 5 rpm (Major Science, Saratoga, CA, USA). Contact times were 30 min, 90 min, to 180 min. The resulting data was fitted to the Chick-Watson model (Equation 2.1) (Haas and Karra 1984)

$$ln\left(\frac{N_t}{N_0}\right) = -k'C^n t$$
Equation 2.1

where N_t/N_0 [-] is the ratio of *E. coli* concentration at time t [min] relative to the initial *E. coli* concentration, k' [mg/g t] is the die-off constant, C [mg/g] is the disinfectant concentration, and n [-] is the coefficient of dilution, which determines the importance of disinfectant concentration. In the Chick-Watson model, if n=1 both time and disinfectant concentration are equally important. If n>1, the disinfectant

concentration is more important than time and vice-versa if n<1 (Tchobanoglous et al. 2003).

The parameterized model (details in SI) was tested against the experimental data and a percentage difference was calculated to determine whether the model over- or underestimated inactivation kinetics.

Inactivation Efficiency of Amended Red Cedar

To test the bacteria inactivation efficiency as a function of antimicrobial amendment loading, batch experiments with *E. coli* solutions at five different concentrations ranging from 10^2 to 10^6 CFU/100ml were prepared in 1.3 mM NaCl solution. These solutions were exposed to unmodified, TPA modified (loading range: 3.6 mg/g to a maximum loading of 9.3 mg/g TPA) and AgNP modified (0.33 mg/g to a maximum loading of 0.68 mg/g AgNP) red cedar (from now on test materials are abbreviated as shown in Table 2.1) at 25 °C in a rotisserie incubator set to 5 rpm (Major Science, Saratoga, CA, USA). The exposure time was 180 minutes. This time was based on a preliminary kinetic study in which a ~50% reduction of *E. coli* was measured when exposed to unmodified red cedar (UM) at 25 °C (data not shown). The inactivation efficiency of the materials was calculated as $\log_{10}$ removal value (LRV):

$$LRV = \log_{10} (C_0) - \log_{10} (C_t) \quad \text{Equation 2.2}$$

Where C_0 is the initial *E. coli* concentration and C_t is the final *E. coli* concentration, which is the sum of the *E. coli* that survived in both the aqueous phase

61

and the *E. coli* attached to the unmodified or modified RC material. NB: Although all the materials were test in the same set of experiments, the inactivation efficiency data for unmodified red cedar, 6TPA and 0.6 Ag were published as part of a proof of concept paper (Kasaraneni et al. 2014) and the data for these three materials was supplemented with four additional amended materials in this paper to compare the whole spectrum of materials (Table 2.1)

To observe the differences in active *E. coli* present on the surface of unmodified and 6mg/g TPA modified red cedar, scanning electron microscope (SEM) images were taken. Each of the wood chips were put in contact with 10^6 CFU/100 ml for three hours in a rotary incubator at 25°C set to 5 rpm (Major Science, Saratoga, CA, USA) and prepared for SEM analysis (details in SI and Pathan et al. (2013)). Control images on silicon wafers were prepared as well to document differences only due to the antimicrobial (Figure S2.2)

Temperature Effect on Inactivation Performance

From the seven materials tested, the three best performing amended materials (6TPA, 9TPA, and 0.6AgNP; abbreviations explained in Table 2.1) along with unmodified red cedar (UM) were selected for testing possible effects of temperature on bacteria inactivation. The materials were exposed to an *E. coli* solution containing 10^6 CFU/100 ml in 1.3 mmol/L NaCl, at temperatures of 25°C, 17.5°C, or 10°C for 180 minutes in a temperature controlled rotisserie incubator set to 5 rpm (Major Science, Saratoga, CA, USA). Bacteria that survived the antimicrobial treatment were counted in the aqueous phase and the solid phase (*E. coli* culturable after attachment to

the solid phase are measured as mentioned in Section "Bacteria Culturing and Enumeration") to determine removal through attachment and inactivation.

Long-term storage of modified materials and its impact on inactivation efficiency

Tests were conducted to determine how long-term storage impacts the inactivation performance of the TPA and AgNP modified materials. Three amended RC sorbents (0.6AgNP, 6TPA, and 9TPA) were stored in a dark at room temperature without mixing under saturated conditions in sterile, deionized water for 120 days at the same ratio as the batch experiments (1:25). The reason deionized water was chosen as the medium for storage was that it provides the greatest concentration gradient from the modified red cedar wood chip into the aqueous phase. Therefore, if any desorption should take place, the gradient is favorable. The 120 day length of storage is equivalent to 4.25 years of an installed tree filter (TF) BMP assuming that the filter matrix in such a BMP would be saturated for a maximum of 48 hours after a rain storm of ≥25 mm, which on average occurs 14 times per year in the Northeast United States, based on a 10-year data set obtained from a NOAA operated meteorological station in Providence, RI (NOAA 2014). The materials were stored under saturated conditions to test the maximum possible degradation over this time period because antimicrobials have been observed to degrade over time when stored under saturated conditions (No et al. 2006). It is assumed that unsaturated or dry storage will have lesser impact on inactivation efficiency over time as degradation occurs more slowly, however this has not been validated.

The inactivation efficiency was quantified immediately after modification (0 days), 60 days (equivalent to ~2.1 years), 94 days (equivalent to ~3.3 years), and 120 days (equivalent to ~ 4.25 years) after modification. At those times, subsamples of the stored material were exposed to 10^6 CFU/100 ml *E. coli* solutions (worst case scenario for stormwater loading (Schueler and Holland 2000)) in 1.3 mM NaCl. Exposure time was, once again, 180 minutes. The exposure temperature was set to 25°C in a temperature controlled rotary incubator that rotated at 5 rpm (Major Science, Saratoga, CA, USA). All modified materials were compared to unmodified red cedar. After 120 days, the storage solutions were tested for desorbed AgNPs or TPA. The storage solution containing AgNP modified red cedar was subsampled and digested using 2% nitric acid and filtered through a 0.45µm filter before analysis in a Perkin Elmer 3100 XL ICP-OES with a method detection limit of 0.01 mg/l for Ag. To test the TPA storage solution, a subsample was prepared following Hach Method 8337 and was analyzed on a Hach DR 2800, which had a method detection limit of 0.2 mg/L for TPA.

The disinfection efficiency at a specific time was modeled using Equation 2.3:

$$LRV(t) = (LRV_0 - LRV_{Final})e^{(-kt)} + LRV_{Final} \qquad \text{Equation 2.3}$$

where LRV_0 is the initial LRV that was achieved by the freshly amended material, LRV_{Final} is the final LRV achieved after the material has been stored for 120 days, k is the disinfection efficiency rate loss constant, and t is the time of storage.

Statistical Analysis

To compare the overall inactivation efficiency of the different materials for all bacteria concentrations tested, a one-way ANOVA was performed. Post-hoc comparisons were carried out using Tukey's Honest Significant Difference. An ANCOVA was carried out to analyze the fraction of culturable attached bacteria and the fraction of culturable bacteria in the aqueous phase. The data were compared based on $\log_{10}$ removal at different temperatures using log-normalized data. In this ANCOVA, the culturable attachment *E. coli* concentrations were the response variable and the explanatory variables were the exposure temperature and the type of material. The model was simplified using a stepwise model simplification and AIC (Akaike's Information Criterion, Akaike 1998) was used as a criterion for the minimal adequate model. The difference in disinfection performance using total *E. coli* survival as the reference at the three different temperatures (10°C, 17.5°C, and 25°C) were compared with a two-way ANOVA, where $\log_{10}$ removal values (LRV) was the response variable and exposure temperature and material type were the factors.

To compare the inactivation kinetics of the different materials, an ANCOVA was carried out where LRV was the response variable and exposure time was the explanatory variable for each different type of red cedar treatment. The comparison between the LRV of the amended materials before and after long term storage was tested using a two-tailed t-test for each material. All statistical analyses had the alpha value set to 0.05 and were carried out using R version 3.0.3.

65

RESULTS AND DISCUSSION

Inactivation Kinetics

The kinetic studies data were evaluated with the Chick-Watson model (Haas and Karra 1984) (Equation 2.1) to determine the concentration-time dependency necessary to achieve a 2 $\log_{10}$ (99%) reduction of total culturable *E. coli*. In addition, the Chick-Watson model parameters differentiate whether the exposure time or antimicrobial loading had a greater impact on the reduction of the number of total culturable *E. coli*.

Over the 180 minute sampling period, the *E. coli* $\log_{10}$ removal value (LRV; Equation 2.2) increased with increased exposure time, following a generally log-linear trend for all materials (Figure 2.1). The order of calculated inactivation rates was as follows: 9TPA > 6TPA > 0.6AgNP > 0.3AgNP > 4TPA ~ 3TPA > UM. Except for 4TPA and 3TPA, the inactivation rates of 9TPA, 6TPA, 0.3AgNP, and 0.6AgNP are statistically different from the unmodified red cedar inactivation kinetics, while 3TPA and 4TPA are similar to unmodified red cedar (Table 2.2).

For both, TPA and AgNP amended red cedar, the coefficient of determination (r^2) for all regression equations created to parameterize the Chick-Watson model was 0.99, indicating that modeling the data using the Chick-Watson model is a valid approach even though the model was developed for aqueous phase inactivation kinetics (Tchobanoglous et al. 2003). The model can be used to describe the inactivation kinetics of the amended materials using first order reaction kinetics.

Verifying the predictions of the model with the experimental data shows that there is good agreement between the modeled and observed data, as the predicted

LRVs for both TPA and AgNP modified RC were within 25% of the observed LRV (Table 2.2).

In the parameterized model, the coefficient of dilution, n, indicates that the loading of TPA is more important than exposure time ($n = 1.99$ and $k' = -0.03$); whereas for AgNP modified red cedar exposure time is key for its disinfection performance ($n = 0.58$ and $k' = -1.18$). The model predicts that with 6TPA a 99% reduction of total number of culturable organisms of *E. coli* can be achieved within 3.7 hrs, while it is 5.9 hrs with 0.6AgNP (Table 2.2, Figure 2.1). The different bacteria inactivation mechanisms of TPA and AgNP support these findings. AgNPs slowly release Ag^+ ions that then diffuse through cell membrane and enter the metabolic pathway of the organism and it therefore takes time to reach the ion concentration required for inactivation. (Sondi and Salopek-Sondi 2004; Kim et al. 2007) On the other hand, while the positive charge of TPA attracts bacteria, it suggested that the long carbon chains on the TPA molecule (SI Figure S2.1) pierce the bacteria cell membrane. Therefore, reduction of total number of culturable organisms by TPA relies heavily on the TPA loading, i.e. the more TPA molecules, the better the chance of contact (Kim,et al., 2010).

Inactivation Efficiency of Amended Red Cedar

Comparing all seven amended materials demonstrates that highly modified materials (0.6AgNP, 6TPA, 9TPA) are overall significantly more effective at

deactivating *E. coli* over a three hour time period compared to unmodified and low modified materials (0.3AgNP, 3TPA, 4TPA; Figure 2.1).

The LRV of unmodified RC was less than 1 and similar results were obtained using low loading on RC (3TPA, 4TPA and 0.3 AgNP; Table 2.1, Figure 2.2). At high loadings (6TPA, 9TPA and 0.6AgNP), *E. coli* reduction increased significantly ($p<0.001$, DF=6, F=32.8, ANOVA table in SI Table S2.1a&b) and the LRV was measured to be up to 3.71 ± 0.38 (>99.9%; Figure 2.2). The LRV for TPA or AgNP modified RC was independent of the initial *E. coli* concentration, which ranged from 10^2 CFU/100 ml to 10^6 CFU/100 ml. Instead the LRV was influenced by the antimicrobial amendment loading on the material. The natural decay in Figure 2.2 depicts the natural die-off of bacteria in the control solution containing only NaCl and cannot be attributed to the antimicrobial.

The SEM images support these findings, as the unmodified red cedar shows much higher numbers of *E. coli* and denser clusters of live bacteria present (Figure 2.3 a&b) on the surface of the wood compared to 6TPA red cedar, which shows fewer bacteria (Figure 2.3 c&d). At higher magnification, the bacteria cells that are present on the 6TPA material are damaged and/or ruptured (Figure 2.3d), compared to those on the unmodified red cedar (Figure 2.3b). The structure of the bacteria cells in the SEM images from Figure 2.3 can be compared to those in Figure S2.2 in the supplemental information where active and TPA treated (inactive) bacteria were analyzed on the SEM on silicon wafers. This visual observation suggests that TPA lowers the number of active *E. coli* on the surface of the wood and prohibits growth of cells on the wood surface.

68

Both, TPA and AgNP modified RC were successful at deactivating *E. coli* but in order to archive significantly higher LRV, a minimum loading of ~6 mg/g is required for TPA and 0.6 mg/g for AgNP. Based on these results, the materials with higher antimicrobial agent loading (6TPA, 9TPA, and 0.6AgNP) were chosen for testing the effect of lower exposure temperatures and storage time on inactivation efficiency.

Temperature Effect on Performance of Amended Red Cedar

The performance of the highly amended materials (6TPA, 9TPA, and 0.6AgNP) was tested at three temperatures (10°C, 17.5°C, and 25 °C). Unmodified RC was used as a baseline comparison.

Over the 180 minute exposure period and at all temperatures (10°C, 17.5°C, and 25 °C), *E. coli* remained culturable in both the aqueous solution and after attachment for all treatments (Figure 2.4). Fewer *E. coli* survived in total when in contact with amended materials at 25 °C and 17.5 °C compared to 10°C (p<0.001, DF=2, F-value=14.78, ANOVA Table in SI Table S2.2a). At 25°C, the type of material impacted the number of total culturable *E. coli* in this order: 9TPA< 6TPA~0.6AgNP< UM, indicating that 9TPA has the highest inactivation value.

Bacteria can be permanently removed through inactivation, but can also be temporarily retained through attachment to surfaces (Mohanty et al. 2013). Generally, more bacteria attach to surfaces at elevated temperatures, compared to lower temperatures (McCaulou et al. 1995; Stevik et al. 2004). The higher modified

materials (6TPA, 0.6 AgNP, and 9 TPA) showed that the survival of bacteria attached onto these surfaces is significantly lower at all temperatures compared to unmodified red cedar (p<0.001, DF=3, F-value=12.317; ANOVA table in SI Table S2.2b; Figure 2.4b).

As the more highly modified materials have a greater concentration of antimicrobial agent on the surface of the red cedar, the likelihood of the bacteria coming in contact with an antimicrobial agent during attachment were greater than for unmodified and low modified materials. As the temperature increased, there are significantly fewer bacteria that survive once they attach to the modified red cedar surface (p<0.001, DF=2, F-value=49.92, ANOVA table in Table S2.2b). This trend was clearly detected when comparing results at 17.5°C and 25°C (Figure 2.4b), whereas no difference in bacteria survival after attachment to the three amended materials was detected at 10°C. However, at 10°C survival after attachment for unmodified red cedar was two orders of magnitude higher compared to modified materials (Figure 2.4b). These results are consistent with previously reported studies, where lower temperatures, such as those used in this study, allowed for higher bacteria survival (Gayán et al. 2011; Raffellini et al. 2011). It is proposed that at lower temperatures the movement of the bacteria in solution is reduced and bacteria generally attach to surfaces in fewer numbers (Stevik et a. 2004), resulting in fewer *E. coli* interacting with the antimicrobial agent. The reduced bacteria motility and attachment, along with a change in their cell membrane structure, making them more rigid at low temperature, (Shivaji and Prakash 2010) contribute to an overall reduced *E. coli* inactivation performance at low temperatures.

Long-term reduction of the disinfection efficiency of modified materials

The three most effective sorbent materials (0.6AgNP, 6TPA, and 9TPA) were tested to quantify if and how saturated bench storage impacts the inactivation performance of the materials. These materials showed changes in efficiency over time that resulted in a 26% to 38% decrease in LRV (Table 2.3, Figure 2.5) compared to freshly prepared material. The decay in removal efficiency of these materials fell into the following order: 9TPA>0.6AgNP>6TPA, where there decrease in inactivation efficiency was significantly different from the original, freshly prepared inactivation efficiency (Figure 2.5, Table S2.4). All models were fitted with r^2> 97%. However, the amended materials still performed significantly better than the unmodified material after the 120 day exposure.

Possible explanations for reduction in performance are: 1) leaching /desorption of TPA and AgNP during storage time, 2) fines clogging the pores of the RC making the antimicrobial inaccessible, 3) degradation of antimicrobial agent, 4) diffusion of TPA and AgNP in to RC thereby becoming inaccessible, and 5) surface aggregation and bridging among TPA polymer molecules or AgNP, depending on the material, making the antimicrobial less accessible. Even though all materials exhibit a decrease in inactivation performance over time (Table 2.3 and Figure 2.5), there was non-significant leaching of either TPA (<0.02%) or AgNP (0%) and Ag^+ ions (0%) from the RC sorbent, even after the full 120 days of storage. As documented in Kasaraneni et al. (2014), all materials were dried for 24 hours and underwent desorption for up to

71

1 week until desorption ceased or the concentrations were below the detection limit of the instruments (0.2 mg/L for TPA and 0.1 µg/L for Ag). Thus, desorption of antimicrobial agents cannot explain the observed lower inactivation performance. However, even though no total silver or silver ions were present in the storage solution when analyzed on the ICP-OES, the concentration of total silver or silver ions may be elevated at the wood chip-water interface, but may not be detected in the bulk sample (Unwin and Bard 1992; Barker et al. 1999; Pfeiffer et al. 2014). This phenomenon may not limit the antimicrobial effectiveness of AgNPs, as the concentration of Ag^+ ions can still be elevated at the interface of the nanoparticle (Pfeiffer et al. 2014).

To test whether eroded red cedar fines might have settled on the wood surface after storage and thus limited access to the antimicrobial coating, all materials were agitated by ultrasound for 10 minutes. Subsequently, the inactivation efficiency of all material was tested again and compared to the non-sonicated materials' performances. The LRV for the sonicated and non-sonicated materials was the same, therefore the covering of actives sites by wood-derived fines could be ruled out as a reason for decreased inactivation efficiency after storage.

The measured decrease in inactivation performance over time could potentially be due to chemical degradation of the antimicrobial material. However, storing aqueous TPA solutions under the same conditions as the amended wood did not decrease the agent's concentration or its inactivation performance. Thus, degradation of the TPA antimicrobial is also not responsible for a decrease in inactivation performance. Similarly, PVP stabilized AgNPs in aqueous solutions have been shown to be stable as well (Zhang et al. 2012). Rather than degrading, the antimicrobial

72

amendments may diffuse from the wood's surface into its interior over time. This would make it more difficult for the bacteria to come in contact with the antimicrobial agent. Existing analytical models for diffusion into wood cannot be applied to describe the diffusion processes of these compounds (Burr and Stamm 1947; Behr et al. 1953) because the TPA and AgNP sorption processes to amend the red cedar do not behave in a linear fashion (Kasaraneni et al. 2014). It would therefore be necessary to develop a complex numerical model as suggested by Rügner et al. (1999) to understand the diffusion dynamics of TPA and AgNP into wood. This was outside of the scope of our research and because the diffusion of comparably large molecules, such as TPA (estimated aqueous diffusion coefficient: $4.3 10^{-10}$ m^2/s), is a very slow process, significant diffusive transport into the wood matrix at the time scale investigated (120 days) was not considered a major contributing factor to the observed decrease in inactivation performance over time. Rather, it is hypothesized that the main reason for the decrease in inactivation efficiency over time is aggregation and bridging of the long carbon chain on TPA polymers and the PVP-stabilized AgNP. Through these processes the antimicrobial amendments enter a lower energy state (Rosen 1975; Rosen and Kunjappu 2012) because bridging/aggregating minimizes contact of the TPA polymer and PVP coated AgNPs with the polar water molecules that surround the wood chips.

While aggregated/bridged TPA and AgNP amendments can explain the decrease in antimicrobial effectiveness, the overall antimicrobial effectiveness of the filter material is not entirely compromised as the amended materials still outperforms the UM red cedar by 3.45 times after 120 days of storage. Further, much of the

decrease in inactivation performance occurs after 60 days of storage, whereas the inactivation performance remains essentially stable for the remainder of the time (days 60-120) (Figure 2.5). Therefore, it can be postulated that the bridging/aggregating occurs within the first 60 days of storage and thereafter the TPA polymer and PVP-stabilized AgNP have reached a stable state of continued inactivation performance.

Limitations

The results in this study indicate that the inactivation performance of amended materials is significantly higher than unmodified materials. However, further testing of these materials under dynamic flow conditions is required to confirm these results. Stormwater is a complex mixture, which can include organic contaminants, heavy metals, inorganic salts, humic substances, along with several species of microorganisms. A study determining the impact of the complex stormwater chemistry conditions and different species of microorganism on the inactivation performance of the amended materials is necessary prior to use of these materials in the field.

Implications and Benefits to Using Antimicrobial Filter Materials

Red cedar wood chips amended with either TPA or AgNP have been shown to increase the removal of *E. coli* from water. Even though similar results could be achieved with chlorine or UV disinfection, both of which occur within minutes (Gayán et al. 2011; Tchobanoglous et al. 2003), these two approaches have not found application in stormwater treatment because of complexity and cost of such treatment (Tchobanoglous et al. 2003). Relative to these technologies, the passive wood

filtration approach described herein does not produce disinfection byproducts, as often observed when using chlorine. As shown by the saturated storage experiments, the antimicrobials also do not leach from the red cedar into the environment, suggesting that the proposed filter media might be safe for use in the environment. Further, using a passive approach of disinfection requires less energy; in particular compared to UV disinfection, which also involves frequent maintenance to ensure proper disinfection (Gayán et al. 2011; Tchobanoglous et al. 2003).

Based on these properties, the red cedar wood chips amended with either TPA or AgNP could find use in stormwater treatment systems. An example is a Tree Filter BMP, which treats conventional stormwater pollutants, such as heavy metals or petroleum hydrocarbons, but could be outfitted with a layer of amended wood chips to provide additional antimicrobial treatment functions. Such a BMP system could potentially remove a much higher percentage of *E. coli* and possibly other bacteria from stormwater runoff than most currently available treatment systems such as *BactoLoxx* (Filtrexx, Goffstown, NH) or *Bacterra* (Filterra Bioretention Designs, Ashland, VA). These currently available systems rely on sorption processes, pH changes, and natural predation by other organisms to achieve the reported removal of up to two $\log_{10}$ units (99%) in *E. coli*, whereas this study suggests that up to 3-$\log_{10}$ (99.9% removal) of *E. coli* may be achieved using the amended red cedar filter materials investigated. This removal far exceeds the 60% reduction in stormwater bacteria levels required in the more recently formulated stormwater treatment manuals (RIDEM 2010).

More importantly, our laboratory study showed that once the wood has been amended, neither TPA nor AgNP showed significant desorption from red cedar, i.e. no detectable leachate for 0.6AgNP and 6TPA, and less than 0.02% of the mass loaded onto 9TPA. Therefore, introducing these materials into BMPs should not disturb native microbial communities such as denitrifiers that have ecological benefits and other stormwater treatment benefits. However, if leaching does occur, quaternary ammonium compounds have been shown to sorb to clay and other soil particles (Oyanedel-Craver and Smith 2006; Oyanedel-Craver et al. 2007; Kasaraneni et al. 2013). Also, the filter material maintained its ability to effectively remove bacteria from aqueous solutions. These are important findings because antimicrobials should not be introduced into the environment and any structural BMP containing modified red cedar should remain effective for several years without major maintenance requirements. Because red cedar is resistant to fungal rot, its use in BMPs is advantageous over other types of wood (Grohs 1999). However, a further study of how long the wood chips can remain in the BMP is required.

Even though both antimicrobials are strongly sorbed to the red cedar, there are benefits to using TPA over AgNP. This is because AgNP amended materials rely on the slow, but continuous release of Ag^+ ions (Kim et al. 2007) and inactivation is time-dependent, as was demonstrated herein. Therefore the antimicrobial treatment of AgNP amended wood is slower and the efficiency is expected to decrease eventually due to a depletion of Ag^+ ions. In comparison to AgNP and other antimicrobials, such as copper (Ren et al. 2009) or other nanoparticles, TPA does not release ions from its matrix into solution. Hence, TPA should retain its antimicrobial efficiency for longer

than AgNP (Shi et al. 2007; Saif et al. 2008; Ferreira and Zumbuehl 2009; Kasaraneni et al. 2014). In addition, a cost benefit analysis of TPA versus AgNP modified materials (Zhang, Smith and Oyanedel-Craver 2012; Kasaraneni et al. 2014) shows that TPA is more cost effective than AgNP.

If the proposed amended red cedar were to be implemented as a filtration matrix in structural best management practices, the 6TPA modified red cedar would be favorable compared to the currently used matrix that consists of a shale-sand mix, or even unmodified red cedar. This is because not only does 1 gram of this material (i.e. 6 mg of TPA) achieve >2 $\log_{10}$ removal after three hours of exposure at room temperature, but it also is effective at removing bacteria at decreased temperatures that could be found in New England (17.5°C). These lower temperatures are closer to a natural BMP operating temperature in most temperate climates. To decrease the effective treatment time to less than 30 minutes, which many BMPs are designed for (RIDEM 2010), an optimal wood:solution ratio would have to be determined before implementing the material in the field. However, introducing any type of bioactive material into the environment will require additional field studies to ensure that no unanticipated consequences result from the well-intended use of antimicrobial wood for stormwater treatment.

TPA solution for testing. The wood was chipped by Scott Ahern and Kevin Broccolo, URI.

REFERENCES

Ahn, J. H., Grant, S. B., Surbeck, C. Q., DiGiacomo, P. M., Nezlin, N. P., Jiang, S. 2005. Coastal water quality impact of stormwater runoff from an urban watershed in southern California. Environmental Science & Technology 39 (16), 5940-5953.

Akaike, H. (1998) Information Theory and an Extension of the Maximum Likelihood Principle. In: Parzen, E., Tanabe, K., Kitagawa, G. (Eds.), Springer New York, 199-213.

Ashbolt, N. J. 2004. Microbial contamination of drinking water and disease outcomes in developing regions. Toxicology 198 (1), 229-238.

Bales, R. C., Hinkle, S. R., Kroeger, T. W., Stocking, K., Gerba, C. P. 1991. Bacteriophage adsorption during transport through porous media: chemical perturbations and reversibility Environmental Science & Technology 25 (12), 2088- 2095.

Barker, A. L., Gonsalves, M., Macpherson, J. V., Slevin, C. J., Unwin, P. R. 1999. Scanning electrochemical microscopy: beyond the solid/liquid interface. Analytica Chimica Acta 385 (1), 223-240.

Behr, E., Briggs, D., Kaufert, F. 1953. Diffusion of dissolved materials through wood. The Journal Of Physical Chemistry 57 (4), 476-480.

Burr, H. K. and Stamm, A. J. 1947. Diffusion in wood. The Journal Of Physical Chemistry 51 (1), 240-261.

Chandrasena, G. I., Deletic, A., McCarthy, D. T. 2013. Survival of *Escherichia coli* in stormwater biofilters Environmental Science and Pollution Research.

Coffman, L. S., Ruby, M., Beach, C. (2008) Bacterra by Filterra® Advanced Bioretention System: Discussion of the Benefits, Mechanisms and Efficiencies for Bacteria Removal. In: ASCE Conf. Proc. 333.

Curriero, F. C., Patz, J. A., Rose, J. B., Lele, S. 2001. The Association Between Extreme Precipitation and Waterborne Disease Outbreaks in the United States, 1948–1994 American Journal of Public Health 91 (8), 1194 - 1199.

Davies, C. M. and Bavor, H. J. 2000. The fate of stormwater-associated bacteria in constructed wetland and water pollution control pond systems Journal of applied microbiology 89 (2), 349 - 360.

Dorfman, M. and Rosselot, K. 2012. Testing the Water: A Guide to Water Quality at Vacation Beaches. 22.

Edberg, S., Rice, E., Karlin, R., Allen, M. 2000. *Escherichia coli*: the best biological drinking water indicator for public health protection. Journal of Applied Microbiology 88 (S1), 106S-116S.

EPA 2001 Protocol for Developing Pathogen TMDLs. Office of Water (4503F), United States Environmental Protection Agency, Washington, DC, 132.

EPA 2011. Performance Standards for Discharges from Newly Developed and Redeveloped Sites. (June 30, 2011), 1-144.

EPA 2012. Recreational Water Quality Criteria. Office of Water 820-F-12-058, 1-58.

Faucette, L., Cardoso-Gendreau, F., Codling, E., Sadeghi, A., Pachepsky, Y., Shelton, D. 2009. Storm water pollutant removal performance of compost filter socks. Journal of Environmental Quality 38 (3), 1233-1239.

Ferreira, L. and Zumbuehl, A. 2009. Non-leaching surfaces capable of killing microorganisms on contact. Journal of Materials Chemistry 19 (42), 7796-7806.

Gayán, E., Monfort, S., Álvarez, I., Condón, S. 2011. UV-C inactivation of *Escherichia coli* at different temperatures Innovative Food Science & Emerging Technologies 12 (4), 531 - 541.

Göbel, P., Dierkes, C., Coldewey, W. G. 2007. Storm water runoff concentration matrix for urban areas. Journal of Contaminant Hydrology 91 (1–2), 26-42.

Grohs, B. M., Wegen, H. -., Kunz, B. 1999. Antifungal activity of red cedar extract and hiba oil on wood-inhabiting moulds. Holz als Roh- und Werkstoff 57 (4), 277-281.

Haas, C. N. and Karra, S. B. 1984. Kinetics of microbial inactivation by chlorine—I Review of results in demand-free systems. Water research 18 (11), 1443-1449.

Kasaraneni, V., Kohm, S. E., Eberle, D., Boving, T., Oyanedel-Craver, V. 2013. Enhanced containment of polycyclic aromatic hydrocarbons through organic modification of soils. Environmental Progress & Sustainable Energy.

Kasaraneni, V. K., Schifman, L. A., Boving, T. B., Oyanedel-Craver, V. 2014. Enhancement of Surface Runoff Quality Using Modified Sorbents. ACS Sustainable Chemistry & Engineering 2 (7), 1609-1615.

Kim, J. S., Kuk, E., Yu, K. N., Kim, J., Park, S. J., Lee, H. J., Kim, S. H., Park, Y. K., Park, Y. H., Hwang, C. 2007. Antimicrobial effects of silver nanoparticles. Nanomedicine: Nanotechnology, Biology and Medicine 3 (1), 95-101.

Kim, H. W., Kim, B. R., Rhee, Y. H. 2010. Imparting durable antimicrobial properties to cotton fabrics using alginate–quaternary ammonium complex nanoparticles Carbohydrate Polymers 79 (4), 1057 - 1062.

Lee, C. M., Lin, T. Y., Lin, C. C., Kohbodi, G. A., Bhatt, A., Lee, R., Jay, J. A. 2006. Persistence of fecal indicator bacteria in Santa Monica Bay beach sediments Water research 40 (14), 2593-2602.

Li, Y. L., Deletic, A., McCarthy, D. T. 2014. Removal of *E. coli* from urban stormwater using antimicrobial-modified filter media Journal of hazardous materials 271, 73 - 81.

Li, Z., Lee, D., Sheng, X., Cohen, R. E., Rubner, M. F. 2006. Two-Level Antibacterial Coating with Both Release-Killing and Contact-Killing Capabilities Langmuir 22 (24), 9820 - 9823.

Mallin, M. A., Williams, K. E., Esham, E. C., Lowe, R. P. 2000. Effect of human development on bacteriological water quality in coastal watersheds. Ecological Applications 10 (4), 1047-1056.

McCaulou, D. R., Bales, R. C., Arnold, R. G. 1995; 2010. Effect of Temperature-Controlled Motility on Transport of Bacteria and Microspheres Through Saturated Sediment Water Resources Research 31 (2), 271 - 280.

McLellan, S. and Salmore, A. 2003. Evidence for localized bacterial loading as the cause of chronic beach closings in a freshwater marina. Water Research 37 (11), 2700-2708.

Mohanty, S. K., Torkelson, A. A., Dodd, H., Nelson, K. L., Boehm, A. B. 2013. Engineering Solutions to Improve the Removal of Fecal Indicator Bacteria by Bioinfiltration Systems during Intermittent Flow of Stormwater Environmental science & technology 47 (19), 10791 - 10798.

Morales, I., Atoyan, J. A., Amador, J. A., Boving, T. 2014. Transport of Pathogen Surrogates in Soil Treatment Units: Numerical Modeling. Water 6 (4), 818-838.

No, H. K., Kim, S. H., Lee, S. H., Park, N. Y., Prinyawiwatkul, W. 2006. Stability and antibacterial activity of chitosan solutions affected by storage temperature and time. Carbohydrate Polymers 65 (2), 174-178.

NOAA, 2014. Annual Climatological Summary for Providence, RI.

Oyanedel-Craver, V. A., Fuller, M., Smith, J. A. 2007. Simultaneous sorption of benzene and heavy metals onto two organoclays. Journal of Colloid and Interface Science 309 (2), 485-492.

Oyanedel-Craver, V. A. and Smith, J. A. 2006. Effect of quaternary ammonium cation loading and pH on heavy metal sorption to Ca bentonite and two organobentonites. Journal of Hazardous Materials 137 (2), 1102-1114.

Oyanedel-Craver, V. A. and Smith, J. A. 2007. Sustainable colloidal-silver-impregnated ceramic filter for point-of-use water treatment. Environmental Science & Technology 42 (3), 927-933.

Parker, J., McIntyre, D., Noble, R. 2010. Characterizing fecal contamination in stormwater runoff in coastal North Carolina, USA. Water Research 44 (14), 4186-4194.

Pathan, A., Bond, J., Gaskin, R. 2010. Sample preparation for SEM of plant surfaces. Materials Today 12, 32-43.

Pfeiffer, C., Rehbock, C., Huhn, D., Carrillo-Carrion, C., de Aberasturi, D. J., Merk, V., Barcikowski, S., Parak, W. J. 2014. Interaction of colloidal nanoparticles with their local environment: the (ionic) nanoenvironment around nanoparticles is different from bulk and determines the physico-chemical properties of the nanoparticles. Journal of the Royal Society, Interface / the Royal Society 11 (96), 20130931.

Raffellini, S., Schenk, M., Guerrero, S., Alzamora, S. M. 2011. Kinetics of *Escherichia coli* inactivation employing hydrogen peroxide at varying temperatures, pH and concentrations. Food Control 22 (6), 920-932.

Rayner, J., Zhang, H., Lantagne, D., Schubert, J., Lennon, P., Craver, V. O. 2013. Laboratory investigation into the effect of silver application on the bacterial removal efficacy of filter material for use on locally-produced ceramic water filters for household drinking water treatment. ACS Sustainable Chemistry & Engineering.

Ren, G., Hu, D., Cheng, E. W., Vargas-Reus, M. A., Reip, P., Allaker, R. P. 2009. Characterisation of copper oxide nanoparticles for antimicrobial applications. International Journal of Antimicrobial Agents 33 (6), 587-590.

RIDEM 2010. Rhode Island Stormwater Design and Installation Standards Manual. pp. 487.

Rose, J. B., Daeschner, S., Easterling, D. R., Curriero, F. C., Lele, S., Patz, J. A. 2000. Climate and waterborne disease outbreaks. Journal-American Water Works Association 92 (9), 77-87.

Rosen, M. J. and Kunjappu, J. T. (2012) Surfactants and interfacial phenomena. John Wiley & Sons, pp. 616.

Rosen, M. 1975. Relationship of structure to properties in surfactants. III. Adsorption at the solid-liquid interface from aqueous solution. Journal of the American Oil Chemists Society 52 (11), 431-435.

Rügner, H., Kleineidam, S., Grathwohl, P. 1999. Long term sorption kinetics of phenanthrene in aquifer materials. Environmental Science & Technology 33 (10), 1645-1651.

Saif, M. J., Anwar, J., Munawar, M. A. 2008. A novel application of quaternary ammonium compounds as antibacterial hybrid coating on glass surfaces. Langmuir 25 (1), 377-379.

Schueler, T. R. and Holland, H. 2000. Microbes and urban watersheds: concentrations, sources, and pathways. The Practice of Watershed Protection, 74-84.

Shi, Z., Neoh, K., Kang, E. 2007. Antibacterial and adsorption characteristics of activated carbon functionalized with quaternary ammonium moieties. Industrial & Engineering Chemistry Research 46 (2), 439-445.

Shivaji, S. and Prakash, J. S. 2010. How do bacteria sense and respond to low temperature? Archives of Microbiology 192 (2), 85-95.

Sondi, I. and Salopek-Sondi, B. 2004. Silver nanoparticles as antimicrobial agent: a case study on *E. coli* as a model for Gram-negative bacteria. Journal of colloid and interface science 275 (1), 177-182.

Song, J., Kong, H., Jang, J. 2011. Bacterial adhesion inhibition of the quaternary ammonium functionalized silica nanoparticles. Colloids and Surfaces B: Biointerfaces 82 (2), 651-656.

Stevik, T. K., Aa, K., Ausland, G., Hanssen, J. F. 2004. Retention and removal of pathogenic bacteria in wastewater percolating through porous media: a review Water Research 38 (6), 1355-1367.

Tchobanoglous, G., Burton, F. L., Stensel, H. D. 2003. Wastewater engineering: treatment and reuse Boston ; McGraw-Hill, pp. 1819.

Torkelson, A., da Silva, A., Love, D., Kim, J., Alper, J., Coox, B., Dahm, J., Kozodoy, P., Maboudian, R., Nelson, K. 2012. Investigation of quaternary ammonium silane-coated sand filter for the removal of bacteria and viruses from drinking water. Journal of applied microbiology 113 (5), 1196-1207.

Unwin, P. R. and Bard, A. J. 1992. Scanning electrochemical microscopy. 14. Scanning electrochemical microscope induced desorption: a new technique for the

measurement of adsorption/desorption kinetics and surface diffusion rates at the solid/liquid interface. The Journal of Physical Chemistry 96 (12), 5035-5045.

Wheeler Alm, E., Burke, J., Spain, A. 2003. Fecal indicator bacteria are abundant in wet sand at freshwater beaches. Water Research 37 (16), 3978-3982.

Zhang, H. and Oyanedel-Craver, V. 2013. Comparison of the bacterial removal performance of silver nanoparticles and a polymer based quaternary amine functiaonalized silsesquioxane coated point-of-use ceramic water filters. Journal of Hazardous Materials.

Zhang, X. and Lulla, M. 2006. Evaluation of pathogenic indicator bacteria in structural best management practices. Journal of Environmental Science and Health Part A 41 (11), 2483-2493.

Zhang, H., Smith, J. A., Oyanedel-Craver, V. 2012. The effect of natural water conditions on the anti-bacterial performance and stability of silver nanoparticles capped with different polymers. Water Research 46 (3), 691-699.

TABLES

Table 2.1. Description of the seven test materials used in the study along with their abbreviations.
The matrix for all test materials was Red Cedar. Antimicrobial agent loadings are categorized as low for 0.3AgNP, 3TPA, and 4TPA, and as high for 0.6AgNP, 6TPA, and 9TPA.

Antimicrobial Agent	Antimicrobial Loading	Abbreviation	Initial aqueous concentrations (mg/l)
None	Unmodified	UM	-
TPA	3.6 mg/g	3TPA	260
	4.5 mg/g	4TPA	450
	6.7 mg/g	6TPA	720
	9.3 mg/g	9TPA	1500
AgNP	0.33 mg/g	0.3Ag	20.8
	0.68 mg/g	0.6Ag	52

Table 2.2. Bacteria inactivation kinetics determined by the Chick-Watson Model (Equation 2.1) for TPA and AgNP modified red cedar. The parameterized model predicts that it takes 1.33 times longer to achieve 3- $\log_{10}$ (99.9%) compared to 2- $\log_{10}$ (99.0%) reduction. Experimental data and the Chick-Watson model predictions are presented in $\log_{10}$ removal values (LRV) with percent differences in parentheses.

Antimicrobial Agent / Model	Antimicrobial Loading	2- $\log_{10}$ reduction (hrs)	3- $\log_{10}$ reduction (hrs)	Experimental Data		Chick Watson Predicted Data	
				90 min	180 min	90 min	180 min
	3 mg/g	11.78	17.63	0.34	0.61	0.25 (25.6)	0.51 (17.1)
TPA	4 mg/g	7.55	11.30	0.40	0.67	0.40 (0.8)	0.80 (-17.8)
$ln\left(\frac{N_t}{N_0}\right) = -0.03C^{1.99}t$	6 mg/g	3.42	5115	0.91	2.16	0.88 (3.3)	1.76 (18.9)
	9 mg/g	1.78	2.66	1.58	3.24	1.69 (-6.8)	3.38 (-3.9)
AgNP	0.3 mg/g	7.34	10.98	0.49	0.83	0.41 (16.6)	0.82 (1.8)
$ln\left(\frac{N_t}{N_0}\right) = -1.18C^{0.58}t$	0.6 mg/g	4.90	7.34	0.68	1.23	0.61 (10.0)	1.23 (1.1)

Table 2.3. Comparison of initial and final $\log_{10}$ removal values (LRV) and the first order rates (incl. percentages) that were observed after storing the amended wood chips in water for 120 days (at 25°C).

Material	LRV_0	LRV_{Final}	k [day^{-1}]	% change
Unmodified red cedar	0.49±0.15	0.41±0.12	0.032	16.33
0.6 mg/g AgNP	1.96±0.23	1.21±0.09	0.022	38.27
6 mg/g TPA	2.23±0.09	1.64±0.05	0.013	26.46
9 mg/g TPA	2.96±0.43	2.04±0.11	0.049	31.08

TOC/ABSTRACT ART
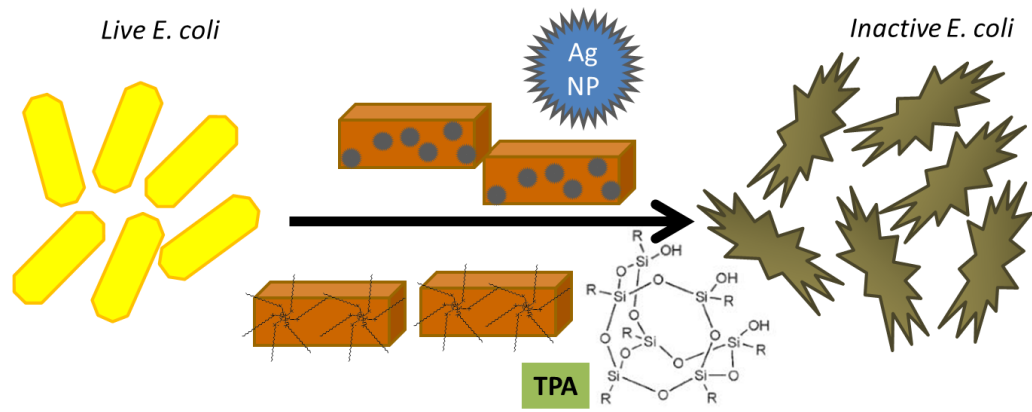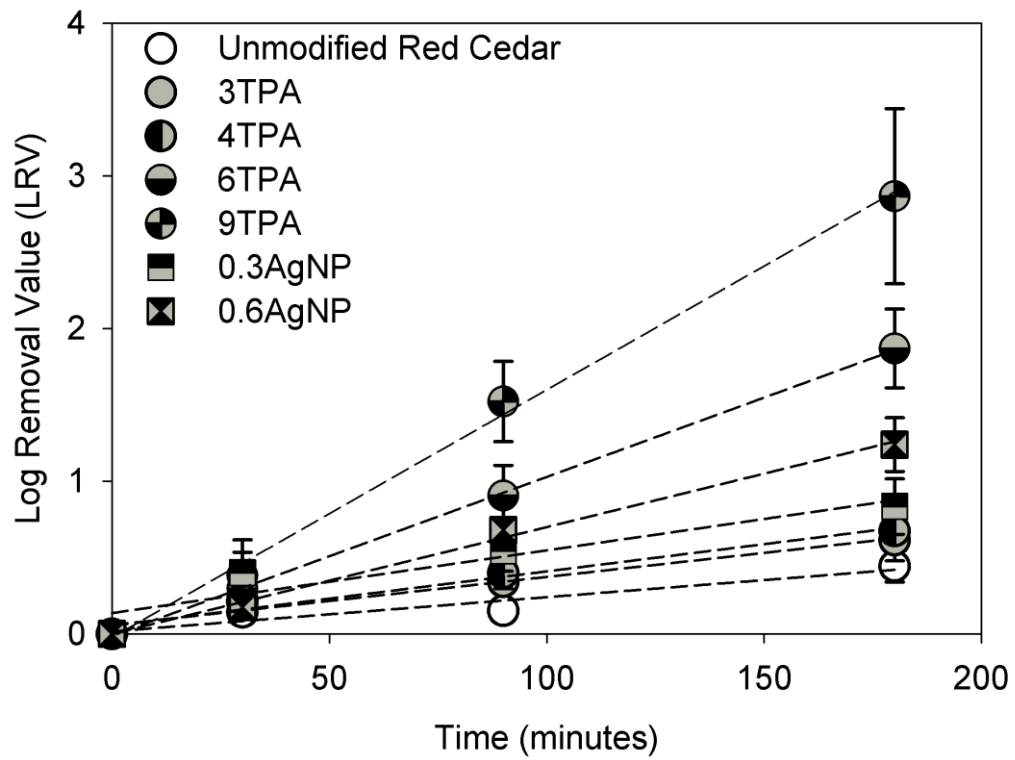
Figure 2.1. Comparison of (average ± standard error) LRV to increased exposure times of the six modified materials and the unmodified red cedar.
A steeper slope indicates a higher inactivation rate, thus a more effective antimicrobial material.
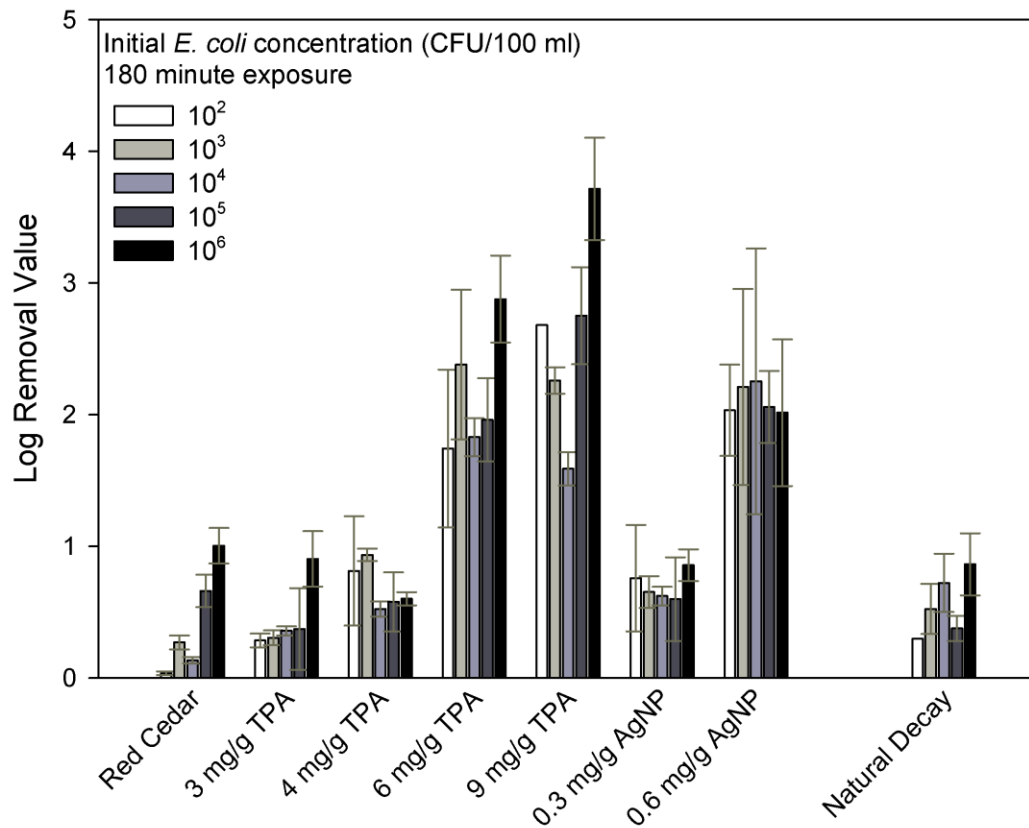
Figure 2.2. Comparison of $\log_{10}$ removal values (LRV) (average ± standard error) for the unmodified red cedar wood chips and the six modifications at different *E. coli* concentrations ranging from 10^2 to 10^6 CFU/100ml.

All materials were exposed for 180 minutes. Natural decay data shows the fraction of *E. coli* die-off that is not due to antimicrobials or removal by attachment. In order to compare the performance of all the materials data for unmodified red cedar, 6TPA, and 0.6 AgNP was obtained from our previously published work (Kasaraneni et al. 2014).
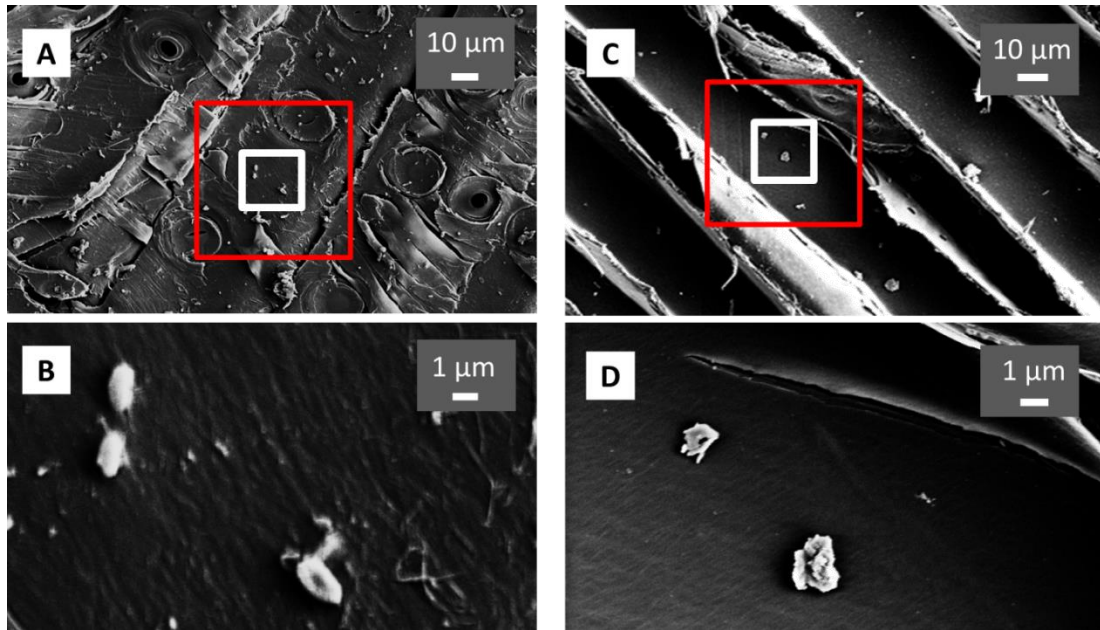
Figure 2.3. SEM images of unmodified red cedar (A and B) and 6TPA (C and D) with clusters of *E. coli* bacteria attached to the surface.

Red squares outline the same size area in both, (A; unmodified red cedar) and (C, 6TPA) for comparison of bacteria cluster densities. White squares indicate what area is represented in figures C and D, which shows unmodified red cedar and red cedar modified with 6 mg/g TPA, respectively. In (D) there a fewer bacteria clusters on the surface of the modified wood and *E. coli* cells walls have been destroyed relative to the well-defined shapes of bacteria in (B). These images were selected after analyzing five different samples for each condition and are therefore representative of the unmodified red cedar and 6mg/g TPA red cedar after being in contact with *E. coli*.
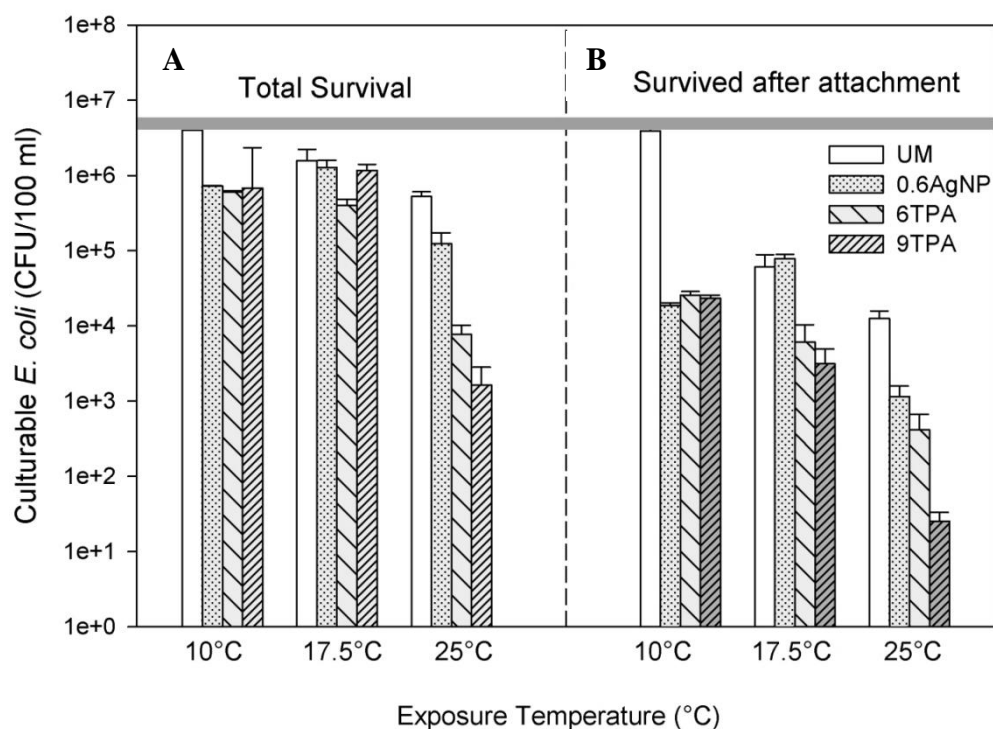
Figure 2.4. Comparison of the effect of temperature (10°C, 17.5°C, and 25°C) on A) the total number (average ± standard error) of surviving culturable *E. coli* and B) number of *E. coli* that were cultivated after being attached for 180 minute to 0.6AgNP, 6TPA, and 9TPA.
The average initial concentration of *E. coli* was in the order of 10^6 CFU/100ml (horizontal grey bar indicates range of initial concentrations achieved for the experiments).
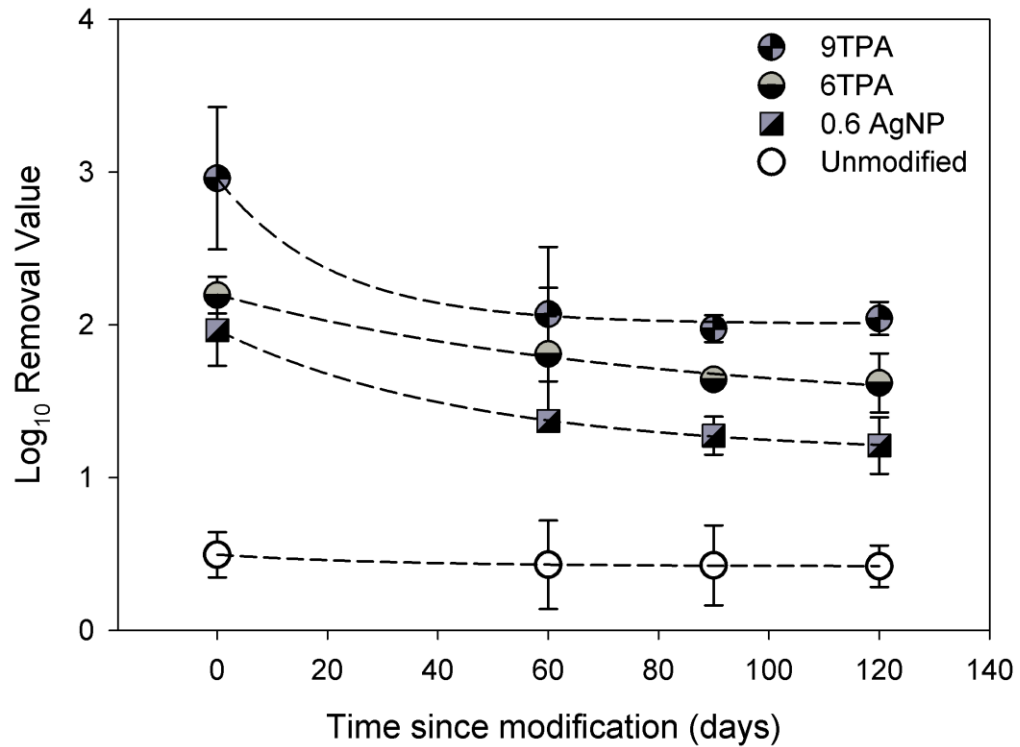
Figure 2.5. Average $\log_{10}$ removal value $\pm$ standard error for the three most effective materials (6TPA, 9TPA, and 0.6Ag) compared to unmodified red cedar at 25°C.
The LRV was determined immediately after modification and at 60, 90, and 120 days after being stored in water. An initial drop in the antimicrobial performance over the first 60 days was followed by a much slower decrease in inactivation performance afterwards.

SUPPORING INFORMATION
Selecting Antimicrobial Filter Media For Improved Stormwater Best

Management Practices

Laura A. Schifman [1*], Varun K. Kasaraneni [2], Ryan K. Sullivan [1], Vinka Oyanedel-Craver [2], Thomas B. Boving [1, 2]

[1] Department of Geosciences, University of Rhode Island, Kingston RI 02881, USA

[2] Department of Civil and Environmental Engineering, University of Rhode Island, Kingston RI 02881, USA

Contents:

Supplemental Text
Methods – Chick-Watson Model Parameterization

To parameterize the model constants k' and n, a two-step approach is required as described in Tchobanoglous, Burton and Stensel (2003) Briefly, a linear regression is fitted to a plot of the natural-log normalized ratio $\ln(N_t/N_o)$ versus the experimental exposure time t for each antimicrobial material. The linear regression equation of each data set is utilized to solve for the theoretical time required to achieve a 99% removal of *E. coli*.

Then, the theoretical time to achieve 99% removal of bacteria is plotted against the disinfectant concentration of the material and a linear regression equation for each type of disinfectant system is fitted to the calculated *C*. The negative inverse of the slope of that linear regression equation equals the coefficient of dilution n. The die-off constant k', is then calculated using

$$n * \ln(y) = \ln\left[\frac{1}{k'} - \ln(\frac{N_t}{N_0})\right] \qquad \text{Supplemental Equation 2.1}$$

where y is the y-intercept and N_t/N_o is the desired ratio of *E. coli* concentration at time t relative to the initial *E. coli* concentration, in this example 99%.

Methods – Sample Preparation for SEM analysis

Briefly, the samples were fixed in 2.5% glutaraldehyde solution for 30 minutes. After fixation, the samples were washed three times with phosphate buffer and then dehydrated for 20 minutes using sequentially increasing ethanol solutions (increments of 10%) containing 40% to 100% ethanol. The samples were exposed to 100% ethanol three times before being chemically dried using Hexamethydisilazane (HMDS). The samples were transferred to a 1:2 HMDS:Ethanol solution for 20 minutes, then a 2:1 HMDS:Ethanol solution, and finally into 100% HMDS. The last step was repeated and the HMDS was left to evaporate in the fume hood overnight. The samples were sputter-coated with a thin layer of gold for 90 seconds under vacuum before the imaging was done in a SIGMA VP Field Emission-Scanning

95

Electron Microscope (Zeiss, USA) with an acceleration voltage of 5kV and a SE2 detector.

Supplemental Tables
Table S2.1a – Performance - ANOVA Table.
ANOVA table for one-way comparison of $\log_{10}$ removal values for the six modified red cedar wood chips and unmodified red cedar wood chips using LRV as the response variable and material as the factor.

	Degrees of Freedom	Sum of Squares	Mean Square	F-Value	P-value
Materials	6	132.25	22.042	32.86	<0.001
Residuals	144	96.58	0.671		

Table S2.1b - Performance - Tukey HSD Summary.
The multiple comparison using Tukey's HSD for the models show differences between the individual materials.

Comparison	Significant?	p-value
Unmodified red cedar vs. 3TPA	N	1.00
Unmodified red cedar vs. 4TPA	N	0.99
Unmodified red cedar vs. 6TPA	Y	<0.001
Unmodified red cedar vs. 9TPA	Y	<0.001
Unmodified red cedar vs. 0.3AgNP	N	0.99
Unmodified red cedar vs. 0.6AgNP	Y	<0.001
4TPA vs. 3TPA	N	0.97
6TPA vs. 3TPA	Y	<0.001
9TPA vs. 03TPA	Y	<0.001
0.3AgNP vs. 3TPA	N	0.97
0.6AgNP vs. 3TPA	Y	<0.001
4TPA vs. 0.3AgNP	N	1.00
6TPA vs. 0.3AgNP	Y	<0.001
9TPA vs. 0.3AgNP	Y	<0.001
0.6AgNP vs. 0.3AgNP	Y	<0.001
6TPA vs. 4TPA	Y	<0.001
9TPA vs. 4TPA	Y	<0.001
0.6AgNP vs. 4TPA	Y	<0.001
9TPA vs. 0.6AgNP	N	0.14
9TPA vs. 6TPA	N	0.14

Table S2.2a – Attachment - ANOVA Table.
ANOVA table for analysis of covariance comparing culturable *E. coli* after attachment for the three most effective materials (0.6 mg/g AgNP, 6 mg/g TPA, 9 mg/g TPA) compared to unmodified red cedar at three different exposure temperatures (10°C, 17.5°C and 25°C) with the final model being: *E. coli* removed by attachment ~ Temperature + Material. There is no interaction term in this model as it went through a stepwise regression and the final model as stated above had a lower AIC value compared to the initial model, which was attachment ~ Temperature * Material.

	Degrees of Freedom	Sum of Squares	Mean Square	F-Value	P-value
Temperature	2	49.504	24.7518	49.921	<0.001
Material	3	18.321	6.107	12.317	<0.001
Residuals	22	10.908	0.496		

Table S2.2b – Attachment – Material - Tukey HSD Summary.
The multiple comparison using Tukey's HSD for the models show differences between the individual materials:

Comparison	Significant?	p-value
Unmodified red cedar vs. 0.6AgNP	Y	<0.001
Unmodified red cedar vs.6TPA	Y(at α=0.90)	0.063
Unmodified red cedar vs.9TPA	Y	<0.001
6TPA vs.0.6AgNP	Y(at α=0.90)	0.062
9TPA vs.0.6AgNP	N	N.S.
9TPA vs.6TPA	N	N.S.

Table S2.2c - Attachment – Temperature - Tukey HSD Summary.
The multiple comparison using Tukey's HSD for the models show differences between the individual materials:

Comparison	Significant?	p-value
10°C vs. 17.5 °C	Y	0.046
10°C vs. 25 °C	Y	<0.001
17.5°C vs. 25 °C	Y	<0.001

Table S2.3 – Inactivation kinetics.
ANOVA table comparing the different models for the inactivation kinetics of the modified red cedar and comparing it to unmodified red cedar.

Model	Estimate	t value	Pr(>|t|)	Significant?
(Intercept)	0.0158	0.28	0.79	N
Time	0.0022	3.98	<0.05	Y
3TPA	0.0419	0.52	0.61	N
4TPA	0.0366	0.45	0.66	N
6TPA	-0.0270	-0.33	0.74	N
9TPA	-0.0399	-0.49	0.63	N
0.3AgNP	0.1201	1.48	0.16	N
0.6AgNP	-0.0173	-0.21	0.83	N
Time*3TPA	0.0009	1.14	0.27	N
Time*4TPA	0.0013	1.66	0.12	N
Time*6TPA	0.0081	10.21	<0.001	Y
Time*9TPA	0.0140	17.52	<0.001	Y
Time*0.3AgNP	0.0019	2.34	<0.05	Y
Time*0.6AgNP	0.0048	5.97	<0.001	Y

Table S2.4 – Long-term storage impact on inactivation efficiency.
Summary table displaying results from t-tests conducted for each material comparing LRV0 to LRV Final. All amended material showed a significant decrease in inactivation after storage under saturated conditions.

Material	Significant change?	p-value
Unmodified Red Cedar	N	0.24
0.6 mg/g AgNP	Y	<0.01
6 mg/g TPA	Y	<0.01
9 mg/g TPA	Y	<0.05

R = CH₂CH₂CH₂N⁺Cl⁻(CH₃)₂(CH₂)₁₇CH₃
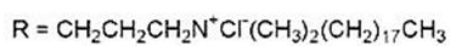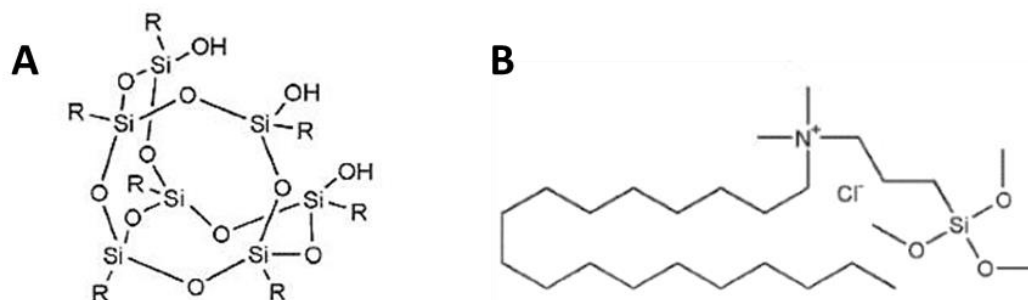
Figure S2.1. Structure of (A) 3-(trihydroxysilyl) propyldimethyloctadecyl ammonium chloride (TPA) and (B) 3-trimethoxysilyl propyldimethyloctadecyl ammonium chloride.
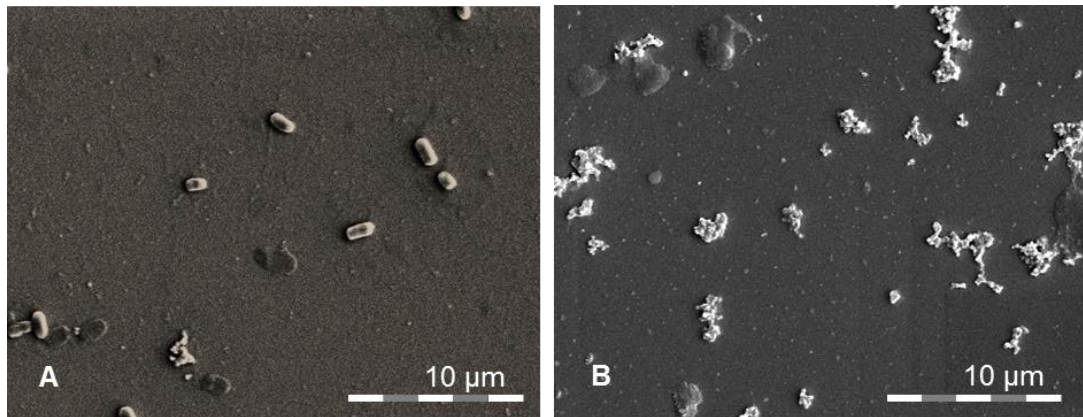
Figure S2.2. SEM images of *E. coli* on a silicon wafers.
In A) the *E. coli* at 104 CFU/100 ml were not exposed to TPA and depict live organisms, whereas in B) *E. coli* at 106 CFU/100ml were exposed to TPA for three hours before SEM imaging, thus depicting damaged organisms.

MANUSCRIPT 3: EVALUATION OF STORMWATER RUNOFF TREATMENT USING A TREE FILTER BMP

Will be merged with Chapter 4 for publication in the Journal of Environmental Engineering

Laura A. Schifman [1*], Varun K. Kasaraneni [2], Ryan K. Sullivan [1], Vinka Oyanedel-Craver [2], Thomas B. Boving [1, 2]

[1] Department of Geosciences, University of Rhode Island, Kingston RI 02881, USA

[2] Department of Civil and Environmental Engineering, University of Rhode Island, Kingston RI 02881, USA

*Corresponding Author: Laura A. Schifman

Department of Geosciences

330 Woodward Hall

University of Rhode Island

Kingston, RI 02881

Email: laura.schifman@gmail.com

ABSTRACT

Stormwater runoff is one of the main contributors of non-point source pollution in the United States, introducing high loads of contaminants into surface water bodies and posing a threat to human health. Even though stormwater treatment standards have not been introduced on a federal level yet, Rhode Island (RI) has set a minimum stormwater contamination reduction standard for structural best management practices (BMP) that reduce nutrients in stormwater (nitrate and phosphate) by 30%, fecal indicator bacteria by 60%, and total suspended solids by 85%. Here the results of an eight month field monitoring project of a subsurface biofiltration BMP (tree filter) are presented and evaluated against Rhode Island's standards. A total of twelve constituents were analyzed (pH, specific conductance, chloride, nitrate, phosphate, total suspended solids, *Escherichia coli* (*E. coli*), copper, nickel, lead, zinc and polycyclic aromatic hydrocarbons (PAH)). We found that throughout the winter sampling period the tree filter met or exceeded RI standards for nitrate, *E. coli*, and lead. During the summer sampling months the stormwater treatment standards for *E. coli* and lead were met. Total suspended solids and PAHs were removed by up to 72% and 68%, respectively; however the minimum removal standards were not met. Suggestions for how to improve the filter system have been provided.

Key words: Tree Filter, Stormwater Treatment, Filtration, Best Management Practice, Water Quality

INTRODUCTION

Several contaminant groups, e.g. heavy metals, organic contaminants, such as polycyclic aromatic hydrocarbons (PAH), pathogens, nutrients, and pesticides accumulate on impervious surfaces during dry periods (Blecken et al. 2012; Boving and Neary 2007; Brown and Peake 2006; Dorfman and Rosselot 2012; Göbel et al. 2007). These contaminants stem from different sources, such as vehicles, agriculture, and wildlife. During storm events, runoff is generated from impervious surfaces like roads or walk ways. The contaminants that have accumulated during the preceding dry period are then flushed into fresh water bodies or coastal waters. Several studies have shown that road side soils and water bodies receive elevated loads of contaminants during the undiluted first flush of a rain storm (Mallin et al. 2000; Van Metre et al. 2000; Lee et al. 2004;Mallin et al. 2009; Lau et al. 2009; Dorfman and Rosselot 2012). These environmental compartments act as sinks and can accumulate some of the contaminants found in runoff, such as heavy metals and organic contaminants (Benfenati et al. 1992; Brown and Peake 2006; Lau et al. 2009; Zehetner et al. 2009). Other contaminants, such as deicing salt or bacteria do not accumulate, but instead are flushed out and have the potential to contaminate surface water bodies after rain events (Ahn et al. 2005; Mallin et al. 2000; Zehetner et al. 2009). The presence of these pollutants impacts groundwater and surface water resources (Casey et al. 2013) and is threatening sensitive species that inhabit these ecosystems (Harless et al. 2011; Karraker and Gibbs 2011).

Even though regulations are in place to prevent the exceedance of total maximum daily loads of contaminants into water bodies (EPA. 2001), very few states have regulations and standards regarding stormwater runoff treatment (EPA 2011; RIDEM 2010; EPA 2012; Bakeman et al. 2012; MDE 2009; RIDEM 2010; VT ANR 2002). The regulations that do exist are usually limited to reducing the total suspended solids (TSS) load by 80-85% before discharging runoff into a surface water body. Some states go further, e.g. in Rhode Island, where regulations require a 30% reduction of both, nitrogen and phosphorous from runoff, in addition to a reduction in bacteria concentration by 60% (EPA 2011; RIDEM 2010). The Rhode Island Stormwater Design and Installation Standard Manual (RISM) (RIDEM 2010) was introduced in 2010 and requires that all developed sites have to meet the above stated stormwater regulations.

To meet these standards, structural best management practices (BMPs) have been introduced (EPA 2005; UNHSC et al. 2007; EPA 2012), ranging in application from flood mitigation through runoff volume reduction and infiltration to stormwater filtration and contaminant removal through sorption (Legret and Colandini 1999; UNHSC et al. 2007). BMPs are generally divided into two categories: structural and non-structural. Non-structural BMPs are guidelines and practices when implemented as part of a design plan can prevent runoff and protect the environment. Therefore non-structural BMPs can be implemented from the single household to the watershed scale. Structural BMPs on the other hand, are location specific and require the construction of a physical device that has the ability to improve water quality. Often

structural BMPs are included in site planning to comply with low impact development requirements (PA DEP 2006; RIDEM 2010).

The Rhode Island Stormwater Treatment Demonstration Facility (RISTDF) was founded in 2011 with the goal of testing conventional and innovative structural BMPs under conditions that are typical for Rhode Island. One of the structural BMPs installed at the RISTDF is a tree filter (TF). A TF is a subsurface filtration system that relies on filtration and sorption to drain and remove contaminants from stormwater runoff using engineered media filled into a buried concrete structure. The TF consists of a catch basin that acts as a sediment trap and an infiltration area where the stormwater runoff gets treated. Once the catch basin has reached its capacity, the water spills over into the tree box from which the runoff infiltrates into the subsurface. Since the box is open on all sides, the runoff can percolate through the filter medium and infiltrate to the groundwater. In addition to the processes that remove contaminants from stormwater, the open construction allows for a tree to be planted in the BMP. Due to its small size, a TF generally takes up less than 1% of its maximum treatment area of up to 0.75 acre (3035 m^2) of paved surface. TF are meant to be installed in urban areas along city streets or within parking lots (UNHSC et al. 2007). TFs contribute to the "greening" of a city and can easily be implemented in landscape architecture designs.

In this study, the contaminant removal efficiency was tested for a TF unit to determine whether the performance complies with the requirements specified in the Rhode Island Stormwater Manual (RISM) requires 85% removal of TSS, 30%

removal of nitrate and phosphate, and 60% removal of bacteria. In addition to the contaminants listed in the RISM (nutrients, TSS, bacteria), the field parameters (temperature, pH, and electrical conductivity), chloride (Cl^-), polycyclic aromatic hydrocarbons (PAH), and heavy metals were analyzed. The objective of this study was to establish whether tree filters meet water quality treatment standards set by RISM under conditions that are typical for Rhode Island.

METHODS

Site Description

In August 2013 a tree box filter was installed at the Rhode Island Stormwater Treatment Demonstration Facility (Figure 3.1). The RISTDF is located on the main campus of the University of Rhode Island. The TF was integrated into a conventional asphalt cover parking lot north of the university that has 458 parking spaces covering 4.9 acres (19830 m^2; Figure 3.1a). The drainage area contributing to the TF is 0.06 acres (242.8 m^2). The site is located over the Chipuxet Aquifer, which is a major source of drinking water in southern Rhode Island. The aquifer is overlain by a thin veneer of loess. Below follow a series of complexly interbedded lenses of sand and gravel with smaller contributions of silt and silty sands (Dickerman 1984). These glacio-fluvial deposits were deposited during the Pleistocene epoch (Dickerman 1984). The stratified material is ~60 m thick and overlies fractured granitic bedrock. The depth to groundwater at the site is approximately 7 m below ground surface (bgs) (Boving et al. 2008).

Meteorological data was obtained from a National Climatic Data Center station that is located less than 0.6 km from the test site. Based on a 20 year record, the site receives an average of 1202 mm of precipitation throughout the year. Average annual snow accumulation is 841 mm. The average number of days per year when precipitation was ≥0.1 inches was 77 days, ≥0.5 inches was 31 days, and ≥ 1 inch was 12 days (NOAA 2014).

The sampling time was divided into the winter (November 2013 to March 2014) and summer (April 2014 through August 2014) season. During the entire sampling period a total precipitation of 1092 mm was received in Kingston, RI. Ten precipitation events were observed that exceeded 1 inch (25.4 mm), six of which occurred during the winter time (November 2013 to March 2014) (water equivalent precipitation). During the winter, a total of 26 snow events were measured at the meteorological station with a total of 1102 mm of snowfall recorded.

Installation

The TF unit is 1.45m*0.9m*1m LWD and includes a catch basin that measures 0.45m*0.9m*1m LWD (Figure 3.2). The catch basin has a capacity of 414 Liters and the infiltration area of the tree filter is 0.91 m^2. The TF is an open concrete structure and, except for four concrete columns, is open at all sides and the bottom (StormTree 2012). For installation approximately 2.1m*2.4m*2.4m LWD of soil was excavated (12 m^3). The excavation pit was back-filled with about 3 m^3 of coarse gravel to a depth

of 0.9m below ground surface (bgs). The TF united was lifted into the pit and placed in a level position. A stainless steel sampling pan with dimensions 0.30m*0.24m*0.033m LWD was installed at the top of the gravel layer, 90 cm below ground (bgs). The pan was filled with coarse gravel and had a resulting pore volume of approximately 1 Liter. A hole at the bottom of the pan was fitted with a brass connector to which 7.9 mm (inner diameter) Teflon tubing was connected. To shield the Teflon tubing from damage and kinking, it was fed through a 6 inch flexible PVC hose reaching to the surface. To measure moisture content, electrical conductivity, and temperature in the tree filter matrix, a Decagon Devices (Pullman, WA, USA) 5TE logger was placed adjacent to the buried sampling pan. The data loggers were accessed from the surface via a data transfer cable buried adjacent to the Teflon tubing. The data loggers were set to take measurements every 10 minutes. Data from the loggers was downloaded using Decagon Devices' ECH2O Utility Software. During sampling events, a portable peristaltic pump (Environmental Sampler, Masterflex, Vernon Hills, IL) was connected to the Teflon tubing and water collected in the buried sampling pan was pumped to the surface (Figure 3.2b).

After the TF concrete structure was placed into the pit, the remaining space was filled with approximately 4 m^3 engineered media composed of 75% coarse sand, 15% expanded shale (Φ=-4; 16 mm), and 10% sphagnum peat to achieve a treatment depth of 0.9m (Figure 3.2c). According to the TF manufacturer, the infiltration rate of the filtration matrix is 0.21 m/hr with the first effluent reaching the sampling port in 30 minutes when the system is saturated.

A red maple tree (*Acer rubrum*) was planted inside the TF (Figure 3.2d). Although there are many other choices of trees, Red Maple was chosen to match surrounding trees in the parking lot. A grate was cut to accommodate the maple tree and placed on top of the concrete structure. Surface runoff can the TF through a curbside opening of 66 cm by 15 cm. Any asphalt removed during the TF installation was patched with commercial black top mix.

The drainage area contributing to the tree box filter is approximately 243 m^2. The drainage area of the TF unit lies close to the entrance of the parking lot and is heavily trafficked every day as the parking facility is a student commuter lot (Figure 3.1b).

Sampling and Analysis

To determine whether the TF meets the standards of RISM, the unit installed at the RISTDF was monitored weekly for eight months starting in November 2013. Runoff that accumulated in the catch basin during prior rain events (influent), grab samples during seven rain events and effluent from the pan were sampled and analyzed for specific conductance, temperature, chloride (Cl$^-$; range 0-1000mg/L), nitrate (NO$_3$; range 0-200 mg/L) using a YSI Professional Plus Multiprobe (Yellow Springs, OH, USA). The pH was measured with a FiveGo Mettler Toledo (Columbus, OH, USA). From July 2014 forward, orthophosphate ((PO$_4^-$)$_3$ was analyzed with a Hach DR2800 Spectrophotometer (Loveland, CO, USA) a following Hach Method

8048 (range 0.06 – 5.00 mg/L). Grab samples during storm events were collected and

analyzed for total suspended solids (TSS) following Standard Method 2540.D.

E. coli (as fecal indicator bacteria) were sampled from the catch basin during

weekly sampling events and during storm events (grab samples). *E. coli* were

quantified as CFU by membrane filtration and 24-hour incubation at 44.5°C using m-

FC broth (Millipore, Billerica, Massachusetts, USA). Heavy metals (Cu, Ni, Pb, Zn)

samples were stabilized with 2% nitric acid (ACS Grade, Fisher Chemical, Pittsburgh,

PA, USA) and digested for a minimum of 24 hours before analyzing with a Perkin

Elmer 3100 XL ICP-OES (Waltham, Massachusetts, USA). The heavy metal method

detection limit was 0.01 mg/l for all compounds. Polycyclic aromatic hydrocarbons

were extracted from the aqueous samples by liquid-liquid extraction following EPA

method 610 and analyzed with a Shimadzu Gas Chromatograph/Mass Spectrometer

QP2010 (Marlborough, MA, USA) following EPA Method 8270d. The GC column

was a fused silica capillary column (30m x 0.25mm ID, 0.25µm, Shimadzu,

Marlborough, MA, USA). Splitless injection with the following temperature program

was used: initial column temperature, 40°C; increase at 25°C min^{-1} to 290°C; increase

at 5°C min^{-1} to 320°C; hold for 2 min. The detector temperature was set at 320°C. The

column flow rate was 1.4 ml/min. PAH quantification was based on a five-point

calibration.

In addition to the 16 priority PAH defined by EPA (EPA 1999), the analysis

included deuterated PAHs (acenaphthene-d10, benzo[a]pyrene-d12,

benz[a]anthracene-d12, phenanthrene-d10, fluoranthene-d10, dibenz[a,h]anthracene-

d4; Ultra Scientific, North Kingston, RI). The deuterated PAH were added to each sample to quantify extraction efficiency. In addition, blank samples and standard checks were run for each sampling campaign and prepared under the same conditions as the field samples. PAH recovery from the liquid-liquid extractions was 40.2 ± 35.4 % for acenaphthene-d10, 41.3 ± 17.3 % for benzo[a]pyrene-d12, 40.7 ± 21.7 % for benz[a]anthracene-d12, 51.1 ± 38.4 % for phenanthrene-d10, 31.1 ± 44.7 % for fluoranthene-d10, and 73.6 ± 31.5 % for dibenz[a,h]anthracene-d14. The deuterated standards were also used to correct for PAH extraction recovery. A method detection limit (MDL) study was conducted and PAHs with molecular weight of 228 g/mol (including Chrysene) the MDL was 5 pg/µl and 10 pg/µl for compounds with molecular weight 252 g/mol and above (Benzo(b)fluoranthene and above).

RESULTS AND DISCUSSION

Stormwater runoff concentrations found in this study are comparable to those found in other studies (Table 3.1). Generally, the pH of the stormwater influent (pH range 6.4 to 11.3) was elevated compared to the effluent (pH range from 5.9 to 7.9). Also, influent pH tended to be higher during winter than summer (Table 3.1). The higher pH of the influent is likely linked to the concrete and the time the influent water is in contact with it. That is, while water remains stagnant in the TF catch basin between storms, the partial dissolution of minerals in the concrete raises the pH of the solution. This effect is most pronounced in new concrete structures, but is expected to diminish over time (Kakade 2014).

Average annual specific conductance in the influent was 1612±3467 µS/cm. It ranged from 18 µS/cm to 164 µS/cm in the summer and 25 µS/cm to 11427 µS/cm in winter (Figure 3.3). The high specific conductance during winter is most likely linked to the use of deicing salts as indicated by elevated chloride concentration during winter (Figure 3.4). A linear regression between the chloride concentration and specific conductance shows that chloride explains 95.5% of the variance in the specific conductance in the influent, and 99.9% of the variance in the effluent. The remainder is assumed to be the contribution of ions that are leaching from the tree filter matrix or the concrete structure.

Chloride concentrations ranged from 2.05 – 12260 mg/L in winter, exceeding the U.S. EPA acute water quality criteria for chloride (860 mg/L) in seven out of the 13 weekly catch basin sampling events. Such high chloride concentrations have been observed in other studies that investigated roadway runoff into urban streams and its impact on aquatic life (Corsi et al. 2010; Karraker and Gibbs 2011; Ledford and Lautz 2014). In the summer, chloride concentrations were significantly lower, ranging from 18.7 - 164.5 mg/L, which is in line with similar results reported by others (Göbel et al. 2007) (Table 3.1).

Nitrate.

Nitrate (N) influent concentrations were higher in winter than in summer. The average nitrate concentrations in the stormwater runoff influent collected from the catch basin were 30.9±31.3 mg/L N in the winter time with a range of 2.3 mg/L to 102

mg/L N. In the summer, the average influent concentrations were 4.8±2.2 mg/L N

with a range of 2.1 mg/L to 8.7 mg/L N (Table 3.1). It is unclear why nitrate

concentrations from grab samples collected during rain events were overall lower

compared to those collected in the catch basin (Table 3.1).The effluent nitrate

concentrations were on average lower than the influent concentrations with 18.9±18.7

mg/L N in winter and 5.8±2.3 mg/L N in summer. Relative to the influent

concentrations from the catch basin, these nitrate values correspond to a 38.6%

reduction in winter, whereas no reduction was observed during summer (Table 3.2,

Figure 3.4). Therefore, the TF performance meets RISM standards (30% nitrate

reduction) in winter but not in the summer. Even though RISM nitrate minimum

removal percentages were met in winter, the nitrate effluent concentrations exceeded

the 10 mg/L threshold set by the U.S. EPA maximum contaminant level (MCLs) (EPA

2009) three times. In the summer the MCL was only exceeded one time.

Several other studies that have investigated nitrate removal by structural BMPs

found nitrate removal highly variable, ranging from 15-99%, and in some cases no

removal was observed (Davis et al. 2009). Studies investigating seasonal variation in

nitrate removal report that removal varied throughout the year with higher removal in

summer compared to winter (Davis et al. 2006; Hatt et al. 2009; Jasper et al. 2014).

One study that also investigated tree filter performance in the field, only reported an

average of 3% nitrate removal (UNHSC et al. 2007) (Table 3.2).

Variability in nitrate removal can be attributed to the compound's transport

behavior, i.e. high mobility and small degree of nitrate sorption, and to properties of

BMPs, such as inadequate treatment layer depth and residence times that are too short for effective denitrification processes to take place (Davis et al. 2006; Hunt et al. 2006; Palmer et al. 2013). For instance, Davis et al. (2001) showed in a laboratory mesocosm study that at least 61 cm of treatment material and a residence time of >2 hours was required to remove effectively nitrate from the solution. Additionally, Jasper et al. (2014) noted that the formation of a biomat was the main contributor to nitrate removal in shallow open water systems, because oxygen levels were reduced in and below the layer compared to the water column. Under those conditions, denitrification accounted for 95% of the nitrate removal (Jasper et al. 2014). In this study, the formation of a biofilm layer on top of the TF substrate is not expected because the filter matrix is designed to drain quickly after each storm. For similar reasons, lower nitrate removal should be expected for systems operating under unsaturated conditions than for filter system under saturated conditions. This behavior was described by Palmer et al. (2013).

Phosphate

Dissolved phosphate concentrations were only measured weekly for two months in the summer during this study and three rain events were grab-sampled during this time period. The phosphate concentrations in both the grab and catch basin samples of the influent (0.43 to 0.62 mg/L) tended to be higher than the effluent concentrations (0.25 to 0.42 mg/L) (Table 3.1). The average removal of phosphate was 43.7% for the samples that were grab sampled, therefore meeting RISM standards.

However, when samples were taken from the catch basin, the removal was lower than 20%, therefore highlighting the importance of sampling the first flush of a rain event.

In general phosphate removal is associated with the attachment to particles and is therefore well correlated with removal of total suspended solids (Berretta and Sansalone 2011). However, the phosphate content of the TSS particles were not investigated in this study. With regard to dissolved phosphate, however, several field studies have shown that the makeup of the biofiltration matrix can have an impact on the removal efficiency because higher organic matter content generally results in higher phosphate removal (Hatt et al. 2009). The TF filter matrix used in this study contained 10% sphagnum peat, which represents an organic matter content higher than in most top natural soils but less than organic soils (Troeh and Thompson 2005). Davis et al. (2006) linked phosphate removal (up to 80%) in biofiltration systems to sorption to clay and silt particles. Particularly clays are not common in the formerly glaciated New England area and their general absence might further limit the performance of the TF investigated herein. But adding clay particles to the TF filter matrix is not desirable because it would likely lower the infiltration rate of this BMP.

In this study, the dissolved phosphate removal correlates well with the total suspended solids removal (R^2=0.73) during the abovementioned storm events (Figure S3.1).

Total Suspended Solids

Total suspended solids were grab-sampled during seven storm events; two winter and five summer storms. The influent TSS concentration in the grab samples ranged from 5 mg/L to 46 mg/L whereas the effluent ranged from 2.2 mg/L to 18.2 mg/L (Table 3.2). Overall, the concentrations of TSS were higher in the grab samples compared to those in the catch basin. The catch basin is designed to collect the influent stormwater and allow the associated particles to settle out, thus the TSS concentration likely decreases as after a storm event.

The TSS removal was similar for the cold and the warm season; i.e, during winter removal was on average 72% compared to 68% in summer. These TSS removal percentages are near, but below the RISM 85% removal standard. However, the number of samples taken during storm events was limited. In a longer term tree filter study documented by UNHSC et al. (2007), a TF system averaged 93% TSS removal throughout a four year observation period (Table 3.2). Other field studies monitoring bioretention BMPs reported TSS reduction to range from 54% to 99% (Davis 2007; Hatt et al. 2009). Here, the removal of TSS likely occurred in the catch basin,

Bacteria

The *E. coli* concentrations in the catch basin and the grab sampled influent had very similar concentrations and ranged from no detected *E. coli* to $5.7*10^4$ CFU/100 (Figure 3.5, Table 3.2). The effluent concentrations ranged from no detected *E. coli* to $4.3*10^4$ CFU/100. The average annual E. *coli* removal percentage was 84.5±20.3% in summer and 75.4±35.5% in winter; both of which exceed the 60% minimum removal

set by RISM. *E. coli* were not detected during all sampling events; in fact very few *E. coli* were detected during most of the summer sampling season until $2*10^4$ CFU/100 ml were detected in August. This is likely due to increased wildlife activity and higher growth rate of the organisms in warmer water temperatures (Chandrasena et al. 2013; Hathaway et al. 2010; Hofmann and Todgham 2010; McCarthy et al. 2012). Part of the complexity of pathogen analysis in stormwater is their intra-event loading unpredictability. Studies have indicated that unlike other contaminants, such as TSS, concentration does not correlate with rainfall intensity, but rather depends on the watershed characteristics and antecedent climate, such as warmer temperatures (Hathaway et al. 2010; McCarthy et al. 2012). Therefore it is common for stormwater *E. coli* concentrations to vary widely, i.e. over several orders of magnitude (Dorfman and Rosselot 2012; Grebel et al. 2013; Mallin et al. 2009; Schueler and Holland 2000).

Similar to the unpredictability of influent *E. coli* concentrations, pathogen removal from runoff is also highly variable (Hathaway et al. 2009; Karim et al. 2004). For instance, Hathaway et al. (2009) investigated four different types of BMPs, dry detention ponds, wet detention ponds, wetlands, and bioretention systems. They found *E. coli* removal to vary from 0-96% with a release of *E. coli* in some cases. Overall, *E. coli* removal in wetland and bioretention systems that underwent changes in soil moisture content due to intermittent stormwater influent was most effective (Hathaway et al 2009). Kibbey et al. (1978) found significantly higher bacteria die-off rates in soils at field capacity compared to saturated soils and attributes this finding to a low tolerance for dryness. It is suspected that high soil moisture content allows

118

pathogens to survive in the subsurface for extended periods of time and also get re-mobilized, possibly being exported during runoff events (Hathaway et al. 2009; Karim et al. 2004; Mohanty et al. 2013; Stevik et al. 2004).

In the TF studied here, the system's high removal percentage can be attributed to the variable moisture content, allowing for less favorable bacteria survival conditions and increased straining in the subsurface (Hathaway et al. 2009; Stevik et al. 2004).

Heavy Metals

The dissolved influent concentrations of heavy metals in the catch basin in winter were as follows: 23.3±39.4 µg/L for copper, 4.9±18.2 µg/L for nickel, 19.5±39.9 µg/L for lead, and 312±710 µg/L for zinc (Table 3.1, Figure 3.6). In summer the concentrations were lower overall. Copper and nickel were not detected, lead was on average 5.6±6.2 µg/L and zinc was 4.4±8.6 µg/L.

The metal removal percentages are shown in Table 3.2. In general, much of the results are inconclusive because of at or below detection limit concentrations (i.e. nickel) or sample contamination issues related to the presence of brass fittings attached to the stainless steel sampling pan. Brass has been shown to leach copper, zinc and lead (Schock and Neff 1988) and for that reason likely caused higher lead, copper, and zinc effluent concentration in both, summer and winter. The leaching assumption is further corroborated by the stormwater runoff pH, which decreased from an average influent range as high as 8.5 to as low as 5.9 in the effluent. At lower

119

pH, a higher portion of zinc and copper is soluble and mobilized, resulting in higher

effluent concentrations (Genç-Fuhrman et al. 2007).

Polycyclic Aromatic Hydrocarbons

During winter the average PAH influent (catch basin) concentration was

4.1 ± 6.8 µg/L with a range of compounds below the detection limit (5 pg/µl for

Naphthalene through Chrysene, 10 pg/µl for Benzo(a)fluoranthene to Indeno(123-

cd)perylene) to a maximum of 17.7 µg/L. In the summer time the average influent

concentration was $5.34.1\pm0.8$ µg/L with a range from 4.8 to 8.0 µg/L (Table 3.1,

Figure 3.7).

Petroleum hydrocarbons, such as PAH, have been removed successfully in

field studies of a tree filter system, with ~65% removal in summer and 99% removal

in winter (UNHSC et al. 2007). Laboratory column studies show that PAH removal

likely occurs through sorption to organic matter and that this process is 80-95%

successful (Hong et al. 2006). In this study removal of PAH was 47.1% in the winter

compared to 7% in the summer. While the overall removal percentages are lower, the

removal trend is similar to that of the UNHSC test site, where summer removal was

lower than in winter. The reason for the overall low removal percentages is unclear

(UNHSC 2007).

Since no grab samples were collected for PAHs and the influent concentration

was based on catch basin water only, it is very likely that PAH in the dissolved phase

have been scavenged and settled out with fine particles by the time the catch basin was

sampled. Therefore, the dissolved PAH concentration in the catch basin may be lower in the analyzed samples and not representative of the actual stormwater PAH concentration.

Recommendations and Suggestions for Improvements of the Tree Filter Technology

Based on the constituents analyzed, the tree filter unit performs well with respect to the removal of nitrate (EPA 2014). The TF also performs well in *E. coli* removal and exceeds RISM bacteria standards throughout the year. Metal removal in this filter unit was not quantifiable or inconclusive for most of the heavy metals.

To improve the nitrate removal from stormwater runoff, the TF system would likely improve by providing a longer residence time for stormwater runoff and/or the creation of an anoxic zone where denitrification could occur. A longer residence time could be achieved through the addition of finer grained material, such as clay or fine organic material. An addition of clay or organic material could also result in a higher percentage of phosphate and PAH removal through attachment/sorption. When designing such a system however, it is important to maintain a high infiltration rate so that the incoming stormwater runoff does not overwhelm the system and bypass it due to ponding and slow infiltration. Determining an optimal mixture of the TF engineered media and structural design demands further research.

To create an anoxic zone that has the potential to improve nitrate removal, continuous saturation of the TF unit is recommended. A structural design change

121

allowing the catch basin to slowly drain the stagnant water into the TF unit would

maintain higher soil saturation between storm events and prevent the microbial

community responsible for denitrification from decomposing. To do this, the catch

basin could have a low permeability membrane on the side facing the infiltration box

that allows the water to slowly drain into the engineered media.

The slow drainage of the catch basin could have multiple advantages, ranging

from improved TSS removal to fewer mosquito breeding grounds in the spring. An

empty catch basin can better capture the first flush of the stormwater influent

containing the highest load of TSS, therefore allowing the particles to settle out

instead of the influent spilling directly into the infiltration area of the TF. As the catch

basin fills up, the particles can settle out and the TSS removal is potentially improved.

If this design for improved TSS removal is successful a higher rate of

phosphate removal is expected as well due to the sorption of phosphate to particles,

especially clay.

122

REFERENCES

Ahn, J. H., Grant, S. B., Surbeck, C. Q., DiGiacomo, P. M., Nezlin, N. P., Jiang, S. (2005). "Coastal Water Quality Impact of Stormwater Runoff from an Urban Watershed in Southern California." *Environ. Sci. Technol.,* 39(16), 5940-5953.

Berretta, C., and Sansalone, J. (2011). "Hydrologic Transport and Partitioning of Phosphorus Fractions." *Journal of Hydrology,* 403(1), 25-36.

Blecken, G. T., Rentz, R., Malmgren, C., Öhlander, B., Viklander, M. (2012). "Stormwater Impact on Urban Waterways in a Cold Climate: Variations in Sediment Metal Concentrations due to Untreated Snowmelt Discharge." *Journal of Soils and Sediments.* 1-16.

Boving, T. B., and Neary, K. (2007). "Attenuation of Polycyclic Aromatic Hydrocarbons from Urban Stormwater Runoff by Wood Filters." *J. Contam. Hydrol.,* 91(1-2), 43-57.

Brown, J. N., and Peake, B. M. (2006). "Sources of Heavy Metals and Polycyclic Aromatic Hydrocarbons in Urban Stormwater Runoff." *Sci. Total Environ.,* 359(1–3), 145-155.

Casey, R. E., Lev, S. M., Snodgrass, J. W. (2013). "Stormwater Ponds as a Source of Long-Term Surface and Ground Water Salinisation." *Urban Water Journal,* 10(3), 145-153.

Chandrasena, G. I., Deletic, A., McCarthy, D. T. (2013). "Survival of *Escherichia Coli* in Stormwater Biofilters " *Environmental Science and Pollution Research.*

Corsi, S. R., Graczyk, D. J., Geis, S. W., Booth, N. L., Richards, K. D. (2010). "A Fresh Look at Road Salt: Aquatic Toxicity and Water-Quality Impacts on Local, Regional, and National Scales." *Environ. Sci. Technol.,* 44(19), 7376-7382.

Davis, A. P., Hunt, W. F., Traver, R. G., Clar, M. (2009). "Bioretention Technology: Overview of Current Practice and Future Needs." *J. Environ. Eng.,* 135(3), 109-117.

Davis, A. P. (2007). "Field Performance of Bioretention: Water Quality." *Environ. Eng. Sci.,* 24(8), 1048-1064.

Davis, A. P., Shokouhian, M., Sharma, H., Minami, C. (2006). "Water Quality Improvement through Bioretention Media: Nitrogen and Phosphorus Removal." *Water Environ. Res.,* 78(3), 284-293.

Davis, A. P., Shokouhian, M., Sharma, H., Minami, C., Winogradoff, D. (2003). "Water Quality Improvement through Bioretention: Lead, Copper, and Zinc Removal." *Water Environ. Res.* 73-82.

Davis, A. P., Shokouhian, M., Sharma, H., Minami, C. (2001). "Laboratory Study of Biological Retention for Urban Stormwater Management." *Water Environ. Res., ,* 5-14.

DeBusk, T. A., Langston, M. A., Schwegler, B. R., Davidson, S. (1997). "An evaluation of filter media for treating storm water runoff." *Proc., Proceedings of the Fifth Biennial Storm Water Research Conference.* 82-89.

Deletic, A. B., and Maksimovic, C. (1998). "Evaluation of Water Quality Factors in Storm Runoff from Paved Areas." *J. Environ. Eng.,* 124(9), 869-879.

Dorfman, M., and Rosselot, K. (2012). *Testing the Water: A Guide to Water Quuality at Vacation Beaches,.*

EPA. (2011). *Performance Standards for Discharges from Newly Developed and Redeveloped Sites,* http://cfpub.epa.gov/npdes/stormwater/rulemaking/performancestandards.cfm Ed., Environmental Protection Agency.

EPA. (2014). "State development of numeric criteria for nitrogen and phosphorus pollution." <http://cfpub.epa.gov/wqsits/nnc-development/> (09/04, 2014).

EPA. (2012). *Recreational Water Quality Criteria, .*

EPA. (2009). "Drinking water contaminants." <http://water.epa.gov/drink/contaminants/#List> (09/04, 2014).

EPA. (2005). *National Management Measures to Control Nonpoint Source Pollution from Urban Areas, .*

EPA. (2001). *Protocol for Developing Pathogen TMDLs,* Office of Water (4503F), United States Environmental Protection Agency, Washington, DC.

EPA. (1999). Compendium Method TO-13A, United States Environmental Protection Agency, Cincinnati, OH, USA.

Genç-Fuhrman, H., Mikkelsen, P. S., Ledin, A. (2007). "Simultaneous Removal of as, Cd, Cr, Cu, Ni and Zn from Stormwater: Experimental Comparison of 11 Different Sorbents." *Water Res.,* 41(3), 591-602.

Gilbert, J. K., and Clausen, J. C. (2006). "Stormwater Runoff Quality and Quantity from Asphalt, Paver, and Crushed Stone Driveways in Connecticut." *Water Res.,* 40(4), 826-832.

Göbel, P., Dierkes, C., Coldewey, W. G. (2007). "Storm Water Runoff Concentration Matrix for Urban Areas." *J. Contam. Hydrol.,* 91(1–2), 26-42.

Grebel, J. E., Mohanty, S. K., Torkelson, A. A., Boehm, A. B., Higgins, C. P., Maxwell, R. M., Nelson, K. L., Sedlak, D. L. (2013). "Engineered Infiltration Systems for Urban Stormwater Reclamation." *Environ. Eng. Sci.,* 30(8), 437-454.

Han, Y., Lau, S., Kayhanian, M., Stenstrom, M. K. (2006). "Characteristics of Highway Stormwater Runoff." *Water Environ. Res.,* 78(12), 2377-2388.

Harless, M. L., Huckins, C. J., Grant, J. B., Pypker, T. G. (2011). "Effects of Six Chemical Deicers on Larval Wood Frogs (Rana Sylvatica)." *Environmental Toxicology and Chemistry,* 30(7), 1637-1641.

Hathaway, J., Hunt, W., Simmons III, O. (2010). "Statistical Evaluation of Factors Affecting Indicator Bacteria in Urban Storm-Water Runoff." *J. Environ. Eng.,* 136(12), 1360-1368.

Hathaway, J., Hunt, W., Jadlocki, S. (2009). "Indicator Bacteria Removal in Storm-Water Best Management Practices in Charlotte, North Carolina." *J. Environ. Eng.,* 135(12), 1275-1285.

Hatt, B. E., Fletcher, T. D., Deletic, A. (2009). "Hydrologic and Pollutant Removal Performance of Stormwater Biofiltration Systems at the Field Scale." *Journal of Hydrology,* 365(3), 310-321.

Ho, Y., John Wase, D., Forster, C. (1995). "Batch Nickel Removal from Aqueous Solution by Sphagnum Moss Peat." *Water Res.,* 29(5), 1327-1332.

Hofmann, G. E., and Todgham, A. E. (2010). "Living in the Now: Physiological Mechanisms to Tolerate a Rapidly Changing Environment " *Annu. Rev. Physiol.,* 72, 127-145.

Hong, E., Seagren, E. A., Davis, A. P. (2006). "Sustainable Oil and Grease Removal from Synthetic Stormwater Runoff using Bench-Scale Bioretention Studies." *Water Environ. Res.,* 78(2), 141-155.

Hunt, W., Jarrett, A., Smith, J., Sharkey, L. (2006). "Evaluating Bioretention Hydrology and Nutrient Removal at Three Field Sites in North Carolina." *J. Irrig. Drain. Eng.,* 132(6), 600-608.

Jasper, J. T., Jones, Z. L., Sharp, J. O., Sedlak, D. L. (2014). "Nitrate Removal in Shallow, Open-Water Treatment Wetlands." *Environ. Sci. Technol.,* .

Kakade, A. (2014) Measuring Concrete Surface pH—A Proposed Test Method. Concrete Repair Bulletin March/April 2014 www.icri.org; Pg. 16-20.

Karim, M. R., Manshadi, F. D., Karpiscak, M. M., Gerba, C. P. (2004). "The Persistence and Removal of Enteric Pathogens in Constructed Wetlands." *Water Res.,* 38(7), 1831-1837.

Karraker, N. E., and Gibbs, J. P. (2011). "Road Deicing Salt Irreversibly Disrupts Osmoregulation of Salamander Egg Clutches." *Environmental Pollution,* 159(3), 833-835.

Kayhanian, M., Suverkropp, C., Ruby, A., Tsay, K. (2007). "Characterization and Prediction of Highway Runoff Constituent Event Mean Concentration." *J. Environ. Manage.,* 85(2), 279-295.

Kibbey, H. J., Hagedorn, C., and McCoy, E. L. _1978_. "Use of fecal streptococci as indicators of pollution in soil." *Appl. Environ. Microbiol.*35_4_, 711–717.

Lau, S., Han, Y., Kang, J., Kayhanian, M., Stenstrom, M. K. (2009). "Characteristics of Highway Stormwater Runoff in Los Angeles: Metals and Polycyclic Aromatic Hydrocarbons." *Water Environ. Res.,* 81(3), 308-318.

Ledford, S. H., and Lautz, L. K. (2014). "Floodplain Connection Buffers Seasonal Changes in Urban Stream Water Quality." *Hydrol. Process.*

Lee, H., Lau, S., Kayhanian, M., Stenstrom, M. K. (2004). "Seasonal First Flush Phenomenon of Urban Stormwater Discharges." *Water Res.,* 38(19), 4153-4163.

Legret, M., and Colandini, V. (1999). "Effects of a Porous Pavement with Reservoir Structure on Runoff Water: Water Quality and Fate of Heavy Metals." *Water Science and Technology,* 39(2), 111-117.

Mallin, M. A., Johnson, V. L., Ensign, S. H. (2009). "Comparative Impacts of Stormwater Runoff on Water Quality of an Urban, a Suburban, and a Rural Stream." *Environ. Monit. Assess.,* 159(1), 475-491.

Mallin, M. A., Williams, K. E., Esham, E. C., Lowe, R. P. (2000). "Effect of Human Development on Bacteriological Water Quality in Coastal Watersheds." *Ecol. Appl.,* 10(4), 1047-1056.

McCarthy, D., Hathaway, J., Hunt, W., Deletic, A. (2012). "Intra-Event Variability of *Escherichia coli* and Total Suspended Solids in Urban Stormwater Runoff." *Water Res.,* 46(20), 6661-6670.

Mohanty, S. K., Torkelson, A. A., Dodd, H., Nelson, K. L., Boehm, A. B. (2013). "Engineering Solutions to Improve the Removal of Fecal Indicator Bacteria by Bioinfiltration Systems during Intermittent Flow of Stormwater " *Environ. Sci. Technol.,* 47(19), 10791 - 10798.

Palmer, E. T., Poor, C. J., Hinman, C., Stark, J. D. (2013). "Nitrate and Phosphate Removal through Enhanced Bioretention Media: Mesocosm Study." *Water Environ. Res.,* 85(9), 823-832.

Reddy, K. R., Xie, T., Dastgheibi, S. (2014). "Evaluation of Biochar as a Potential Filter Media for the Removal of Mixed Contaminants from Urban Storm Water Runoff." *J. Environ. Eng*.

RIDEM. (2010). *Rhode Island Stormwater Design and Installation Standards Manual*.

Schock, M. R., and Neff, C. H. (1988). "Trace Metal Contamination from Brass Fittings." *Journal (American Water Works Association),*47-56.

Schueler, T. R., and Holland, H. (2000). "Microbes and Urban Watersheds: Concentrations, Sources, and Pathways." *The Practice of Watershed Protection,* 74-84.

Stevik, T. K., Aa, K., Ausland, G., Hanssen, J. F. (2004). "Retention and Removal of Pathogenic Bacteria in Wastewater Percolating through Porous Media: A Review " *Water Res.,* 38(6), 1355-1367.

StormTree, LLC. 2012. Tree Box Filter bioretention stormwater management system <www.stormtree.com> Accessed August 30th 2013.

Surbeck, C. Q., Jiang, S. C., Ahn, J. H., Grant, S. B. (2006). "Flow Fingerprinting Fecal Pollution and Suspended Solids in Stormwater Runoff from an Urban Coastal Watershed." *Environ. Sci. Technol.,* 40(14), 4435-4441.

Troeh, F. R., Thompson L. M. Soils and Soil Fertility. 6th ed. Ames, Iowa: Blackwell Pub., 2005

Tromp, K., Lima, A. T., Barendregt, A., Verhoeven, J. T. (2012). "Retention of Heavy Metals and Poly-Aromatic Hydrocarbons from Road Water in a Constructed Wetland and the Effect of De-Icing." *J. Hazard. Mater.,* 203, 290-298.

UNHSC, Roseen, R., Ballestero, T., Houle, J. (2007). *UNH Stormwater Center 2007 Annual Report.* University of New Hampshire, Cooperative Institute for Coastal and Estuarine Environmental Technology, Durham, NH., http://ciceet.unh.edu/unh_stormwater_report_2007/index.php.

Van Metre, P. C., Mahler, B. J., Furlong, E. T. (2000). "Urban Sprawl Leaves its PAH Signature." *Environ. Sci. Technol.,* 34(19), 4064-4070.

Zehetner, F., Rosenfellner, U., Mentler, A., Gerzabek, M. H. (2009). "Distribution of Road Salt Residues, Heavy Metals and Polycyclic Aromatic Hydrocarbons Across a Highway-Forest Interface." *Water, Air, & Soil Pollution,* 198(1), 125-132.

TABLES

Table 3.1.Summary of winter (November - March) and summer (April - September) average ± standard deviation catch basin and grab sample (n=7) influent concentrations and ranges in parentheses along with reported literature values.

Constituents measured: pH, specific conductance (SC, μs/cm), Cl⁻ (mg/L), NO_3^- as N (mg/L), PO_4^{2-} (mg/L), TSS (mg/L), *E. coli* (CFU/100 ml), Cu (μg /L), Ni (μg /L), Pb (μg /L), Zn (μg/L), and ∑PAH16 (μg/L).

Constituent	Units	WINTER Catch Basin	WINTER Grab Sample	SUMMER Catch Basin	SUMMER Grab Sample	Literature Values	Reference
pH	-	8.5 ± 1.8 (6.3 – 11.3)	8.4 ± 2.5 (6.6 – 10.2)	8.1 ± 1.2 (6.4 – 9.7)	6.8 ± 0.4 (6.2 – 7.1)	4.5 – 10.1	a, b, c, l, o, s
SC	μs/cm	3630 ± 4611 (26 – 11427)	3757 ± 4076 (875 – 6640)	67 ± 37 (18 – 164)	91 ± 27 (50 – 110)	25 – 30800	a, d, e
Cl⁻	mg/L	4230.4 ± 4923.0 (2.1 – 12260.0)	4742.3 ± 4162.3 (1800 – 7686)	60.6 ± 40.4 (18.7 – 164.5)	81.0 ± 34.4 (50 - 111)	0.2 – 11200	a, d, e, l, s
NO_3^- as N	mg/L	30.9 ± 31.3 (2.4 – 102.0)	20.1 ± 15.2 (9.4 – 30.9)	4.8 ± 2.1 (2.1 – 8.7)	7.1 ± 2.1 (4.1 – 8.6)	0.02 – 34.7	a, b, c, f, g, h, n, s
$(PO_4^-)_3$	mg/L	-	-	0.47 ± 0.12 (0.43 – 0.62)	0.51±0.15 (0.34 – 0.75)	0.005 – 2.3	a, b, c, g, n
TSS	mg/L	28.8 ± 20.2 (3.5 – 58.0)	46.3 ± 13.8 (36.5 – 56.0)	10.1 ± 12.4 (0.5 – 46)	22.1 ± 15.9 (5.0 – 46.0)	1 – 46000	a, c, g, h, p, r
E. coli	CFU/100 ml	$1*10^4 ± 2*10^4$ (0 – $6*10^4$)	$4*10^3 ± 6*10^3$ (0 - $8*10^3$)	$4*10^3 ± 8*10^3$ ($2*10^1$ – $2*10^4$)	$6*10^3 ± 7*10^3$ (0 – $2*10^4$)	110 – 10^6	a, g, h, q
Copper*	μg /L	22.3 ± 39.4 (b.d. – 151.0)		b.d.		6 – 1800	a, g
Nickel*	μg /L	4.9 ± 18.2 (b.d. – 68)		b.d.		4 – 170	a, g, h, m, q
Lead*	μg /L	19.5 ± 39.9 (b.d. – 156.0)		5.6 ± 6.2 (0.7 – 18.9)		2 – 525	a, g, h, q, r
Zinc*	μg /L	312 ± 710 (b.d. – 2577)		4.4 ± 8.6 (n.d. – 26.6)		25 – 13000	a, l
∑PAH₁₆*	μg /L	4.1 ± 6.8 (b.d. – 17.7)		5.3 ± 0.8 (4.8 – 8.0)		0 – 22.6	g, i, j, k, p

*Grab samples were not analyzed for PAH and heavy metals; b.d. below method detection limit

References: a=(Göbel et al. 2007), b=(Reddy et al. 2014), c=(Kayhanian et al. 2007), d= (Ledford and Lautz 2014), e= (Corsi et al. 2010), f= (Han et al. 2006), g= (Grebel et al. 2013), h= (Hatt et al. 2009), i= (Dorfman and Rosselot 2012), j= (Schueler and Holland 2000), k= (Mallin et al. 2000), l= (Boving and Neary 2007), m=(Chong et al. 2013), n= (Mallin et al. 2009), o= (Deletic and Maksimovic 1998), p= (Surbeck et al. 2006), q= (Gilbert and Clausen 2006), r= (Davis et al. 2009), s=(Jasper et al. 2014)

Table 3.2. Winter (November - March) and summer (April - September) average ± standard deviation effluent concentrations and TF removal calculated based on Table 3.1 data for catch basin and grab sample influent concentrations.
Also, literature reported removal values, RISM minimum removal and StormTree © reported removal for the parameters of interest are provided. Bolded values signify when TF removal met or exceeded RISM standards. Constituents measured: pH, specific conductance (SC, µs/cm), Cl$^-$ (mg/L), NO$_3^-$ as N (mg/L), PO$_4^{2-}$ (mg/L), TSS (mg/L), *E. coli* (CFU/100 ml), Cu (µg /L), Ni (µg /L), Pb (µg /L), Zn (µg/L), and ∑PAH16 (µg/L).

Constituent	WINTER			SUMMER			RISM Removal %	StormTree© Reported TF Removal %	Reported Removal	Reference
	Effluent	% Change Catch Basin	% Change Grab Sample	Effluent	% Change Catch Basin	% Change Grab Sample				
pH	7.1±0.56 (6.4 – 7.9)	16.9	23.0	6.5±0.23 (5.9 – 6.9)	19.8	3.9	-	-	-	-
SC	1708±2541 (17 – 7579)	52.9	60.2	97±42 (56 – 216)	-45.9	-40.7	-	-	-	-
Cl$^-$	2068±3224.2 (2.4 – 9000.0)	51.1	61.7	74.31±38.81 (17.5 – 130.0)	-22.6	-31.3	-	-	-	-
NO$_3^-$ as N	18.9±18.7 (1.9 – 53.6)	**38.6**	22.0	5.8±2.3 (2.1 – 11.9)	-22.2	-12.1	30	>48	3–99	h, r, s, t, u
(PO$_4^-$)$_3^-$	-	-	-	0.35±0.08 (0.25 – 0.62)	19.9	**43.7**	30	>63	65–80	h, t
TSS	28.5 ± 22.4 (4.5 – 77.5)	56.3	72.1	7.7±5.4 (2.2 – 19.7)	32.9	68.2	85	>85	54–99	h, u, v
E. coli	6*10^3±2*10^4 (0 – 4*10^4)	**75.4**	**89.9**	1*10^3±4*10^3 (0 – 1*10^4)	**84.9**	**92.7**	60	-	0–96	w, x
Copper*	135.0±105.4 (b.d. – 388.0)	^		70.1±32.9 (30.0 – 127.5)	^		-	58–88	67–99	h, y
Nickel*	4.4±10.8 (b.d. – 31.0)	9.7		b.d.	**-**		-	58–88	+	z
Lead*	105.1±82.8 (b.d. – 278.0)	^		64.2±57.4 (n.d. – 130.3)	^		-	58–88	80–99	h, y
Zinc*	5488±7888 (b.d. – 23050)	^		2062±739 (1212 – 3526)	^		-	58–88	84–99	h, y
∑PAH$_{16}$*	2.2±4.9 (b.d. – 15.4)	47.1		4.9±0.3 (3.9 – 5.3)	7.0		-	>85	18.5–99	l, u

*Grab samples were not analyzed for PAH and heavy metals; ^ Potential metal release from brass fitting on sampling pan therefore not quantifiable; +Nickel release reported by authors in study (z); b.d. concentration is below detection on the instrument.
References: h= (Hatt et al. 2009), i= (Dorfman and Rosselot 2012), j= (Schueler and Holland 2000), k= (Mallin et al. 2000), l= (Boving and Neary 2007), m=(Chong et al. 2013), n= (Mallin et al. 2009), o= (Deletic and Maksimovic 1998), p= (Surbeck et al. 2006), q= (Gilbert and Clausen 2006), r= (Davis et al. 2009), s=(Jasper et al. 2014), t= (Davis et al. 2006), u= (UNHSC et al. 2007), v= (Davis 2007), w= (Karim et al. 2004), x= (Hathaway et al. 2009), y= (Davis et al. 2003), z=(Tromp et al. 2012), aa=(Boving and Neary 2007)

FIGURES
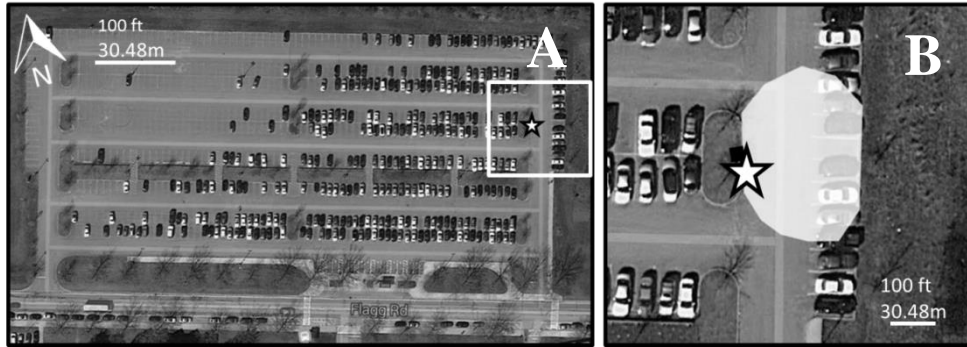
Figure 3.1. A) Overview of the RISTDF parking lot where the tree filter unit was installed (white star). The box outlined in white is magnified in B) where the TF catchment area is outlined in white.
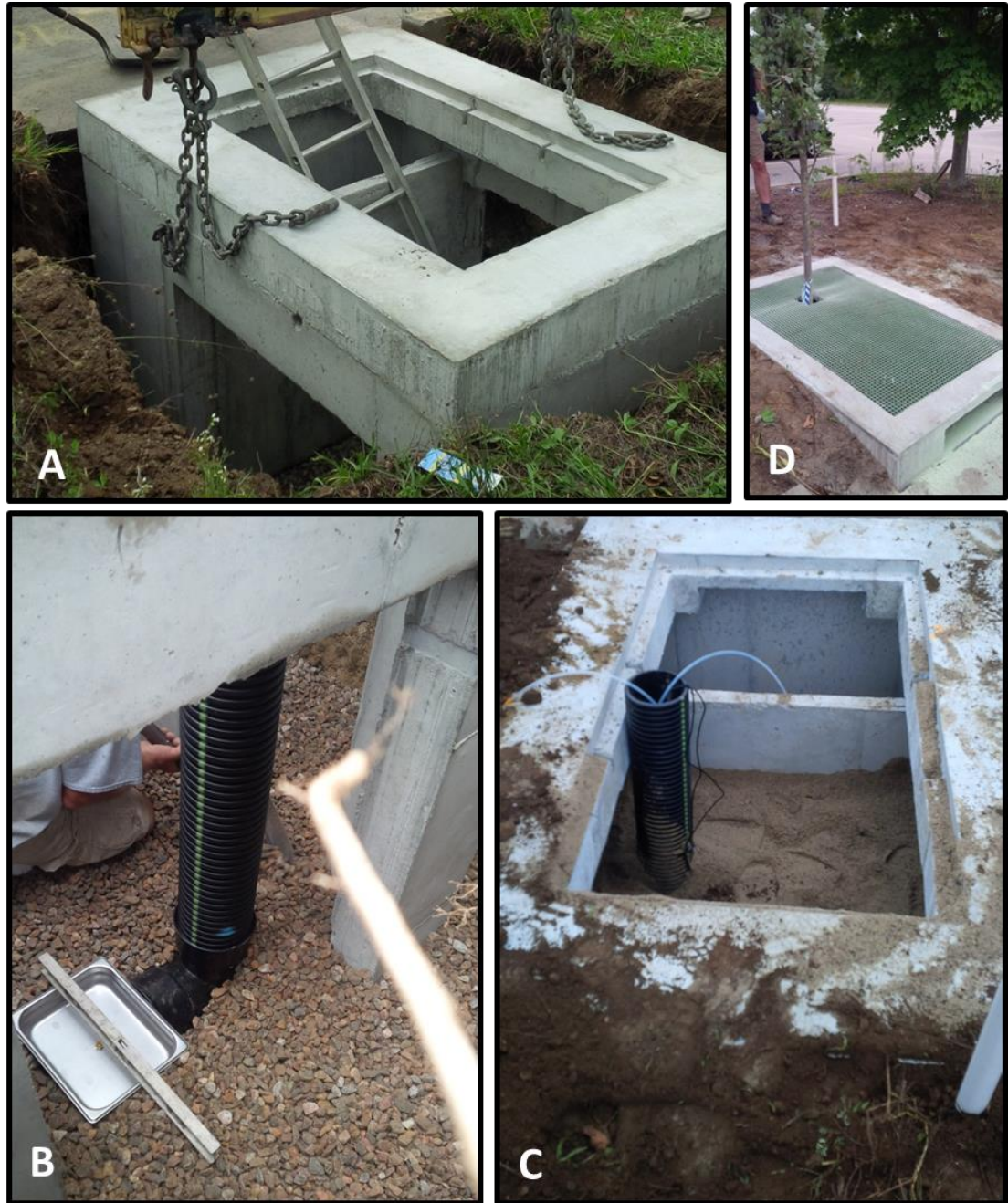
Figure 3.2. Tree Filter installation.
(A) the open concrete box is lowered into the ground on top of a 0.9m coarse gravel bed that was used to backfill the excavated soil. (B) the sampling pan is installed on top of the gravel bed to allow for effluent sampling. The tubing is fed to the surface in the black casing that is surrounded by the engineered media (~0.9 cm depth fill), (C) along with the empty catch basin. (D) the tree has been planted and the grate put in place.

132
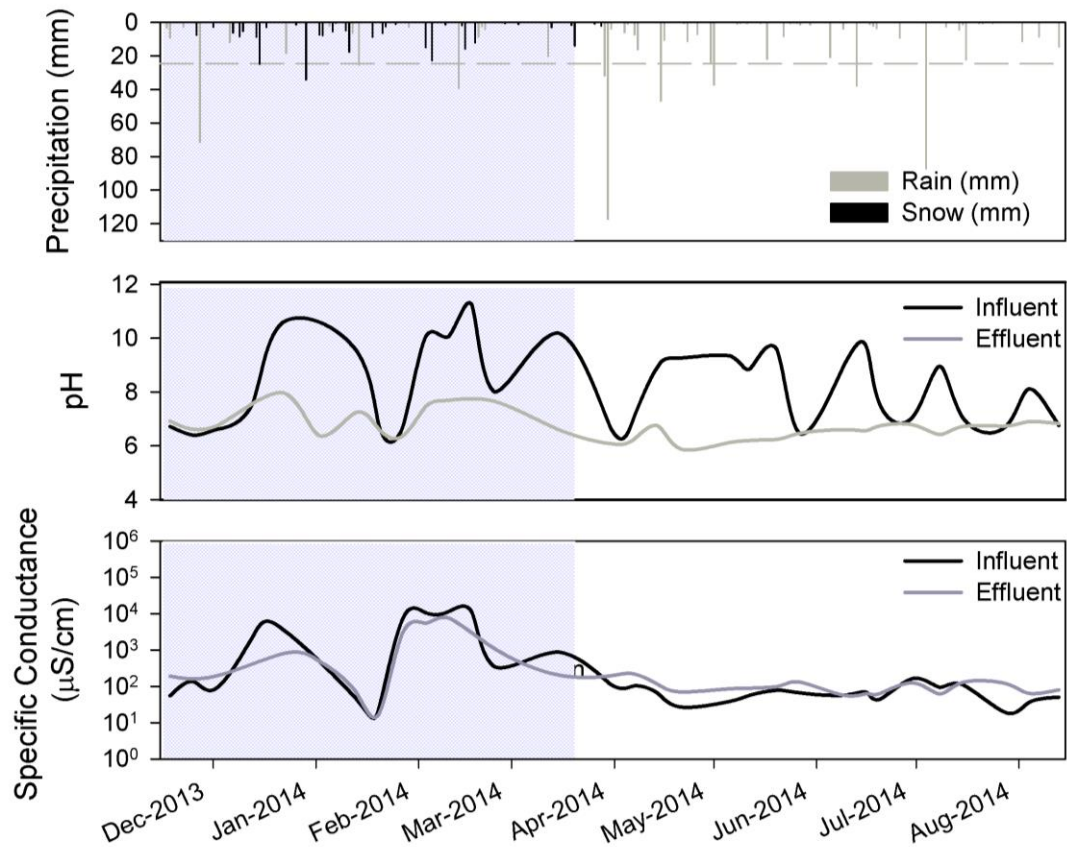
Figure 3.3. Rain and snow (melt water equivalent) precipitation throughout the sampling period along with trends of pH and specific conductance in µS/cm in stormwater influent and tree filter effluent throughout the sampling period.
Grey area represents winter months from 11/18/2013 until 3/20/2014, white areas represent summer months.
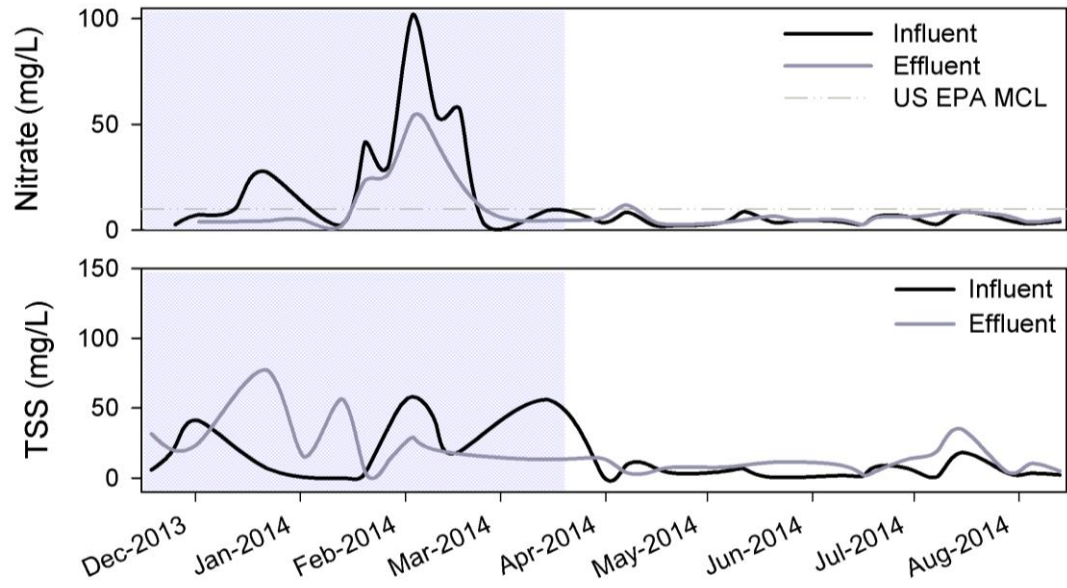
Figure 3.4.Concentrations of nitrate and total suspended solids throughout the sampling period found in influent stormwater and effluent from the tree filter.
Influent concentrations shown here depict catch basin concentrations of nitrate and TSS. Grey area represents winter months from 11/18/2013 until 3/20/2014, white areas represent summer months.
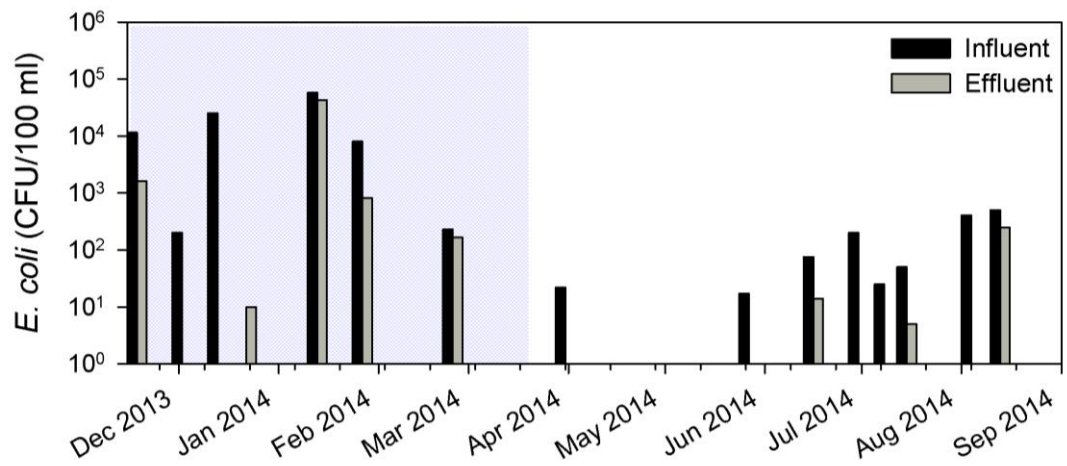
Figure 3.5. Concentrations of *E. coli* throughout the sampling period found in influent stormwater and effluent from the tree filter.
These results show both, catch basin and grab samples. Grey area represents winter months from 11/18/2013 until 3/20/2014, white areas represent summer months.
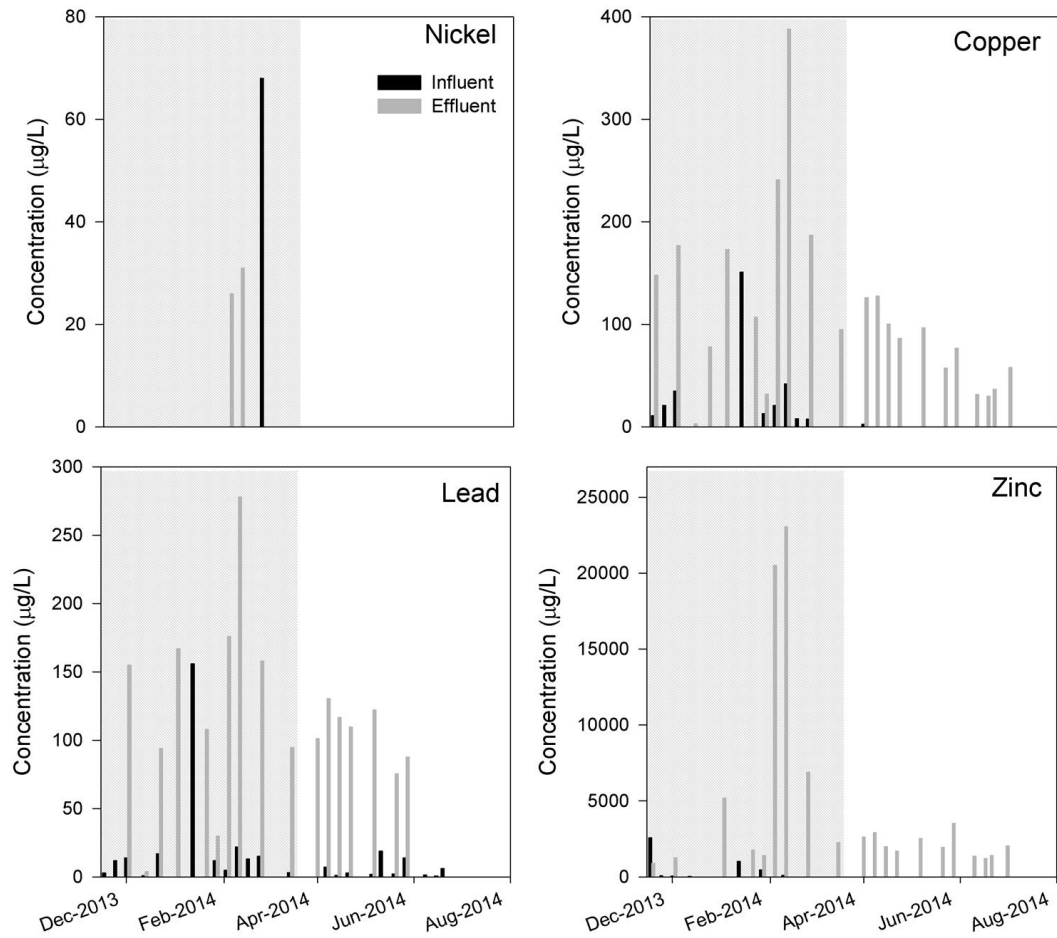
Figure 3.6. Concentrations of nickel, copper, lead, and zinc throughout the sampling period found in influent stormwater collected in the catch basin and effluent from the tree filter. Grey area represents winter months from 11/18/2013 until 3/20/2014, white areas represent summer months.

136
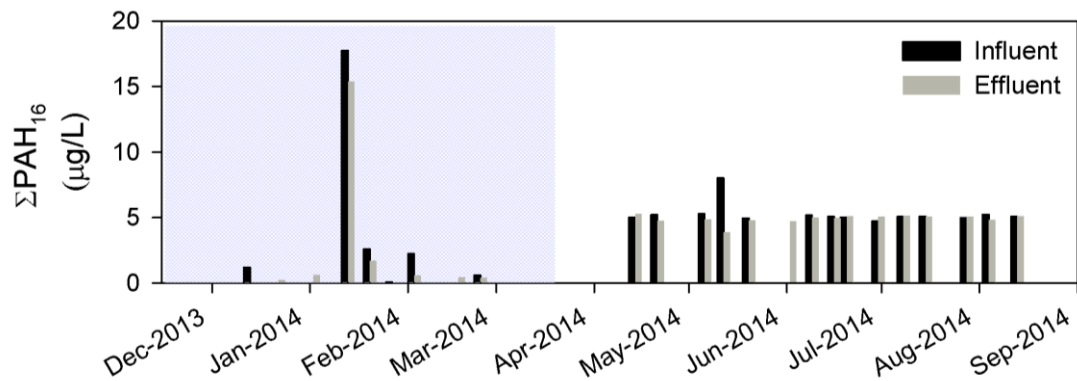
Figure 3.7. Concentrations of PAH throughout the sampling period found in influent stormwater collected from the catch basin and effluent from the tree filter.
Grey area represents winter months from 11/18/2013 until 3/20/2014, white areas represent summer months.

SUPPORTING INFORMATION

Evaluation of Stormwater Runoff Treatment using a Tree Filter BMP

Laura A. Schifman[1], Varun K. Kasaraneni[2], Ryan K. Sullivan[1], Vinka Oyanedel-Craver[2], Thomas B. Boving[1,2]

[1]Department of Geosciences, 9 E. Alumni Avenue, University of Rhode Island, Kingston, RI 02881
[2]Department of Civil and Environmental Engineering, 1 Lippitt Road, University of Rhode Island, Kingston, RI 02881

Contents:

Supplemental Figures

Figure S3.1. Relationship between dissolved phosphate and total suspended solids removal for four storm events that were monitored.
The relationship can be explained by y=-54.5*1.3x and has an R^2 of 0.73.

MANUSCRIPT 4: BACTERIA REMOVAL FROM STORMWATER RUNOFF USING TREE FILTERS: PILOT SCALE TESTING OF AN INNOVATIVE SYSTEM

Will be merged with Chapter 3 for publication in the Journal of Environmental Engineering

Laura A. Schifman [1*], Varun K. Kasaraneni [2], Ryan K. Sullivan [1], Vinka Oyanedel-Craver [2], Thomas B. Boving [1, 2]

[1] Department of Geosciences, University of Rhode Island, Kingston RI 02881, USA

[2] Department of Civil and Environmental Engineering, University of Rhode Island, Kingston RI 02881, USA

*Corresponding Author: Laura A. Schifman

Department of Geosciences

330 Woodward Hall

University of Rhode Island

Kingston, RI 02881

Email: laura.schifman@gmail.com

ABSTRACT

Stormwater runoff is one of the main contributors of non-point source pollution in the United States, introducing high loads of contaminants into surface water bodies and posing a threat to the ecosystem and human health. Stormwater treatment standards have not yet been introduced on a federal level, however increasingly more states require at least primary treatment of stormwater runoff to prevent water quality degradation of surface waters. In this study we compare the results of an eight month field monitoring of two tree filter (TF) systems. A TF is a type of a structural best management practices (BMP) for road runoff treatment. One conventional TF, containing a sand/shale mix, was compared with an innovative unit that contained red cedar wood chips amended with the antimicrobial 3-(trihydroxysilyl)propyldimethyloctadecyl ammonium chloride (TPA). *Escherichia coli* (*E. coli*) was selected as test bacteria to measure the treatment effectiveness of both TF units. In addition, polycyclic aromatic hydrocarbons (PAH), nutrients (nitrate, phosphate), heavy metals (Cu, Ni, Zn, Pb) as well as chloride and total suspended solids were investigated. We found that the innovative TF exhibited higher nitrate, phosphate, TSS, and $\sum PAH_{16}$, removal, but only a marginal increase in *E. coli* removal compared to the conventional TF. Overall, both the conventional and the innovative tree filters exceeded Rhode Island's standards for bacteria removal, making them good candidates for BMP use in the Northeastern United States.

INTRODUCTION

Stormwater runoff mobilizes microorganisms and other contaminants into surface and ground water bodies, potentially impairing their quality (Schueler and Holland 2000; Ahn et al. 2005; Göbel et al. 2007; Parker et al. 2010) and compromising ecosystem and human health (Stewart et al. 2008; Dorfman and Rosselot 2012; EPA 2012). *Escherichia coli* (*E. coli*) and fecal coliforms are typically monitored in watersheds as their presence is an fecal indicator bacteria (EPA 2001; EPA 2012). In runoff from roads and other transportation structures, *E. coli* concentrations often exceed 10^4 colony-forming units (CFU) per 100 ml (Schueler and Holland 2000; EPA 2001; Ahn et al. 2005). Besides bacteria, stormwater runoff also contains other contaminants, such as heavy metals, including lead, copper, zinc, and nickel; petroleum hydrocarbons, particularly polycyclic aromatic hydrocarbons (PAHs), and nutrients, like nitrate and phosphate (Göbel et al. 2007; Lau et al. 2009; Herngren et al. 2010).

Coastal areas are particularly vulnerable to stormwater runoff contamination, as high contaminant loads are introduced through untreated surface water runoff during storm events, resulting in beach closings and impacting the economic activities of coastal communities (Mallin et al. 2000; McLellan and Salmore 2003; Ahn et al. 2005; Lee et al. 2006; Parker et al. 2010; Dorfman and Rosselot 2012). Despite the risks associated with contaminants stemming from stormwater runoff, very few stormwater treatment regulations exist. Currently, Rhode Island is the only state in the United States that has defined statewide standards and requires any new construction

142

to include stormwater best management practices (BMP) that remove at least 85% of total suspended solids (TSS), 60% of influent bacteria, and 30% of nitrogen and phosphorous (RIDEM 2010; EPA 2011).

There may be several BMP technologies that can treat TSS very effectively, for example, stormwater bioretention systems (UNHSC et al. 2007; Davis et al. 2009). But only a few commercial systems advertise effective bacterial removal capacities. Examples of such systems include *BactoLoxx* (Filtrexx, Goffstown, NH), which relies on proprietary flocculation agents that result in settling out bacteria (Faucette et al. 2009), and *Bacterra* (Filterra Bioretention Designs, Ashland, VA), which relies on physical filtration and predation in a biomat layer (Coffman et al. 2008). While the manufacturer supplied bacteria removal efficiency of these two stormwater BMPs reaches up to 99%, these treatments are not geared towards the simultaneous removal of other contaminants. For that purpose, supplementary filter media must be added (Coffman et al. 2008; Faucette et al. 2009). Other BMPs, such as biofiltration systems, that simultaneously target more than one class of contaminants, e.g. heavy metals and PAHs, have limited bacteria removals capacities, ranging from 0-80%. From a public health perspective, this is not considered sufficient (Schueler and Holland 2000; EPA 2001; Ahn et al. 2005).

Besides overall low removal efficiencies, recent studies of bacteria removal in a wide range of structural BMPs concluded that bacteria treatment was ineffective and unreliable, as the removal of pathogens primarily relied on attachment and not deactivation (Stevik et al. 2004; Zhang and Lulla 2006). This is because sorbed

143

pathogens can remain viable during attachment (Davies and Bavor 2000; Mohanty et al. 2013) and therefore can be remobilized or detached during intermittent flow conditions (Mohanty et al. 2013). Bacteria remobilization or detachment is especially relevant in areas with high water tables, because insufficient soil depth may prevent effective pathogen treatment, therefore increasing the risk of bacterial contamination of groundwater resources (Morales et al. 2014). New approaches are therefore needed to enhance the inactivation of pathogenic organisms in stormwater runoff, possibly together with other co-contaminants, and implement these technologies in the next generation of BMPs.

Herein, we investigated if innovative stormwater treatment approaches can be based on antimicrobial compounds that have found wide-spread application in many consumer products or water filtration materials. Several studies have shown that materials amended with antimicrobials are significantly more effective at removing bacteria from aqueous solutions and retaining them either on porous media (Mohanty et al. 2013) or inactivating them by damaging the bacterial cell structure (Zhang and Oyanedel-Craver 2013; Schifman et al. in prep. a). For instance, Schifman et al. (in prep.a) tested antimicrobial amended material for the use in stormwater BMPs. It was found that under laboratory conditions, red cedar (*Thuja plicata*) wood chips amended with 3-(trihydroxysilyl)propyldimethyloctadecyl ammonium chloride (TPA) were effective at removing *E. coli* from aqueous solution by at least 99% (2 $\log_{10}$ removal). These findings suggest that it might be possible to amend antimicrobial properties to

144

the matrix of existing BMP systems, such as tree filters (Schifman et al. in prep a.; Schifman et al. in prep. b), thereby achieving simultaneous treatment of chemical and bacteriological contaminants.

The objective of this pilot-scale study was to compare a conventional sand/expanded shale based tree filter BMP to an innovative one amended with TPA/Red Cedar wood chips. The primary focus was on quantifying the removal of bacteria from stormwater runoff. It was hypothesized that the antimicrobial media, which has been extensively tested in the laboratory for its ability to simultaneously remove heavy metals, PAHs, and *E. coli,* will show an increased pollutant and bacteria removal capability in the field compared to the conventional filter (Kasaraneni et al. 2014; Schifman et al. in prep. a; Schifman et al. in prep. b). The results from this study are expected to shed light on the potential of this simultaneous treatment approach for possibly implementation in full scale stormwater runoff BMP systems in the future.

METHODS

Site Description

A conventional asphalt covered parking lot on the northern end of the University of Rhode Island, Kingston campus holds 458 parking spaces and is heavily used by commuting students. This parking lot covers 4.9 acres (19830 m^2; Figure 4.1a) and, together with adjacent roadways, it is part of the Rhode Island Stormwater Demonstration Facility (RISTDF). The test area is located over the Chipuxet Aquifer in southern Rhode Island. Beneath is a thin layer of loess, a Pleistocene glacio-fluvial

aquifer contains complexly interbedded lenses of sand and gravel with smaller contributions of deposits of silt and silty sands (Dickerman 1984). The stratified material is about 60 m thick and overlies fractured granitic bedrock. The depth to groundwater at the site is approximately 7 m below ground surface (bgs) (Boving et al. 2008).

Installation

In August 2013 two tree filters were installed at the Rhode Island Stormwater Treatment Demonstration Facility (RISTDF, Figure 4.1). One conventional TF unit contained a mixture of sand and expanded shale as the filter media (0.64 m^3). The innovative TF unit had 30 kg (0.10 m^3) of bioactive red cedar wood chips added the sand and expanded shale mix (1.13 m^3) . The conventional TF unit is 1.45m*1m*0.9m LWD and includes a catch basin that measures 0.45m*1m *0.9m LWD. The innovative TF unit is slightly larger (1.73m*1.25m*0.9m LWD) and includes a catch basin that measures 0.45m*1.25m*0.9m LWD. The TF units are open concrete structures that allow the filtered runoff to infiltrate into the ground and replenish the aquifer (Figure 4.2). For installation 2.1m*2.4m*2.4m LWD of soil was excavated and filled with coarse gravel until 0.9m bgs. A stainless steel sampling pan with dimensions 0.30m*0.24m*0.033m LWD was installed at the top of the gravel layer in both filters 0.9 meters below the infiltration surface. The pan was filled with coarse gravel. Based on an estimated 30% porosity of the gravel, the pore volume represented by the sampling pan is ~ 1 Liter. A 5 mm hole in the bottom of the pan is connected to

146

a 7.9 mm (inner diameter Teflon tube which was fed through a PVC pipe to the surface. The tubing permits pumping of the filter effluent collected in the pan beneath (Figure 4.2). Once the TF was placed inside the excavation pit, the remaining space was filled with engineered media composed of 75% coarse sand, 15% of expanded shale (Φ=-4; 16 mm), and 10% sphagnum peat to a depth of 0.7 m bgs. (Figure 4.2). A red maple tree (*Acer rubrum*) was planted in the unit to complete the tree filter system (Figure 4.2). Red maple was chosen to match the surrounding trees in the parking lot.

Meteorological data was obtained from a National Climatic Data Center station that is located less than 0.6 km from the test site. Based on a 20 year record, the site receives on average 1202 mm of precipitation throughout the year. Average annual snow accumulation is 841 mm. The average number of days per year when precipitation was ≥ 0.1 inches was 77 days, ≥ 0.5 inches was 31 days, and ≥ 1 inch was 12 days (NOAA 2014).

The sampling time was divided into the winter (November 2013 to March 2014) and summer (April 2014 through August 2014) season. During the entire sampling period a total precipitation of 1092 mm was received in Kingston, RI. Ten precipitation events were observed that exceeded 1 inch (25.4 mm), six of which occurred during the winter time (November 2013 to March 2014) (water equivalent precipitation). During the winter, a total of 26 snow events were measured at the meteorological station with a total of 1102 mm of snowfall recorded.

Red Cedar TF Preparation

A quaternary ammonium compound, 3-(trihydroxysilyl) propyl-dimethyl-octadecyl ammonium chloride (TPA), was the antimicrobial agent used in this study. In prior laboratory studies, TPA was identified as a stable amendment to red cedar wood chips (Kasaraneni et al. 2014; Schifman et al. in prep. a). Although TPA loadings of up to 9 mg per gram wood were found possible (Kasaraneni et al. 2014), for cost reasons the loading selected for this pilot experiment was 6 mg/g. The red cedar chips were prepared for TPA loading by first washing the wood to remove fines and leaching out soluble matter. For that, the wood was soaked in frequently exchanged clean water for a minimum of 2 weeks. The wood chips were then mixed with an aqueous solution containing 75 mg/L TPA (Figure S4.1). The ratio of the red cedar mass to TPA solution was 1g to 25 ml, as based on previous experiments. The mix was stirred for 9 days to reach the 6 mg/g TPA load as suggested by Kasaraneni et al. (2014). Afterwards, the wood chips were dried, weighed, and stored in a dark and dry location before being added to the tree filter. A total of 30 kg of TPA amended Red Cedar was mixed into the top 0.5 m of sand/shale mix already inside the tree filter.

Sampling and Analysis

From November 2013 until August 2014, both runoff into the catch basin and effluent from the sampling pan installed were sampled weekly. Since it is possible that the catch basin samples do not reflect the true stormwater influent samples additional

grab samples were analyzed during seven rain storms. *E. coli* (as fecal indicator bacteria) were quantified using membrane filtration and 24-hour incubation at 44.5°C using m-FC broth (Millipore, Billerica, MA, USA) and reported as CFU/100 ml. While the main focus was on bacteria concentrations, all samples were analyzed for pH (FiveGo Mettler Toledo, Columbus, OH, USA) and for specific conductance, temperature, chloride Cl^-(range 0-1000mg/L), nitrate (NO_3^-, range 0-200 mg/L) using a YSI Professional Plus Multiprobe electrodes (Yellow Springs, OH, USA). Orthophosphate (PO_4^-)$_3$ was quantified with a Hach DR2800 Spectrophotometer (Loveland, CO, USA) following Hach Method 8048 (range 0.06 – 5.00 mg/L). Total suspended solids (TSS) were measured following Standard Method 2540.D. Heavy metals (Cu, Ni, Pb, Zn) samples were stabilizing with 2% nitric acid (ACS grade, Fisher Chemical, Pittsburgh, PA, USA) and digested for a minimum of 24 hours before analysis with a Perkin Elmer 3100 XL ICP-OES (Waltham, MA, USA). The method detection limit was 0.01 mg/l for all metals. Polycyclic aromatic hydrocarbons (PAH) were extracted from the aqueous samples by liquid-liquid extraction following EPA method 610 analyzed with a Shimadzu Gas Chromatograph/Mass Spectrometer QP2010 (Marlborough, MA, USA) following EPA Method 8270d. The GC column was a fused silica capillary column (30m x 0.25mm ID, 0.25μm, Shimadzu, Marlborough, MA, USA). Splitless injection was used in combination with the following temperature program: initial column temperature, 40°C; increase at 25°C min^{-1} to 290°C; increase at 5°C min^{-1} to 320°C; hold for 2 min. The detector

temperature was set at 320°C. The column flow rate is 1.4 ml/min. PAH quantification is carried out using a five-point calibration plot.

In addition to the 16 priority PAH defined by the U.S.EPA (EPA 2006) the analysis included deuterated PAH (acenaphthene-d10, benzo[a]pyrene-d12, benz[a]anthracene-d12, phenanthrene-d10, fluoranthene-d10, dibenz[a,h]anthracene-d4; Ultra Scientific, North Kingston, RI). The deuterated PAH were added to each sample to quantify extraction efficiency. In addition, blank samples and standard checks were run for each sampling campaign and prepared under the same conditions as at the field samples. PAH recovery from the extractions was 40.2 ± 35.4 % for acenaphthene-d10, 41.3 ± 17.3% for benzo[a]pyrene-d12, 40.7 ± 21.7 % for benz[a]anthracene-d12, 51.1 ± 38.4 % for phenanthrene-d10, 31.1 ± 44.7 % for fluoranthene-d10, and 73.6 ± 31.5 % for dibenz[a,h]anthracene-d14. The deuterated standards were also used to correct for PAH extraction recovery. The method detection limits was 5 pg/µl for PAHs with molecular weight of 228 g/mol (including Chrysene) and 10 pg/µl for compounds with molecular weight 252 g/mol and above (Benzo(b)fluoranthene and above).

A two tailed t-test was carried out using R software version 3.0.3 to statistically compare the storm event removal percentages for TSS, nitrate, phosphate, *E. coli*, and PAH from the two tree filters. Metals were not statistically analyzed because metal data was inconclusive.

Controlled Field Tracer Experiments

Field tracer experiments were carried out on each TF using a solution containing NaCl as a conservative tracer and a green fluorescent protein (GFP) strain of *E. coli* (BTF 132) (Biomérieux, Hazelwood, MO, USA) as a bacterial tracer. GFP labelled *E. coli* are ideal for use as a bacterial tracer (Pinheiro et al. 2008) because bacteria colonies glow green under UV light. This allows for differentiating *E. coli* added as a tracer from those native to the TF system.

The GFP *E. coli* were cultured in LB broth (10 g/L sodium chloride, 10 g/L tryptone, and 5 g/L yeast extract, Sigma Aldrich, St. Louis, MO, USA) at 37.5 °C for 13 hrs. After culturing, the bacteria were removed from the LB broth, washed and stored in phosphate buffer solution (11.2 g/L K_2HPO_4, 4.8 g/L KH_2PO_4, and 20 mg/L ethylenediaminetetraacetic acid, all Sigma Aldrich; pH: 7.3). *E. coli* concentration for all samples was determined using the membrane filtration technique, applying m-FC with Rosalic Acid Broth Millipore, (Billerica, MA, USA) with subsequent incubation at 44.5 °C for 24-48 hrs.

The two tracer tests were carried out on separate days one week apart in September 2014. No major rain events were observed immediately prior to or during the tracer test period. In both instances clean, non-chlorinated water was pumped into the TF at about 3 L/min (circa 200 L) to create similar initial conditions in both TF filters. The water was pumped into the TF directly, bypassing the catch basin using an electric submersible pump and garden hose (Figure 4.2). The water flow was metered with a 2.5 m^3/hr ISTEC Flowmeter (Sparta, NJ, USA). After approximately 70

minutes of pumping clean water, the tracer solution containing NaCl and GFP *E. coli* was injected. The NaCl concentration was 888 mg/L (428 liters) and 969 mg/L (392 liters) for the conventional and the innovative TF experiment, respectively (Table 4.2). The initial concentration (C_o) of GFP *E. coli* in the solution was $6.90*10^5$ CFU/100 ml and $8.32*10^6$ CFU/100 ml for the conventional and the innovative tree filter, respectively (Table 4.2). The tracer solutions were pumped over the course of 120 minutes and 145 minutes, respectively (Table 4.2). Afterwards, an additional 207 L of clean, non-chlorinated water was pumped through each of the two TF for approximately 70 minutes.

Periodic influent samples were taken throughout the tracer test to monitor natural decay of *E. coli* in the tracer solution. Using a Masterflex Environmental Sampler (Vernon Hills, IL, USA), effluent was pumped constantly from the buried sampling pan inside the TF at a rate of 200 ml/min for the conventional and 225 ml/min for the innovative system. Every 5 minutes, the effluent was metered for specific conductance using a YSI Professional Plus Multimeter logger (Yellow Springs, OH, USA) (Figure S2). Every 15 minutes samples were collected for bacteria analysis and immediately processed at the field laboratory at the RISTDF site.

RESULTS

Catch Basin Water Quality

Overall, both tree filters had similar influent contaminant concentrations during storm events and catch basin samples were similar to grab samples, except

TSS, where concentrations in the grab samples were elevated compared to the catch basin (Table 4.3). As a result, all further discussion on TSS is based on grab samples as the influent. For the remaining constituents the catch basin water samples are used as a base comparison as these concentrations did not differ from the grab samples.

All constituents that were analyzed occurred at higher concentrations during winter months except for PAHs, for which concentrations were higher during the summer (Table 4.3). There were higher loads of chloride measured in the catch basin in winter, up to 29,480 mg/L, compared to the summer where the maximum concentration observed was 74.5 mg/L. Nitrate concentrations averaged 44.9±61.3 mg/L as N throughout the year, however were generally higher in winter where they reached up to 249.6 mg/L as N. Phosphate concentrations were only measured in summer and averaged 0.49±0.26 mg/L. Total suspended solids were higher in winter, averaging 52.7±28.9 mg/L compared to summer 231±15.9 mg/L. Concentrations of heavy metals were also elevated in winter compared to summer (Table 4.3). Detected PAH concentrations were on average lower in winter (1.9±5.2 µg/L) compared to summer (4.5±2.1 µg/L). One sampling event in winter resulted in much higher $\sum PAH_{16}$ concentration (21.1 µg/L). Influent *E. coli* concentrations in the catch basin during winter ($1.7*10^4$ CFU/100ml) were about one order of magnitude higher than observed in summer ($2.3*10^3$ CFU/100ml).

DISCUSSION

Rhode Island received 43.6 inches (1107.4 mm) of snow during the winter sampling period starting in November and lasting through March, with most snowfall

153

occurring in January and February (NOAA 2014). This period coincides with the highest amount of measurable chloride. The high chloride concentrations in this time can be attributed to the use of salt on surfaces surrounding the study area (Figure 4.3a).

Nitrate, similar to chloride, is very mobile. Studies suggest nitrate concentrations in forests spike at the end of the winter period (Kurian et al. 2013). While there are no forests at the site, there are leaves and other tree residues accumulating on the parking lot surface. These organic materials are incorporated into snow piles during winter. The nitrates associated with these organic residues appear to be exported during snowmelt, therefore contributing to higher loads during the late winter sampling period (Figure 4.3b) (Kurian et al. 2013). Once the snow cover has melted, the nitrate loading from stormwater runoff decreased, which correlates with the chloride concentrations (Table 4.3, Figure 4.3).

Total suspended solids (TSS) display similar trends in winter, where higher loads of particles are transported through runoff during melting or rain events (Figure 4.3c); this is apparent in both, catch basin and grab samples (Table 4.3). The grab samples did exhibit higher concentrations of TSS, likely because most particles are removed in the catch basin after the stormwater enters the TF unit.

In part, the high concentrations of TSS in the winter time can be attributed to the parking lot being treated with a sand/salt mix (Pers. comm. Joseph Paradise, URI). Even though the concentration of TSS decreases in summer, elevated loads of TSS can still be observed during rain events following longer antecedent dry periods.

154

Contaminant Removal

Water Quality and chloride

Both tree filters were evaluated for their ability to remove contaminants from stormwater. In both TFs, the pH in the effluent decreased relative to the catch basin in summer and winter. The chloride effluent concentrations in winter were lower by 51.1% in the conventional TF compared to the influent. In the innovative TF, chloride effluent concentrations decreased by 23.5% during the summer (Table 4.4). It is unclear why or how chloride was apparently removed because this ion is not expected to sorb or otherwise interact with the TF filter matrix.

Total Suspended Solids

TSS analysis is based on seven grab samples taken during rain events because the catch basin is not a representative sample for this analysis (Table 4.3). During these events the TSS removal was higher in summer for both filters (84.9% and 90.3% for the conventional and innovative filter, respectively) compared to winter (75.4% and 80.2%, for the conventional and innovative filter, respectively). Neither filters met the RISM standard of 85% TSS removal. However more frequent grab sampling during storm events is needed to validate these results. Comparing these two systems statistically shows that there is no significant difference in TSS removal in winter ($p=0.3$), while there is a significant difference in TSS removal in summer ($p<0.05$).

Nitrate

Nitrate removal was higher in winter, where the conventional TF achieved removal of 38.6% and the red cedar TF removed 62.6% (Table 4.4). During winter,

155

the catch basin nitrate concentrations were also significantly higher compared to summer, during which the EPA MCL for nitrate (10 mg/L) was rarely exceeded (Table 4.3, Figure 4.3 b). However, in summer nitrate concentrations in the effluent often exceed those of the catch basin (8.4% in the innovative tree filter and 22.2% in the conventional tree filter). However, effluent concentrations only exceeded the 10 mg/L MCL set by EPA four times out of the 18 summer sampling events. The opposite was observed during winter. Nitrate was always effectively removed in both filters in winter, where influent concentrations were higher than in summer (Table 4.4 and 4.5). Statistical comparison of the two systems indicates that there is no difference in nitrate removal for either season ($p>0.05$).

Although in this study only nitrate was measured, other organic and inorganic nitrogen species are often found in stormwater runoff (Kim et al. 2003; Davis et al. 2006; Jasper et al. 2014). When these other nitrogen species are present in stormwater runoff and accumulate in BMPs, they can be converted to nitrate through biologically mediated nitrification during dry periods. This is because dry periods reduce the water content in the tree filter and conditions become more aerobic, favoring nitrification (Kim et al. 2003). When this occurs nitrate can be released from the system during the next storm event.

Kim et al. (2003) tested seven materials i.e., alfalfa, leaf mulch compost, newspaper, sawdust, wheat straw, wood chips, and elemental sulfur, for their ability to remove nitrate in laboratory column studies. It was found that the materials that were effective electron donors, such as wood chips, newspaper, and sawdust outperformed

washed filter sand. Nitrate reduction was observed during steady state flow conditions

as well as intermittent flow conditions (Kim et al. 2003). On this background, during

more frequent rain or melt events, as is observed at this test site, the filter may turn

anaerobic, creating conditions that are favorable for denitrification (Kim et al. 2003).

When this occurs wood chips in the innovative filter can act as effective electron

donors and denitrification can occur, resulting in more effective nitrate removal in the

innovative tree filter system. Because the soil oxygen content was not measured in this

study, a definite statement cannot be provided if conditions inside the TF were aerobic

or anaerobic.

Phosphate

Phosphate removal, though only studied in the summer months, was more

effective in the innovative filter (46.5% removal, p=0.08) compared to the

conventional sand/shale TF unit (31.5% removal) (Table 4.4). Similar results have

been reported in other studies where organic based filter media, such as biochar, peat,

or mulch outperformed a sand mixture in the removal of phosphates (Chang et al.

2010; Yao et al. 2011). In general, phosphate removal in other BMP studies indicated

that not just the filter media but also the initial phosphate content of the filter media

may play a role in the removal efficiency of phosphate (Davis et al. 2006; Hunt et al.

2006; Davis 2007; Davis et al. 2009).

Heavy Metals

For heavy metals, the contaminant removal was not quantifiable for copper and zinc because during both sampling seasons these two metals apparently leached from the brass fitting connected to the stainless steel sampling pan (Schock and Neff 1988). Nickel aqueous phase concentrations were at or near the method detection limit (10 µg/L) during the entire sampling campaign, particularly during summer. During winter, nickel removal was 9.7% removal in the conventional TF compared to 97.1 % in the red cedar tree filter (Table 4.4). Because of at or near the method detection limit concentrations during summer, nickel removals for that period were not calculated. For lead, the effluent concentrations during both, winter and summer, were elevated compared to the catch basin influent in both filters. Leaching tests were conducted using shale and red cedar samples placed into deionized water. These tests indicated that lead was not leaching from either material (data not shown).

Polycyclic aromatic hydrocarbons

The red cedar TF was significantly more effective (p-value<0.05) than the conventional shale TF at removing $\sum PAH_{16}$ from runoff in both seasons (Table 4.4). During winter, $\sum PAH_{16}$ removal by the red cedar filter was 80.6% compared to 47.1% for the conventional filter. During summer $\sum PAH_{16}$ removal in the red cedar filter was only marginally more effective with 21.2% removal compared to 7% conventional TF (p-value=0.06).

Using wood as a matrix for stormwater filtration, in particular for treating

PAH, has been previously tested in the field and in the laboratory (Boving and Zhang

2004; Boving and Neary 2007; Neary and Boving 2011; Kasaraneni et al. 2014). In a

laboratory study by Kasaraneni et al. (2014), it was shown that red cedar amended

with 6 mg/g TPA had a 69.8 times higher sorption capacity for the PAH compound

fluorene compared to expanded shale. Similarly, for acenapthene, TPA amended red

cedar had a 58.1 times higher affinity than expanded shale. A field study by Boving

and Neary (2007) found that Aspen wood filters deployed in stormwater detention

ponds removed on average between 18.5% and 35.6% of PAHs.

Even though $\sum PAH_{16}$ is being used as the reference for the much large class of

PAH compounds, not all 16 target PAH were detected each time and the relative

distribution of compounds also varied from sample to sample. In the winter, when

PAHs were present in the runoff an average of 42% of the time, 4.8 compounds were

detected compared to 9.6 compounds in the summer time, when PAHs were detected

74% of the time. Commonly the compounds detected in the winter were low

molecular weight compounds, i.e. those with 3 or fewer benzene rings (naphthalene

through anthracene), compared to the summer where a greater number of high

molecular compounds, those with 4 or more benzene rings, were detected. This shift

can be attributed to runoff and ambient temperatures that influence the solubility of

PAHs that already have limited solubility (Schwarzenbach et al. 2002). This shift is

also supported by a study conducted in Rhode Island that showed that the PAH

atmospheric deposition profile in the winter time has a strong signature of low

molecular compounds, whereas in summer the fraction of higher molecular weight

PAH compounds increased (Schifman and Boving in review).

E. coli

Overall, both tree filters achieved *E. coli* removal that exceeds the RISM

standard of 60%. Similar removal capabilities have been observed in other studies that

investigated bacteria straining and removal through filtration (Hathaway et al. 2009;

Chandrasena et al. 2013).

Comparing the *E. coli* removal by season, lower removal percentages were

observed in winter compared to summer (Table 4.4). During both periods, the red

cedar TF outperformed the conventional shale TF. However, the removal differences

were statistically insignificant (P>0.1). These observations were confirmed by the

field tracer test results, which showed that GFP *E. coli* removal was 2.09 $\log_{10}$ cycles

and 2.02 $\log_{10}$ cycles in the conventional and amended TF, respectively. All data

suggests that there is no difference in the removal capability of the conventional and

innovative TF.

There are several possible explanations for why no significant differences

between the conventional and amended TF were found during this pilot scale study.

Foremost, only a comparably small amount of amended cedar wood (30 kg) was

applied. This amount represents less than 1% of the TF volume. Greater amounts of

amended wood are required to ensure greater removal. Second, because of the small

amount of amended wood material, the contact time between the infiltrating

stormwater and the bioactive matrix was insufficient. In prior laboratory experiments

by Schifman et al. (in prep a), it was determined that a three hour contact time using TPA modified red cedar resulted in 2.2 log removal. In the pilot scale test described herein, the residence time was 20 minutes, therefore the residence time in the layer containing the antimicrobial wood chips is likely less than 10 minutes. Third, the TPA loading to the cedar wood was 6 mg/g, but up to 9 mg/g can be achieved as shown by Kasaraneni et al. (2014). Higher TPA loading should result in greater bacteria removal percentages. Finally, the TPA amended red cedar was only applied on the top 0.5 m of the TF system instead of being homogenously mixed into the entire filter media. It is expected that better mixing would increase the contact of the infiltrating bacteria with antimicrobially active wood chips, possibly leading to more efficient bacteria removal.

CONCLUSIONS

Two tree filter units, one conventional with a sand/shale mix and one innovative containing antimicrobially amended red cedar wood chips, were compared for their contaminant removal capabilities in a field pilot study. Over the course of an 8 month period, the water in the TF catch basin and the effluent was sampled for twelve constituents. Additional stormwater grab samples were collected during some storm events. Overall, the innovative TF exhibited higher nitrate, phosphate, TSS, and $\sum PAH_{16}$ removal, However, the *E. coli* removal was insignificantly different from the conventional systems.

Even though *E. coli* removal by TPA amended red cedar wood chips was extensively and successfully tested in the laboratory (Kasaraneni et al. 2014; Schifman et al. in prep. a), this pilot scale field study demonstrated that the laboratory results were difficult to replicate in the field. Possible reasons for this are 1) co-contaminants, such a high salt load during winter, may reduce the antimicrobial effectiveness of the TPA, 2) insufficient amounts of reactive material were added to the TF system, preventing sufficient contact time of the infiltrating stormwater with the matrix and, 3) the amended red cedar should have been mixed with engineered matrix more evenly, allowing for more contact between the bacteria and TPA red cedar during treatment.

At the time of the installation of the TF, the units were filled entirely with conventional sand/shale matrix. Later on, this prevented the replacement with TPA amended wood chips or better mixing of the filter matrix afterwards. If a similar study is to be repeated, it is recommended to add much more TPA amended red cedar wood chips to the system and mix it more thoroughly with the conventional sand/shale matrix before packing the TF unit with the mix. Also, the ratio of wood chips to conventional sand/shale matrix should be increased to realize contact times longer than the approximately 10 minutes in this study. It is very likely that these improvements will show that TPA amended tree filters can lower the bacteria concentrations more significantly than conventional TF systems.

162

REFERENCES

Ahn, J. H., Grant, S. B., Surbeck, C. Q., DiGiacomo, P. M., Nezlin, N. P., Jiang, S. (2005). "Coastal Water Quality Impact of Stormwater Runoff from an Urban Watershed in Southern California." *Environ. Sci. Technol.,* 39(16), 5940-5953.

Boving, T. B., and Neary, K. (2007). "Attenuation of Polycyclic Aromatic Hydrocarbons from Urban Stormwater Runoff by Wood Filters." *J. Contam. Hydrol.,* 91(1-2), 43-57.

Boving, T. B., and Zhang, W. (2004). "Removal of Aqueous-Phase Polynuclear Aromatic Hydrocarbons using Aspen Wood Fibers." *Chemosphere,* 54(7), 831-839.

Chandrasena, G. I., Deletic, A., McCarthy, D. T. (2013). "Survival of *Escherichia Coli* in Stormwater Biofilters " *Environmental Science and Pollution Research.*

Chang, N., Wanielista, M., Daranpob, A. (2010). "Filter Media for Nutrient Removal in Natural Systems and Built Environments: II—Design and Application Challenges." *Environ. Eng. Sci.,* 27(9), 707-720.

Chong, M. N., Sidhu, J., Aryal, R., Tang, J., Gernjak, W., Escher, B., Toze, S. (2013). "Urban Stormwater Harvesting and Reuse: A Probe into the Chemical, Toxicology and Microbiological Contaminants in Water Quality." *Environ. Monit. Assess.,* 185(8), 6645-6652.

Coffman, L. S., Ruby, M., Beach, C. (2008). "Bacterra by filterra® advanced bioretention system: Discussion of the benefits, mechanisms and efficiencies for bacteria removal." *Proc., ASCE Conf. Proc. 333.*

Corsi, S. R., Graczyk, D. J., Geis, S. W., Booth, N. L., Richards, K. D. (2010). "A Fresh Look at Road Salt: Aquatic Toxicity and Water-Quality Impacts on Local, Regional, and National Scales." *Environ. Sci. Technol.,* 44(19), 7376-7382.

Davies, C. M., and Bavor, H. J. (2000). "The Fate of Stormwater-Associated Bacteria in Constructed Wetland and Water Pollution Control Pond Systems " *J. Appl. Microbiol.,* 89(2), 349 - 360.

Davis, A. P., Hunt, W. F., Traver, R. G., Clar, M. (2009). "Bioretention Technology: Overview of Current Practice and Future Needs." *J. Environ. Eng.,* 135(3), 109-117.

Davis, A. P. (2007). "Field Performance of Bioretention: Water Quality." *Environ. Eng. Sci.,* 24(8), 1048-1064.

Davis, A. P., Shokouhian, M., Sharma, H., Minami, C. (2006). "Water Quality Improvement through Bioretention Media: Nitrogen and Phosphorus Removal." *Water Environ. Res.,* 78(3), 284-293.

Davis, A. P., Shokouhian, M., Sharma, H., Minami, C., Winogradoff, D. (2003). "Water Quality Improvement through Bioretention: Lead, Copper, and Zinc Removal." *Water Environ. Res.,* , 73-82.

Davis, A. P., Hunt, W. F., Traver, R. G., Clar, M. (2009). "Bioretention Technology: Overview of Current Practice and Future Needs " *J. Environ. Eng.,* 135(3), 109 - 117.

Deletic, A. B., and Maksimovic, C. (1998). "Evaluation of Water Quality Factors in Storm Runoff from Paved Areas." *J. Environ. Eng.,* 124(9), 869-879.

Dorfman, M., and Rosselot, K. (2012). *Testing the Water: A Guide to Water Quuality at Vacation Beaches*.

EPA. (2012). *Recreational Water Quality Criteria*.

EPA. (2011). *Performance Standards for Discharges from Newly Developed and Redeveloped Sites,* http://cfpub.epa.gov/npdes/stormwater/rulemaking/performancestandards.cfm Ed., Environmental Protection Agency, .

EPA. (2006). "Current national recommended water quality criteria." <http://www.epa.gov/ost/criteria/wqcriteria.html#priority> .

EPA. (2001). *Protocol for Developing Pathogen TMDLs,* Office of Water (4503F), United States Environmental Protection Agency, Washington, DC.

EPA. (1999). Compendium Method TO-13A, United States Environmental Protection Agency, Cincinnati, OH,USA.

Faucette, L., Cardoso-Gendreau, F., Codling, E., Sadeghi, A., Pachepsky, Y., Shelton, D. (2009). "Storm Water Pollutant Removal Performance of Compost Filter Socks." *J. Environ. Qual.,* 38(3), 1233-1239.

Gilbert, J. K., and Clausen, J. C. (2006). "Stormwater Runoff Quality and Quantity from Asphalt, Paver, and Crushed Stone Driveways in Connecticut." *Water Res.,* 40(4), 826-832.

Göbel, P., Dierkes, C., Coldewey, W. G. (2007). "Storm Water Runoff Concentration Matrix for Urban Areas." *J. Contam. Hydrol.,* 91(1–2), 26-42.

Grebel, J. E., Mohanty, S. K., Torkelson, A. A., Boehm, A. B., Higgins, C. P., Maxwell, R. M., Nelson, K. L., Sedlak, D. L. (2013). "Engineered Infiltration Systems for Urban Stormwater Reclamation." *Environ. Eng. Sci.,* 30(8), 437-454.

Han, Y., Lau, S., Kayhanian, M., Stenstrom, M. K. (2006). "Characteristics of Highway Stormwater Runoff." *Water Environ. Res.,* 78(12), 2377-2388.

Hathaway, J., Hunt, W., Jadlocki, S. (2009). "Indicator Bacteria Removal in Storm-Water Best Management Practices in Charlotte, North Carolina." *J. Environ. Eng.,* 135(12), 1275-1285.

Hatt, B. E., Fletcher, T. D., Deletic, A. (2009). "Hydrologic and Pollutant Removal Performance of Stormwater Biofiltration Systems at the Field Scale." *Journal of Hydrology,* 365(3), 310-321.

Herngren, L., Goonetilleke, A., Ayoko, G. A., Mostert, M. M. M. (2010). "Distribution of Polycyclic Aromatic Hydrocarbons in Urban Stormwater in Queensland, Australia." *Environmental Pollution,* 158(9), 2848-2856.

Hunt, W., Jarrett, A., Smith, J., Sharkey, L. (2006). "Evaluating Bioretention Hydrology and Nutrient Removal at Three Field Sites in North Carolina." *J. Irrig. Drain. Eng.,* 132(6), 600-608.

Jasper, J. T., Jones, Z. L., Sharp, J. O., Sedlak, D. L. (2014). "Nitrate Removal in Shallow, Open-Water Treatment Wetlands." *Environ. Sci. Technol .*

Karim, M. R., Manshadi, F. D., Karpiscak, M. M., Gerba, C. P. (2004). "The Persistence and Removal of Enteric Pathogens in Constructed Wetlands." *Water Res.,* 38(7), 1831-1837.

Kasaraneni, V. K., Schifman, L. A., Boving, T. B., Oyanedel-Craver, V. (2014). "Enhancement of Surface Runoff Quality using Modified Sorbents." *ACS Sustainable Chem. Eng.,* 2(7), 1609-1615.

Kayhanian, M., Suverkropp, C., Ruby, A., Tsay, K. (2007). "Characterization and Prediction of Highway Runoff Constituent Event Mean Concentration." *J. Environ. Manage.,* 85(2), 279-295.

Kim, H., Seagren, E. A., Davis, A. P. (2003). "Engineered Bioretention for Removal of Nitrate from Stormwater Runoff." *Water Environ. Res*, 355-367.

Kurian, L. M., Lautz, L. K., Mitchell, M. J. (2013). "Winter Hydrology and NO_3- Concentrations in a Forested Watershed: A Detailed Field Study in the Adirondack Mountains of New York1." *JAWRA Journal of the American Water Resources Association,* 49(2), 264-283.

Lau, S., Han, Y., Kang, J., Kayhanian, M., Stenstrom, M. K. (2009). "Characteristics of Highway Stormwater Runoff in Los Angeles: Metals and Polycyclic Aromatic Hydrocarbons." *Water Environ. Res.,* 81(3), 308-318.

Ledford, S. H., and Lautz, L. K. (2014). "Floodplain Connection Buffers Seasonal Changes in Urban Stream Water Quality." *Hydrol. Process*.

Lee, C. M., Lin, T. Y., Lin, C. C., Kohbodi, G. A., Bhatt, A., Lee, R., Jay, J. A. (2006). "Persistence of Fecal Indicator Bacteria in Santa Monica Bay Beach Sediments " *Water Res.,* 40(14), 2593-2602.

Mallin, M. A., Johnson, V. L., Ensign, S. H. (2009). "Comparative Impacts of Stormwater Runoff on Water Quality of an Urban, a Suburban, and a Rural Stream." *Environ. Monit. Assess.,* 159(1), 475-491.

Mallin, M. A., Williams, K. E., Esham, E. C., Lowe, R. P. (2000). "Effect of Human Development on Bacteriological Water Quality in Coastal Watersheds." *Ecol. Appl.,* 10(4), 1047-1056.

McLellan, S., and Salmore, A. (2003). "Evidence for Localized Bacterial Loading as the Cause of Chronic Beach Closings in a Freshwater Marina." *Water Res.,* 37(11), 2700-2708.

Mohanty, S. K., Torkelson, A. A., Dodd, H., Nelson, K. L., Boehm, A. B. (2013). "Engineering Solutions to Improve the Removal of Fecal Indicator Bacteria by Bioinfiltration Systems during Intermittent Flow of Stormwater " *Environ. Sci. Technol.,* 47(19), 10791 - 10798.

Morales, I., Atoyan, J. A., Amador, J. A., Boving, T. (2014). "Transport of Pathogen Surrogates in Soil Treatment Units: Numerical Modeling." *Water,* 6(4), 818-838.

Neary, K., and Boving, T. B. (2011). "The Fate of the Aqueous Phase Polycyclic Aromatic Hydrocarbon Fraction in a Detention Pond System." *Environmental Pollution,* 159(10), 2882-2890.

Parker, J., McIntyre, D., Noble, R. (2010). "Characterizing Fecal Contamination in Stormwater Runoff in Coastal North Carolina, USA." *Water Res.,* 44(14), 4186-4194.

Pinheiro, L. B., Gibbs, M. D., Vesey, G., Smith, J. J., Bergquist, P. (2008). "Fluorescent Reference Strains of Bacteria by Chromosomal Integration of a Modified Green Fluorescent Protein Gene." *Appl. Microbiol. Biotechnol.,* 77(6), 1287-1295.

Reddy, K. R., Xie, T., Dastgheibi, S. (2014). "Evaluation of Biochar as a Potential Filter Media for the Removal of Mixed Contaminants from Urban Storm Water Runoff." *J. Environ. Eng*.

RIDEM. (2010). *Rhode Island Stormwater Design and Installation Standards Manual,* .

Schifman, L. A., and Boving, T. B. (in review). "Spatial and Seasonal Variation in PAH Sources and Atmospheric Deposition Patterns in a Small Northeastern State in the United States."

Schifman, L. A., Kasaraneni, V. K., Sullivan, R. K., Oyanedel-Craver, V., Boving, T. (in prep. a). "Selecting an Antimicrobial Filter Media for Improved Stormwater Best Management Practices."

Schifman, L. A., Kasaraneni, V. K., Sullivan, R. K., Oyanedel-Craver, V., Boving, T. (in prep. b). "Evaluation of Stormwater Runoff using a Tree Filter BMP."

Schock, M. R., and Neff, C. H. (1988). "Trace Metal Contamination from Brass Fittings." *Journal (American Water Works Association),*47-56.

Schueler, T. R., and Holland, H. (2000). "Microbes and Urban Watersheds: Concentrations, Sources, and Pathways." *The Practice of Watershed Protection,* 74-84.

Schwarzenbach, R. P., Gschwend, P. M., Imboden, D. M. (2002). *Environmental Organic Chemistry,* 2nd Ed., John Wiley & Sons, Inc., Hoboken, New Jersey, USA.

Stevik, T. K., Aa, K., Ausland, G., Hanssen, J. F. (2004). "Retention and Removal of Pathogenic Bacteria in Wastewater Percolating through Porous Media: A Review " *Water Res.,* 38(6), 1355-1367.

Stewart, J. R., Gast, R. J., Fujioka, R. S., Solo-Gabriele, H. M., Meschke, J. S., Amaral-Zettler, L. A., del Castillo, E., Polz, M. F., Collier, T. K., Strom, M. S. (2008). "The Coastal Environment and Human Health: Microbial Indicators, Pathogens, Sentinels and Reservoirs." *Environ. Health,* 7(Suppl 2), S3.

Surbeck, C. Q., Jiang, S. C., Ahn, J. H., Grant, S. B. (2006). "Flow Fingerprinting Fecal Pollution and Suspended Solids in Stormwater Runoff from an Urban Coastal Watershed." *Environ. Sci. Technol.,* 40(14), 4435-4441.

Tromp, K., Lima, A. T., Barendregt, A., Verhoeven, J. T. (2012). "Retention of Heavy Metals and Poly-Aromatic Hydrocarbons from Road Water in a Constructed Wetland and the Effect of De-Icing." *J. Hazard. Mater.,* 203, 290-298.

UNHSC, Roseen, R., Ballestero, T., Houle, J. (2007). *UNH Stormwater Center 2007 Annual Report.* University of New Hampshire, Cooperative Institute for Coastal and Estuarine Environmental Technology, Durham, NH., http://ciceet.unh.edu/unh_stormwater_report_2007/index.php.

Yao, Y., Gao, B., Inyang, M., Zimmerman, A. R., Cao, X., Pullammanappallil, P., Yang, L. (2011). "Removal of Phosphate from Aqueous Solution by Biochar Derived from Anaerobically Digested Sugar Beet Tailings." *J. Hazard. Mater.,* 190(1), 501-507.

Zhang, H., and Oyanedel-Craver, V. (2013). "Comparison of the Bacterial Removal Performance of Silver Nanoparticles and a Polymer Based Quaternary Amine Functiaonalized Silsesquioxane Coated Point-of-use Ceramic Water Filters." *J. Hazard. Mater*.

Zhang, X., and Lulla, M. (2006). "Evaluation of Pathogenic Indicator Bacteria in Structural Best Management Practices." *Journal of Environmental Science and Health Part A,* 41(11), 2483-2493.

TABLES

Table 4.1. Tree filter (TF) and catch basin dimensions for the conventional and TPA amended red cedar system.

Measure	Conventional Sand/Shale Tree Filter	Innovative Red Cedar Tree Filter*
Catch Basin Length (m)	0.45	0.45
Catch Basin Width (m)	0.91	1.25
Catch Basin Depth (m)	1.00	0.97
Catch Basin Volume (L)	409.5	542.6
Infiltration Area (m^2)	0.90	1.59
Contributing Area (m^2)	238	2978

*30 kg of bioactive red cedar wood chips added

Table 4.2. Conditions during the field tracer experiments.

Condition	Conventional	Innovative Red
Date of Tracer Test	Sept. 14th 2014	Sept. 20th 2014
Average Ambient Temperature (°C)	14	13
Number of days since last rain event (amount mm)	1 (6.7)	7 (6.7)
Experiment duration (hh:mm)	4:19	4:49
Influent Area (m^2)	0.29	0.29
Effluent Pan Area (m^2)	0.072	0.072
Ratio of Influent Area : Effluent Pan Area (-)	4.0	4.0
Tracer Volume injected (L)	428	392
Influent flow rate (L/min)	3.45	2.97
Effluent flow rate (ml/min)	200	225
Mass of NaCl injected (g)	380	380
NaCl concentration (mg/L)	888.63	969.99
GFP *E. coli* concentration injected (CFU/100 ml)	$6.90*10^5$	$8.32*10^6$

Table 4.3. Stormwater runoff concentrations for both TF filters measured weekly in the catch basin during the winter (November through March) and summer (April through September) and from grab samples (total n=7) along with literature values.
Reported are the average ± standard deviation for the runoff collected in the TF catch basin. TSS values were determined from grab samples of storm water entering the TF and were collected during rain events (n=7).

Constituent	Units	WINTER		SUMMER		Literature Values	Reference
		Catch Basin	Grab Sample	Catch Basin	Grab Sample		
pH	-	8.3 ± 1.6 (6.0 – 11.3)	8.5 ± 1.9 (6.6 – 10.2)	7.7 ± 1.1 (6.0 – 9.7)	6.6 ± 0.4 (6.0 – 7.1)	4.54 – 10.1	a, b, c, l, o, s
SC	µs/cm	4286 ± 5616 (20 – 20115)	6422 ± 6732 (875 - 15831)	92 ± 70 (18 – 378)	86 ± 44 (17 – 158)	25 – 30800	a, d, e
Chloride	mg/L	4796.8 ± 6937.7 (2.1 – 29480.0)	4049 ± 3150 (1800 - 7686)	89.0 ± 74.5 (18.7 – 366.6)	84.9 ± 47.0 (29.6 – 171.6)	0.2 – 11200	a, d, e, l, s
Nitrate as N	mg/L	44.9 ± 61.3 (1.4 – 249.6)	60.9 ± 82.6 (9.4 – 184.1)	5.8±3.8 (2.1 – 19.2)	7.9 ± 5.1 (2.4 – 18.5)	0.02 – 34.7	a, b, c, f, g, h, n, s
Phosphate	mg/L	-	-	0.49 ± 0.26 (0.0 - 0.94)	0.6 ± 0.2 (0.03 – 0.94)	0.005 – 2.3	a, b, c, g, n
TSS*	mg/L	32.2 ± 26.4 (1.8 – 92.0)	52.7 ± 28.9 (26.3 – 92.0)	10.3 ± 10.9 (0.5 – 46)	23.1 ± 15.9 (2.5 – 56.0)	1 – 46000	a, c, g, h, p, r
Copper	µg /L	60.3 ± 246.4 (b.d. – 1356)		2.2 ± 7.9 (b.d. – 36.3)		6 – 1800	a, g, h, q
Nickel	µg /L	3.3 ± 13.2 (b.d. - 68)		b.d.		4 – 170	a, g
Lead	µg /L	44.7 ± 163.1 (b.d. – 893.0)		6.9 ± 13.24 (b.d. – 118.0)		2 – 525	a, g, h, m, q
Zinc	µg /L	364.3 ± 1157.0 (b.d. – 5899.0)		27.1 ± 36.3 (n.d. – 118.0)		25 – 13000	a, g, h, q, r
$\sum PAH_{16}$	µg /L	1.9 ± 5.2 (b.d. – 21.1)		4.5 ± 2.1 (b.d. – 8.0)		0 – 22.6	a, l
E. coli	CFU/100 ml	$2*10^4 \pm 4*10^4$ $(0 – 2*10^5)$	$3*10^3 \pm 5*10^3$ $(0 – 8*10^3)$	$2*10^3 \pm 6*10^3$ $(0 – 2*10^4)$	$4*10^3 \pm 6*10^3$ $(0 – 2*10^4)$	$110 – 10^6$	g, i, j, k, p

*Results based on grab samples during rain storm, not on weekly sampling (n=6).
b.d. below method detection limit
References: a=(Göbel et al. 2007), b=(Reddy et al. 2014), c=(Kayhanian et al. 2007), d= (Ledford and Lautz 2014), e= (Corsi et al. 2010), f= (Han et al. 2006), g= (Grebel et al. 2013), h= (Hatt et al. 2009), i= (Dorfman and Rosselot 2012), j= (Schueler and Holland 2000), k= (Mallin et al. 2000)(Mallin et al. 2009), l= (Boving and Neary 2007), m=(Chong et al. 2013), n= (Mallin et al. 2009), o= (Deletic and Maksimovic 1998), p= (Surbeck et al. 2006), q= (Gilbert and Clausen 2006), r= (Davis et al. 2009), s=(Jasper et al. 2014)

Table 4.4. Summary of winter and summer average ± standard deviation TF removal rates were calculated based on Table 4.3 catch basin data, except for TSS*. For reference, literature reported removal values, RISM minimum removal requirements and StormTree © reported removal values for the parameters of interest are provided.
Bolded values meet or exceed RISM minimum removal percentages for the given contaminant.

Constituent	Units	Shale Tree Filter		Red Cedar Tree Filter		RISM Minimum Removal %	Reported TF Removal %	Literature Reported Removal %	Reference
		Winter % Change	Summer % Change	Winter % Change	Summer % Change				
pH	-	16.9	19.8	13.0	15.8	-	-	-	-
SC	µs/cm	52.9	-45.9	7.8	25.2	-	-	-	-
Chloride	mg/L	51.1	-22.6	-10.2	23.5	-	-	-	-
Nitrate as N	mg/L	**38.6**	-22.2	**62.9**	-8.4	30	>48	3–99	h, r, s, t, u
Phosphate	mg/L	~	**31.5**	-	**46.5**	30	>63	65–80	h, t
TSS*	mg/L	72.1	68.2	**91.4**	80.1	85	>85	54–99	h, u, v
Copper	µg /L	^	^	^	^	-	58–88	67–99	h, y
Nickel[#]	µg /L	9.7	~	97.1	~	-	58–88	+	z
Lead	µg /L	^	^	^	^	-	58–88	80–99	h, y
Zinc	µg /L	^	^	^	^	-	58–88	84–99	h, y
∑PAH$_{16}$	µg /L	47.1	7.0	80.6	21.2	-	>85	18.5–99	l, u
E. coli	CFU/100 ml	**75.4**	**84.9**	**80.15**	**90.29**	60	-	0–96	w, x

*Results based on grab samples during rain storm, not on weekly sampling (n=7).

^ Metal release from brass fitting on sampling pan.

+ Nickel release reported by authors, therefore not quantifiable.

~ Not measured in the case of Phosphate and not detected in influent, therefore unable to calculate removal rates.

- No standard set in RISM, no reported removal values for tree filters or other BMPs

[#] Only detected 4 times during sampling campaign.

References: a=(Göbel et al. 2007), b=(Reddy et al. 2014), c=(Kayhanian et al. 2007), d= (Ledford and Lautz 2014), e= (Corsi et al. 2010), f= (Han et al. 2006), g= (Grebel et al. 2013), h= (Hatt et al. 2009), i= (Dorfman and Rosselot 2012), j= (Schueler and Holland 2000), k= (Mallin et al. 2000)(Mallin et al. 2009), l= (Boving and Neary 2007), m=(Chong et al. 2013)), n= (Mallin et al. 2009), o= (Deletic and Maksimovic 1998), p= (Surbeck et al. 2006), q= (Gilbert and Clausen 2006), r= (Davis et al. 2009), s=(Jasper et al. 2014), t= (Davis et al. 2006), u= (UNHSC et al. 2007), v= (Davis 2007), w= (Karim et al. 2004), x= (Hathaway et al. 2009), y= (Davis et al. 2003), z=(Tromp et al. 2012), aa=(Boving and Neary 2007)

Table 4.5. Summary of field tracer test results and parameters tested.

Parameter	Conventional Sand/Shale Tree Filter	Innovative Red Cedar Tree Filter
Tracer Volume recovered (L)	51.8	60.3
Ratio Volume Injected : Volume recovered (-)	8.3	6.5
Expected Volume Recovered (L)	107	98
Volume Recovered % Error	51.5%	38.5%
Wetting Front (min)	30	23
Arrival time of tracer (min)	16	25
Mass of NaCl recovered (g)	35.2	48
Expected Mass of NaCl (g)	46.0	58.5
NaCl Mass Recovered % Error	23.5%	18.5%
GFP *E.* coli concentration recovered (CFU/100	$2.68*10^3$	$4.78*10^4$
Expected GFP *E.* coli concentration (CFU/100 ml)	$3.32*10^5$	$5.12*10^6$
Log_{10} Removal Value	2.09	2.02
% Removal	99.2	99.1

FIGURES
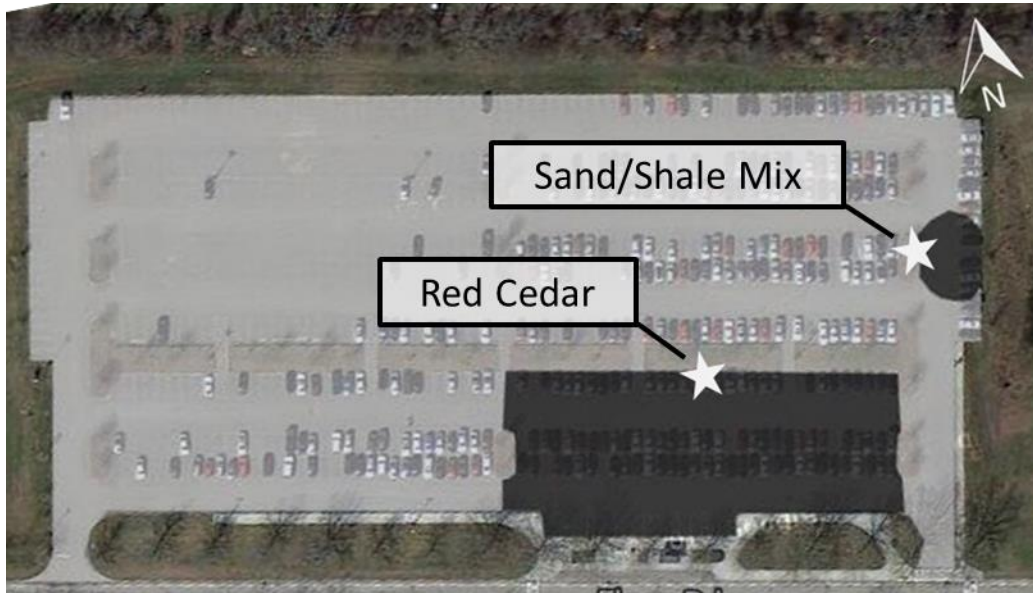
Figure 4.1. Overview of the parking lot where the two TF units are installed.
The stars denote the location of the tree filter. The contributing areas of both filters are outlined in dark grey; for the sand/shale mix TF the contributing area is 238 m^2 or 0.059 acres and for the red cedar TF the contributing area is 2978 m^2 or 0.736 acres, however a drain exists adjacent to the tree filter, thus capturing at least ½ of the runoff.

175
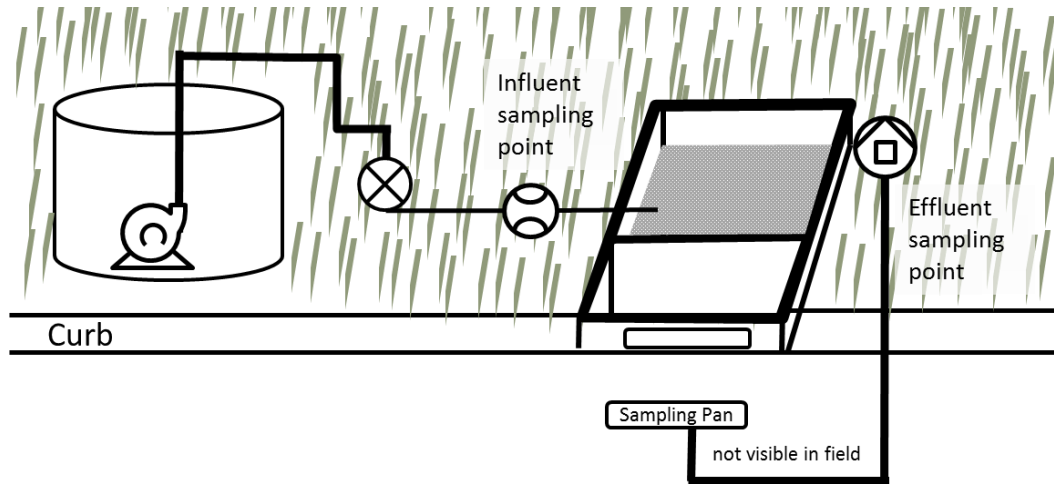
Figure 4.2. Schematic describing the setup of the field tracer experiment.
A submersible pump was used to pump the solution into the TF at ~3 L/min. Influent samples were taken immediately out of the hose whereas effluent samples were taken from a stainless steel sampling pan installed 28 inches (71 cm) below the infiltration surface.
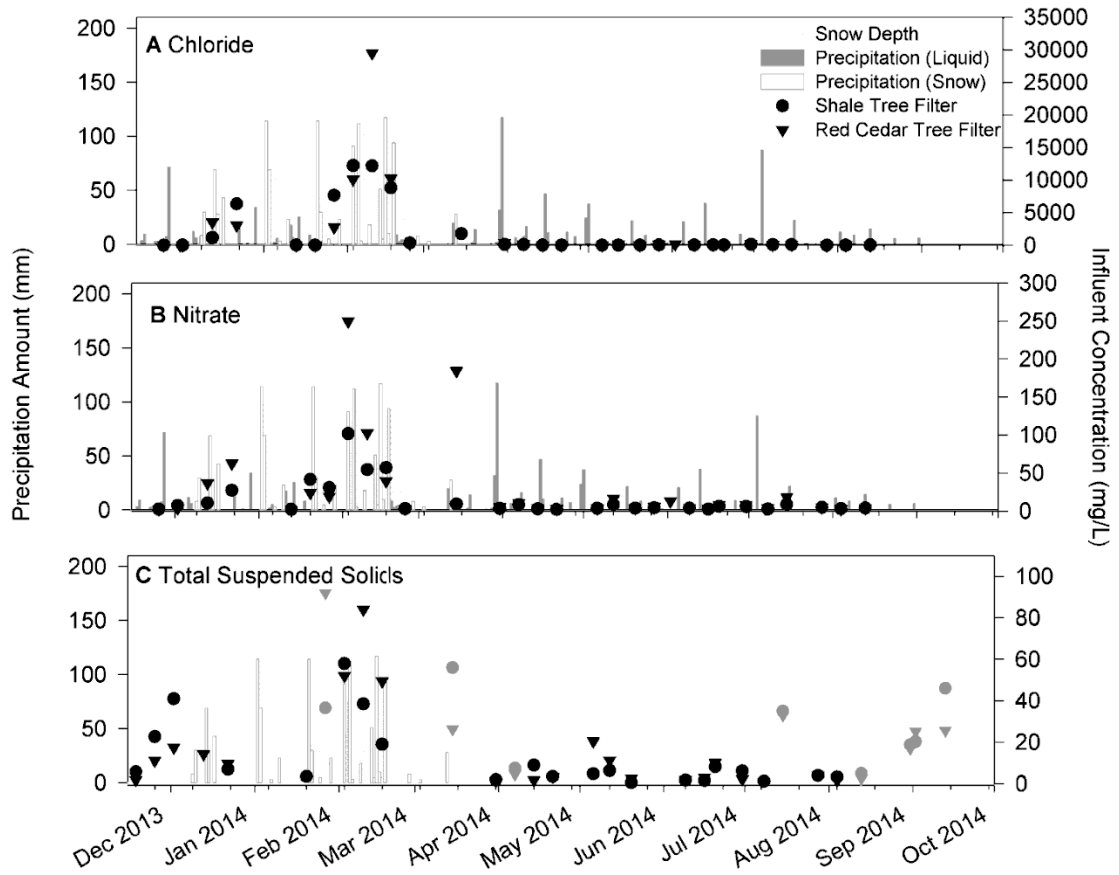
Figure 4.3. Relationship between snow depth, daily snow fall and influent concentrations of
A) Chloride, B) Nitrate, and C) total suspended solids measured in both tree filters.
The grey points in C) indicate grab samples during storm events.

177
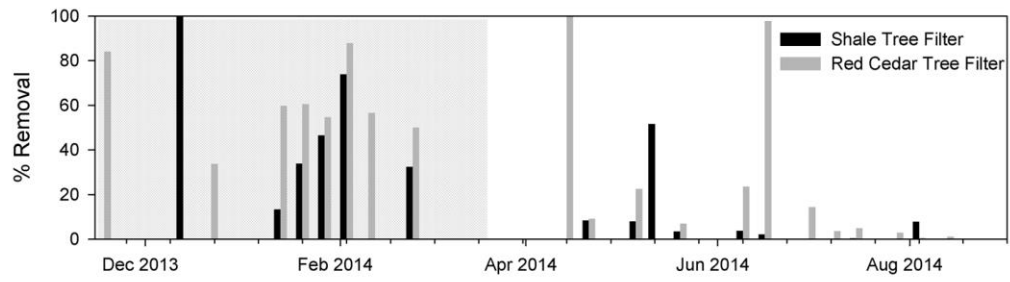
Figure 4.5. Comparison of PAH removal percentages achieved by the two different filter units over the course of the sampling period.
The gray area indicates the period during which snow was present and therefore the influent consisted of a combination of runoff and snowmelt.

178
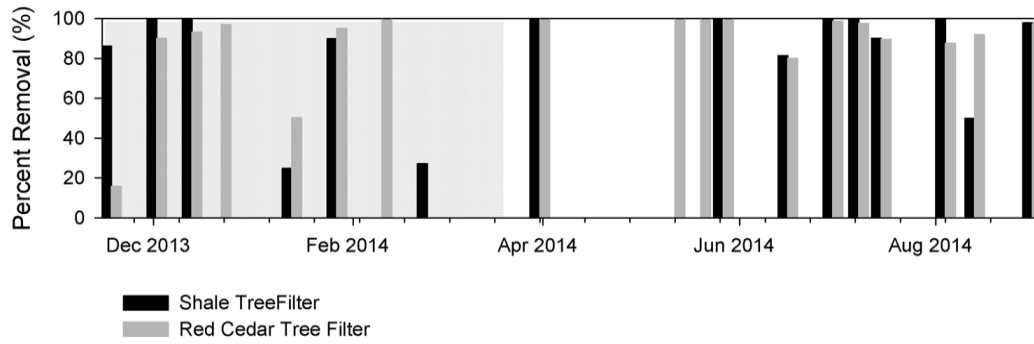
Figure 4.6. Comparison of *E. coli* removal percentages achieved by the two different filter units over the course of the sampling period.
The gray area indicates the period during which snow was present and therefore the influent consisted of a combination of runoff and snowmelt.

179

SUPPLEMENTAL INFORMATION

Bacteria Removal from Stormwater Runoff using Tree Filters: A comparison of a

conventional and an innovative system

Laura A. Schifman[1], Varun K. Kasaraneni[2], Ryan K. Sullivan[1], Vinka Oyanedel-Craver[2], Thomas B. Boving[1,2]

[1]Department of Geosciences, 9 E. Alumni Avenue, University of Rhode Island, Kingston, RI 02881
[2]Department of Civil and Environmental Engineering, 1 Lippitt Road, University of Rhode Island, Kingston, RI 02881

Contents:

Supplemental Figures

Figure S4.1. Mixing tank used to amend the red cedar wood chips with TPA.
The chain has a paddle attached that ensured proper mixing of the solution and the wood chips
during the amendment period that lasted 9 days.

Figure S4.2. Sampling set up during the field tracer experiment.
Effluent was pumped up to the surface using the Masterflex Environmental Sampler into a
Teflon beaker. The YSI Professional Plus logger was set up to log specific conductivity at five
minute intervals. At 15 minute intervals bacteria samples were taken from the effluent.

APPENDICES

**APPENDIX I – SUPPORTING CO-AUTHORED PUBLICATION:
ENHANCEMENT OF SURFACE RUNOFF QUALITY USING MODIFIED
SORBENTS**

Varun K. Kasaraneni *†, Laura A. Schifman ‡,Thomas B. Boving †‡, and Vinka
Oyanedel-Craver*†

† Department of Civil and Environmental Engineering,University of Rhode Island, 1
Lippitt Rd., Kingston, Rhode Island 02881, United States
‡ Department of Geosciences, University of Rhode Island, 9 E. Alumni Ave.,
Kingston, Rhode Island 02881, United States

ABSTRACT

The objective of this study was to develop and test nanoparticle and polymer based bioactive amended sorbents to enhance stormwater runoff treatment in best management practices (BMPs). Red cedar wood and expanded shale were the sorbents tested. Red cedar wood chips (RC) were modified with 3-(trihydroxysilyl) propyldimethyloctadecyl ammonium chloride (TPA) and silver nanoparticles (AgNP) at different mass loadings (0.36 mg/g, 0.67 mg/g, 0.93 mg/g for TPA and 0.33 mg/g and 0.68 mg/g for AgNP) to simultaneously improve the sorption of organic and inorganic contaminants and pathogenic deactivation in BMPs treating stormwater runoff. Unmodified expanded shale is often used as a filter material for stormwater treatment and was used as a base comparison. The results showed that TPA and AgNP loading onto red cedar increased the Langmuir maximum sorption coefficient (Q) for polycyclic aromatic hydrocarbons, up to 35 fold and 29 fold, respectively compared to unmodified red cedar. In case of heavy metals, Q for Lead increased with increased loading of TPA and AgNPs, whereas no significant change in the Q value for cadmium was observed, while for zinc and nickel sorption slightly decreased. The Langmuir maximum sorption coefficient of copper was higher for modified red cedar, however no correlation was observed with TPA or AgNPs loadings.

The log reduction value (LRV) for *Escherichia coli* using unmodified red cedar was <1 log, while modified red cedar exhibited LRV up to 2.90±0.50 log for 0.67 mg/g TPA-RC and up to 2.10±0.90 log for 0.68 mg/g AgNP-RC. Although

184

AgNP modified red cedar shows a comparable performance to TPA-RC, the high cost of production may limit the use of AgNP amended materials. While TPA modified red cedar has advantages of lower cost and lower toxicity, the fate, transport and environmental implications of TPA in natural environments has not been fully evaluated. The findings from this study show that if BMPs were to incorporate the modified red cedar, stormwater treatment of PAH and *E.coli* could be enhanced and the quality of the treated water will improve.

Keywords: Stormwater runoff treatment, Bacteria deactivation, Nanomaterials, Poly(trihydroxysilyl)propyldimethyloctadecyl ammonium chloride, Organic and inorganic contaminants, filter media, Sorption, Best management practices.

INTRODUCTION

Stormwater runoff contains polycyclic aromatic hydrocarbons (PAH), heavy metals, and pathogens that are discharged into natural surface and ground water bodies, impairing ecosystems and compromising human health [1-3]. During and after precipitation events, these contaminants commonly exceed the maximum contaminant level (MCL) standards in runoff and receiving water bodies [1, 4, 5.] High concentrations of heavy metals and petroleum hydrocarbons, such as PAHs [3] can compromise the ability to use stormwater for recharging aquifers or apply it in grey-water operations. The concentrations of *Escherichia coli* (*E.coli*) in runoff can exceed 10^4 colony-forming units (CFU) per 100 ml [1, 6] making stormwater runoff one of the major contributors of pathogens into surface and coastal waters [5, 7]. The sources of pathogens in stormwater runoff are attributed to wildlife or pets [8] and, to some degree to human fecal contamination [7]. Exposure to pathogens can lead to serious illness, such as gastroenteritis or cholera [5, 9].Ideally, structural BMPs should simultaneously attenuate organic, inorganic, and microbiological contaminants. However, most stormwater BMPs are only effective in treating heavy metals and petroleum hydrocarbons [10-12] through filtration and sorption [11-13]. They are largely ineffective in treating pathogens [14-17]. Previous studies showed that materials such as organoclays amended with quaternary ammonium compounds exhibit higher sorption for PAHs and metals [18-21]. 3-(trihydroxysilyl) propyldimethyloctadecyl ammonium chloride (TPA) is a quaternary ammonium polymer used as a disinfectant material in environmental and medical applications such as ceramic filters [22] and prosthetic devices [23]. Silver

nanoparticles (AgNPs) are another well-known antimicrobial agent. Impregnating filters media with AgNPs effectively removes pathogens from aqueous solutions [24, 25]. To our knowledge these nanoparticles and the TPA polymer have never been used for stormwater runoff treatment.

One commonly used BMP are tree filters, which consist of a subsurface biofiltration system that combines filtration, sorption, and phytoremediation processes for contaminant removal. However, previous studies have shown that contaminant removal is limited [13]. Hence, there is a need to find filter materials that can treat a variety of pollutants and can enhance the stormwater treatment performance of BMPs, such as tree filters. Hence, the objective of this study was to develop and test filter materials amended with nanoparticles or polymers that are capable of simultaneously removing PAHs, metals and pathogens from stormwater runoff. For this study, red cedar (RC) wood chips and expanded shale (ES) were selected as the filter matrices. Expanded shale is a commonly used filter material in commercial tree filters, while the rot-resistance of red cedar, even under saturated conditions [26], makes it a promising filter material. Here, we investigated the efficacy of TPA and AgNPs as amendments to RC and compared the contaminant removal performance to the unmodified expanded shale. The ultimate goal of this study is to offer new, multifunctional filter materials for stormwater treatment.

METHODS

Materials

Untreated red cedar wood was obtained locally (Liberty Cedar, West Kingston, RI). The wood was chipped and the fraction of RC chips retained between 10 mm and 3.3 mm sieves was used for the experiments. This sieve size was chosen to avoid fines and larger wood chips as the former can reduce hydraulic conductivity and the latter could induce preferential flow paths. Expanded shale (ES; trade name: Norlite), sorted between 13 mm and 19 mm (the size of ES used in tree filters), was obtained from Read Custom Soils (Hanover, MA). Both materials were washed and soaked in deionized water for a minimum of two weeks to leach out soluble matter. A 5% solution of 3-(trihydroxysilyl) propyldimethyloctadecyl ammonium chloride solution (TPA) (EPA product Reg.No.83019-2) was obtained from Biosafe (Pittsburgh, PA). AgNPs were synthesized via Tollens method as described elsewhere [27], using polyvinylpyrrolidone (PVP, average molecular weight: 29,000 g/mol, Sigma Aldrich) as a stabilizer.

Two common stormwater PAH compounds, Acenaphthene and Fluorene (purity grade of 98% or higher), were obtained from Sigma Aldrich. The PAH solutions were prepared as described elsewhere [21]. PAH standards and deuterated PAH standards were obtained from Ultra Scientific, USA. Metal reference standards containing 1000 mg/L $\pm$ 1% certified cadmium, copper, lead, nickel and zinc were obtained from Fisher Chemical. Sodium sulfate (Na_2SO_4), disodium phosphate (Na_2HPO_4) and

188

sodium nitrate ($NaNO_3$) were obtained from Sigma Aldrich. A nonpathogenic wild strain of *Escherichia coli* (*E. coli*) was obtained from IDEXX laboratories.

Material Characterization

The hydrodynamic size of AgNPs was measured with dynamic light scattering (DLS) using a Zetasizer (Nano ZS, ZEN 3600, Malvern) at 25°C in 1.3 mmol/L ionic strength medium comprised of NaCl. The surface area of the sorbents was measured using a multipoint BET method (Quantachrome NOWA 2200) with N_2 as the sorbate. The hydrophobicity of the materials was determined by measuring contact angle of deionized water to modified red cedar using a contact angle goniometer (Rame-Hart)

Laboratory Analysis

TPA concentrations were analyzed using Hach Method 8337 on a Hach DR 2800 Spectrophotometer. Metals, along with AgNPs (measured as total silver), were analyzed using a Perkin Elmer inductively coupled plasma optical emission spectrometer (ICP-OES) 3100 XL. The fraction of silver nanoparticles and Ag ions were measured by filtering the samples through Amicon ultra-14 centrifugal filters (Millipore) at 3500 rpm for 30 minutes.

All PAH Samples were prepared according to EPA method 610 and analyzed using a gas chromatograph coupled with a mass spectrometer (Shimadzu GC-MS QP2010). PAH samples were spiked with acenaphthene-d10 to quantify the extraction efficiency.

189

E. coli concentrations were determined using membrane filtration, applying m-FC broth with Rosolic Acid (Millipore) and incubating the samples at 44.5 ˚C for 24 hrs. To enumerate *E. coli* sorbed onto the solid phase, samples were sonicated (QSonica, Q125) twice for 10 minutes at 20% amplitude in phosphate buffer solution. The liquid phase was then analyzed by the aforementioned method.

Experimental methodology

The laboratory experiments were divided into two phases: during the first phase, the loading capacity and stability of TPA and AgNPs amendments on RC and ES were tested. This was achieved through batch sorption isotherms (loading capacity) followed by sequential desorption for a week (stability). In the second phase, building on the isotherm results obtained during the first phase, RC was modified with different TPA and AgNPs loadings and evaluated in batch experiments for sorption capacity of PAHs and heavy metals, and also *E.coli* disinfection performance.

Phase I

Nanoparticle and polymer loading capacity of sorbents

Batch isotherms were carried out in triplicates to determine the loading capacity of TPA and AgNP onto the sorbent materials. For all experiments, a 1.3 mmol/L ionic strength medium using sodium chloride (NaCl) was used as a background solution in order to mimic surface water conditions in Rhode Island [27]. Detailed experimental procedures are in the supporting information Text S1. After

conducting the sorption experiment the samples were decanted and dried at 60°C.

Desorption of TPA and AgNP from modified sorbent materials was determined

through sequential desorption in DI water for a minimum of 24 hrs and up to 168 hrs,

i.e. until aqueous concentrations were below the method detection limit of 0.2 mg/L

for TPA and 0.01 mg/l for Ag. The method detection limit for Ag is below EPA MCL

of 0.1mg/l, while for TPA no EPA MCL limit is defined. TPA is categorized as

slightly toxic with oral LD_{50} above 5000 mg/l. The results from the desorption

experiment were reported as total silver and TPA, respectively. The fraction of

desorbed AgNPs and Ag ions were also measured and reported in supporting

information Table S2.

Phase II

Organic and inorganic contaminant removal efficiency of the modified sorbents

Using the results obtained in Phase I, RC was modified at different loadings of

TPA and AgNPs to assess the ability to remove organic, inorganic, and

microbiological contaminants as a function of loading. This process was required to

adapt the lab-scale amending procedure to a large scale due to the large amount of the

material required to perform all tests; details of this procedure is presented in the

supplemental information Text S2. Due to disintegration of ES when agitated for

modification, this material was no longer tested. However, unmodified ES was used

as baseline comparison for modified RC.

Batch tests were carried out to determine the sorption capacity of the modified and unmodified sorbent materials for PAHs and heavy metals. A synthetic stormwater runoff stock solution, containing PAHs, metals and inorganic salts, was prepared (Table S3). For this part of the study all experimental solutions were adjusted to a pH of 5.5. Details of batch test are described in the supporting information Text S3. Visual MINTEQ Ver.3.0, an equilibrium speciation software, was used to determine the speciation of metals in the synthetic runoff.

Microbiological contaminant removal efficiency by the modified sorbents

Two of the modified RC sorbents (0.6 mg/g TPA-RC and 0.6 mg/g AgNP-RC) along with unmodified RC and ES were selected to test bacteria deactivation efficiency. Five different initial *E. coli* concentrations relevant to stormwater runoff, ranging from 10^2-10^6 CFU/100ml were used in the experiments [6,7]. Detailed experimental procedures are provided in supporting information Text S4.

Cost analysis and limitations

The cost for the preparation of modified red cedar was calculated based on material cost incurred from lab scale modifications. The total initial cost calculation for incorporating modified red cedar in a full scale tree filter BMP system was based on a 5 cm thick layer of modified RC for a tree box filter with dimensions 1.22m x 1.83m and drainage area of 0.5 acre.

RESULTS AND DISCUSSION

Material Characterization

The average hydrodynamic size of AgNPs was 38.5±3.5 nm. The surface area of the modified RC increased with increasing loading of AgNPs and TPA for example, the surface area increased from 4.89±0.092 m^2/g for UM-RC to 7.98 ±0.42 m^2/g and 6.01±0.23 m^2/g for 0.9 TPA-RC and 0.6 AgNP-RC respectively. The contact angle of deionized water for modified RC increased with loading of TPA and AgNPs (Table S4). The contact angle was greater than 90° for, 0.9TPA-RC and was greater than 70° for 0.6TPA-RC 0.6AgNp-RC indicating that modification with TPA and AgNPs made the material more hydrophobic.

Phase I

Nanoparticle and polymer loading capacity of sorbents

The TPA batch sorption on RC showed that between 37% and 98 % of the initial mass of TPA in the aqueous phase was sorbed to the RC, with a maximum loading of 0.93 ± 0.03 mg/g. For expanded shale (ES) the total mass of TPA sorbed was in the range of 30% to 75%, with a maximum loading of 0.30 ± 0.03 mg/g. During the sequential desorption study, only 0.54 ± 0.30% of the TPA initial mass sorbed was released from RC, while for ES it was 1.13 ± 0.60%.

The higher sorption of TPA to RC is likely due to stronger interaction with the wood's molecules, such as lignin and cellulose [28]. The non-linear shape of the sorption isotherm model (Figure S1a) supports that TPA predominantly sorbs onto RC rather

193

than diffusing into it, which would have been by linear sorption isotherm, indicative of, Fickian transport processes. In comparison, ES contains little or no organic matter due to the extreme heating during expansion process [29]. This likely resulted in fewer sorption sites for TPA. The linearity of the ES isotherm (Figure S1 a) indicates that TPA may be partitioning into to porous spaces in the shale.

The amount of AgNP sorption to RC depended on the initial concentration of the AgNP solution. That is, RC sorbed up to 97% when the initial concentrations of AgNP were below 21 mg/L. However, the AgNP sorption to RC decreased to 75% and 10% when initial concentrations were at 52 and 104 mg/L, respectively. Maximum loading of AgNPs to RC was 0.63 ± 0.10 mg/g.

Independent of the initial solution concentration, ES sorbed 96% to 99% of the initial mass of AgNPs with a maximum loading of 0.40 ± 0.02 mg/g. In the case of AgNPs, desorption was variable for RC and depended on the AgNP mass sorbed to the sorbent. That is, 2.50 ± 2.94 % were desorbed if the AgNP loading was low (0.33 mg/g) and 14.4 ± 9.28 % if the loading was high (0.63 mg/g) (Figure 1b). Depending on the initial aqueous phase concentration of AgNP, between 88% and 98% of the mass desorbed is in the form AgNPs, while the remainder is in form of Ag ions (Table S2). For ES, desorption of AgNP was <0.01% relative to the initial mass of AgNP sorbed, regardless of the initial aqueous phase AgNP concentration or mass sorbed (Figure 1b). The fraction of AgNPs and Ag ions desorbed from ES were below method detection limit. The uptake of AgNPs can be due to trapping of AgNPs in the

194

pores of the sorbent material and sorption due to van der Waal forces of attraction between AgNPs and the sorbents.

At concentrations below 52 mg/L, the hydrodynamic size of AgNPs is ≤40 nm, whereas at higher concentrations (104 mg/l), the average hydrodynamic size of AgNPs increased to >80 nm, due to aggregation. This phenomenon was confirmed by TEM imaging (Figure S2). The larger size could have hindered the sorption of AgNPs to the micropores in wood chips, whereas it did not reduce the uptake by ES, due to the large pores present in expanded shale [29].

Phase II

Organic and inorganic contaminant removal efficiency of the modified sorbents

The results of the batch isotherm experiments for PAHs and heavy metals onto unmodified ES as well as unmodified and modified RC are nonlinear (Figure 2). Assuming that the number of sorption sites is limited, the results were fitted to the Langmuir model:

$$q = \frac{Qb\, C_e}{(1+bC_e)} \qquad \text{Equation 1}$$

where q is the amount of solute sorbed (µg/g), Q is the Langmuir maximum amount of solute that can be absorbed by the sorbent (µg/g), b is the Langmuir adsorption coefficient, and C_e is the equilibrium aqueous solute concentration (µg/l). The results from batch experiments show that during the experimental conditions RC and ES had reached saturation, indicating a limited number of sorption sites (Figure S3), thus

confirming the appropriateness of the Langmuir type isotherm model. In order to compare the performance of all the materials the Langmuir type model was applied to all datasets. The isotherm parameters for PAHs and metals for all sorbents were obtained using SigmaPlot 11 (Systat Software Inc.) (Table 2). Except for ES, the goodness-of-fit using the Langmuir model was high (R^2 >0.90) for all isotherms.

Polycyclic Aromatic Hydrocarbons

The Langmuir maximum sorption capacity of PAH for ES is much lower compared to both unmodified and modified RC (Table 2), which may be a result of the vitrification process the expanded shale has undergone during thermal expansion, making it more inert by removing potential organic sorption sites [29]. In case of RC, the value of Q for acenaphthene and fluorene increased with increased loadings of TPA and AgNPs (Figure 2). For example, for acenaphthene, *Q* increased from 48.6 µg/g for UM-RC to 1703.5 µg/g for 0.9TPA-RC and to 1429.2 µg/g for 0.6AgNP-RC (Table 2).

Finally, the modification with TPA and AgNPs increased the hydrophobicity of the RC as confirmed by contact angle measurements (Table S4). While the C_{18} chain of the TPA molecule is enhancing the hydrophobicity of RC, in case of AgNP-RC it is the PVP coating on AgNPs. The increase in surface hydrophobicity of RC resulted in increase of PAH sorption after the amendment of RC with both AgNP and TPA. This is due to hydrophobic interactions between PAH and modified RC . In addition PAHs can also partition on to organic phase created by TPA and PVP on modified RC.

196

Heavy Metals

The results obtained from the Visual MINTEQ model show that at pH 5.5, the

metal speciation in the synthetic stormwater is dominated (73.5 % to 87.6 %) by the

divalent cations (Pb^{+2}, Cd^{+2},Zn^{+2},Ni^{+2}, and Cu^{+2}) and otherwise consists of

predominantly sulfate salts of e.g. $PbSO_4$ (Table S6). The percentage of metals

available for sorption was taken into account for batch isotherm calculations and the

Langmuir isotherm model was used for quantitative comparison of the sorption

capacity between the unmodified and modified materials.

Of all sorbents tested, the unmodified ES exhibited the lowest *Q* for all metals

(Table 2). In case of RC, *Q* for Pb increased from 85.14 µg/g for unmodified RC to

625 µg/g for 0.9TPA-RC and 153.8 µg/g 0.6AgNP-RC (Table 2). For Cu, the TPA

and AgNPs amendments enhanced the sorption of Cu compared to unmodified RC.

However, no correlation could be identified between amendment loading and Cu

sorption (Table 2). The modification of RC with TPA and AgNPs did not have an

impact on *Q* for Cd and slightly decreased in case of Zn and Ni. (Table 2).

The enhanced maximum sorption capacity *Q* of modified RC for Pb and Cu, as

well as the unchanged *Q* for Cd indicates that modification of RC is not limiting the

retention of these metals, in fact increases it. The hydroxyl groups present in the TPA

molecule provides attractive sorption sites for metals, whereas the oxygen and

nitrogen present in PVP can form metal complexes [30]. The increase in Pb and Cu

sorption could be due to bonding with hydroxyl groups on TPA and formation of

complexes with PVP present on AgNPs. In addition, the increase in surface area of

modified RC (Table S4) likely provided more sorption sites for these metals.

However, the reasons for the slight decrease in Q for Zn and Ni (Table 2) is unclear.

No correlations with physiochemical properties or interactions with the amendments

were found to explain the different sorption behavior of these metals to modified RC.

Therefore, further studies are required to gain insight on the sorption behavior of these

metals onto modified RC.

Microbiological contaminant removal efficiency of the modified sorbents

Two modified sorbents (0.6TPA-RC and 0.6AgNP-RC) were tested for

bacteria deactivation efficiency and compared to unmodified RC and ES. The

disinfection performance of the materials was calculated as log removal value (LRV):

$$\text{LRV} = \log (\text{initial } E. \text{ coli concentration}) - \log (\text{final } E. \text{ coli concentration})$$

Equation 2

The final E. coli concentration is the total E. coli present in the aqueous phase and

sorbed to the sorbents. The average LRV for the unmodified RC and ES was always

below 1 (Figure 3). For the modified materials, the average LRVs ranged from 1.74 ±

1.04 log to 2.90 ± 0.50 log for 0.6TPA-RC. In case of 0.6AgNP-RC, the average LRV

ranged from 2.03 ± 0.60 log to 2.10 ± 0.90 log. Overall, the deactivation performance

shows that the modified materials are significantly more effective at deactivating

bacteria compared to unmodified ES and RC ($p<0.001$) (Figure 3). Previous studies

198

showed that the impregnation of TPA and AgNPs onto surfaces enhanced the deactivation of *E. coli* [22] Several mechanisms have been suggested for disinfection using AgNPs. These include damage to bacteria by pitting the cell membrane, lysis of cells caused by silver ion release, or damage of the cell by the reactive oxygen species formed on the surface of the AgNPs. The biotoxicity of TPA has been explained mainly by the positively charged quaternary amine groups attracting *E. coli* and C_{18} groups piercing membrane and causing cell disruption [31].

Cost analysis and limitations

The contaminant removal performance and bacterial deactivation of both, TPA and AgNP modified RC compare well and significantly enhanced water quality compared to unmodified RC. However, the selection of which antimicrobial agent to use for modification will be driven by the costs of amending the materials. The initial modification cost for RC using AgNP is higher compared to TPA (Table S7). For instance, to modify 1 kg RC at similar loadings (~0.6 mg/g), an AgNP modification costs $57.90/kg for versus $10.30/kg for TPA (Table S7). When installing these amendments in a field scale BMP, such as a tree filter, less than 8% of the total initial cost incur in case of TPA amendment compared to 35 % increase for AgNP. The toxicological data as determined by previous studies also suggests that TPA is less toxic compared to AgNPs (Table S8). Further, the antimicrobial performance of AgNPs primarily depends on silver ion release. Over time, the silver ion release from AgNP may decrease, and thus could result in the reduction of antimicrobial efficiency.

Overall, TPA has a cost advantage over AgNPs in addition to lower toxicity and better contaminant removal performance. The long-term performance of TPA is currently unknown and requires further studies. These need to include investigations of TPA behavior at different water chemistry conditions.

In summary, this study reveals that conventional materials such as unmodified expanded shale and red cedar have very limited pathogen treatment capabilities. However, RC amended with TPA and AgNPs both increased antimicrobial properties by orders of magnitude. The amendments also enhanced PAH sorption while not hindering the sorption of most metals. These findings show that modified sorbent materials can enhance the stormwater treatment efficiency of BMP filters. The high cost involved in amending the sorbent with AgNP and its higher toxicity may prevent the use of AgNP modified materials in BMPs. Conversely, TPA modified RC has the advantage of lower cost, lower toxicity and higher contaminant and pathogen removal performance, making it the overall better choice as a filter medium for use in BMPs, such as tree filters. However, the long term performance and effectiveness of TPA modified RC under natural environmental conditions has yet to be studied.

TABLES

Table 1: Amendment loadings achieved by exposing red cedar to aqueous solutions of either TPA or AgNPs.

Bioactive agent	Concentrations (mg/l)	Amendments (Abbreviation)
TPA	26	0.36 mg/g TPA Red Cedar (0.3TPA-RC)
	72	0.67 mg/g TPA Red Cedar (0.6TPA-RC)
	150	*0.93 mg/g TPA Red Cedar (0.9TPA-RC)
AgNP	20.8	0.33 mg/g AgNP Red Cedar (0.3AgNP-RC)
	52	*0.68 mg/g AgNP Red Cedar (0.6AgNP-RC)

*Maximum possible loading.

Table 2: Langmuir maximum sorption capacity (Q) for PAHs and metals for all sorbents. Both, Langmuir adsorption coefficients (b) and goodness-of-fit values (R^2) are provided in the supplementary information.

Contaminant		ES	Unmodified-RC	0.3TPA-RC	0.6TPA-RC	0.9TPA-RC	0.3AgNP-RC	0.6AgNP-RC
Acenaphthene	Q (µg/g)	2.3	48.6	114.6	133.7	1703.5	282.7	1429.2
Fluorene	Q (µg/g)	1.2	26.1	43.9	83.8	391.1	87.7	380.0
Lead	Q (µg/g)	33	85.14	193.3	352.6	625.1	148.4	153.8
Cadmium	Q (µg/g)	6.3	13.0	13.7	11.8	14.2	13.8	15.1
Copper	Q (µg/g)	18.7	62.3	173.4	81.8	93.2	127.1	97.06
Zinc	Q (µg/g)	31.7	124.9	95.6	84.1	95.7	106.7	45.8
Nickel	Q (µg/g)	11.6	35.3	13.25	15.8	20.36	14.23	9.2

FIGURES
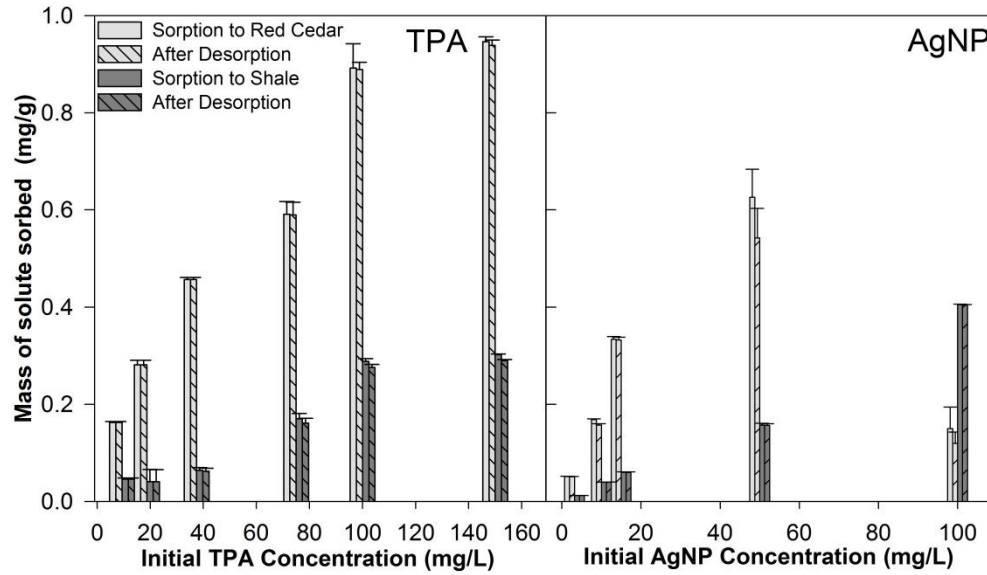
Figure 1: Polymer and nanoparticle loading capacity of sorbents. Mass sorbed during sorption experiments and mass retained after desorption for (a) TPA and (b) AgNPs on red cedar (RC) and expanded shale (ES). The data suggests that once amended, the active compounds remain largely fixed on the substrate.
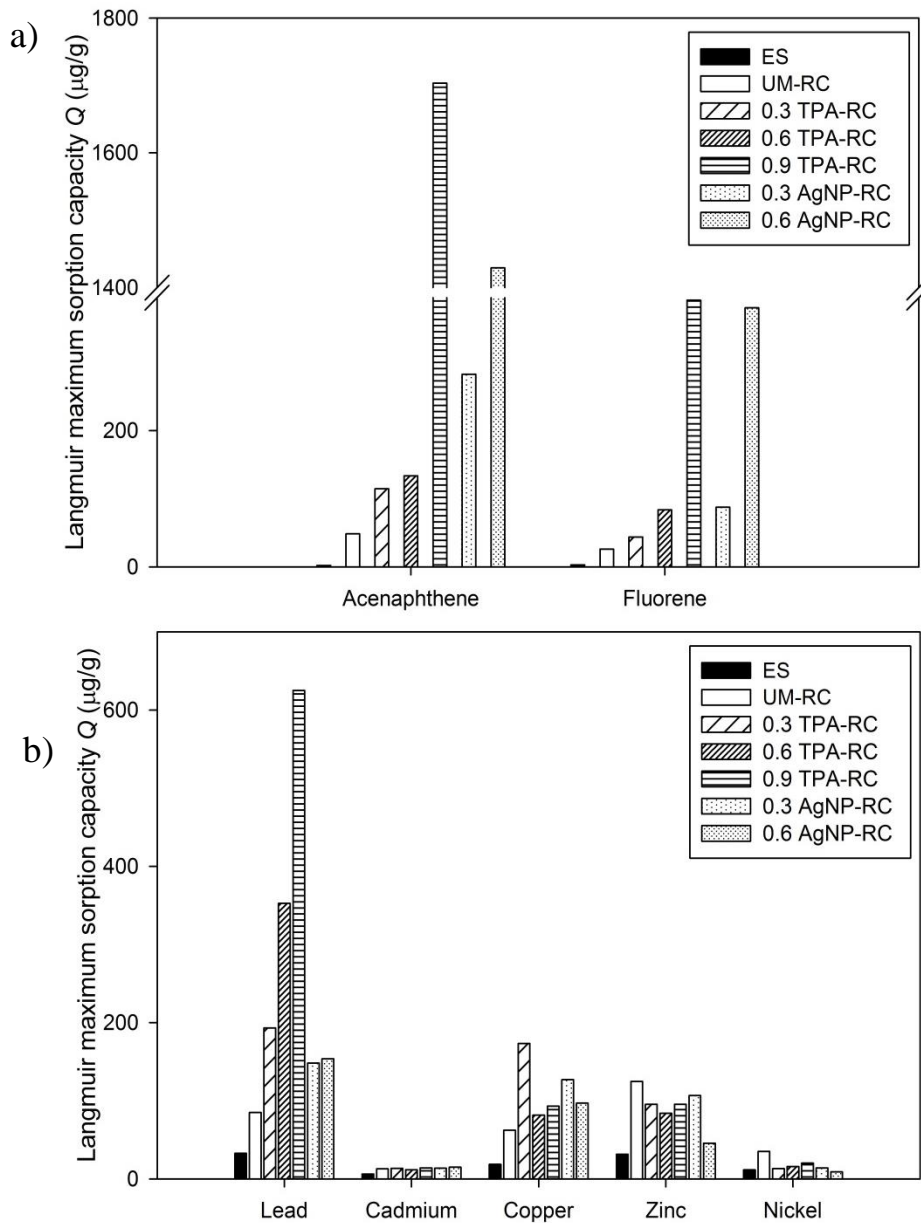
Figure 2: Langmuir maximum sorption coefficient *Q* of a) PAHs and b) heavy metals for expanded shale (ES), unmodified red cedar (UM-RC) and RC modified with TPA and AgNPs.
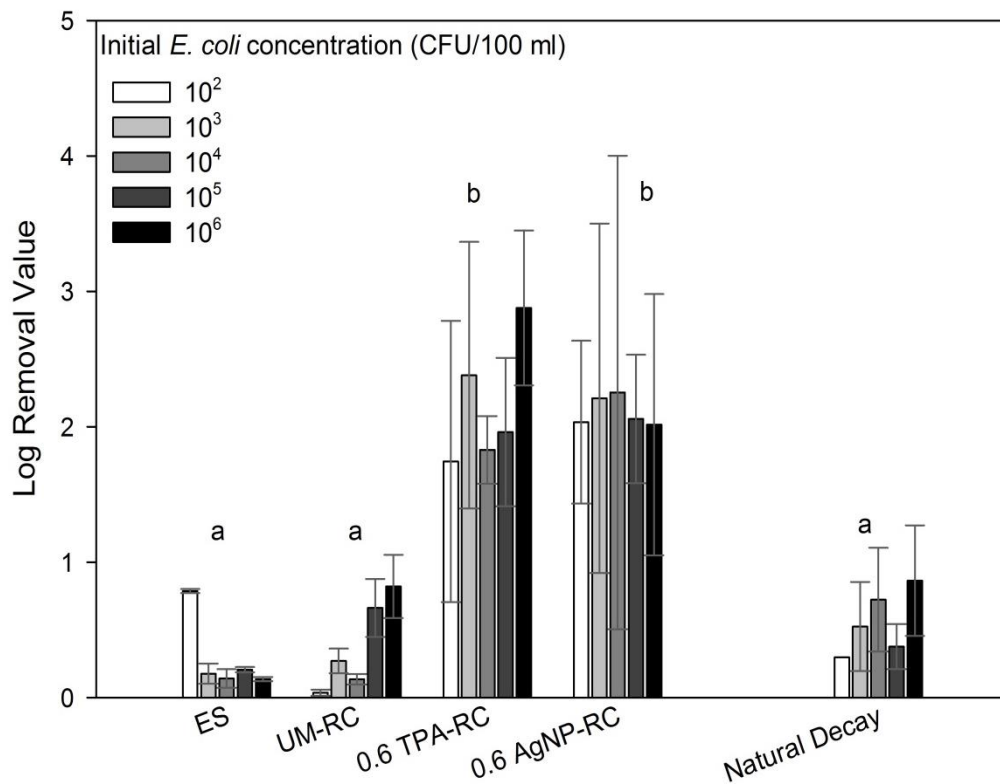
Figure 3: Deactivation of *E. coli* at increasing concentrations using unmodified and modified materials (0.6 TPA-RC, and 0.6Ag-RC). Both the 0.6 TPA-RC and 0.6Ag-RC were significantly more effective at deactivating *E. coli* compared to the unmodified materials (p<0.001). The data presented is an average of nine samples. Individual significant differences between the materials are indicated by the letters a and b in the figure.

ACKNOWLEDGEMENTS

SUPPORTING INFORMATION

Experimental procedures Text S1-S4, supporting graphics and images in Figures S1-S3 and additional information in Tables S1-S8. This material is available free of charge via the Internet at http://pubs.acs.org.

For Table of Contents Use Only

Enhancement of Surface Runoff Quality Using Modified Sorbents

[1]Kasaraneni, Varun K*; [2]Schifman, Laura A.; [1,2]Boving, Thomas B; [1]Oyanedel-Craver, Vinka*

[1]Department of Civil and Environmental Engineering, University of Rhode Island, 1 Lippitt Rd, Kingston, RI USA 02881

[2]Department of Geosciences, University of Rhode Island, 9 E. Alumni Ave, Kingston, RI USA 02881

*Corresponding author

Phone: 401 874 2784. Fax: 401 874 2786.

E-mail: craver@mail.uri.edu.   vkasaraneni@my.uri.edu.
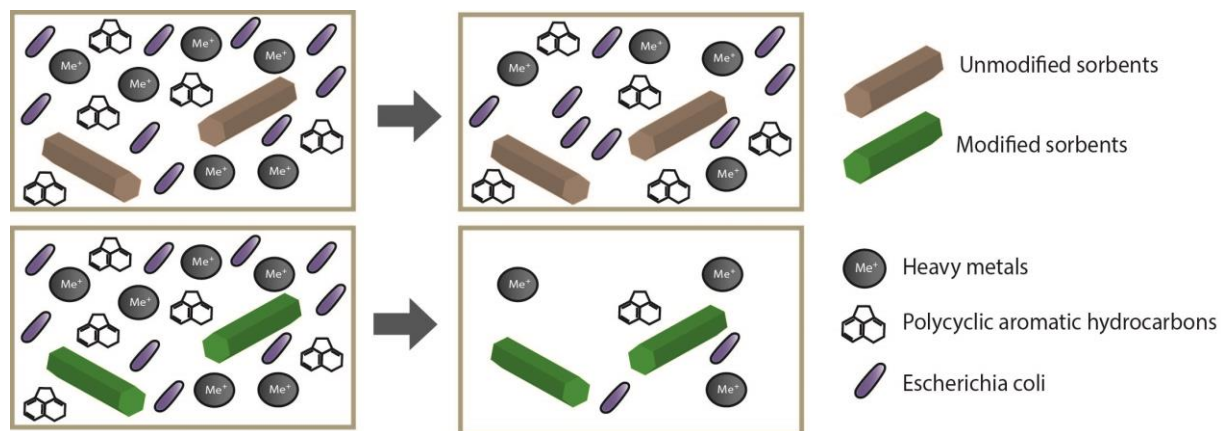
Synopsis

Developed and tested materials for stormwater runoff treatment. Use of these modified materials can effectively retain pollutants, such as PAHs, heavy metals, and bacteria, and prevent them from entering in to water bodies during and after storm events.

207

REFERENCES

(1). Ahn, J. H.; Grant, S. B.; Surbeck, C. Q.; DiGiacomo, P. M.; Nezlin, N. P.; Jiang, S. Coastal water quality impact of stormwater runoff from an urban watershed in southern California. *Environ. Sci. Technol.* **2005**, *39*, 5940-5953.

(2). Brown, J. N.; Peake, B. M. Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff. *Sci. Total Environ.* **2006**, *359*, 145-155.

(3). Göbel, P.; Dierkes, C.; Coldewey, W. G. Storm water runoff concentration matrix for urban areas. *J. Contam. Hydrol.* **2007**, *91*, 26-42.

(4). McLellan, S.; Salmore, A. Evidence for localized bacterial loading as the cause of chronic beach closings in a freshwater marina. *Water Res.* **2003**, *37*, 2700-2708.

(5). Dorfman, M.; Rosselot, K. Testing the Water: A Guide to Water Quuality at Vacation Beaches. *Natural Resources Defense Council* **2012**, *22*.

(6). Schueler, T. R.; Holland, H. Microbes and urban watersheds: concentrations, sources, and pathways. *The Practice of Watershed Protection* **2000**, 74-84.

(7). Parker, J.; McIntyre, D.; Noble, R. Characterizing fecal contamination in stormwater runoff in coastal North Carolina, USA. *Water Res.* **2010**, *44*, 4186-4194.

(8). Mallin, M. A.; Williams, K. E.; Esham, E. C.; Lowe, R. P. Effect of human development on bacteriological water quality in coastal watersheds. *Ecol. Appl.* **2000**, *10*, 1047-1056.

(9). Stewart, J. R.; Gast, R. J.; Fujioka, R. S.; Solo-Gabriele, H. M.; Meschke, J. S.; Amaral-Zettler, L. A.; del Castillo, E.; Polz, M. F.; Collier, T. K.; Strom, M. S. The coastal environment and human health: microbial indicators, pathogens, sentinels and reservoirs. *Environ. Health* **2008**, *7*, S3.

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

(11). Boving, T. B.; Neary, K. Attenuation of polycyclic aromatic hydrocarbons from urban stormwater runoff by wood filters. *J. Contam. Hydrol.* **2007**, *91*, 43-57.

(12). Genç-Fuhrman, H.; Mikkelsen, P. S.; Ledin, A. Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater: Experimental comparison of 11 different sorbents. *Water Res.* **2007***, 41*, 591-602.

(13). UNHSC; Roseen, R.; Ballestero, T.; Houle, J. UNH Stormwater Center 2007 Annual Report. **2007**.

(14). Zhang, X.; Lulla, M. Evaluation of pathogenic indicator bacteria in structural best management practices. *Journal of Environmental Science and Health Part A* **2006***, 41*, 2483-2493.

(15). Scholes, L.; Revitt, D. M.; Ellis, J. B. A systematic approach for the comparative assessment of stormwater pollutant removal potentials. *J. Environ. Manage.* **2008***, 88*, 467-478.

(16). Davis, A. P.; Hunt, W. F.; Traver, R. G.; Clar, M. Bioretention technology: Overview of current practice and future needs. *J. Environ. Eng.* **2009***, 135*, 109-117.

(17). Li, H.; Davis, A. P. Water quality improvement through reductions of pollutant loads using bioretention. *J. Environ. Eng.* **2009***, 135*, 567-576.

(18). Celis, R.; Hermosin, M. C.; Cornejo, J. Heavy metal adsorption by functionalized clays. *Environ. Sci. Technol.* **2000***, 34*, 4593-4599.

(19). Oyanedel-Craver, V. A.; Smith, J. A. Effect of quaternary ammonium cation loading and pH on heavy metal sorption to Ca bentonite and two organobentonites. *J. Hazard. Mater.* **2006***, 137*, 1102-1114.

(20). Lee, S. M.; Tiwari, D. Organo and inorgano-organo-modified clays in the remediation of aqueous solutions: An overview. *Appl. Clay. Sci.* **2012***, 59*, 84-102.

(21). Kasaraneni, V.; Kohm, S. E.; Eberle, D.; Boving, T.; Oyanedel-Craver, V. Enhanced containment of polycyclic aromatic hydrocarbons through organic modification of soils. *Environmental Progress & Sustainable Energy* **2013**.

(22). Zhang, H.; Oyanedel-Craver, V. Comparison of the bacterial removal performance of silver nanoparticles and a polymer based quaternary amine functiaonalized silsesquioxane coated point-of-use ceramic water filters. *J. Hazard. Mater.* **2013**.

(23). Oosterhof, J. J.; Buijssen, K. J.; Busscher, H. J.; van der Laan, Bernard FAM; van der Mei, Henny C Effects of quaternary ammonium silane coatings on mixed fungal and

bacterial biofilms on tracheoesophageal shunt prostheses. *Appl. Environ. Microbiol.* **2006**, *72*, 3673-3677.

(24). Dankovich, T. A.; Gray, D. G. Bactericidal paper impregnated with silver nanoparticles for point-of-use water treatment. *Environ. Sci. Technol.* **2011**, *45*, 1992-1998.

(25). Rayner, J.; Zhang, H.; Lantagne, D.; Schubert, J.; Lennon, P.; Craver, V. O. Laboratory investigation into the effect of silver application on the bacterial removal efficacy of filter material for use on locally-produced ceramic water filters for household drinking water treatment. *ACS Sustainable Chemistry & Engineering* **2013**.

(26). Bilby, R. E.; Heffner, J. T.; Fransen, B. R.; Ward, J. W.; Bisson, P. A. Effects of immersion in water on deterioration of wood from five species of trees used for habitat enhancement projects. *N. Am. J. Fish. Manage.* **1999**, *19*, 687-695.

(27). Zhang, H.; Smith, J. A.; Oyanedel-Craver, V. The effect of natural water conditions on the anti-bacterial performance and stability of silver nanoparticles capped with different polymers. *Water Res.* **2012**, *46*, 691-699.

(28). Boving, T. B.; Rowell, R. In *Environmental Applications of Lignocellolusic Filter Materials;* Rowell, R., Ed.; Sustainable Development in the Forest Products Industry; UFP Editions: Lisbon, Portugal, 2010.

(29). Forbes, M. G.; Dickson, K. R.; Golden, T. D.; Hudak, P.; Doyle, R. D. Dissolved phosphorus retention of light-weight expanded shale and masonry sand used in subsurface flow treatment wetlands. *Environ. Sci. Technol.* **2004**, *38*, 892-898.

(30). Tokman, N.; Akman, S.; Ozeroglu, C. Determination of lead, copper and manganese by graphite furnace atomic absorption spectrometry after separation/concentration using a water-soluble polymer *Talanta* **2004**, *63*, 699-703.

(31). Kim, H. W.; Kim, B. R.; Rhee, Y. H. Imparting durable antimicrobial properties to cotton fabrics using alginate–quaternary ammonium complex nanoparticles. *Carbohydr. Polym.* **2010**, *79*, 1057-1062.

**APPENDIX II – SAMPLING PROTOCOL DEVELOPED FOR RHODE
ISLAND STORMWATER DEMONSTRATION FACILITY**

OVERVIEW

Objective: Water quality parameters and runoff contaminants sampled 1/week at all
three tree filters. Contaminants are measured in the catch basin, the influent, and
effluent (sampling pan at bottom of tree filter unit) of the tree filter matrix.
Soil/Water quality parameters: pH, Electrical Conductance, Temperature, Soil
Moisture
Contaminants: *E. coli,* Polycyclic Aromatic Hydrocarbons[1], Heavy Metals[2], Nitrate
(NO_3^-), Phosphate (PO_4^-), Chloride (Cl^-),Total Suspended Solids (TSS)
Field Gear:
Latex Gloves
Environmental Sampler peristaltic pump with Tygon tubing
11x1 L amber glass bottles with Teflon lined caps (4 influent samples, 4 effluent
samples, 3 catch basin samples -> 11 total). Labelled appropriately (Example: TF type
& sample type (influent, pan, or catch basin), initials, date).
pH meter, YSI Multimeter with Electrical Conductivity, Nitrate, Chloride and
Temperature probes
Small cooler with ice (packs)
Laptop computer with ECH2O utility software installed

Weekly Sampling Procedure:
Label all bottles appropriately prior to appropriately (Example: TF type & sample type
(influent, pan, or catch basin), initials, date).
Download data from the *Decagon* field data loggers (EC, Temperature, Soil Moisture)
for all Tree Filters -> need to being laptop computer with ECH2O Utility software
installed
One (1) Liter amber glass bottle should be filled with one liter of stormwater runoff
collected from the catch basin of each tree filter.
The amber bottle collecting the influent sample (attached to the tree filter) should be
replaced with an empty bottle.
Connect portable pump to hose(s) inside TF and pump contents of the (buried)
sampling pan into a one (1) L amber glass bottle.

---

[1] Polycyclic Aromatic Hydrocarbons to be analyzed: Naphthalene, Acenaphthylene , Acenaphthene,
Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysene,
Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(e)pyrene, Benzo(a)pyrene,
Dibenzo(a,h)anthracene, Indeno(1,2,3-cd)pyrene, Benzo(ghi)perylene.
[2] Heavy Metals to be analyzed: Cadmium (Cd), Copper (Cu), Nickel (Ni), Lead (Pb), Sodium (Na), Zinc
(Zn).

For each sample record the water quality parameters (pH, EC, temperature) on attached field sampling data sheet.

Return all samples to Dr. Craver's lab within 6 hrs. Use cooler to transport samples and to protect them.

Monthly Sampling Procedure:

Pump the catch basin dry after taking your sample using the sump pump.

Collect the accumulated sediment/solids from the catch basin in buckets (available in the shed).

Weigh the accumulated sediment in the lab to determine the amount of build up over time.

TREE FILTER SAMPLING LOCATIONS

Catch Basin Sampling Location ↓

←Pan Sampling Location

Influent Bottle and Data Logger Sampling Location ↓
(beneath grate)

SAMPLING PROCEDURES
Water Quality Parameters, Nitrate, Chloride, Data Loggers, and Climate
(Standard Method 4500 pH, Standard Method 2510 EC, Standard Method 2550 temperature)
Supplies
Data sheet
11x1L amber glass bottles labelled appropriately prior to sampling (Example: TF type & sample type (influent, pan, or catch basin), initials, date).
3x1L clean amber glass bottles to replace the influent bottles at each tree filter
Peristaltic pump "Environmental Sampler" with flexible tubing (Ensure that the pump is charged before going into the field)
Calibrated pH Meter
pH 4 buffer, pH 7 buffer, pH 10 buffer solutions to calibrate
Calibrated Multimeter with Electrical Conductance, Nitrate, and Chloride Probes
1413 µS calibration solution
Thermometer (may be included in a field meter)
Analytical balance, capable of weighing to 0.001 g
Computer and communication cable for *Decagon* field data loggers
Procedure
Calibrate all water quality meters according to the manufacturer's instructions before going into the field to ensure proper functionality.
Fill out the data sheet (Date, personnel, weather, air temperature, last precipitation date and type, precipitation amount since last sampling)
Collect one liter of the catch basin sample by submerging the bottle in the catch basin. Collect the installed influent bottle and replace it with a clean bottle.
Collect one liter of the sample in the submerged pan, by attaching the flexible tubing to the tubing in the monitoring tube below the tree filter grate. Insert the flexible tubing in the peristaltic pump and pump out the pan into the appropriate bottle until dry.
Take the electrical conductivity, temperature, pH, Chloride, and Nitrate readings for all samples. Allow all readings to stabilize and record the results in the appropriate data sheet.
To download the data from the data loggers plug the connection chord into the communication port in the data logger and the USB end into the computer.
Open the ECH2O Utility software and connect to the device.
Select the data you want to download and save the data in an excel file.
Save the file on dropbox under
>FlaggRoad>Data>DataLogger>FilterTYPEXXXX>YYYYMMDD
Check to see if the data was downloaded properly before you delete the data on the datalogger, tell it to start collecting data again, and disconnect from the software.

Bacteria (Standard Method 9222.D – Membrane Filtration using m_ColiBlue24 Culture Media and Standard Method 9230 – Fecal Streptococcus and Enterococcus Groups)

Supplies

46 autoclaved 250 mL polyethylene bottles (2 dilutions per sample per test (2 tests), 11 samples, 2 phosphate buffer blanks)

46x 100 mL Autoclaved phosphate buffer solution

11.2 g/L dibasic potassium phosphate

9.6 g/L monobasic potassium phosphate

0.02 g/L Ethylenediaminetetraacetic acid (EDTA)

Micropipette capable of measuring 1mL and 10mL

Autoclaved graduated cylinder

23x 2 mL ampoules of m-ColiBlue24 (for *E.coli* and total coliform)

46x Sterile 0.45 μm filters with 47 mm diameter

23x 47 mm petri dishes with absorbent pad

23x 47 mm petri dishes with 5 mL m Enterococcus Agar (for enterococci)

Suspend 42 g of the powder in 1 L of purified water. Mix thoroughly.

Heat with frequent agitation and boil for 1 minute to completely dissolve the powder.

DO NOT AUTOCLAVE.

Cool to 45-50°C and dispense into 50 x 9 mm Petri dishes to a depth of 4-5 mm (approximately 4-6 mL).

Incubator set to 44.8°C

Incubator set to 37°C

Thermometer

Forceps

Hot plate

1 liter beakers filled with water for sterilization of filter funnels on hot plate

Vacuum filtration manifold for membrane filtration

Isopropyl alcohol (ACS grade)

Analytical balance, capable of weighing to 0.001 g

Procedure (follow the same procedure for both pathogens until step 8, then be careful to follow the separate instructions for E. coli and enterococci sample preparation)

At the lab, sterilize the workbench and filtration manifold using isopropyl alcohol. Ensure that no isopropyl alcohol residual is present.

Sterilize the filter funnels by placing them in boiling water for 15 minutes

Label XX autoclaved polyethylene bottles appropriately (Pathogen (*E. coli* or enterococci), Sample (TF type & sample type (influent, pan, or catch basin)), personnel, date).

Dilute all samples twice (once for *E. coli* and once for Enterococci) in the following manner into labeled bottles filled with 100 ml phosphate buffer each:

A: 10 mL of sample into 100 mL of phosphate buffer solution (dilution factor: 10)

B: 1 mL of sample into 100 mL of phosphate buffer solution (dilution factor: 100)

Prepare one blank containing 100 mL of phosphate buffer solution only.

216

Prepare the manifold by placing a 0.45 μm filter paper on the filtration disks using sterilized forceps

Place the filtration funnel on the manifold and allow to cool.

Pour the sample through the filter and turn on the vacuum filtration to allow all water to drain.

E. coli preparation

Prepare the petri dishes for *E. coli* with adsorbent pads by adding one ampoule of m-ColiBlue24 broth to each petri dish and carefully place the filter into the petri dish using forceps.

Pat the petri dish on the counter to ensure that the filter paper is placed on the adsorbent pad without air bubbles and is covered in culture medium.

Immediately incubate the petri dishes in the incubator at 44.8°C for 24 hours.

After 24 hours of incubation count the bacteria using the colony counter pen and record the results, ensuring to adjust for the dilution factor.

Blue colonies represent *E. coli* and red colonies represent total coliform.

Enterococci preparation

Obtain petri dishes for *enterococci* containing 5 mL m Enterococcus Agar (without adsorbent pads, prepared previously)

Carefully place the filter into the petri dish using forceps after the sample has passed through the vacuum filtration.

Pat the petri dish on the counter to ensure that the filter paper is placed on the culture medium without air bubbles.

Allow the petri dishes to stand for 30 minutes on the bench top.

Invert the petri dish and place into the incubator at 37°C for 24 hours.

After 24 hours of incubation read the bacteria using the colony counter pen and record the results, ensuring to adjust for the dilution factor.

Total Suspended Solids (EPA Method 160.2)

Supplies

Gelman A/E or Whatman 943 AH glass fiber filter paper (0.45 µm pore size)

Gooch crucible or similar and suction flask attached to vacuum filtration unit with glass flask to capture filtrate

Graduated cylinder

Drying oven, 103-105°C

Desiccator

Forceps

Aluminum weighing dishes (numbered)

Analytical balance, capable of weighing to 0.1 mg

TSS Filtration file in Dropbox

Procedure

Clean a Gelman A/E or Whatman 943 AH glass fiber filter paper with 20 ml of deionized water three successive times using the filtration unit. ***Only handle filter papers with forceps from now on***

Place the filter paper into an aluminum weighing dish and dry in the oven at 103-105°C until dry.

Store the weighing paper in an aluminum weighing dish in a desiccator until further use.

Before use, weigh the dry filter paper on a balance and record the weight.

Place the filter on the vacuum filtration unit and wet it with some deionized water to seat it against the fritted support.

Shake the sample to ensure proper mixing and filter 250 ml for an influent sample and 200 ml for a pan sample (record how much you filtered in the TSS filtration sheet in Dropbox) through the **pre-weighed** glass fiber filter under vacuum and collect the filtrate in a glass flask. Ensure that you collect more than 10 mg of solids.

Carefully remove the filter paper with the collected solids using forceps from the vacuum filtration set up and dry in an oven at 103-105°C for at least one hour or until a constant weight is reached.

Capture the filtrate from the flask in a pre-labelled bottle for Heavy Metal and PAH analysis.

Rinse the flask several times with deionized water before proceeding with the next filtration.

Once the filter paper is dry, weigh the filter paper and calculate the non-filterable residue as follows:

$$TSS\left(\frac{mg}{L}\right)$$
$$= \frac{(Weight\ of\ filter\ paper\ and\ residue\ (mg) - weight\ of\ filter\ paper(mg)) * 1000}{Volume\ of\ sample\ filtered\ (mL)}$$

Heavy Metals (Standard Method 3120)
Supplies
15 mL falcon tubes labelled appropriately (Sample (TF type & sample type (influent, pan, or catch basin)), personnel, date)
Nitric Acid (HNO$_3$, Trace Metal grade)
Inductively Coupled Plasma – Optical Emission Spectrometer
Procedure
Take 10 ml of the filtrate from the TSS sample preparation and place it into a 15 ml plastic falcon tube.
Add nitric acid to the sample so the solution now contains 2% nitric acid (0.2 mL for 10 mL)
Place the sample into the fridge and allow the sample to digest overnight.
If not analyzed within 2 days, freeze one day after digestion to store the sample.
Turn on the ICP-OES (located in Bliss 114) and allow to warm up (~70 minutes)
Check all gases to ensure that enough resources are available to complete the analysis
Ensure that enough 5% nitric acid solution is present in the eluent container. If not, prepare more using deionized water and Nitric Acid.
Prepare a blank sample containing deionized water only.
Place samples into the autosampler starting at position 9
Open the WinLab software on the desktop
Create a new Sample Info File
Record the sample names according to their positions in the auto sampler.
Select the "Stormwater" method.
Save the Sample Info File using the following format: YYYYMMDD
Click Analyze, *Rebuild List*, and *Analyze Samples*
Record all results in the excel sheet on Dropbox.
Dispose of the samples in the designated hazardous waste accumulation container.

Polycyclic Aromatic Hydrocarbons (EPA Method 610)

Supplies

Graduated cylinder (glass)

Aluminum foil

250 mL volumetric flask wrapped in aluminum foil and labelled appropriately (Example: TF type & sample type (influent, pan, or catch basin), initials, date).

Cyclohexane (ACS grade)

Extraction standard (deuterated PAHs @ 20mg/L)

500 mL amber glass bottles with Teflon screw tops

2 mL amber vials with Teflon screw tops

2 mL glass transfer pipettes with bulb

10 mL glass transfer pipettes with bulb

GC Extraction data file in Dropbox

Gas Chromatograph-Mass Spectrometer

Procedure

Measure 240 ml of the pan sample and 200 ml of the influent sample and add to the appropriately labelled 500 mL amber glass bottles. Record the sample volume of your extractions in the GC Extraction data file on Dropbox.

Add 20 µL of extraction standard with a concentration of 20 mg/L . Record the volume of internal standard you added to your extractions in the GC Extraction data file on Dropbox.

Add 10 ml of cyclohexane. Record the volume of cyclohexane you added to your extractions in the GC Extraction data file on Dropbox.

Cap the amber glass bottles ensuring that there is a tight seal and mix the contents of the bottles for 1 minute. Let rest for 1 minute. Repeat this three times.

Allow the aqueous phase to separate from the organic phase.

Transfer the samples to the pre-labelled 250 mL volumetric flasks.

Skim off the organic phase of the sample using a 2 mL glass transfer pipette and transfer at least 1.5 mL of the sample into a labelled 2 mL amber GC vial.

Place the samples into the autosampler along with a blank (position 1) containing cyclohexane only. Arrange the samples from low to high concentration.

Check if the vials in the injection tray have enough solvent in them. If not, refill them with cyclohexane.

On the Desktop connected to the GCMS navigate to: C/GCMSSolution/Data/Varun/Data/FlagRoad/

If we are in a new month make a new folder and name it: YYYY-MM, if have a folder for this month open it

In C/GCMSSolution/Data/Varun/Data/FlagRoad/YYYY-MM create a new folder with the name in the following format: MM-DD

Open the shortcut on the desktop to GCMSSolutions' Analysis Editor software and create a new batch file.

In the batch file record the sample name and ID (can be the same for both fields)

Adjust the vial number according to the sample locations in the autosampler
Select the most recent method that was used to calibrate the instrument (dated)
Select the most recent tuning file that was created during the last calibration (dated)
Set the injection amount to 2
Set the data file name
Right click the "Data File" tab.
Click the "Folder" tab and select "Place in designated folder" and navigate to
C/GCMSSolution/Data/Varun/Data/FlagRoad/YYYY-MM/MM-DD
Click the "Data File Name" tab and select "Create name from XXXX"
In the selection menu remove the Sample ID and Sample Description from the list,
keep Sample Name in the list.
Press OK to save.
The Data File fields should now appear yellow.
Delete the following fields from the table:
level, internal standard amount, sample report, sample description
Save the batch file in the following format YYYMMDD_Runoff under
GCMSSolutions>Data>Varun>Data>Flag Road>YYYY-MM>MM-DD>
Close the Analysis Editor and open GCSolutions' Real Time Analysis
Close the Method window and select Open…
Navigate to your folder where you saved the batch file:
GCMSSolutions>Data>Varun>Data>Flag Road>YYYY-MM>MM-DD> and make
sure you can open batch file in the browser window (make sure you are able to see
batch files in the windows explorer window by selecting the batch file option from the
drop down list in the windows explorer menu)
Open your batch file
Check if all parameters are correct (especially if all vial number positions correspond
to the vial placement in the autosampler)
Click the green start button and start the run
Each run is set to take ~ 20 minutes to analyze the samples, and the column has to cool
back down again, so you can calculate about 40 minutes per run. This means you can
come back the next day when you analyze the metal samples and read the bacteria to
note down the results from the GCMS run.
Dispose of the remaining liquid from the extractions and the samples in the designated
hazardous waste accumulation container.

Phosphate (USEPA1 PhosVer 3® (Ascorbic Acid) Method)
Supplies
10 mL glass sample cells for Hach Spectrophotometer
PhosVer® 3 Phosphate Reagent powder pillows
Hach Spectrophotometer
Kimwipes
Procedure
Turn on the Hach Spectrophotometer.
Select the "Stored Program" button on the touch screen and select search by Program
Number
Enter 490 and hit enter
Select the 490 P React PP Method.
***The following steps have to be followed for every sample (i.e. every sample has a
blank and an unknown) ***
Prepare the sample: Take 10 ml of the filtrate from the TSS sample preparation and
place it into the sample cell.
Add the contents of the PhosVer 3 Phosphate Reagent Powder Pillow to the sample
cell.
Swirl and shake the sample cell to dissolve the powder, taking care not to spill the
sample.
Allow the reaction to complete for two minutes.
In the meantime, prepare the blank by filling the sample cell with 10 mL of sample.
Wipe the sample cell containing the blank to remove finger prints and water drops
using a Kimwipe
Insert the sample cell containing the blank into the machine with the fill line facing
towards the right.
Hit the "Zero" button.
Remove the sample cell and dispose of the blank.
Wipe the sample cell containing the sample to remove finger prints and water drops
using a Kimwipe
Insert the sample cell containing the sample into the machine with the fill line facing
towards the right.
Hit the "Read" button.
Record the results immediately, as this instrument does not store your data.
Dispose of the samples in the designated hazardous waste accumulation container.

WEEKLY SAMPLING DATA SHEET

Date: _____   **Personnel:** _____

Weather: Dry   Rainy   Snow   **Temperature:** ____°C

Last Precipitation Date and Type: _____ Rain   Snow   **Amount since last sample:** _____ mm

CATCH BASIN PARAMETERS (WEEKLY)

Parameter/Tree Filter	Shale Filter w/ tree	Red Cedar Filter w/ tree	½ Shale filter w/o tree	½ Red Cedar filter w/o tree
pH				
EC				
Temp				
NO_3^-				
PO_4^{--}				
Cl^-				

PAN PARAMETERS (WEEKLY)

Parameter/Tree Filter	Shale Filter w/ tree	Red Cedar Filter w/ tree	½ Shale filter w/o tree	½ Red Cedar filter w/o tree
pH				
EC				
Temp				
NO_3^-				
PO_4^{--}				
Cl^-				

MONTHLY SAMPLING DATA SHEET

SOLIDS ACUMULATION (EVERY THREE MONTHS)

Parameter/Tree Filter	Shale Filter w/ tree	Red Cedar Filter w/ tree	½ Shale filter w/o tree	½ Red Cedar filter w/o tree
Solids (kg)				

NOTES

WHAT TO DO IF SOMETHING GOES WRONG

Safety

Make yourself aware of the safety features in all labs. This includes the eye wash stations, fire extinguishers, emergency showers, exits, and so forth.

Always wear personal protective equipment (PPE) when working in the lab. This includes googles and latex gloves at minimum. Work in a fume hood, especially when working with Nitric Acid and Organic Solvents.

Know where the MSDS sheets are kept in case you have a question about the chemical you are working with or you need to access it in the case of an emergency.

Always work in the lab when other people are around. This ensures that someone is there to help if a question arises or there is an emergency.

Prevent emergencies by working during day light hours and when you are well rested. If you start to feel tired and notice that your attention is fading, take a break or better yet, stop your work and continue the next day.

Emergency

An emergency constitutes something like injury in the lab (cut, burn, chemical spill/burn). If this happens please call the campus emergency number at 401.874.2121. If a chemical is involved have the MSDS information available and rinse the affected area with copious amounts of water.

Disposal of Hazardous Waste

You will generate hazardous waste during sample preparation. Collect the waste in a labelled container ("Hazardous Waste") and dispose of it in the designated 5 gallon polyethylene containers in 111. When you dispose of the waste, make sure that the compounds that are in your sample are also listed on the hazardous waste label that is placed on the bottle. If the compound is not yet listed, add it to the label.

I screwed up in the procedure

If you think you screwed up in the sample preparation, don't fret. Try to think about what you did and where the mistake occurred. Write down exactly when you realized you made a mistake and write down what you did wrong. Notify either Laura at laura.schifman@gmail.com or Varun at vkasaraneni@my.uri.edu.

I don't know how to proceed

If you are stuck and don't know how to proceed, please don't hesitate to ask! Either Laura or Varun should be in the lab to help.

ORDERING INFORMATION AND HOW TO RE-ORDER
If supplies are running low, meaning there are enough supplies for only two weeks of sampling left, please copy the desired items along with their vendor information, catalog number and weblink, and pricing information into an email and send it to Tom Boving at boving@uri.edu and cc both, Laura and Varun at laura.schifman@gmail.com and vkasaraneni@my.uri.edu.

Analyte	Vendor	Item	Catalog Number / Web link	Unit	Price per Unit
Pathogens	Fisher	PALL LIFE SCIENCE DIVISION GN-6 METRICEL S-PK 47MM	NC0301418	200/pack	$166.38
	Fisher	Petri-Pad Dish with Pad	PD20 047 S0	150/pack	$62.97
	Fisher	Potassium Phosphate Dibasic	P288-500	500 g	$79.64
	Fisher	Potassium Phosphate Monobasic	P285-500	500 g	$52.85
	Fisher	m Enterococcus Agar (m Azide Agar)	DF0746-17-0	500 g dehydrated	$169.49
	Fisher	2-Propanol (Certified ACS Plus), Fisher Chemical	A416-4	4 L Bottle	$75.09
	Fisher	Millipore™ m-ColiBlue24™ Broth Culture Media (Total Coliform + E.coli)	M00PMCB24	Pack of 50	$107.54
Heavy Metals	Fisher	Falcon™ 15mL Conical Centrifuge Tubes	05-527-90	500/pack	$174.20
	Fisher	Nitric Acid (TraceMetal ™ Grade), Fisher Chemical	A509-P212	2.5 L bottle	$113.31

227

	Manufacturer	Description	Catalog #	Size	Price
TSS	Fisher	PALL GELMANN 47MM GLASS FILTER	NC9063501	Pack of 100	$66.37
Phosphate	Hach	PhosVer® 3 Phosphate Reagent Powder Pillows, 10 mL, pk/100)	2106069	Pack of 100 pillows	$30.29
PAHs	Fisher	Cyclohexane (Certified ACS), Fisher Chemical	C556-4	4 L bottle	$106.32
	Fisher	GC Vials 2ml Amber	03-377D	Pack of 100	$29.79
	Fisher	Robovial* Caps with Pre-Inserted Septa	03-378-31	Pack of 100	$31.48
	Ultra Scientific	PAH Mixture 16 Analyte(s) @ 100 µg/mL	PM-611-1	1 ml	$33.30
	Ultra Scientific	Deuterated PAH Mixture 7 Analyte(s) @ 200 µg/mL	ISM-750-1	1 ml	$146.45

BIBLIOGRAPHY

Aquaterra, EU-Aquaterra, European Integrated Project, Integrated soil and Groundwater Modelling, Partners, Deliverables, Tübingen, Germany, Europe, EU: Data and results 2011.

Abumaizar, R.J., Smith, E.H., 1999. Heavy metal contaminants removal by soil washing. J. Hazard. Mater. 70, 71-86 doi: 10.1016/S0304-3894(99)00149-1.

Accardi-Dey, A.M., Gschwend, P.M., 2003. Reinterpreting literature sorption data considering both absorption into organic carbon and adsorption onto black carbon. Environ. Sci. Technol. 37, 99-106.

Adhikari, H., Barnes, D.L., Schiewer, S., White, D.M., 2007. Total Coliform Survival Characteristics in Frozen Soils J. Environ. Eng. 133, 1098 - 1105 doi: 10.1061/(ASCE)0733-9372(2007)133:12(1098).

Agarwal, T., Bucheli, T.D., 2011. Is black carbon a better predictor of polycyclic aromatic hydrocarbon distribution in soils than total organic carbon? Environmental Pollution 159, 64-70.

Ahmad, A., Rafatullah, M., Danish, M., 2007. Sorption studies of Zn (II)-and Cd (II) ions from aqueous solution on treated sawdust of sissoo wood. European Journal of Wood and Wood Products 65, 429-436.

Ahn, J.H., Grant, S.B., Surbeck, C.Q., DiGiacomo, P.M., Nezlin, N.P., Jiang, S., 2005. Coastal water quality impact of stormwater runoff from an urban watershed in southern California. Environ. Sci. Technol. 39, 5940-5953.

Akaike, H., 1998. Information Theory and an Extension of the Maximum Likelihood Principle, in: Parzen, E., Tanabe, K., Kitagawa, G. (Eds.). Springer New York, pp. 199-213.

Alig, R.J., Kline, J.D., Lichtenstein, M., 2004. Urbanization on the US landscape: looking ahead in the 21st century. Landscape Urban Plann. 69, 219-234 doi: 10.1016/j.landurbplan.2003.07.004.

Allen, J.O., Dookeran, N.M., Smith, K.A., Sarofim, A.F., Taghizadeh, K., Lafleur, A.L., 1996. Measurement of polycyclic aromatic hydrocarbons associated with size-segregated atmospheric aerosols in Massachusetts. Environ. Sci. Technol. 30, 1023-1031.

Anderson, S.T., Parry, I.W.H., Sallee, J.M., Fischer, C., 2011. Automobile Fuel Economy Standards: Impacts, Efficiency, and Alternatives. Review of Environmental Economics and Policy 5, 89-108 doi: 10.1093/reep/req021.

Aprill, W., Sims, R.C., 1990. Evaluation of the use of prairie grasses for stimulating polycyclic aromatic hydrocarbon treatment in soil. Chemosphere 20, 253-265.

Aryal, R.K., Furumai, H., Nakajima, F., Boller, M., 2005. Dynamic behavior of fractional suspended solids and particle-bound polycyclic aromatic hydrocarbons in highway runoff. Water Res. 39, 5126-5134 doi: 10.1016/j.watres.2005.09.045.

Ashbolt, N.J., 2004. Microbial contamination of drinking water and disease outcomes in developing regions. Toxicology 198, 229-238.

Baek, S., Field, R., Goldstone, M., Kirk, P., Lester, J., Perry, R., 1991. A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior. Water Air Soil Pollut. 60, 279-300.

Baek, S.O., Field, R.A., Goldstone, M.E., Kirk, P.W., Lester, J.N., Perry, R., 1991. A review of atmospheric polycyclic aromatic hydrocarbons: Sources, fate and behavior. Water, Air, & Soil Pollution 60, 279-300 doi: 10.1007/BF00282628.

Bailey, S.E., Olin, T.J., Bricka, R.M., Adrian, D.D., 1999. A review of potentially low-cost sorbents for heavy metals. Water Res. 33, 2469-2479 doi: 10.1016/S0043-1354(98)00475-8.

Bakeman, S., Gariepy, D., Howie, D., Killelea, J., Labib, F., and Obrien, E., 2012. 2012 Stormwater Management Manual for Western Washington. , 1-1039.

Bales, R.C., Hinkle, S.R., Kroeger, T.W., Stocking, K., Gerba, C.P., 1991. Bacteriophage adsorption during transport through porous media: chemical perturbations and reversibility Environ. Sci. Technol. 25, 2088 - 2095 doi: 10.1021/es00024a016.

Bamford, H.A., Poster, D.L., Baker, J.E., 1999. Temperature dependence of Henry's law constants of thirteen polycyclic aromatic hydrocarbons between 4°C AND 31°C. Environmental Toxicology and Chemistry 18, 1905-1912 doi: 10.1002/etc.5620180906.

Barbosa, A., Fernandes, J., David, L., 2012. Key issues for sustainable urban stormwater management. Water Res. 46, 6787-6798.

Bari, M.A., Baumbach, G., Brodbeck, J., Struschka, M., Kuch, B., Dreher, W., Scheffknecht, G., 2011. Characterisation of particulates and carcinogenic polycyclic aromatic hydrocarbons in wintertime wood-fired heating in residential areas. Atmos. Environ. 45, 7627-7634 doi: 10.1016/j.atmosenv.2010.11.053.

Barker, A.L., Gonsalves, M., Macpherson, J.V., Slevin, C.J., Unwin, P.R., 1999. Scanning electrochemical microscopy: beyond the solid/liquid interface. Anal. Chim. Acta 385, 223-240.

Barthel, P., Thuens, S., Shunthirasingham, C., Westgate, J.N., Wania, F., Radke, M., 2012. Application of XAD-resin based passive air samplers to assess local (roadside) and regional patterns of persistent organic pollutants. Environmental Pollution 166, 218-225.

Behr, E., Briggs, D., Kaufert, F., 1953. Diffusion of dissolved materials through wood. J. Phys. Chem. 57, 476-480.

Benfenati, E., Valzacchi, S., Mariani, G., Airoldi, L., Fanelli, R., 1992. PCDD, PCDF, PCB, PAH, cadmium and lead in roadside soil: relationship between road distance and concentration. Chemosphere 24, 1077-1083.

Berretta, C., Sansalone, J., 2011. Hydrologic transport and partitioning of phosphorus fractions. Journal of Hydrology 403, 25-36.

Bettez, N.D., Groffman, P.M., 2012. Denitrification potential in stormwater control structures and natural riparian zones in an urban landscape. Environ. Sci. Technol. 46, 10909-10917.

Bilby, R.E., Heffner, J.T., Fransen, B.R., Ward, J.W., Bisson, P.A., 1999. Effects of immersion in water on deterioration of wood from five species of trees used for habitat enhancement projects. N. Am. J. Fish. Manage. 19, 687-695.

Blaustein, R.A., Pachepsky, Y., Hill, R.L., Shelton, D.R., Whelan, G., 2013. *Escherichia coli* survival in waters: Temperature dependence Water Res. 47, 569 - 578 doi: 10.1016/j.watres.2012.10.027.

Blecken, G.T., Rentz, R., Malmgren, C., Öhlander, B., Viklander, M., 2012. Stormwater impact on urban waterways in a cold climate: variations in sediment metal concentrations due to untreated snowmelt discharge. Journal of Soils and Sediments, 1-16.

Boonyatumanond, R., Murakami, M., Wattayakorn, G., Togo, A., Takada, H., 2007. Sources of polycyclic aromatic hydrocarbons (PAHs) in street dust in a tropical Asian mega-city, Bangkok, Thailand. Sci. Total Environ. 384, 420-432 doi: 10.1016/j.scitotenv.2007.06.046.

Bopp, S., Weiß, H., Schirmer, K., 2005. Time-integrated monitoring of polycyclic aromatic hydrocarbons (PAHs) in groundwater using the Ceramic Dosimeter passive sampling device. Journal of Chromatography A 1072, 137-147 doi: 10.1016/j.chroma.2004.12.049.

Boving, T.B., Rowell, R., 2010. Environmental Applications of Lignocellolusic Filter Materials, in: Rowell, R. (Ed.). UFP Editions, Lisbon, Portugal.

Boving, T.B., Stolt, M.H., Augenstern, J., Brosnan, B., 2008. Potential for localized groundwater contamination in a porous pavement parking lot setting in Rhode Island. Environ. Geol. 55, 571-582.

Boving, T.B., Grathwohl, P., 2001. Tracer diffusion coefficients in sedimentary rocks: correlation to porosity and hydraulic conductivity. J. Contam. Hydrol. 53, 85-100.

Boving, T., Stolt, M., Augenstern, J., Brosnan, B., 2008. Potential for localized groundwater contamination in a porous pavement parking lot setting in Rhode Island. Environmental Geology 55, 571-582 doi: 10.1007/s00254-007-1008-z.

Boving, T.B., Neary, K., 2007. Attenuation of polycyclic aromatic hydrocarbons from urban stormwater runoff by wood filters. J. Contam. Hydrol. 91, 43-57.

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

Boyd, S., Brixie, J., 1994. Treatment of contaminated soils with organoclays to reduce leachable pentachlorophenol. J. Environ. Qual. 23, 1283-1290.

Brändli, R.C., Hartnik, T., Henriksen, T., Cornelissen, G., 2008. Sorption of native polyaromatic hydrocarbons (PAH) to black carbon and amended activated carbon in soil. Chemosphere 73, 1805-1810.

Breakwell, I.K., Homer, J., Lawrence, M.A.M., McWhinnie, W.R., 1995. Studies of organophilic clays: the distribution of quaternary ammonium compounds on clay surfaces and the role of impurities. Polyhedron 14, 2511-2518.

Brennan, F.P., Grant, J., Botting, C.H., O'Flaherty, V., Richards, K.G., Abram, F., 2013; 2012. Insights into the low-temperature adaptation and nutritional flexibility of a soil-persistent *Escherichia coli* FEMS Microbiol. Ecol. 84, 75 - 85 doi: 10.1111/1574-6941.12038.

Brown, J.N., Peake, B.M., 2006. Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff. Sci. Total Environ. 359, 145-155 doi: 10.1016/j.scitotenv.2005.05.016.

Brun, G.L., Vaidya, O.C., Léger, M.G., 2004. Atmospheric Deposition of Polycyclic Aromatic Hydrocarbons to Atlantic Canada: Geographic and Temporal Distributions and Trends 1980-2001. Environ. Sci. Technol. 38, 1941-1948 doi: 10.1021/es034645l.

Brunk, B.K., Jirka, G.H., Lion, L.W., 1997. Effects of Salinity Changes and the Formation of Dissolved Organic Matter Coatings on the Sorption of Phenanthrene: Implications for Pollutant Trapping in Estuaries. Environ. Sci. Technol. 31, 119-125 doi: 10.1021/es9602051.

Brusseau, M.L., Hu, Q., Srivastava, R., 1997. Using flow interruption to identify factors causing nonideal contaminant transport. J. Contam. Hydrol. 24, 205-219.

Burr, H.K., Stamm, A.J., 1947. Diffusion in wood. J. Phys. Chem. 51, 240-261.

Carrera, G., Fernández, P., Vilanova, R.M., Grimalt, J.O., 2001. Persistent organic pollutants in snow from European high mountain areas. Atmos. Environ. 35, 245-254.

Casey, R.E., Lev, S.M., Snodgrass, J.W., 2013. Stormwater ponds as a source of long-term surface and ground water salinisation. Urban Water Journal 10, 145-153.

Celis, R., Hermosin, M.C., Cornejo, J., 2000. Heavy metal adsorption by functionalized clays. Environ. Sci. Technol. 34, 4593-4599.

Chandrasena, G.I., Deletic, A., McCarthy, D.T., 2013. Survival of *Escherichia coli* in stormwater biofilters Environmental Science and Pollution Research doi: 10.1007/s11356-013-2430-2.

Chang, N., Wanielista, M., Daranpob, A., 2010. Filter media for nutrient removal in natural systems and built environments: II—Design and application challenges. Environ. Eng. Sci. 27, 707-720.

Chedgy, R.J., Lim, Y.W., Breuil, C., 2009. Effects of leaching on fungal growth and decay of western redcedar. Can. J. Microbiol. 55, 578-586.

Chefetz, B., Deshmukh, A.P., Hatcher, P.G., Guthrie, E.A., 2000. Pyrene Sorption by Natural Organic Matter. Environ. Sci. Technol. 34, 2925-2930 doi: 10.1021/es9912877.

Chen, S.C., Liao, C.M., 2006. Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources. Sci. Total Environ. 366, 112-123.

Chen, Y., Schnitzer, M., Scanning Electron Microscopy Of A Humic Acid And Of A Fulvic Acid And Its Metal And Clay Complexes. Soil Sci. Soc. Am. J. 40, 682-686.

Chiou, C.T., Mortland, M.M., Boyd, S.A., 1988. Sorption characteristics of organic compounds on hexadecyltrimethylammonium-smectite. Soil Sci. Soc. Am. J. 52, 652-657.

Chiou, C.T., McGroddy, S.E., Kile, D.E., 1998. Partition Characteristics of Polycyclic Aromatic Hydrocarbons on Soils and Sediments. Environ. Sci. Technol. 32, 264-269 doi: 10.1021/es970614c.

Choi, S., Baek, S., Chang, Y., Wania, F., Ikonomou, M.G., Yoon, Y., Park, B., Hong, S., 2008. Passive Air Sampling of Polychlorinated Biphenyls and Organochlorine Pesticides at the Korean Arctic and Antarctic Research Stations: Implications for Long-Range Transport and Local Pollution. Environ. Sci. Technol. 42, 7125-7131 doi: 10.1021/es801004p.

Chong, M.N., Sidhu, J., Aryal, R., Tang, J., Gernjak, W., Escher, B., Toze, S., 2012. Urban stormwater harvesting and reuse: a probe into the chemical, toxicology and microbiological contaminants in water quality. Environ. Monit. Assess. , 1-8.

Christie, S., Raper, D., Lee, D.S., Williams, P.I., Rye, L., Blakey, S., Wilson, C.W., Lobo, P., Hagen, D., Whitefield, P.D., 2012. Polycyclic aromatic hydrocarbon emissions from the combustion of alternative fuels in a gas turbine engine. Environ. Sci. Technol. 46, 6393-6400.

Coffman, L.S., Ruby, M., Beach, C., 2008. Bacterra by Filterra® Advanced Bioretention System: Discussion of the Benefits, Mechanisms and Efficiencies for Bacteria Removal. 93.

Coleman, N.J., Lee, W.E., Slipper, I.J., 2005. Interactions of aqueous Cu^2, Zn^2 and Pb^2 ions with crushed concrete fines. J. Hazard. Mater. 121, 203-213.

Comero, S., Capitani, L., Gawlik, B., 2009. Positive Matrix Factorisation (PMF)–An introduction to the chemometric evaluation of environmental monitoring data using PMF. Office for Official Publications of the European Communities, Luxembourg.

Conte, E., Milani, R., Morali, G., Abballe, F., 1997. Comparison between accelerated solvent extraction and traditional extraction methods for the analysis of the herbicide diflufenican in soil. Journal of Chromatography A 765, 121-125 doi: 10.1016/S0021-9673(96)00948-X.

Cooper, D., 2001. Exhaust emissions from high speed passenger ferries. Atmos. Environ. 35, 4189-4200.

Cornelissen, G., Breedveld, G.D., Kalaitzidis, S., Christanis, K., Kibsgaard, A., Oen, A.M.P., 2006. Strong sorption of native PAHs to pyrogenic and unburned carbonaceous geosorbents in sediments. Environ. Sci. Technol. 40, 1197-1203.

Cornelissen, G., Gustafsson, Ö., 2005. Importance of unburned coal carbon, black carbon, and amorphous organic carbon to phenanthrene sorption in sediments. Environ. Sci. Technol. 39, 764-769.

Cornelissen, G., Gustafsson, Ö., Bucheli, T.D., Jonker, M.T.O., Koelmans, A.A., van Noort, P.C.M., 2005. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. Environ. Sci. Technol. 39, 6881-6895.

Cornelissen, G., Gustafsson, Ö., 2004. Sorption of phenanthrene to environmental black carbon in sediment with and without organic matter and native sorbates. Environ. Sci. Technol. 38, 148-155.

Cornelissen, G., Kukulska, Z., Kalaitzidis, S., Christanis, K., Gustafsson, Ö., 2004. Relations between environmental black carbon sorption and geochemical sorbent characteristics. Environ. Sci. Technol. 38, 3632-3640.

Corsi, S.R., Graczyk, D.J., Geis, S.W., Booth, N.L., Richards, K.D., 2010. A fresh look at road salt: aquatic toxicity and water-quality impacts on local, regional, and national scales. Environ. Sci. Technol. 44, 7376-7382.

Crawley, M.J., 2005. Statistics: An Introduction using R . J. Wiley, Chichester, West Sussex, England.

Cui, L., Zhu, X., Ma, M., Ouyang, Y., Dong, M., Zhu, W., Luo, S., 2008. Phosphorus sorption capacities and physicochemical properties of nine substrate materials for constructed wetland. Arch. Environ. Contam. Toxicol. 55, 210-217.

Curriero, F.C., Patz, J.A., Rose, J.B., Lele, S., 2001. The Association Between Extreme Precipitation and Waterborne Disease Outbreaks in the United States, 1948–1994 Am. J. Public Health 91, 1194 - 1199 doi: 10.2105/AJPH.91.8.1194.

Czimczik, C.I., Masiello, C.A., 2007. Controls on black carbon storage in soils. Global Biogeochem. Cycles 21, GB3005.

Dankovich, T.A., Gray, D.G., 2011. Bactericidal paper impregnated with silver nanoparticles for point-of-use water treatment. Environ. Sci. Technol. 45, 1992-1998.

Davies, C.M., Bavor, H.J., 2000. The fate of stormwater-associated bacteria in constructed wetland and water pollution control pond systems J. Appl. Microbiol. 89, 349 - 360 doi: 10.1046/j.1365-2672.2000.01118.x.

Davis, A.P., Hunt, W.F., Traver, R.G., Clar, M., 2009. Bioretention technology: Overview of current practice and future needs. J. Environ. Eng. 135, 109-117.

Davis, A.P., 2007. Field performance of bioretention: Water quality. Environ. Eng. Sci. 24, 1048-1064.

Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., 2006. Water quality improvement through bioretention media: Nitrogen and phosphorus removal. Water Environ. Res. 78, 284-293.

Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., Winogradoff, D., 2003. Water quality improvement through bioretention: Lead, copper, and zinc removal. Water Environ. Res., 73-82.

Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., 2001. Laboratory study of biological retention for urban stormwater management. Water Environ. Res. , 5-14.

Davis, A.P., Hunt, W.F., Traver, R.G., Clar, M., 2009. Bioretention Technology: Overview of Current Practice and Future Needs J. Environ. Eng. 135, 109 - 117 doi: 10.1061/(ASCE)0733-9372(2009)135:3(109).

de Paiva, L.B., Morales, A.R., Valenzuela Díaz, F.R., 2008. Organoclays: Properties, preparation and applications. Appl. Clay. Sci. 42, 8-24 doi: 10.1016/j.clay.2008.02.006.

De Ridder, K., Lefebre, F., Adriaensen, S., Arnold, U., Beckroege, W., Bronner, C., Damsgaard, O., Dostal, I., Dufek, J., Hirsch, J., 2008. Simulating the impact of urban sprawl on air quality and population exposure in the German Ruhr area. Part II: Development and evaluation of an urban growth scenario. Atmos. Environ. 42, 7070-7077.

DeBell, L.J., Talbot, R.W., Dibb, J.E., Munger, J.W., Fischer, E.V., Frolking, S.E., 2004. A major regional air pollution event in the northeastern United States caused by extensive forest fires in Quebec, Canada. Journal of Geophysical Research: Atmospheres (1984–2012) 109.

DeBusk, T.A., Langston, M.A., Schwegler, B.R., Davidson, S., 1997. An evaluation of filter media for treating storm water runoff. , 82-89.

Del Vento, S., Dachs, J., 2007. Atmospheric Occurrence and Deposition of Polycyclic Aromatic Hydrocarbons in the Northeast Tropical and Subtropical Atlantic Ocean. Environ. Sci. Technol. 41, 5608-5613 doi: 10.1021/es0707660.

Delbem, M.F., Valera, T.S., Valenzuela-Diaz, F.R., Demarquette, N.R., 2010. Modification of a Brazilian smectite clay with different quaternary ammonium salts Química Nova 33, 309 - 315 doi: 10.1590/S0100-40422010000200015.

Deletic, A.B., Maksimovic, C., 1998. Evaluation of water quality factors in storm runoff from paved areas. J. Environ. Eng. 124, 869-879.

DiBlasi, C.J., Li, H., Davis, A.P., Ghosh, U., 2008. Removal and fate of polycyclic aromatic hydrocarbon pollutants in an urban stormwater bioretention facility. Environ. Sci. Technol. 43, 494-502.

Dickerman, D.C., 1984. Aquifer tests in the stratified drift, Chipuxet River basin, Rhode Island. Available from OFSS, USGS Box 25425, Fed.Ctr.Denver, CO 80225, USGS Water-Resources Investigations Report 83-4321, 1984.39 p, 16 Fig, 7 Tab, 24.

Dickhut, R., Canuel, E., Gustafson, K., Liu, K., Arzayus, K., Walker, S., Edgecombe, G., Gaylor, M., MacDonald, E., 2000. Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay region. Environ. Sci. Technol. 34, 4635-4640.

Doick, K.J., Klingelmann, E., Burauel, P., Jones, K.C., Semple, K.T., 2005. Long-term fate of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in an agricultural soil. Environ. Sci. Technol. 39, 3663-3670.

Domany, Z., Galambos, I., Vatai, G., Bekassy-Molnar, E., 2002. Humic substances removal from drinking water by membrane filtration. Desalination 145, 333-337.

Donath, S., Militz, H., Mai, C., 2006. Treatment of wood with aminofunctional silanes for protection against wood destroying fungi. Holzforschung 60, 210-216.

Donath, S., Militz, H., Mai, C., 2007. Weathering of silane treated wood Holz als Roh- und Werkstoff 65, 35 - 42 doi: 10.1007/s00107-006-0131-y.

Dorfman, M., Rosselot, K., 2012. Testing the Water: A Guide to Water Quuality at Vacation Beaches. Natural Resources Defense Council 22.

Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L., Weathers, K.C., 2001. Acidic Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management Strategies: The effects of acidic deposition in the northeastern United States include the acidification of soil and water, which stresses terrestrial and aquatic biota. Bioscience 51, 180-198.

Dunne, E.J., Coveney, M.F., Marzolf, E.R., Hoge, V.R., Conrow, R., Naleway, R., Lowe, E.F., Battoe, L.E., 2012. Efficacy of a large-scale constructed wetland to

remove phosphorus and suspended solids from Lake Apopka, Florida. Ecol. Eng. 42, 90-100.

Edberg, S., Rice, E., Karlin, R., Allen, M., 2000. *Escherichia coli*: the best biological drinking water indicator for public health protection. J. Appl. Microbiol. 88, 106S-116S.

Edwards, N.T., 1983. Polycyclic Aromatic Hydrocarbons (PAH's) in the Terrestrial Environment - A Review. J. Environ. Qual. 12, 427-441.

EPA, 2014. State Development of Numeric Criteria for Nitrogen and Phosphorus Pollution. 2014.

EPA, 2013. EPA Positive Matrix Factorization (PMF) 5.0 model. Research Triangle Park, NC 5.0 doi: http://www.epa.gov/heasd/products/pmf/pmf.html.

EPA, 2012. Recreational Water Quality Criteria. Office of Water 820-F-12-058, 1-58.

EPA, 2011. Performance Standards for Discharges from Newly Developed and Redeveloped Sites. 1-144.

EPA, 2009. Drinking Water Contaminants. 2014.

EPA, 2006. Current national recommended water quality criteria.

EPA, 2005. National Management Measures to Control Nonpoint Source Pollution from Urban Areas. EPA-841-B-05-004, 1-518.

EPA, 2001. Protocol for Developing Pathogen TMDLs. Office of Water (4503F), United States Environmental Protection Agency, Washington, DC.

EPA, 1988. Ambient Water Quality Criteria for Chloride. EPA 440/ 5-88-001.

Esen, F., Tasdemir, Y., Cindoruk, S.S., 2010. Determination of mass transfer rates and deposition levels of polycyclic aromatic hydrocarbons (PAHs) using a modified water surface sampler. Atmospheric Pollution Research 1, 177-183.

Faucette, L., Cardoso-Gendreau, F., Codling, E., Sadeghi, A., Pachepsky, Y., Shelton, D., 2009. Storm water pollutant removal performance of compost filter socks. J. Environ. Qual. 38, 1233-1239.

Ferreira, L., Zumbuehl, A., 2009. Non-leaching surfaces capable of killing microorganisms on contact. Journal of Materials Chemistry 19, 7796-7806.

Fetter, C.W., 2000. Applied Hydrogeology (4th Edition) , 4 ed. Prentice Hall <SKU> 4e85e1c19db2de0608001638.

Fletcher, T.D., Deletic, A., Mitchell, V.G., Hatt, B.E., 2008. Reuse of urban runoff in Australia: A review of recent advances and remaining challenges. J. Environ. Qual. 37, S-116-S-127.

Forbes, M.G., Dickson, K.R., Golden, T.D., Hudak, P., Doyle, R.D., 2004. Dissolved phosphorus retention of light-weight expanded shale and masonry sand used in subsurface flow treatment wetlands. Environ. Sci. Technol. 38, 892-898.

Franz, T.P., Eisenreich, S.J., Holsen, T.M., 1998. Dry Deposition of Particulate Polychlorinated Biphenyls and Polycyclic Aromatic Hydrocarbons to Lake Michigan. Environ. Sci. Technol. 32, 3681-3688 doi: 10.1021/es980107a.

Freeman, D.J., Cattell, F.C., 1990. Woodburning as a source of atmospheric polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 24, 1581-1585.

Fuerhacker, M., Haile, T.M., Monai, B., Mentler, A., 2011. Performance of a filtration system equipped with filter media for parking lot runoff treatment. Desalination 275, 118-125.

Futalan, C.M., Kan, C., Dalida, M.L., Hsien, K., Pascua, C., Wan, M., 2011. Comparative and competitive adsorption of copper, lead, and nickel using chitosan immobilized on bentonite. Carbohydr. Polym. 83, 528-536.

Gabrieli, J., Decet, F., Luchetta, A., Valt, M., Pastore, P., Barbante, C., 2010. Occurrence of PAH in the seasonal snowpack of the Eastern Italian Alps. Environmental Pollution 158, 3130-3137.

Galarneau, E., 2008. Source specificity and atmospheric processing of airborne PAHs: implications for source apportionment. Atmos. Environ. 42, 8139-8149.

Garban, B., Blanchoud, H., Motelay-Massei, A., Chevreuil, M., Ollivon, D., 2002. Atmospheric bulk deposition of PAHs onto France: trends from urban to remote sites. Atmos. Environ. 36, 5395-5403.

Garcia-Alonso, S., Pérez-Pastor, R., Sevillano-Castaño, M., Escolano, O., García-Frutos, F., 2008. Influence of particle size on the quality of PAH concentration measurements in a contaminated soil. Polycyclic Aromatic Compounds 28, 67-83.

Gayán, E., Monfort, S., Álvarez, I., Condón, S., 2011. UV-C inactivation of Escherichia coli at different temperatures Innovative Food Science & Emerging Technologies 12, 531 +- 541 doi: 10.1016/j.ifset.2011.07.008.

Genç-Fuhrman, H., Mikkelsen, P.S., Ledin, A., 2007. Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater: Experimental comparison of 11 different sorbents. Water Res. 41, 591-602 doi: 10.1016/j.watres.2006.10.024.

German Industrial Standard DIN 19739-2, 2003.
Air and soil quality - Measurement of atmospheric deposition of organic trace substances; Funnel adsorber method - Part 2: Determination of polynuclear aromatic hydrocarbons. , 1-17.

Gigliotti, C.L., Dachs, J., Nelson, E.D., Brunciak, P.A., Eisenreich, S.J., 2000. Polycyclic aromatic hydrocarbons in the New Jersey coastal atmosphere. Environ. Sci. Technol. 34, 3547-3554.

Gigliotti, C.L., Totten, L.A., Offenberg, J.H., Dachs, J., Reinfelder, J.R., Nelson, E.D., Glenn, Eisenreich, S.J., 2005. Atmospheric Concentrations and Deposition of Polycyclic Aromatic Hydrocarbons to the Mid-Atlantic East Coast Region. Environ. Sci. Technol. 39, 5550-5559 doi: 10.1021/es050401k.

Gilbert, J.K., Clausen, J.C., 2006. Stormwater runoff quality and quantity from asphalt, paver, and crushed stone driveways in Connecticut. Water Res. 40, 826-832.

Göbel, P., Dierkes, C., Coldewey, W.G., 2007. Storm water runoff concentration matrix for urban areas. J. Contam. Hydrol. 91, 26-42 doi: 10.1016/j.jconhyd.2006.08.008.

Gocht, T., 2005. Die vier Griechischen Elemente: Massenbilanzierung von polyzyklischen aromatischen Kohlenwasserstoffen (PAK) in Kleineinzugsgebieten des ländlichen Raumes.

Gocht, T., Ligouis, B., Hinderer, M., Grathwohl, P., 2007. Accumulation of polycyclic aromatic hydrocarbons in rural soils based on mass balances at the catchment scale. Environmental Toxicology and Chemistry 26, 591-600 doi: 10.1897/06-287R.1.

Gocht, T., Barth, J.A.C., Epp, M., Jochmann, M., Blessing, M., Schmidt, T.C., Grathwohl, P., 2007. Indications for pedogenic formation of perylene in a terrestrial soil profile: Depth distribution and first results from stable carbon isotope ratios. Appl. Geochem. 22, 2652-2663.

Gocht, T., Klemm, O., Grathwohl, P., 2007. Long-term atmospheric bulk deposition of polycyclic aromatic hydrocarbons (PAHs) in rural areas of Southern Germany. Atmos. Environ. 41, 1315-1327.

Gocht, T., Moeckel, C., Chaemfa, C., Thomas, G.O., Jones, K.C., 2007. Validation of an passive atmospheric deposition sampler for polybrominated diphenyl ethers. J. Environ. Monit. 9, 1176-1182.

Golomb, D., Barry, E., Fisher, G., Varanusupakul, P., Koleda, M., Rooney, T., 2001. Atmospheric deposition of polycyclic aromatic hydrocarbons near New England coastal waters. Atmos. Environ. 35, 6245-6258.

Gouin, T., Wilkinson, D., Hummel, S., Meyer, B., Culley, A., 2010. Polycyclic aromatic hydrocarbons in air and snow from Fairbanks, Alaska. Atmospheric Pollution Research 1, 9-15.

Gouin, T., Harner, T., Blanchard, P., Mackay, D., 2005. Passive and Active Air Samplers as Complementary Methods for Investigating Persistent Organic Pollutants in the Great Lakes Basin. Environ. Sci. Technol. 39, 9115-9122 doi: 10.1021/es051397f.

Grabińska-Sota, E., 2011. Genotoxicity and biodegradation of quaternary ammonium salts in aquatic environments. J. Hazard. Mater. 195, 182-187.

Grebel, J.E., Mohanty, S.K., Torkelson, A.A., Boehm, A.B., Higgins, C.P., Maxwell, R.M., Nelson, K.L., Sedlak, D.L., 2013. Engineered infiltration systems for urban stormwater reclamation. Environ. Eng. Sci. 30, 437-454.

Grimmer, G., Jacob, J., Naujack, K.W., Dettbarn, G., 1981. Profile of the polycyclic aromatic hydrocarbons from used engine oil — inventory by GCGC/MS — PAH in environmental materials, Part 2. Fresenius' Journal of Analytical Chemistry 309, 13-19 doi: 10.1007/BF00493445.

Grohs, B.M., Wegen, H.-., Kunz, B., 1999. Antifungal activity of red cedar extract and hiba oil on wood-inhabiting moulds. Holz als Roh- und Werkstoff 57, 277-281.

Grynkiewicz, M., Polkowska, Ż., Namieśnik, J., 2002. Determination of polycyclic aromatic hydrocarbons in bulk precipitation and runoff waters in an urban region (Poland). Atmos. Environ. 36, 361-369 doi: 10.1016/S1352-2310(01)00266-7.

Gunasekara, A.S., Xing, B., 2003. Sorption and Desorption of Naphthalene by Soil Organic Matter. J. Environ. Qual. 32, 240-246.

Guo, H., Lee, S., Ho, K., Wang, X., Zou, S., 2003. Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. Atmos. Environ. 37, 5307-5317.

Gustafsson, Ö., Haghseta, F., Chan, C., MacFarlane, J., Gschwend, P.M., 1996. Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. Environ. Sci. Technol. 31, 203-209.

Haas, C.N., Karra, S.B., 1984. Kinetics of microbial inactivation by chlorine—I Review of results in demand-free systems. Water Res. 18, 1443-1449.

Han, Y., Lau, S., Kayhanian, M., Stenstrom, M.K., 2006. Characteristics of highway stormwater runoff. Water Environ. Res. 78, 2377-2388.

Harless, M.L., Huckins, C.J., Grant, J.B., Pypker, T.G., 2011. Effects of six chemical deicers on larval wood frogs (Rana sylvatica). Environmental Toxicology and Chemistry 30, 1637-1641.

Harrison, R.M., Smith, D., Luhana, L., 1996. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. Environ. Sci. Technol. 30, 825-832.

Hartigan, J.A., Wong, M.A., 1979. Algorithm AS 136: A K-Means Clustering Algorithm Applied Statistics 28, 100 doi: 10.2307/2346830.

Hartmann, P.C., Quinn, J.G., Cairns, R.W., King, J.W., 2005. Depositional history of organic contaminants in Narragansett Bay, Rhode Island, USA. Mar. Pollut. Bull. 50, 388-395.

Harvey, R.G., 1991. Polycyclic Aromatic Hydrocarbons: Chemistry and Carcinogenicity. Cambridge University Press, Cambridge, England.

Hathaway, J., Hunt, W., Simmons III, O., 2010. Statistical evaluation of factors affecting indicator bacteria in urban storm-water runoff. J. Environ. Eng. 136, 1360-1368.

Hathaway, J., Hunt, W., Jadlocki, S., 2009. Indicator bacteria removal in storm-water best management practices in Charlotte, North Carolina. J. Environ. Eng. 135, 1275-1285.

Hatt, B.E., Fletcher, T.D., Deletic, A., 2009. Hydrologic and pollutant removal performance of stormwater biofiltration systems at the field scale. Journal of Hydrology 365, 310-321.

Hayward, S.J., Gouin, T., Wania, F., 2010. Comparison of four active and passive sampling techniques for pesticides in air. Environ. Sci. Technol. 44, 3410-3416.

He, J., Balasubramanian, R., 2010. A comparative evaluation of passive and active samplers for measurements of gaseous semi-volatile organic compounds in the tropical atmosphere. Atmos. Environ. 44, 884-891.

Herngren, L., Goonetilleke, A., Ayoko, G.A., Mostert, M.M.M., 2010. Distribution of polycyclic aromatic hydrocarbons in urban stormwater in Queensland, Australia. Environmental Pollution 158, 2848-2856 doi: 10.1016/j.envpol.2010.06.015.

Herrera, P., Burghardt, R., Huebner, H.J., Phillips, T.D., 2004. The efficacy of sand-immobilized organoclays as filtration bed materials for bacteria. Food Microbiol. 21, 1-10.

Hindarso, H., Ismadji, S., Wicaksana, F., Mudjijati, a., Indraswati, N., 2001. Adsorption of benzene and toluene from aqueous solution onto granular activated carbon. Journal of Chemical & Engineering Data 46, 788-791.

Ho, Y., John Wase, D., Forster, C., 1995. Batch nickel removal from aqueous solution by sphagnum moss peat. Water Res. 29, 1327-1332.

Hofmann, G.E., Todgham, A.E., 2010. Living in the now: physiological mechanisms to tolerate a rapidly changing environment Annu. Rev. Physiol. 72, 127-145 doi: 10.1146/annurev-physiol-021909-135900; 10.1146/annurev-physiol-021909-135900.

Hong, E., Seagren, E.A., Davis, A.P., 2006. Sustainable oil and grease removal from synthetic stormwater runoff using bench-scale bioretention studies. Water Environ. Res. 78, 141-155.

Hopke, P.K., 1991. Receptor Modeling for Air Quality Management. Elsevier.

Hsieh, C., Davis, A.P., Needelman, B.A., 2007. Bioretention column studies of phosphorus removal from urban stormwater runoff. Water Environ. Res. 79, 177-184.

Hu, S., Fruin, S., Kozawa, K., Mara, S., Winer, A.M., Paulson, S.E., 2009. Aircraft emission impacts in a neighborhood adjacent to a general aviation airport in Southern California. Environ. Sci. Technol. 43, 8039-8045.

Huang, L., Ou, Z., Boving, T.B., Tyson, J., Xing, B., 2009. Sorption of copper by chemically modified aspen wood fibers. Chemosphere 76, 1056-1061 doi: 10.1016/j.chemosphere.2009.04.030.

Huang, L., Boving, T.B., Xing, B., 2006. Sorption of PAHs by Aspen Wood Fibers as Affected by Chemical Alterations. Environ. Sci. Technol. 40, 3279-3284 doi: 10.1021/es0524651.

Huang, X.-., McConkey, B.J., Babu, T.S., Greenberg, B.M., 1997. Mechanisms of photoinduced toxicity of photomodified anthracene to plants: Inhibition of photosynthesis in the aquatic higher plant Lemna gibba (duckweed). Environmental Toxicology and Chemistry 16, 1707-1715 doi: 10.1002/etc.5620160819.

Huang, X., El-Alawi, Y., Penrose, D.M., Glick, B.R., Greenberg, B.M., 2004. A multi-process phytoremediation system for removal of polycyclic aromatic hydrocarbons from contaminated soils. Environmental Pollution 130, 465-476.

Huang, X., Zeiler, L.F., Dixon, D.G., Greenberg, B.M., 1996. Photoinduced Toxicity of PAHs to the Foliar Regions ofBrassica napus (Canola) andCucumbis sativus(Cucumber) in Simulated Solar Radiation. Ecotoxicol. Environ. Saf. 35, 190-197.

Hunt, W., Jarrett, A., Smith, J., Sharkey, L., 2006. Evaluating bioretention hydrology and nutrient removal at three field sites in North Carolina. J. Irrig. Drain. Eng. 132, 600-608.

Jacob, J., 1996. The significance of polycyclic aromatic hydrocarbons as environmental carcinogens. Pure & Appl. Chem. 68, 301-308.

Jacob, J., 2008. The significance of polycyclic aromatic hydrocarbons as environmental carcinogens. 35 years research on PAH—a retrospective. Polycyclic Aromatic Compounds 28, 242-272.

Jasper, J.T., Jones, Z.L., Sharp, J.O., Sedlak, D.L., 2014. Nitrate Removal in Shallow, Open-Water Treatment Wetlands. Environ. Sci. Technol. .

Jaward, F.M., Farrar, N.J., Harner, T., Sweetman, A.J., Jones, K.C., 2004. Passive air sampling of polycyclic aromatic hydrocarbons and polychlorinated naphthalenes across europe. Environmental Toxicology and Chemistry 23, 1355-1364 doi: -10.1897/03-420.

Jaynes, W., Vance, G., 1996. BTEX sorption by organo-clays: cosorptive enhancement and equivalence of interlayer complexes. Soil Sci. Soc. Am. J. 60, 1742-1749.

Jeng, H.C., Andrew, J., Bradford, H.B., 2005. Indicator organisms associated with stormwater suspended particles and estuarine sediment. Journal of environmental science and health 40, 779-791.

Johnsen, A.R., Wick, L.Y., Harms, H., 2005. Principles of microbial PAH-degradation in soil. Environmental Pollution 133, 71-84.

Johnson, D.C., Coleman, N.J., Lane, J., Hills, C.D., Poole, A.B., A preliminary investigation of the removal of heavy metal species from aqueous media using crushed concrete fines, in: Anonymous . Elsevier, pp. 1044-1049.

Jonker, M.T.O., Koelmans, A.A., 2002. Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: Mechanistic considerations. Environ. Sci. Technol. 36, 3725-3734.

Karim, M.R., Manshadi, F.D., Karpiscak, M.M., Gerba, C.P., 2004. The persistence and removal of enteric pathogens in constructed wetlands. Water Res. 38, 1831-1837.

Karraker, N.E., Gibbs, J.P., 2011. Road deicing salt irreversibly disrupts osmoregulation of salamander egg clutches. Environmental Pollution 159, 833-835.

Kasaraneni, V., Kohm, S.E., Eberle, D., Boving, T., Oyanedel-Craver, V., 2013. Enhanced containment of polycyclic aromatic hydrocarbons through organic modification of soils. Environmental Progress & Sustainable Energy .

Kasaraneni, V.K., Schifman, L.A., Boving, T.B., Oyanedel-Craver, V., 2014. Enhancement of Surface Runoff Quality Using Modified Sorbents. ACS Sustainable Chem. Eng. 2, 1609-1615 doi: 10.1021/sc500107q.

Katsoyiannis, A., Sweetman, A.J., Jones, K.C., 2011. PAH molecular diagnostic ratios applied to atmospheric sources: a critical evaluation using two decades of source inventory and air concentration data from the UK. Environ. Sci. Technol. 45, 8897-8906.

Kaushal, S.S., Groffman, P.M., Band, L.E., Elliott, E.M., Shields, C.A., Kendall, C., 2011. Tracking nonpoint source nitrogen pollution in human-impacted watersheds. Environ. Sci. Technol. 45, 8225-8232.

Kavouras, I.G., Koutrakis, P., Tsapakis, M., Lagoudaki, E., Stephanou, E.G., Von Baer, D., Oyola, P., 2001. Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHs) using multivariate methods. Environ. Sci. Technol. 35, 2288-2294.

Kayhanian, M., Suverkropp, C., Ruby, A., Tsay, K., 2007. Characterization and prediction of highway runoff constituent event mean concentration. J. Environ. Manage. 85, 279-295.

Khalili, N.R., Scheff, P.A., Holsen, T.M., 1995. PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions. Atmos. Environ. 29, 533-542.

Kim, H., Seagren, E.A., Davis, A.P., 2003. Engineered bioretention for removal of nitrate from stormwater runoff. Water Environ. Res., 355-367.

Kim, H.W., Kim, B.R., Rhee, Y.H., 2010. Imparting durable antimicrobial properties to cotton fabrics using alginate–quaternary ammonium complex nanoparticles. Carbohydr. Polym. 79, 1057-1062.

Kim, J.S., Kuk, E., Yu, K.N., Kim, J., Park, S.J., Lee, H.J., Kim, S.H., Park, Y.K., Park, Y.H., Hwang, C., 2007. Antimicrobial effects of silver nanoparticles. Nanomedicine: Nanotechnology, Biology and Medicine 3, 95-101.

Klement, J., 2008. Determining the effectiveness of aspen (Populus tremula) wood fibers and ponderosa pine (Pinus ponderosa) bark pellets for removal of storm runoff contaminants: a field-scale study in Providence, RI. , 256.

Kong, M., Chen, X.G., Xing, K., Park, H.J., 2010. Antimicrobial properties of chitosan and mode of action: a state of the art review. Int. J. Food Microbiol. 144, 51-63.

Krauss, M., Wilcke, W., Zech, W., 2000. Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in forest soils: depth distribution as indicator of different fate. Environmental Pollution 110, 79-88.

Krein, A., Schorer, M., 2000. Road runoff pollution by polycyclic aromatic hydrocarbons and its contribution to river sediments. Water Res. 34, 4110-4115 doi: 10.1016/S0043-1354(00)00156-1.

Kroetz, K.M., Friedland, A.J., 2008. Comparing costs and emissions of northern New England space heating fuel options. Biomass Bioenergy 32, 1359-1366.

Kurian, L.M., Lautz, L.K., Mitchell, M.J., 2013. Winter Hydrology and NO3− Concentrations in a Forested Watershed: A Detailed Field Study in the Adirondack Mountains of New York1. JAWRA Journal of the American Water Resources Association 49, 264-283.

Larsen, R.K., Baker, J.E., 2003. Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. Environ. Sci. Technol. 37, 1873-1881.

Lau, S., Han, Y., Kang, J., Kayhanian, M., Stenstrom, M.K., 2009. Characteristics of Highway Stormwater Runoff in Los Angeles: Metals and Polycyclic Aromatic Hydrocarbons. Water Environ. Res. 81, 308-318 doi: doi:10.2175/106143008X357237".

Lau, S., Stenstrom, M.K., 2005. Metals and PAHs adsorbed to street particles. Water Res. 39, 4083-4092 doi: 10.1016/j.watres.2005.08.002.

Ledford, S.H., Lautz, L.K., 2014. Floodplain connection buffers seasonal changes in urban stream water quality. Hydrol. Process. .

Lee, J.H., Gigliotti, C.L., Offenberg, J.H., Eisenreich, S.J., Turpin, B.J., 2004. Sources of polycyclic aromatic hydrocarbons to the Hudson River Airshed. Atmos. Environ. 38, 5971-5981.

Lee, S.M., Tiwari, D., 2012. Organo and inorgano-organo-modified clays in the remediation of aqueous solutions: An overview. Appl. Clay. Sci. 59, 84-102.

Lee, C.M., Lin, T.Y., Lin, C.C., Kohbodi, G.A., Bhatt, A., Lee, R., Jay, J.A., 2006. Persistence of fecal indicator bacteria in Santa Monica Bay beach sediments Water Res. 40, 2593-2602 doi: 10.1016/j.watres.2006.04.032.

Lee, H., Lau, S., Kayhanian, M., Stenstrom, M.K., 2004. Seasonal first flush phenomenon of urban stormwater discharges. Water Res. 38, 4153-4163 doi: 10.1016/j.watres.2004.07.012.

Legret, M., Colandini, V., Le Marc, C., 1996. Effects of a porous pavement with reservoir structure on the quality of runoff water and soil. Sci. Total Environ. 189-190, 335-340.

Legret, M., Colandini, V., 1999. Effects of a porous pavement with reservoir structure on runoff water: Water quality and fate of heavy metals. Water Science and Technology 39, 111-117.

Li, H., Davis, A.P., 2009. Water quality improvement through reductions of pollutant loads using bioretention. J. Environ. Eng. 135, 567-576.

Li, L., Qian, J., Ou, C., Zhou, Y., Guo, C., Guo, Y., 2014. Spatial and temporal analysis of Air Pollution Index and its timescale-dependent relationship with meteorological factors in Guangzhou, China, 2001–2011. Environmental Pollution 190, 75-81.

Li, Y.L., Deletic, A., McCarthy, D.T., 2014. Removal of *E. coli* from urban stormwater using antimicrobial-modified filter media J. Hazard. Mater. 271, 73 - 81 doi: 10.1016/j.jhazmat.2014.01.057.

Li, Z., Lee, D., Sheng, X., Cohen, R.E., Rubner, M.F., 2006. Two-Level Antibacterial Coating with Both Release-Killing and Contact-Killing Capabilities Langmuir 22, 9820 - 9823 doi: 10.1021/la0622166.

Liguori, L., Heggstad, K., Hove, H.T., Julshamn, K., 2006. An automated extraction approach for isolation of 24 polyaromatic hydrocarbons (PAHs) from various marine matrixes. Anal. Chim. Acta 573–574, 181-188 doi: 10.1016/j.aca.2006.01.082.

Lima, A.L.C., Farrington, J.W., Reddy, C.M., 2005. Combustion-derived polycyclic aromatic hydrocarbons in the environment—a review. Environmental Forensics 6, 109-131.

Lima, A.L.C., Eglinton, T.I., Reddy, C.M., 2003. High-resolution record of pyrogenic polycyclic aromatic hydrocarbon deposition during the 20th century. Environ. Sci. Technol. 37, 53-61.

Limousin, G., Gaudet, J., Charlet, L., Szenknect, S., Barthes, V., Krimissa, M., 2007. Sorption isotherms: A review on physical bases, modeling and measurement. Appl. Geochem. 22, 249-275.

Liu, L., Liu, Y., Lin, J., Tang, N., Hayakawa, K., Maeda, T., 2007. Development of analytical methods for polycyclic aromatic hydrocarbons (PAHs) in airborne particulates: A review. Journal of Environmental Sciences 19, 1-11.

Liu, Y., Beckingham, B., Ruegner, H., Li, Z., Ma, L., Schwientek, M., Xie, H., Zhao, J., Grathwohl, P., 2013. Comparison of sedimentary PAHs in the rivers of Ammer (Germany) and Liangtan (China): differences between early-and newly-industrialized countries. Environ. Sci. Technol. 47, 701-709.

Lo, I.M.C., Yang, X., 1999. EDTA extraction of heavy metals from different soil fractions and synthetic soils. Water, Air, & Soil Pollution 109, 219-236.

Logan, B.E., 1999. Environmental Transport Processes . John Wiley & Sons, New York.

Lohmann, R., MacFarlane, J., Gschwend, P., 2005. Importance of black carbon to sorption of native PAHs, PCBs, and PCDDs in Boston and New York harbor sediments. Environ. Sci. Technol. 39, 141-148.

Lohmann, R., Gioia, R., Jones, K.C., Nizzetto, L., Temme, C., Xie, Z., Schulz-Bull, D., Hand, I., Morgan, E., Jantunen, L., 2009. Organochlorine Pesticides and PAHs in the Surface Water and Atmosphere of the North Atlantic and Arctic Ocean. Environ. Sci. Technol. 43, 5633-5639 doi: 10.1021/es901229k.

Lohmann, R., Northcott, G.L., Jones, K.C., 2000. Assessing the Contribution of Diffuse Domestic Burning as a Source of PCDD/Fs, PCBs, and PAHs to the U.K. Atmosphere. Environ. Sci. Technol. 34, 2892-2899 doi: 10.1021/es991183w.

Luo, L., Lin, S., Huang, H., Zhang, S., 2012. Relationships between aging of PAHs and soil properties. Environmental Pollution 170, 177-182.

MacKay, A.A., Gschwend, P.M., 2000. Sorption of Monoaromatic Hydrocarbons to Wood. Environ. Sci. Technol. 34, 839-845 doi: 10.1021/es9900858.

Mackay, D., Shiu, W.Y., Kuo-Ching Ma, Sum Chi Lee, Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Second Edition . TF-CRC.

Mahler, B.J., Van Metre, P.C., Bashara, T.J., Wilson, J.T., Johns, D.A., 2005. Parking lot sealcoat: an unrecognized source of urban polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 39, 5560-5566.

Maliszewska-Kordybach, B., 1993. The effect of temperature on the rate of disappearance of polycyclic aromatic hydrocarbons from soils. Environmental Pollution 79, 15-20.

Mallin, M.A., Johnson, V.L., Ensign, S.H., 2009. Comparative impacts of stormwater runoff on water quality of an urban, a suburban, and a rural stream. Environ. Monit. Assess. 159, 475-491.

Mallin, M.A., Ensign, S.H., Wheeler, T.L., Mayes, D.B., 2002. Pollutant removal efficacy of three wet detention ponds. J. Environ. Qual. 31, 654-660.

Mallin, M.A., Williams, K.E., Esham, E.C., Lowe, R.P., 2000. Effect of human development on bacteriological water quality in coastal watersheds. Ecol. Appl. 10, 1047-1056.

Manoli, E., Samara, C., 1999. Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis. TrAC Trends in Analytical Chemistry 18, 417-428.

Manouchehri, N., Besancon, S., Bermond, A., 2006. Major and trace metal extraction from soil by EDTA: Equilibrium and kinetic studies. Anal. Chim. Acta 559, 105-112 doi: 10.1016/j.aca.2005.11.050.

Marini, M., Bondi, M., Iseppi, R., Toselli, M., Pilati, F., 2007. Preparation and antibacterial activity of hybrid materials containing quaternary ammonium salts via sol–gel process. European Polymer Journal 43, 3621-3628 doi: 10.1016/j.eurpolymj.2007.06.002.

Martin, H., 2000. Development of passive samplers for time-integrated deposition and groundwater monitoring: adsorption cartridges and ceramic dosimeters.

Masclet, P., Mouvier, G., Nikolaou, K., 1986. Relative decay index and sources of polycyclic aromatic hydrocarbons. Atmospheric Environment (1967) 20, 439-446.

Masiello, C., 2004. New directions in black carbon organic geochemistry. Mar. Chem. 92, 201-213.

Mastral, A.M., Callan, M.S., 2000. A Review on Polycyclic Aromatic Hydrocarbon (PAH) Emissions from Energy Generation. Environ. Sci. Technol. 34, 3051-3057 doi: 10.1021/es001028d.

May, W.E., Wise, S.A., 1984. Liquid chromatographic determination of polycyclic aromatic hydrocarbons in air particulate extracts. Anal. Chem. 56, 225-232.

McCarthy, D., Mitchell, V., Deletic, A., Diaper, C., 2007. *Escherichia coli* in urban stormwater: explaining their variability. Water Science & Technology 56, 27-34.

McCarthy, D., Hathaway, J., Hunt, W., Deletic, A., 2012. Intra-event variability of *Escherichia coli* and total suspended solids in urban stormwater runoff. Water Res. 46, 6661-6670.

McCarthy, D., Deletic, A., Mitchell, V., Fletcher, T., Diaper, C., 2008. Uncertainties in stormwater *E. coli* levels. Water Res. 42, 1812-1824.

McCaulou, D.R., Bales, R.C., Arnold, R.G., 1995; 2010. Effect of Temperature-Controlled Motility on Transport of Bacteria and Microspheres Through Saturated Sediment Water Resour. Res. 31, 271 - 280 doi: 10.1029/94WR02569.

McLellan, S., Salmore, A., 2003. Evidence for localized bacterial loading as the cause of chronic beach closings in a freshwater marina. Water Res. 37, 2700-2708.

MDE, 2009. Maryland Stormwater Design Manual Volume I - Stormwater Management Criteria.

Mellouk, H., Khezami, L., Rezzoug, S., Capart,R., 2008. Total Valorisation Of Red Cedar (Thuja Plicata) Sawmills Wastes. Isolation Of Extractives And Production Of Activated Carbon From The Solid Residue. BioResources 3.

Melymuk, L., Robson, M., Helm, P.A., Diamond, M.L., 2013. Application of land use regression to identify sources and assess spatial variation in urban SVOC concentrations. Environ. Sci. Technol. 47, 1887-1895.

Menon, R., MacKay, A., Hailey, J., Bloom, M., Burgess, A., Swanson, J., 1987. An NMR determination of the physiological water distribution in wood during drying. J Appl Polym Sci 33, 1141-1155.

Miguel, A.H., Pereira, P.A., 1989. Benzo (k) fluoranthene, benzo (ghi) perylene, and indeno (1, 2, 3-cd) pyrene: new tracers of automotive emissions in receptor modeling. Aerosol Science and Technology 10, 292-295.

Mohanty, S.K., Torkelson, A.A., Dodd, H., Nelson, K.L., Boehm, A.B., 2013. Engineering Solutions to Improve the Removal of Fecal Indicator Bacteria by Bioinfiltration Systems during Intermittent Flow of Stormwater Environ. Sci. Technol. 47, 10791 <last_page> 10798 doi: 10.1021/es305136b.

Moldanová, J., Fridell, E., Popovicheva, O., Demirdjian, B., Tishkova, V., Faccinetto, A., Focsa, C., 2009. Characterisation of particulate matter and gaseous emissions from a large ship diesel engine. Atmos. Environ. 43, 2632-2641.

Morales, I., Atoyan, J.A., Amador, J.A., Boving, T., 2014. Transport of Pathogen Surrogates in Soil Treatment Units: Numerical Modeling. Water 6, 818-838.

Moreno-Castilla, C., Rivera-Utrilla, J., Joly, J., López-Ramón, M., Ferro-García, M., Carrasco-Marin, F., 1995. Thermal regeneration of an activated carbon exhausted with different substituted phenols. Carbon 33, 1417-1423.

Mostert, M.M.R., Ayoko, G.A., Kokot, S., 2010. Application of chemometrics to analysis of soil pollutants. TrAC Trends in Analytical Chemistry 29, 430-445.

Motelay-Massei, A., Ollivon, D., Garban, B., Chevreuil, M., 2003. Polycyclic aromatic hydrocarbons in bulk deposition at a suburban site: assessment by principal component analysis of the influence of meteorological parameters. Atmos. Environ. 37, 3135-3146.

Motelay-Massei, A., Ollivon, D., Garban, B., Tiphagne-Larcher, K., Zimmerlin, I., Chevreuil, M., 2007. PAHs in the bulk atmospheric deposition of the Seine river basin: source identification and apportionment by ratios, multivariate statistical techniques and scanning electron microscopy. Chemosphere 67, 312-321.

Mukherji, S., Peters, C.A., Weber Jr, W.J., 1997. Mass transfer of polynuclear aromatic hydrocarbons from complex DNAPL mixtures. Environ. Sci. Technol. 31, 416-423.

Nam, J.J., Thomas, G.O., Jaward, F.M., Steinnes, E., Gustafsson, O., Jones, K.C., 2008. PAHs in background soils from Western Europe: Influence of atmospheric deposition and soil organic matter. Chemosphere 70, 1596-1602.

Naumova, Y.Y., Offenberg, J.H., Eisenreich, S.J., Meng, Q., Polidori, A., Turpin, B.J., Weisel, C.P., Morandi, M.T., Colome, S.D., Stock, T.H., 2003. Gas/particle distribution of polycyclic aromatic hydrocarbons in coupled outdoor/indoor atmospheres. Atmos. Environ. 37, 703-719.

Neary, K., Boving, T.B., 2011. The fate of the aqueous phase polycyclic aromatic hydrocarbon fraction in a detention pond system. Environmental Pollution 159, 2882-2890.

No, H.K., Kim, S.H., Lee, S.H., Park, N.Y., Prinyawiwatkul, W., 2006. Stability and antibacterial activity of chitosan solutions affected by storage temperature and time. Carbohydr. Polym. 65, 174-178.

NOAA, National Oceanic and Atmospheric Administration, 2014. Annual Climatological Summary for Providence, RI.

Norrström, A., Jacks, G., 1998. Concentration and fractionation of heavy metals in roadside soils receiving de-icing salts. Sci. Total Environ. 218, 161-174.

Ohashi, H., Nakazawa, H., 1996. The microstructure of humic acid-montmorillonite composites. Clay Minerals 31, 347-354.

Okuda, T., Kumata, H., Naraoka, H., Takada, H., 2002. Origin of atmospheric polycyclic aromatic hydrocarbons (PAHs) in Chinese cities solved by compound-specific stable carbon isotopic analyses. Org. Geochem. 33, 1737-1745.

Ola, E., Abo, S.M., Kotek, R., White, W.C., Reeve, J.A., Hauser, P., Kim, J.H., 2004. Unusual polymerization of 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride on PET substrates. Polymer 45, 3215-3225.

Olivella, M.À., 2006. Polycyclic aromatic hydrocarbons in rainwater and surface waters of Lake Maggiore, a subalpine lake in Northern Italy. Chemosphere 63, 116-131 doi: 10.1016/j.chemosphere.2005.07.045.

Oosterhof, J.J., Buijssen, K.J., Busscher, H.J., van der Laan, Bernard FAM, van der Mei, Henny C, 2006. Effects of quaternary ammonium silane coatings on mixed fungal and bacterial biofilms on tracheoesophageal shunt prostheses. Appl. Environ. Microbiol. 72, 3673-3677.

Orr, C.H., Leifert, C., Cummings, S.P., Cooper, J.M., 2012. Impacts of Organic and Conventional Crop Management on Diversity and Activity of Free-Living Nitrogen

Fixing Bacteria and Total Bacteria Are Subsidiary to Temporal Effects. PLoS ONE 7, e52891.

Ortega-Gómez, E., Fernández-Ibáñez, P., Ballesteros Martín, M.M., Polo-López, M.I., Esteban García, B., Sánchez Pérez, J.A., 2012. Water disinfection using photo-Fenton: Effect of temperature on Enterococcus faecalis survival Water Res. 46, 6154 - 6162 doi: 10.1016/j.watres.2012.09.007.

Oyanedel-Craver, V.A., Fuller, M., Smith, J.A., 2007. Simultaneous sorption of benzene and heavy metals onto two organoclays. J. Colloid Interface Sci. 309, 485-492.

Oyanedel-Craver, V.A., Smith, J.A., 2006. Effect of quaternary ammonium cation loading and pH on heavy metal sorption to Ca bentonite and two organobentonites. J. Hazard. Mater. 137, 1102-1114.

Oyanedel-Craver, V.A., Smith, J.A., 2007. Sustainable colloidal-silver-impregnated ceramic filter for point-of-use water treatment. Environ. Sci. Technol. 42, 927-933.

Öztürk, N., Bektaş, T.E., 2004. Nitrate removal from aqueous solution by adsorption onto various materials. J. Hazard. Mater. 112, 155-162.

PA DEP, 2006. Pennsylvania Stormwater Best Management Practices Manual. 1, 1-642.

Paatero, P., Tapper, U., 1994. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. Environmetrics 5, 111-126.

Palma, G., Freer, J., Baeza, J., 2003. Removal of metal ions by modified Pinus radiata bark and tannins from water solutions. Water Res. 37, 4974-4980 doi: 10.1016/j.watres.2003.08.008.

Palmer, E.T., Poor, C.J., Hinman, C., Stark, J.D., 2013. Nitrate and phosphate removal through enhanced Bioretention media: Mesocosm study. Water Environ. Res. 85, 823-832.

Park, K.S., Sims, R.C., Dupont, R.R., 1990. Transformation of PAHs in soil systems. J. Environ. Eng. 116, 632-640.

Park, J., Wade, T.L., Sweet, S., 2001. Atmospheric distribution of polycyclic aromatic hydrocarbons and deposition to Galveston Bay, Texas, USA. Atmos. Environ. 35, 3241-3249 doi: 10.1016/S1352-2310(01)00080-2.

Parker, J., McIntyre, D., Noble, R., 2010. Characterizing fecal contamination in stormwater runoff in coastal North Carolina, USA. Water Res. 44, 4186-4194.

Pathan, A., Bond, J., Gaskin, R., 2010. Sample preparation for SEM of plant surfaces. Materials Today 12, 32-43.

Paune, F., Caixach, J., Espadaler, I., Om, J., Rivera, J., 1998. Assessment on the removal of organic chemicals from raw and drinking water at a Llobregat river water works plant using GAC. Water Res. 32, 3313-3324.

Peltonen, K., Kuljukka, T., 1995. Air sampling and analysis of polycyclic aromatic hydrocarbons. Journal of Chromatography A 710, 93-108.

Pfeiffer, C., Rehbock, C., Huhn, D., Carrillo-Carrion, C., de Aberasturi, D.J., Merk, V., Barcikowski, S., Parak, W.J., 2014. Interaction of colloidal nanoparticles with their local environment: the (ionic) nanoenvironment around nanoparticles is different from bulk and determines the physico-chemical properties of the nanoparticles. J. R. Soc. Interface 11, 20130931 doi: 10.1098/rsif.2013.0931 [doi].

Pinheiro, L.B., Gibbs, M.D., Vesey, G., Smith, J.J., Bergquist, P., 2008. Fluorescent reference strains of bacteria by chromosomal integration of a modified green fluorescent protein gene. Appl. Microbiol. Biotechnol. 77, 1287-1295.

Plaschke, M., Römer, J., Klenze, R., Kim, J., 1999. In situ AFM study of sorbed humic acid colloids at different pH. Colloids Surf. Physicochem. Eng. Aspects 160, 269-279.

Raffellini, S., Schenk, M., Guerrero, S., Alzamora, S.M., 2011. Kinetics of *Escherichia coli* inactivation employing hydrogen peroxide at varying temperatures, pH and concentrations. Food Control 22, 920-932.

Rance, G.A., Marsh, D.H., Bourne, S.J., Reade, T.J., Khlobystov, A.N., 2010. van der Waals interactions between nanotubes and nanoparticles for controlled assembly of composite nanostructures. ACS nano 4, 4920-4928.

Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos. Environ. 42, 2895-2921.

Ravindra, K., Bencs, L., Wauters, E., De Hoog, J., Deutsch, F., Roekens, E., Bleux, N., Berghmans, P., Van Grieken, R., 2006. Seasonal and site-specific variation in vapour and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities. Atmos. Environ. 40, 771-785.

Ray, S., Khillare, P., Agarwal, T., Shridhar, V., 2008. Assessment of PAHs in soil around the International Airport in Delhi, India. J. Hazard. Mater. 156, 9-16.

Rayner, J., Zhang, H., Lantagne, D., Schubert, J., Lennon, P., Craver, V.O., 2013. Laboratory investigation into the effect of silver application on the bacterial removal efficacy of filter material for use on locally-produced ceramic water filters for household drinking water treatment. ACS Sustainable Chemistry & Engineering.

Reading, H.G., 1996. Sedimentary Environments: Processes, Facies, and Stratigraphy. Blackwell Science.

Reddad, Z., Gerente, C., Andres, Y., Le Cloirec, P., 2002. Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. Environ. Sci. Technol. 36, 2067-2073.

Reddy, K.R., Xie, T., Dastgheibi, S., 2014. Evaluation of Biochar as a Potential Filter Media for the Removal of Mixed Contaminants from Urban Storm Water Runoff. J. Environ. Eng. .

Reeves, R.L., Grant, S.B., Mrse, R.D., Copil Oancea, C.M., Sanders, B.F., Boehm, A.B., 2004. Scaling and management of fecal indicator bacteria in runoff from a coastal urban watershed in southern California. Environ. Sci. Technol. 38, 2637-2648.

Ren, D., Colosi, L.M., Smith, J.A., 2013. Evaluating the sustainability of ceramic filters for point-of-use drinking water treatment. Environ. Sci. Technol. 47, 11206-11213.

Ren, G., Hu, D., Cheng, E.W., Vargas-Reus, M.A., Reip, P., Allaker, R.P., 2009. Characterisation of copper oxide nanoparticles for antimicrobial applications. Int. J. Antimicrob. Agents 33, 587-590.

Ribes, S., Van Drooge, B., Dachs, J., Gustafsson, Ø., Grimalt, J.O., 2003. Influence of soot carbon on the soil-air partitioning of polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 37, 2675-2680.

RIDEM, 2010. Rhode Island Stormwater Design and Installation Standards Manual. , 487.

Rockne, K.J., Shor, L.M., Young, L.Y., Taghon, G.L., Kosson, D.S., 2002. Distributed Sequestration and Release of PAHs in Weathered Sediment:‰ The Role of Sediment Structure and Organic Carbon Properties. Environ. Sci. Technol. 36, 2636-2644 doi: 10.1021/es015652h.

Roesner, L.A., Bledsoe, B.P., Brashear, R.W., 2001. Are best-management-practice criteria really environmentally friendly? J. Water Resour. Plann. Manage. 127, 150-154.

Rogers, S., Ong, S., Kjartanson, B., Golchin, J., Stenback, G., 2002. Natural attenuation of polycyclic aromatic hydrocarbon-contaminated sites: review. Pract. Periodical Hazard. , Toxic, Radioact. Waste Manage. 6, 141-155.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R., 1997. Sources of fine organic aerosol. 8. Boilers burning No. 2 distillate fuel oil. Environ. Sci. Technol. 31, 2731-2737.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R., 1993. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environ. Sci. Technol. 27, 636-651.

Rose, J.B., Daeschner, S., Easterling, D.R., Curriero, F.C., Lele, S., Patz, J.A., 2000. Climate and waterborne disease outbreaks. Journal-American Water Works Association 92, 77-87.

Rosen, M., 1975. Relationship of structure to properties in surfactants. III. Adsorption at the solid-liquid interface from aqueous solution. Journal of the American Oil Chemists Society 52, 431-435.

Rosen, M.J., Kunjappu, J.T., 2012. Surfactants and Interfacial Phenomena doi: 10.1002/9781118228920.

Rügner, H., Kleineidam, S., Grathwohl, P., 1999. Long term sorption kinetics of phenanthrene in aquifer materials. Environ. Sci. Technol. 33, 1645-1651.

Sabaté, J., Viñas, M., Solanas, A.M., 2006. Bioavailability assessment and environmental fate of polycyclic aromatic hydrocarbons in biostimulated creosote-contaminated soil. Chemosphere 63, 1648-1659.

Sabin, L.D., Lim, J.H., Stolzenbach, K.D., Schiff, K.C., 2005. Contribution of trace metals from atmospheric deposition to stormwater runoff in a small impervious urban catchment. Water Res. 39, 3929-3937.

Saif, M.J., Anwar, J., Munawar, M.A., 2008. A novel application of quaternary ammonium compounds as antibacterial hybrid coating on glass surfaces. Langmuir 25, 377-379.

Saim, N., Dean, J.R., Abdullah, M.P., Zakaria, Z., 1998. An Experimental Design Approach for the Determination of Polycyclic Aromatic Hydrocarbons from Highly Contaminated Soil Using Accelerated Solvent Extraction. Anal. Chem. 70, 420-424 doi: 10.1021/ac970473x.

Saim, N., Dean, J.R., Abdullah, M.P., Zakaria, Z., 1997. Extraction of polycyclic aromatic hydrocarbons from contaminated soil using Soxhlet extraction, pressurised and atmospheric microwave-assisted extraction, supercritical fluid extraction and accelerated solvent extraction. Journal of Chromatography A 791, 361-366 doi: 10.1016/S0021-9673(97)00768-1.

Schifman, L.A., Boving, T.B., submitted. Spatial and seasonal variation in PAH sources and atmospheric deposition patterns in a small northeastern state in the United States.

Schifman, L.A., Kasaraneni, V.K., Sullivan, R.K., Oyanedel-Craver, V., Boving, T., in prep a. Selecting an antimicrobial filter media for improved stormwater best management practices.

Schifman, L.A., Kasaraneni, V.K., Sullivan, R.K., Oyanedel-Craver, V., Boving, T., in prep b. Evaluation of Stormwater Runoff Using a Tree Filter BMP.

Schmidt, M.W.I., Noack, A.G., 2000. Black carbon in soils and sediments: analysis, distribution, implications, and current challenges. Global Biogeochem. Cycles 14, 777-793.

Schnitzer, M., Khan, S.U., 1978. Soil Organic Matter. Elsevier Science.

Schock, M.R., Neff, C.H., 1988. Trace metal contamination from brass fittings. Journal (American Water Works Association) , 47-56.

Scholes, L., Revitt, D.M., Ellis, J.B., 2008. A systematic approach for the comparative assessment of stormwater pollutant removal potentials. J. Environ. Manage. 88, 467-478.

Schoonover, J.E., Lockaby, B.G., 2006. Land cover impacts on stream nutrients and fecal coliform in the lower Piedmont of West Georgia. Journal of Hydrology 331, 371-382.

Schueler, T.R., Holland, H., 2000. Microbes and urban watersheds: concentrations, sources, and pathways. The Practice of Watershed Protection , 74-84.

Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2002. Environmental Organic Chemistry, 2 ed. John Wiley & Sons, Inc., Hoboken, New Jersey, USA.

Schwarz, K., Gocht, T., Grathwohl, P., 2011. Transport of polycyclic aromatic hydrocarbons in highly vulnerable karst systems. Environmental Pollution 159, 133-139.

Selvakumar, A., Borst, M., 2006. Variation of microorganism concentrations in urban stormwater runoff with land use and seasons. J Water Health 4, 109-124.

Shahin, U., Yi, S., Paode, R.D., Holsen, T.M., 2000. Long-Term Elemental Dry Deposition Fluxes Measured around Lake Michigan with an Automated Dry Deposition Sampler. Environ. Sci. Technol. 34, 1887-1892 doi: 10.1021/es9907562.

Shannigrahi, A., Fukushima, T., Ozaki, N., 2005. Comparison of different methods for measuring dry deposition fluxes of particulate matter and polycyclic aromatic hydrocarbons (PAHs) in the ambient air. Atmos. Environ. 39, 653-662.

Shen, G., Tao, S., Wang, W., Yang, Y., Ding, J., Xue, M., Min, Y., Zhu, C., Shen, H., Li, W., Wang, B., Wang, R., Wang, W., Wang, X., Russell, A.G., 2011. Emission of Oxygenated Polycyclic Aromatic Hydrocarbons from Indoor Solid Fuel Combustion. Environ. Sci. Technol. 45, 3459-3465 doi: 10.1021/es104364t.

Shen, H., Huang, Y., Wang, R., Zhu, D., Li, W., Shen, G., Wang, B., Zhang, Y., Chen, Y., Lu, Y., Chen, H., Li, T., Sun, K., Li, B., Liu, W., Liu, J., Tao, S., 2013. Global Atmospheric Emissions of Polycyclic Aromatic Hydrocarbons from 1960 to 2008 and Future Predictions. Environ. Sci. Technol. doi: 10.1021/es400857z.

Sheu, H., Lee, W., Su, C., Chao, H., Fan, Y., 1996. Dry Deposition of Polycyclic Aromatic Hydrocarbons in Ambient Air. J. Envir. Engrg. 122, 1101-1109 doi: 10.1061/(ASCE)0733-9372(1996)122:12(1101).

Shi, Z., Neoh, K., Kang, E., 2007. Antibacterial and adsorption characteristics of activated carbon functionalized with quaternary ammonium moieties. Ind Eng Chem Res 46, 439-445.

Shivaji, S., Prakash, J.S., 2010. How do bacteria sense and respond to low temperature? Arch. Microbiol. 192, 85-95.

Simcik, M.F., Eisenreich, S.J., Lioy, P.J., 1999. Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. Atmos. Environ. 33, 5071-5079.

Skog, K.E., Watterson, I.A., 1984. Residential fuelwood use in the United States. J. For. 82, 742-747.

Slob, A.F.L., Rijnveld, M., Chapman, A.S., Strosser, P., 2007. Challenges of linking scientific knowledge to river basin management policy: AquaTerra as a case study. Environmental Pollution 148, 867-874.

Smith, J.A., Jaffe, P.R., Chiou, C.T., 1990. Effect of ten quaternary ammonium cations on tetrachloromethane sorption to clay from water. Environ. Sci. Technol. 24, 1167-1172.

Smith, M.J., Flowers, T.H., Duncan, H.J., Alder, J., 2006. Effects of polycyclic aromatic hydrocarbons on germination and subsequent growth of grasses and legumes in freshly contaminated soil and soil with aged PAHs residues. Environmental Pollution 141, 519-525.

Soller, J.A., Schoen, M.E., Varghese, A., Ichida, A.M., Boehm, A.B., Eftim, S., Ashbolt, N.J., Ravenscroft, J.E., 2014. Human health Risk implications of multiple sources of faecal indicator bacteria in a recreational waterbody. Water Res. .

Sondi, I., Salopek-Sondi, B., 2004. Silver nanoparticles as antimicrobial agent: a case study on *E. coli* as a model for Gram-negative bacteria J. Colloid Interface Sci. 275, 177-182 doi: 10.1016/j.jcis.2004.02.012.

Song, J., Kong, H., Jang, J., 2011. Bacterial adhesion inhibition of the quaternary ammonium functionalized silica nanoparticles. Colloids and Surfaces B: Biointerfaces 82, 651-656.

Stein, E.D., Tiefenthaler, L.L., Schiff, K.C., 2007. Sources, patterns and mechanisms of storm water pollutant loading from watersheds and land uses of the greater Los Angeles area, California, USA. Southern California Coastal Water Research Project Techincal Report 510.

Stevik, T.K., Aa, K., Ausland, G., Hanssen, J.F., 2004. Retention and removal of pathogenic bacteria in wastewater percolating through porous media: a review Water Res. 38, 1355-1367 doi: 10.1016/j.watres.2003.12.024.

Stewart, J.R., Gast, R.J., Fujioka, R.S., Solo-Gabriele, H.M., Meschke, J.S., Amaral-Zettler, L.A., del Castillo, E., Polz, M.F., Collier, T.K., Strom, M.S., 2008. The coastal environment and human health: microbial indicators, pathogens, sentinels and reservoirs. Environ. Health 7, S3.

Surbeck, C.Q., Jiang, S.C., Ahn, J.H., Grant, S.B., 2006. Flow fingerprinting fecal pollution and suspended solids in stormwater runoff from an urban coastal watershed. Environ. Sci. Technol. 40, 4435-4441.

Syring, S.M., Krishnamurthy, R., MacKay, A.A., 2009. Attenuation of Roadway-Derived Heavy Metals by Wood Chips. J. Environ. Eng. 135, 747-757.

Taty-Costodes, V.C., Fauduet, H., Porte, C., Delacroix, A., 2003. Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of Pinus sylvestris. J. Hazard. Mater. 105, 121-142 doi: 10.1016/j.jhazmat.2003.07.009.

Tchobanoglous, G., Burton, F.L., Stensel, H.D. 2003.Wastewater Engineering: Treatment and Reuse . Boston ; McGraw-Hill.

Tillman Jr, F.D., Bartelt-Hunt, S.L., Craver, V.A., Smith, J.A., Alther, G.R., 2005. Relative metal ion sorption on natural and engineered sorbents: batch and column studies. Environ. Eng. Sci. 22, 400-410.

Tobiszewski, M., Namieśnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environmental Pollution 162, 110-119.

Tokman, N., Akman, S., Ozeroglu, C., 2004. Determination of lead, copper and manganese by graphite furnace atomic absorption spectrometry after separation/concentration using a water-soluble polymer Talanta 63, 699-703 doi: 10.1016/j.talanta.2003.12.018 [doi].

Tomšič, B., Klemenčič, D., Simončič, B., Orel, B., 2011. Influence of antimicrobial finishes on the biodeterioration of cotton and cotton/polyester fabrics: leaching versus bio-barrier formation. Polym. Degrad. Stab. 96, 1286-1296.

Torkelson, A., da Silva, A., Love, D., Kim, J., Alper, J., Coox, B., Dahm, J., Kozodoy, P., Maboudian, R., Nelson, K., 2012. Investigation of quaternary ammonium silane-coated sand filter for the removal of bacteria and viruses from drinking water. J. Appl. Microbiol. 113, 1196-1207.

Tromp, K., Lima, A.T., Barendregt, A., Verhoeven, J.T., 2012. Retention of heavy metals and poly-aromatic hydrocarbons from road water in a constructed wetland and the effect of de-icing. J. Hazard. Mater. 203, 290-298.

Tuccillo, M.E., 2006. Size fractionation of metals in runoff from residential and highway storm sewers. Sci. Total Environ. 355, 288-300 doi: 10.1016/j.scitotenv.2005.03.003.

UNHSC, Roseen, R., Ballestero, T., Houle, J., 2007. UNH Stormwater Center 2007 Annual Report. .

Unwin, P.R., Bard, A.J., 1992. Scanning electrochemical microscopy. 14. Scanning electrochemical microscope induced desorption: a new technique for the measurement of adsorption/desorption kinetics and surface diffusion rates at the solid/liquid interface. J. Phys. Chem. 96, 5035-5045.

Valderrama, C., Gamisans, X., de las Heras, X., Farran, A., Cortina, J., 2008. Sorption kinetics of polycyclic aromatic hydrocarbons removal using granular activated carbon: Intraparticle diffusion coefficients. J. Hazard. Mater. 157, 386-396.

van den Elshout, S., Léger, K., Nussio, F., 2008. Comparing urban air quality in Europe in real time: A review of existing air quality indices and the proposal of a common alternative. Environ. Int. 34, 720-726.

Van Metre, P.C., Majewski, M.S., Mahler, B.J., Foreman, W.T., Braun, C.L., Wilson, J.T., Burbank, T.L., 2012. PAH volatilization following application of coal-tar-based pavement sealant. Atmos. Environ. .

Van Metre, P.C., Mahler, B.J., Furlong, E.T., 2000. Urban Sprawl Leaves Its PAH Signature. Environ. Sci. Technol. 34, 4064-4070 doi: 10.1021/es991007n.

Venkataraman, C., Lyons, J.M., Friedlander, S.K., 1994. Size distributions of polycyclic aromatic hydrocarbons and elemental carbon. 1. Sampling, measurement methods, and source characterization. Environ. Sci. Technol. 28, 555-562.

Viglianti, C., Hanna, K., de Brauer, C., Germain, P., 2006. Removal of polycyclic aromatic hydrocarbons from aged-contaminated soil using cyclodextrins: Experimental study. Environmental Pollution 140, 427-435 doi: 10.1016/j.envpol.2005.08.002.

Viskari, E.-., Rekilä, R., Roy, S., Lehto, O., Ruuskanen, J., Kärenlampi, L., 1997. Airborne pollutants along a roadside: Assessment using snow analyses and moss bags. Environmental Pollution 97, 153-160.

VT ANR, 2002. The Vermont Stormwater Management Manual Volume II - Technical Guidance. , 1-260.

Wang, J.Z., Guan, Y.F., Ni, H.G., Luo, X.L., Zeng, E.Y., 2007. Polycyclic aromatic hydrocarbons in riverine runoff of the Pearl River Delta (China): concentrations, fluxes, and fate. Environ. Sci. Technol. 41, 5614-5619.

Wang, Z., Chen, S., Xu, Y., Tang, J., 2012. Aging Effects on Sorption-desorption Behaviors of PAHs in Different Natural Organic Matters. J. Colloid Interface Sci. .

Wania, F., Mackay, D., Hoff, J.T., 1999. The Importance of Snow Scavenging of Polychlorinated Biphenyl and Polycyclic Aromatic Hydrocarbon Vapors. Environ. Sci. Technol. 33, 195-197 doi: 10.1021/es980806n.

Wauchope, R.D., Getzen, F.W., 1972. Temperature dependence of solubilities in water and heats of fusion of solid aromatic hydrocarbons. J. Chem. Eng. Data 17, 38-41 doi: 10.1021/je60052a020.

Wheeler Alm, E., Burke, J., Spain, A., 2003. Fecal indicator bacteria are abundant in wet sand at freshwater beaches. Water Res. 37, 3978-3982.

Wilcke, W., 2007. Global patterns of polycyclic aromatic hydrocarbons (PAHs) in soil. Geoderma 141, 157-166.

Wilcke, W., Müller, S., Kanchanakool, N., Niamskul, C., Zech, W., 1999. Polycyclic aromatic hydrocarbons in hydromorphic soils of the tropical metropolis Bangkok. Geoderma 91, 297-309.

Williams, E.S., Mahler, B.J., Van Metre, P.C., 2012. Coal-tar pavement sealants might substantially increase children's PAH exposures. Environmental Pollution 164, 40-41 doi: 10.1016/j.envpol.2012.01.010.

Williams, P., Benton, L., Warmerdam, J., Sheehan, P., 2002. Comparative Risk Analysis of Six Volatile Organic Compounds in California Drinking Water. Environ. Sci. Technol. 36, 4721-4728 doi: 10.1021/es020725y.

Wong, F., Harner, T., Liu, Q., Diamond, M.L., 2004. Using experimental and forest soils to investigate the uptake of polycyclic aromatic hydrocarbons (PAHs) along an urban-rural gradient. Environmental Pollution 129, 387-398.

Wright, W.R., Sautter, E.H., 1988. Soils of Rhode Island Landscapes. University of Rhode Island Agricultural Experiment Station in cooperation with the United States Department of Agriculture, Soil Conservation Service. , 1-63.

Yang, W., Lampert, D., Zhao, N., Reible, D., Chen, W., 2012. Link between black carbon and resistant desorption of PAHs on soil and sediment. Journal of Soils and Sediments , 1-11.

Yang, Y., Hofmann, T., Pies, C., Grathwohl, P., 2008. Sorption of polycyclic aromatic hydrocarbons (PAHs) to carbonaceous materials in a river floodplain soil. Environmental Pollution 156, 1357-1363 doi: 10.1016/j.envpol.2008.02.024.

Yao, Y., Gao, B., Inyang, M., Zimmerman, A.R., Cao, X., Pullammanappallil, P., Yang, L., 2011. Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings. J. Hazard. Mater. 190, 501-507.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org. Geochem. 33, 489-515.

Zehetner, F., Rosenfellner, U., Mentler, A., Gerzabek, M.H., 2009. Distribution of road salt residues, heavy metals and polycyclic aromatic hydrocarbons across a highway-forest interface. Water, Air, & Soil Pollution 198, 125-132.

Zhang, H., Oyanedel-Craver, V., 2013. Comparison of the bacterial removal performance of silver nanoparticles and a polymer based quaternary amine functiaonalized silsesquioxane coated point-of-use ceramic water filters. J. Hazard. Mater..

Zhang, H., Oyanedel-Craver, V., 2011. Evaluation of the disinfectant performance of silver nanoparticles in different water chemistry conditions. J. Environ. Eng. 138, 58-66.

Zhang, X., Lulla, M., 2006. Evaluation of pathogenic indicator bacteria in structural best management practices. Journal of Environmental Science and Health Part A 41, 2483-2493.

Zhang, Y., Tao, S., 2009. Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. Atmos. Environ. 43, 812-819.

Zhang, H., Oyanedel-Craver, V., 2012. Evaluation of the Disinfectant Performance of Silver Nanoparticles in Different Water Chemistry Conditions RID G-6346-2010. J. Environ. Eng. -ASCE 138, 58-66 doi: 10.1061/(ASCE)EE.1943-7870.0000460.

Zhang, H., Smith, J.A., Oyanedel-Craver, V., 2012. The effect of natural water conditions on the anti-bacterial performance and stability of silver nanoparticles capped with different polymers. Water Res. 46, 691-699 doi: 10.1016/j.watres.2011.11.037.

Zhu, L., Li, Y., Zhang, J., 1997. Sorption of organobentonites to some organic pollutants in water. Environ. Sci. Technol. 31, 1407-1410.