PERVIOUS CONCRETE RESEARCH FACILITY: WINTER PERFORMANCE AND ENHANCEMENT OF POLLUTANTS REMOVAL

Vinka Oyanedel Craver, PhD.
Varun Kasaraneni
Steven Kohm
University of Rhode Island

March, 2014

URITC PROJECT NO. 500- 2302- 0000- 0002595

PREPARED FOR

UNIVERSITY OF RHODE ISLAND TRANSPORTATION CENTER

DISCLAIMER

This report, prepared in cooperation with the University of Rhode Island Transportation Center, does not constitute a standard, specification, or regulation. The contents of this report reflect the views of the author(s) who is (are) responsible for the facts and the accuracy of the data presented herein. This document is disseminated under the sponsorship of the Department of Transportation, University Transportation Centers Program, in the interest of information exchange. The U.S. Government assumes no liability for the contents or use thereof.

Technical Report Documentation Page

	Technical Report 1	ocumentation Page				
1	Government Accession 1 N/A	No. 3. Reci N/A	ipient's Catalog No.			
4. Title and Subtitle		5. Rep	ort Date			
		ecember 2013				
PERVIOUS CONCRETE RESE	WINTER					
PERFORMANCE AND EN	HANCEMENT OF	6. Per	forming Organization (Code		
POLLUTANTS REMOVAL	1					
7. Author(s)			orming Organization R	Report No.		
Vinka Oyanedel-Craver, Varun Kas	araneni, Steven Kohi	n				
Performing Organization Name and Addr	ngg	10 W/	ork Unit No. (TRAIS)			
University of Rhode Island	222	10. WC	or cliit No. (TRAIS)			
Civil and Environmental Engine	perina	11. 0	4 4 C 4N			
1 Lippitt Rd, Bliss Hall 2013	cing		ntract or Grant No.	2505		
11 ,		300)- 2302- 0000- 000	12393		
Kingston, RI, 02881 12. Sponsoring Agency Name and Address		12 Tv	pe of Report and Perio	d Covered		
University of Rhode Island Trans	nortation Center	15. 1y	pe of Report and Ferro	u Covereu		
		Pood				
Carlotti Administration Building	, /3 Lower College F					
Kingston, RI 02881		14. Sp	onsoring Agency Code			
15. Supplementary Notes This project was funded under the	EHWA Endoral Land	. Highway Tashnalage	Danlarmant Initi	ativas and		
This project was funded under the		0 , 0,	1 2	anves and		
Partnership Program (TDIPP). Or tl	ie Coordinated Techr	lology implementation	Program (CTIP).			
16. Abstract						
10. Austract						
The purpose of the current study	was to design and to	et a narous medium the	t can notantially b	a annliad in		
pervious pavement systems. The pr						
sorption capacity, thereby mitigatin						
studies were carried out in three pha						
effectiveness of the organic amendr						
compound Naphthalene; and (iii) de						
pervious pavement systems (i.e., po	, 55		,			
removal. The PAH compounds acer	naphthene and flourer	ne were used for the sec	cond part of the stu	ıdy		
17. Key Words		18. Distribution Statement				
SOIL AMENDMENT, POLY	No restriction. Th	is document is ava	ilable to the			
HYDROCARBONS, STORMWA	Public through the URI Transportation Center,					
		Carlotti Administration Building, 75 Lower College				
	Rd., Kingston, RI		23.1.01 2011050			
	Ino a i =:			00 n :		
19. Security Classif. (of this report)	20. Security Classif. (21. No. of Pages	22. Price		
Unclassified	lassified		N/A			
	l					

Form DOT F 1700.7 (8-72)

Reproduction of completed page authorized

TABLE OF CONTENTS

P	erviou	us concrete research facility: winter performance and enhancement of pollutants remove	/al i
1	Inti 1.1	roduction	
2	Lit	erature review	1
3	Exj 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8	perimental Methods. Overview of experimental methodology Materials. Synthesis and characterization of organically modified soil amendments Sorption isotherms. Column experiments. HYDRUS 1D. Autosampler Research and educational facility.	2 3 4 5
4	Res 4.1 4.2 4.3	sults and Discussions Synthesis and characterization of organically modified soil amendments Sorption isotherms Column experiments with unmodified, organically modified, and blended Rhode Island glacizath soils Performance of convention and organically modified pervious concrete Autosampler Research and educational facility	6 7 ial 8 10
5	Co	nclusions	13
6	Re	ferences	13
7	AP	PPENDICES	16

LIST OF TABLES AND FIGURES

- TABLE 1. Soil Organic Carbon, Particle Size, and Hydraulic Conductivity Properties
- TABLE 2. Freundlich sorption parameters from batch and column studies of modified Soils
- TABLE 3. Column Intrinsic Parameters and Naphthalene Retardation
- TABLE 4. Column Intrinsic Parameters and Retardation factors
- FIGURE 1. Sorption isotherms for the sorption of naphthalene on (a) Glacial Outwash Soil (Linearized Langmuir model). qe is aqueous naphthalene / mass of naphthalene sorbed per unit mass of soil (b) Modified soils (HDTMA, BHDH and blend) Freundlich model.
- FIGURE 2. Observed and predicted BTCs of naphthalene for a) RI glacial outwash b) HDTMA modified soil c) BHDH modified soil d) Blended modified soil.
- FIGURE 3. BTCs of acenaphthene and flourene in column experiments for a) concrete b) aggregate c) RI glacial outwash soil d) blend of organo clay-glacial outwash soil.
- FIGURE 4. Pictures of the Teledyne ISCO 6712 Portable Sampler purchased to be deployed at the Stormwater Demonstration Facility
- FIGURE 5. Progress on the implementation of the RISDF

1 INTRODUCTION

The construction of permeable parking, rural roads and bike path as an alternative to impermeable surfaces has been shown to be an effective method of stormwater source control. The main design criterion for infiltration systems has usually been the reduction of peak discharge through the retention of stormwater flow. To date although some effort has been directed towards the use of such systems for the treatment of retained pollutants there has been little thought put into gaining a fundamental understanding of the chemical and microbiological processes taking place.

Previous research has demonstrated the ability of a permeable pavement to retain suspended solids [1]. Limited research has been conducted concerning water-purification properties of pervious concrete. Few studies examined the growth of microorganisms within pervious concrete by observing the consumption of the dissolved oxygen [2],[3] however these study have not been systematically and long term performed. For example, the studies do not consider different hydraulic retention time, temperature and salinity changes associated with typical changes in weather conditions during the year.

1.1 Research objectives

- Determine the effectives of pervious concrete for the removal of organic and inorganic compounds dissolved in urban stormwater runoff.
- Selection of an autosampler for the *Rhode Island Stormwater Management and Treatment Demonstration Facility*
- Create an educational facility for local schools visits

2 LITERATURE REVIEW

Impermeable surfaces such as conventional concrete and asphalt have the potential to generate large volumes of contaminated storm-water runoff during precipitation events. Stormwater runoff is a source of organic and inorganic contaminants that can end up polluting natural bodies of water [4]. Of particular concern are polycyclic aromatic hydrocarbons (PAHs), which are a family of organic compounds containing two or more benzene rings.

PAHs are ubiquitous in the environment and present in the soil, water, and air. Most PAHs are acutely toxic and suspected human carcinogens [5]. The Safe Drinking Water Act enforces a maximum contaminant level of 0.0002 mg/L for PAHs [6]. Acute oral toxicity of PAHs range from 50 to 2000 mg/kg of body weight depending on the specific compound [5]. One of the main characteristics of PAH is that, as the number of benzene rings increases, the solubility in aqueous solutions decreases. Due to the hydrophobic properties of these compounds, PAHs are rapidly sorbed onto sediment particles and subsequently deposited. As previously demonstrated, the rerelease of PAHs into clean or less contaminated waters is possible [7], [8]. After a rainfall event, PAHs are carried into the drainage infrastructure and are eventually transported into ground and surface waters. Hoffman et al. [7] reported that urban runoff entering Narragansett Bay was responsible for 71% percent of the total inputs of higher molecular weight PAHs and 36% of

total PAHs. Another study, spanning from 1993 to 2001, showed that storm-water runoff contributes about 51% of all PAHs to the San Francisco Bay [9].

As vehicles produce the greatest concentration of PAHs during ignition and acceleration [10], roads and parking lots are ideal locations for containing the transport of these contaminants before they are discharged into natural ecosystems. In most major American cities, parking lots account for 10 to 15% of the total impervious area [11], and impervious areas in urban and suburban settings are expected to increase in the future. In addition to automotive-related releases, coats of pavement sealants and oil leakages are also important sources of PAHs [7], [12], [13], [14].

Engineered systems can mitigate the discharge of PAHs from parking lots, thereby drastically reducing the influx of contaminants into water resources. For example, pervious pavement has been used to reduce both the volume and contaminant load in storm runoff [15], [16], [17] [18]. In addition pervious concrete pavements can elevate pH of runoff from acidic nature [19]. However, conventional pervious pavements systems have a limited contaminant removal capacity [20]. The pollutant removal performance of the pervious pavement systems is not consistent over time and also depends on location [20].

Previous studies have demonstrated that, by increasing the fraction of carbon (f_{oc}) of a sorbent, the sorption of PAHs increases [21], [22], [23]. Several approaches have been suggested to increase the f_{oc} of soils or other engineered materials [21], [24], such as activated carbon [25], [26], which can be expensive, can be labor intensive, and may require frequent maintenance.

The purpose of the current study was to design and test a porous medium that can potentially be applied in pervious pavement systems. The principle goals were to identify a material capable of enhancing the PAH sorption capacity, thereby mitigating the influx of PAHs into the deeper subsurface. The necessary laboratory studies were carried out in three phases: (i) synthesis of organically modified soils; (ii) testing of the effectiveness of the organic amendments to Rhode Island glacial outwash soil and organoclay to sorb the PAH compound Naphthalene; and (iii) determination of whether any of the conventional construction components of pervious pavement systems (i.e., porous concrete, aggregate, including unmodified soil) contribute to PAH removal. The PAH compounds acenaphthene and flourene were used for the second part of the study.

3 EXPERIMENTAL METHODS

3.1 Overview of experimental methodology

The experiment was divided into three phases. The first phase involved the synthesis and characterization of the organically modified soil amendments. Second, the performance of the modified soil in terms of PAH sorption was assessed using naphthalene as the model PAH. This phase involved both batch isotherms and column experiments. Naphthalene was chosen due to its high aqueous solubility. The third phase focused on the assessment of PAH-retaining capabilities of conventional and organically modified pervious pavement elements. In these column experiments, acenaphthene and fluorene were used as model PAHs. These PAHs were selected as they have high aqueous solubility, have higher molecular weight, and are commonly found at contaminated sites.

3.2 Materials

Naphthalene, fluorine, and acenapthene (purity grade of 98% or higher) were obtained from Aldrich Inc. Analytical grade solvents (dichloromethane and methanol) were obtained from Fisher Scientific. Aqueous solutions were prepared in deionized water free of detectable traces of PAH and with a pH near neutral. PAH are non ionic compounds, there is no influence of pH on the characteristics of PAH in the aqueous phase. Further the pH of runoff originating from traffic areas ranges between 6.4 and 7.9 [4]. The pH used for our experiments is 7.0, which is well within the narrow range of natural conditions. A gas chromatograph with flame ionization detector (Shimadzu GC-17A/FID) and a gas chromatograph/mass spectrometer (Shimadzu GC-MS QP2010) were used to quantify PAH compounds. Only glass vessels were used, and care was taken to prevent PAH photo degradation. Hexadecyltrimethyl ammonium chloride (HDTMA) and Benzyldimethylhexadecyl ammonium chloride (BHDH) were obtained from sigma Aldrich, with a purity of 99%; they were used as received.

The PAH-saturated solutions were prepared following a method described by Wang et al. [27]. In brief, PAHs were dissolved in 1 mL of dichloromethane in a 4 L Erlenmeyer flask. As the solvent volatilized, a thin film of PAH formed on the glass. The flask was then filled with deionized water, which was allowed to saturate and equilibrate with the PAH over the course of one week. The initial concentration (C_0) of all three target PAHs in the aqueous phase was determined using the gas chromatograph.

A bulk sample (20 kg) of Rhode Island glacial outwash soil was collected at the Peckham farm research site near the University of Rhode Island campus. The soil was fully dried and sieved through a number 10 sieve (2.0 mm). The fraction of soil passing through the sieve was sterilized in an autoclave. Aggregate material was obtained from the Cherenzia Excavation site in Rhode Island. The aggregates confirmed to ASTM C 33, Size No. 67 (3/4 in. to No. 4). In addition, Portland type II cement was obtained from the Home Depot in Middletown, Rhode Island. Pervious concrete was prepared following one of the compaction techniques described in Putman et al. [28]. Briefly, concrete was mixed and placed in 2-inch layers by compacting using a 15.9 mm diameter steel rod, rodding it 15 times. The pervious concrete had a void content of 15% to 18%, which is typical for this type of material [29]. The porosity (equation 1) of the materials was determined using the volume of voids which was determined by identifying the difference in weight between the dry sample and a water-saturated sample.

$$\Phi = V_V / V_T \tag{1}$$

3.3 Synthesis and characterization of organically modified soil amendments

The cation exchange capacity (CEC) of the soil was determined by the Soil, Water, and Plant Testing Laboratory at Colorado State University. A characterization of the soil particle size distribution was conducted on all modified and unmodified soils through sieve and hydrometer analysis using ASTM 136 and 152 H methods [30]. The hydraulic conductivity of the concrete, aggregate, and soils was determined using the falling head permeameter method [31]. HDTMA and BHDH are long-chained cations with a relatively high carbon content; therefore, they are considered to be an attractive choice for increasing the $f_{\rm oc}$ of the porous matrices. Equation 2 was developed by Boyd et al. [32] to determine the mass of QAC with respect to the mass of soil and CEC.

$$f = M_{cation} / (CEC * M_{soil} * GMW_{cation} * z)$$
 (2)

where CEC is the cation exchange capacity in milli-equivalents per gram or soil, f is the fraction of CEC exchanged, M_{cation} is the mass of cation used in grams, M_{soil} is the mass of soil in grams, GMW_{cation} is the formula weight of cation in grams per mole, and z represents the moles of charge per equivalent moles per milli-equivalent of exchange capacity

The wet method developed by Breakwell et al. [33] was used to modify the soils. Briefly, the amount of QAC necessary to produce 100 grams of 100% CEC modified soil was calculated using Boyd's equation. The QAC was dissolved into 400 mL of deionized water using a stir bar and a glass beaker. Soil was mixed into the QAC solution and agitated for 3 days at 150 rpm in an incubator at 20°C. The contents of the glass beaker were carefully decanted after settling, and the soil was placed into the oven for 6 hours at 100° C to dry. The residual chloride ions were removed by rinsing with deionized water until electrical conductivities were below 1 µs/cm. Once dried, the modified soils were analyzed using a Carlo Erba EA1108 Carbon Hydrogen and Nitrogen analyzer to quantify the amount of carbon.

The second approach for introducing f_{oc} involved mixing the glacial outwash soil with commercial organoclay (PM-199; CETCO Oil Field Services). To maintain a point of reference in isotherm and column experiments, the mass of the total organic carbon in the blend was calculated to match the mass of total organic carbon in the BHDH-modified soil. This resulted in a 1:18 ratio of commercial organoclay and Rhode Island glacial outwash.

3.4 Sorption isotherms

A series of batch isotherms were carried out for all sorbents to study the static interaction between sorbent and aqueous PAH. A constant mass (different for each soil) of the particular sorbent was exposed to increasing concentrations (ranging from 2 to 22 mg/l) of the aqueous naphthalene solution. Kinetic investigation showed that it took 30 hr to reach equilibrium between the aqueous phase and the sorbent. Based on this finding, the isotherms tests were carried out for at least 48 hours at 20°C. Afterwards, all samples were centrifuged for 10 min at 2500 rpm to remove any particulates from the aqueous phase. After the liquid-liquid extraction with dichloromethane following EPA method 610, the naphthalene concentration was determined using GC-MS. The Langmuir equation (Equation 3) was used to model sorption data for the glacial outwash material while the Freundlich equation (Equation 4) was used to model the sorption of all other materials.

$$\frac{C_{\rm s}}{C_{\rm e}} = \frac{1}{\alpha\beta} + \frac{C_{\rm s}}{\beta} \tag{3}$$

$$C_s = K_f C_e^n \tag{4}$$

where C_e is the concentration of naphthalene in solution at equilibrium [M/L³], C_s is the mass of naphthalene sorbed per dry unit weight of sorbent [M/M], α is a Langmuir adsorption constant and β is the Langmuir maximum amount of naphthalene that can be absorbed by the sorbent, n is the unitless Freundlich exponent, and K_f is the Freundlich sorption coefficient [L³/(M-M^(1-N))].

3.5 Column experiments

Column experiments were conducted to study the sorption and desorption of PAHs under dynamic, flow-through conditions. For the concrete and aggregate materials, larger glass columns (length: 15.0 cm, ID: 8.5 cm) were used, whereas smaller ones (length: 5.0 cm, ID: 2.5 cm) were used for soil. Columns filled with porous concrete and aggregate were connected to a Masterflex L/S pump with Teflon tubing. The columns packed with soil were connected to an Accuject Series I injector pump with Teflon tubing. Conservative tracer tests with sodium chloride (NaCl) were performed to determine pore velocity and dispersion coefficient. After determining the column intrinsic parameters, an aqueous solution saturated with the target PAH was pumped through the columns. Effluent samples were collected until breakthrough, which defined as C/Co equaling one (i.e., the effluent concentration is equal to the influent concentration). The flow velocities were held constant at 2 mL/min for soil columns and 20 mL/min for concrete and aggregate columns. After breakthrough, the influent was switched to deionized water to study desorption. The pumping of deionized water continued until at least 90% of the PAH was recovered. This same procedure was repeated for concrete, aggregate, and all other soil media.

3.6 HYDRUS 1D

HYDRUS-1D (version 4.14) software was used to stimulate solute transport through unmodified and modified soils. Parameters obtained from sorption isotherms, soil characterization, and column experiments were used to predict the BTCs for naphthalene in unmodified and modified soils. Langmuir and Freundlich isotherm coefficients were obtained from isotherm experiments. Dispersion coefficient and bulk densities were obtained from column tracer experiments. Hydraulic conductivities were obtained from falling head permeameter tests. HYDRUS-1D was also used to estimate the adsorption coefficient from column experiments using the inverse solution to the Levenberg-Marquardt nonlinear parameter optimization method.

3.7 Autosampler

Selection of a programmable autosampler for collecting stormwater samples of diverse volumes at different distribution methods such as sequential and continuous sampling, is essential for the developing of the stormwater runoff management program at URI. This portable sampler will be installed at Rhode Island Stormwater Demostration Facility (RISDF) as part of field testing the Tree Filters. It will be used to collect runoff samples pre and after treatment using tree filters. A preset program for storm event will make sampling efficient.

3.8 Research and educational facility

As a result of efforts to comply with local and national stormwater quality discharge standards as well as current regulations for environment protection, the Rhode Island Department of Transportation (RIDOT) has installed many structural Best Management Practices (BMP's) in an attempt to lessen pollutant loads to receiving waterways. For instance, between 1997 and 2007 more than 70 hydrodynamic separators units were installed by RI DOT. The selection of the various, commercially available BMP systems relies mostly on unverified manufacturer's

data or is based on performance reports from other parts of the country where local environmental conditions are much different than those in Rhode Island. In general, there is insufficient data for science-based selection of the most appropriate BMP for addressing specific applications in Rhode Island. Therefore, a group of investigator from the Civil and Environmental Engineering Department will performed a joint project to provide RI DOT and the URI transportation community with a new facility where BMP structures can be evaluated against the manufacturer's claims and under environmental conditions prevailing in our state. This facility will be known as the "Rhode Island Stormwater Management and Treatment Demonstration Facility" (RI SDF).

4 RESULTS AND DISCUSSIONS

4.1 Synthesis and characterization of organically modified soil amendments

A CEC of 5.6 milli-equivalents of exchangeable cations per 100 grams of glacial outwash soil (meq/100g) was measured. These results were consistent with the CEC values determined by Wright et al. (1998) [33]. The results from soil modification, particle size analysis, and hydraulic conductivity measurements are summarized in Table 1. Also shown are the initial f_{oc} and the percentage of f_{oc} increase resulting from the soil modification.

TABLE 1. Soil Organic Carbon, Particle Size, and Hydraulic Conductivity Properties

Soil Type	f _{oc} [%]	f _{oc} Increase [%]	D ₁₀ [mm]	Uniformity Index (U) [-]	Porosity (n) [-]	Hydraulic Conductivity (K) [cm/s]
Unmodified						
Glacial						
Outwash	1.70		0.070	9.286	0.54	1.53E-03
HDTMA	2.90	70.6	0.030	13.333	0.504	6.73E-04
BHDH	2.94	72.9	0.040	12.500	0.56	9.33E-04
Blend	2.94	72.9	0.090	6.667	0.52	2.93E-03

 f_{oc} = Fraction of Organic Carbon; D_{10} =effective grain size; Blend is 1:18 mix of organical variation and glacial outwash soil.

Quaternary ammonium cations HDTMA and BHDH increased the fraction of organic carbon in the Rhode Island glacial outwash soil by 70.6% and 72.9%, respectively. The f_{OC} increase in the blend was calculated to match the organic carbon in the BHDH-modified soil. This resulted in mix of 1:18 commercial organoclay and glacial outwash. The hydraulic conductivities of the modified soils were an order of magnitude smaller than the unmodified soil. Decreases in effective grain size (D_{10}) and porosity were also observed, although the reasons for these decreases were not investigated. Conversely, adding the PM-199 organoclay to the unmodified soil increased the effective grain size D_{10} of the blend while decreasing the uniformity coefficient and increasing the hydraulic conductivity. Thus, a material with increased hydraulic conductivity, such as this organoclay-glacial outwash blend, will be best suited for application below permeable pavement because it will aid in faster drainage of storm water.

4.2 Sorption isotherms

Kinetic investigation revealed an equilibrium time of 30 hours (data not shown) between the soils and naphthalene, which is consistent with prior research [35], [36]. The sorption isotherm results for the glacial outwash fit the Langmuir model, in which a limited number of sorption sites are available that can be fully saturated during isotherm experimentation. The use of the Langmuir model for glacial outwash materials is consistent with the results of Appert-Collin et al. [37], who exposed saturated aqueous naphthalene solutions to soils with low organic carbon material. Correlation coefficients values, R², of the glacial outwash Langmuir fit were 0.997. Figure 1a shows the results of the naphthalene-soil isotherm experiments for glacial outwash.

The maximum amount of naphthalene that can be sorbed by the glacial outwash, β , was determined to be 0.48 mg naphthalene per gram of soil. The adsorption constant related to binding energy, α , was 0.24 L/g. The predicted α from column experiments was 0.18 L/g. In contrast to the unmodified soil (Fig. 1a), the isotherms experiments on the modified soils and naphthalene demonstrated that sorption sites were not exhausted within the range of PAH concentrations tested. For this reason, the isotherm data for the modified soil were fitted with the Freundlich isotherm model (R²=0.98). As expected, Freundlich constants (K_F; Table 2) increased with increasing organic carbon content of the soils, leading to increased naphthalene sorption. Of the modified soils, the organoclay-glacial outwash blend (1:18 ratio) exhibited the greatest K_f value (114.2). Although the Freundlich model suggested that no upper limit exists for sorption in the experimental concentration range, in reality one is likely to exist, although it remains to be determined what this limit is.

TABLE 2. Freundlich sorption parameters from batch and column studies of modified Soils

	Batch Isotherm			Column study	
Soil	K _F	N	\mathbb{R}^2	K_{F}	N
HDTMA	36.90	1.23	0.99	5.50	1.58
BHDH	54.30	1.28	0.98	19.3	1.04
Blend	114.20	1.18	0.97	89.9	1.12

N is the unitless Freundlich linearity exponent; Kf is the Freundlich sorption coefficient and R^2 is the correlation coefficient.

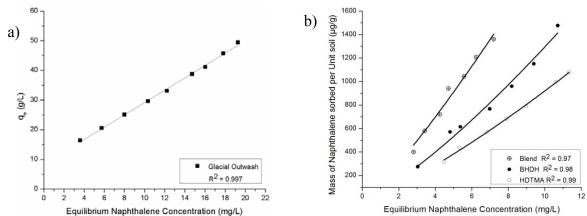


FIGURE 1. Sorption isotherms for the sorption of naphthalene on (a) Glacial Outwash Soil (Linearized Langmuir model). q_e is aqueous naphthalene / mass of naphthalene sorbed per unit mass of soil (b) Modified soils (HDTMA, BHDH and blend) Freundlich model. Origin data analysis software was used for fitting. Freundlich Model power fit was used to obtain Freundlich Isotherm constants.

4.3 Column experiments with unmodified, organically modified, and blended Rhode Island glacial outwash soils

Parameters for the four column experiments, including pore volume, pore water velocity, and dispersion coefficients, are shown in Table 3. Observed and predicted naphthalene BTCs for all soils are plotted in dimensionless terms of relative concentration (C/Co) and pore volumes (Figure 2).

TABLE 3. Column Intrinsic Parameters and Naphthalene Retardation

Soil	Pore Volume [-]	Bulk Density [g/cm3]	Velocity [cm/min]	Dispersion [cm2/min]	Retardation factor CXT fit
G. O [*]	13.23	1.43	0.75	0.60	54.3
HDTMA	12.37	1.58	0.96	0.77	76
BHDH	12.75	1.45	0.82	0.73	304
Blend	13.75	1.15	0.76	0.26	438

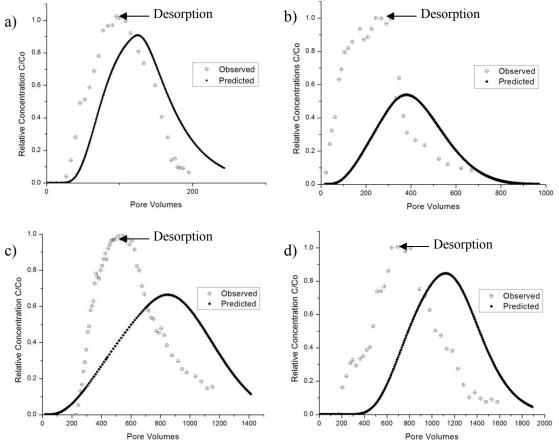


FIGURE 2. Observed and predicted BTCs of naphthalene for a) RI glacial outwash b) HDTMA modified soil c) BHDH modified soil d) Blended modified soil. The injected naphthalene concentrations were 30±2mg/l and flow rates were maintained at 2ml/min. Desorption experiment started once the relative concentration reached 1

Column experiments supported the results obtained from the batch isotherms. Unmodified glacial outwash soil had the fastest breakthrough and the lowest retardation factor of 54.3. These results are consistent with the outwash having the lowest f_{oc} . Of the modified soils fitted with the Freundlich isotherm model, the HDTMA soil had the lowest retardation factor R=76 and the lowest K_F =36.9, versus R=304 and K_F =54.3 for BHDH-modified soil. Although the HDTMA and BHDH soils had very similar f_{oc} values (2.90% and 2.94%, respectively), their Freundlich sorption coefficients differed (Table 2) which may be due to the presence of the benzyl group in the BHDH. Naphthalene is composed of two fused benzene rings, and the similar structure between the sorbent and solute can facilitate and greatly increase sorption. This would be consistent with the findings in other studies focusing on OAC-modified sorbents containing benzyl groups [38]. The column that exhibited the greatest retardation of naphthalene was the blended commercial organoclay-glacial outwash material. This sorbent retarded naphthalene by R=438, which correlates with the blended material having the largest K_F of 114.2 and f_{oc} = 2.94 Although the BHDH and Blended soils had very similar foc values (2.94%), there is higher sorption of naphthalene by the blended material. This due to the Quaternary Ammonium Chloride (QAC) used in preparation of oraganoclay PM-199 which is dialkyldimethyl ammonium chloride. The proprietary alkyl groups are shown are not revealed.

The higher sorption of naphthalene by blend can be attributed to the hydrophobicity of the hydrocarbon chain in the ammonium salt used to produce PM-199. [36]

The CXT fit model [39] was used to determine column intrinsic parameters and the retardation factors for naphthalene. CXT fit allows for inverse estimation of transport parameters from a laboratory study. The program uses convection dispersion equation with a data set, using the non-linear least-squares parameter optimization method. Together with experimental data, including hydraulic conductivity, bulk density, and isotherm coefficients from sorption studies, parameters determined with CXT fit were used as inputs to predict BTCs with HYDRUS. The predicted BTC (Figure 2) compared poorly with the measured batch experimental data. Similarly, the predicted adsorption isotherm coefficients (Table 2) for column experiment data were lower than the values from batch experiments. Maraga et al. [40] also reported that their batch study overestimated adsorption coefficients of benzene and dimethylphthalate compared with the results from the column study. Similarly, Lee et al. [41] reported a poor match of their predicted BTCs relative to the ones measured for naphthalene. However, the Langmuir coefficients predicted from column experiments for glacial outwash are in close agreement with isotherm coefficients. The fraction of type 1 adsorption sites at which sorption is assumed to be instantaneous was set to one, and the first-order rate constant was set to zero for the calculation of BTCs and the inverse solution. HYDRUS permits chemical non-equilibrium (adsorptiondesorption process) and physical non-equilibrium (possible heterogeneity of soil). As none of these processes were considered in the modeling of the results, this could be a reason for the poor prediction of BTCs. Additional experiments are required to obtain the parameters needed to include chemical and physical non-equilibrium processes. The HYDRUS modeling was test if the results can be replicated using this computational tool. The results suggest that HYDRUS and the current results will support a more thorough future modeling study regarding determining the life time and optimizing the ratio of organolay to glacial outwash. More data and modeling effort is needed to obtain an optimal fit. The breakthrough curves obtained using the isotherm data was used to compare the experimental data and modeling data. This allowed us to determine how effective the modeling data is when compared to laboratory scale/field scale results.

Performance of convention and organically modified pervious concrete 4.4

As potential parts of a pervious pavement system, the capacities of porous concrete and aggregate for retaining PAH of different molecular weights were determined through column experiments (Table 4).

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

PV is pore volume, R_f is Retardation factor * The column volume of concrete and aggregate columns were 850 cm² ** Column volume is 24.5 cm³

The sorption and desorption results for acenaphthene and flourene are shown in Figures 3a and 3b. The PAH retardation factor for concrete was R_f =1, indicating that this material has no PAH sorption capacity. For the aggregate, the retardation factor is R_f =11 and R_f =7 for acenaphthene and flourene, respectively. Due to the very low organic matter, the retardation of PAHs in concrete and aggregate is significantly lower compared to in soils [21], [22], [23]. Similarly, low retardation was found in the case of the glacial outwash soil (R=16.5; Fig. 3c). By far, the greatest retardation (R=4125.6for acenaphthene) was achieved with the blend of organoclay-glacial outwash, which reinforces that increasing f_{oc} leads to an increase in PAH sorption capacity. Retardation of fluorene for the organoclay–glacial outwash blend column was not calculated because C/C_0 =1 was not reached during this experiment.

Commercial organoclay ranges in cost between one to two dollars per pound. If the organoclay – glacial outwash blending ratio and bulk density used in the study was kept constant, the cost of the organoclay material would average about \$200.00 per cubic meter. However, the thickness of the modified section could be reduced to decrease the cost. Also, the QAC loading on the soil could be optimized to further reduce prices. The cost-benefit analysis and optimization of the enhanced sorption section is beyond the context of this study but will be a subject of our future studies.

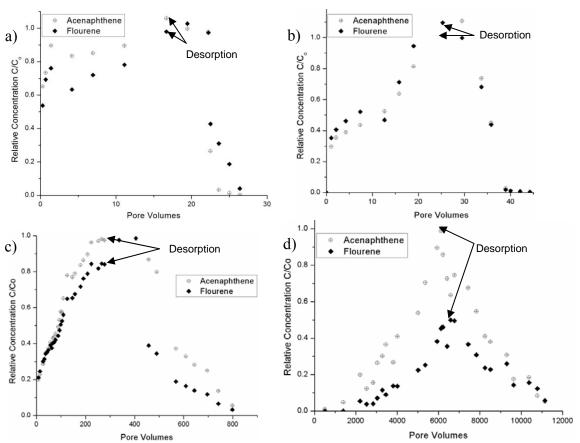


FIGURE 3. BTCs of acenaphthene and flourene in column experiments for a) concrete b) aggregate c) RI glacial outwash soil d) blend of organo clay-glacial outwash soil. Desorption experiment started once the relative concentration reached 1.0. The influent concentrations of acenaphthene and fluorene were 1.6 ± 0.2 mg/l and 0.6 ± 0.2 mg/l respectively.

4.5 Autosampler

Teledyne ISCO 6712 Portable Sampler (Figure 4) was chosen as an autosampler for stormwater monitoring. The sampler can be programmed for collecting stormwater samples of diverse volumes at different distribution methods such as sequential and continuous sampling. The programming capabilities enable us to choose sample collection start time and sampling times. The sample collection can also be started remotely. A maximum of 48 samples can be collected continuously providing a good sampling distribution during and after the storm event. Samples can be collected in either plastic or glass containers depending on the analytes



FIGURE 4. Pictures of the Teledyne ISCO 6712 Portable Sampler purchased to be deployed at the Stormwater Demonstration Facility

4.6 Research and educational facility

The contribution of this project to the overall facility consisted on the involvement of the PI and graduate students will the logistic and implementation of infrastructure to the facility. The facility is still in the construction phase due to several delays related with permit and coordination with the University. It is expected that the facility will be completed with supplemental fund provided by RIDOT on December of 2013. Figure 5 presents the progress on the implementation of the RISDF.



FIGURE 5. Progress on the implementation of the RISDF

5 CONCLUSIONS

The adverse effects of contaminants commonly present in storm-water runoff can be minimized using BMPs, such as pervious pavement systems. The results of this study demonstrated that conventional pervious pavement components, such as porous concrete, aggregate, and unmodified soil, have little capacity to retain PAHs from the aqueous phase. The modification of glacial outwash using QAC increased the fraction of organic carbon in the soil and greatly enhanced the PAH sorption capacity of the soils. After flushing several hundred pore volumes of PAH saturated water, the modified soil media removed up to 74% of PAHs (i.e., irreversible sorption). Thus, modified soil media, such as a blend of organoclay and glacial outwash, could find applications in BMPs in order to reduce contaminant flux into surface water or groundwater. These modified organoclay–glacial outwash blends can potentially be incorporated as a layer beneath pervious pavement. In addition to retaining PAHs, their higher hydraulic conductivity relative to the unmodified soil is an added advantage. However, cost is an important factor when incorporating modified materials into permeable pavement design. Currently, the cost of commercial organoclay ranges from one to two dollars per pound, which may prevent the widespread application of this promising amendment.

6 REFERENCES

- 1. Pratt, C. J., Mantle, J. D. G., & Schofield, P. A. (1995). UK research into the performance of permeable pavement, reservoir structures in controlling stormwater discharge quantity and quality. Water Science and Technology, 32(1), 63-69.
- 2. Luck, J. D., Workman, S. R., Coyne, M. S., & Higgins, S. F. (2008). Solid material retention and nutrient reduction properties of pervious concrete mixtures. Biosystems engineering, 100(3), 401-408.
- 3. Park, S. B., & Tia, M. (2004). An experimental study on the water-purification properties of porous concrete. Cement and Concrete Research, 34(2), 177-184.
- 4. Gobel P., Dierkes C., Coldewey W.G., (2007). Storm Water Runoff Concentration Matrix for Urban Areas. Journal of Contaminant Hydrology, 91, 26-42.
- 5. Eisler, R., (1987). Polycyclic Aromatic Hydrocarbon Hazard to Fish, Wildlife, and Invertabrates: A Synoptic Review. Patuxent Wildlife Research Center Contaminant Hazard Reviews, 1, 1-55.
- 6. EPA (2009). Unites States Environmental Protection Agency. Technical Fact Sheet on Polycyclic Aromatic Hydrocarbons. EPA Safewater.
- 7. Hoffman, E. J., Mills G. L., Latimer J. S., and Quinn J. G., (1984). Urban Runoff as a Source of Polycyclic Aromatic Hydrocarbons to Coastal Waters. Environmental Science and Technology, 18,580-587.
- 8. 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, 2882-2890.
- 9. Oros, D. R., Ross J. R.M., Spies. R. M., Mumley. T., (2007). Polycyclic Aromatic Hydrocarbon (PAH) Contamination in San Francisco Bay: A 10-year Retrospective of Monitoring in an Urbanized Estuary. Environmental Research, 105,101-118.

- 10. Joneck, M., and Prinz, R. (1996). Organic and Inorganic pollutants in roadside soils from streets with different traffic densities in Bavaria. (Berlin). Wasser und Boden 48, 49–54.
- 11. Wong, Eva. (2005). Cool Pavements. Reducing Urban Heat Islands: Compendium of Strategies. EPA. Washington D.C
- 12. Jiries A.G., Hussein H.H., Lintelmann J. (2003). Polycyclic aromatic hydrocarbon in rain and street runoff in Amman, Jordan. Journal Environmental Science (China), 15,848-853.
- 13. 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. Environmental Science and Technology, 39, 5560-5566.
- 14. Legret M, Odie L, Demare D, Jullien A. (2005). Leaching of heavy metals and polycyclic aromatic hydrocarbons from reclaimed asphalt pavement. Water Research, 39, 3675-85.
- 15. Kadurupokune, N., and N. Jayasuriya (2009). Pollutant load removal efficiency of pervious pavements: is clogging an issue? Water science and technology,60,1787–1794
- 16. Luck, J.D., Workman S.R., Coyne M.S., Higgins S.F., (2008). Solid material retention and nutrient reduction properties of pervious concrete mixtures. Biosystems Engineering, 100,401–408.
- 17. Luck, J.D., Workman S.R., Coyne M.S., Higgins S.F., (2009). Consequences of manure filtration through pervious concrete during simulated rainfall events. Biosystems Engineering, 102,417–423.
- 18. Kuang, X., Fu, Y., (2012). "Coupled infiltration and filtration behaviours of concrete porous pavement for stormwater management", Hydrological Processes.
- 19. Kuang, X., Sansalone, J., (2011). "Cementitious Porous Pavement in Stormwater Quality Control: pH and Alkalinity Elevation", Water Science & Technology, 63, 2992–2998
- 20. Brattebo B. O., Booth, B. D., (2003). Long-term stormwater quantity and quality performance of permeable pavement systems. Water Research, 18, 4369–4376.
- 21. Jonker, M.T.O., and Koelmans A.A., (2002). Sorption of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls to Soot and Soot-like Materials in the Aqueous Environment: Mechanistic Considerations. Environmental Science and Technology, 36, 3725–3734.
- 22. Cornelissen, G., Breedveld, G.D., Kalaitzidis, S., Christanis, K., Kibsgaard A., and Oen A.M., (2006). Strong Sorption of Native PAHs to Pyrogenic and Unburned Carbonaceous Geosorbents in Sediments. Environmental Science and Technology, 40, 1197–1203.
- 23. Brändli, R.C., Hartnik, T., Henriksen, T., and Cornelissen G., (2008). Sorption of native polyaromatic hydrocarbons (PAH) to black carbon and amended activated carbon in soil. Chemosphere, 73, 1805-1810.
- 24. Li, R., Wen, B., Zhang, S., Pei, Z., Shan X., (2009). Influence of organic amendments on the sorption of pentachlorophenol on soils. Journal of Environmental Sciences, 21, 474–480.
- 25. Zimmerman, J.R., Ghosh, U., Millward, R.N., Bridges, T.S., and Luthy R.G. (2004). Addition of Carbon Sorbents to Reduce PCB and PAH Bioavailability in Marine Sediments: Physicochemical Tests Environmental Science and Technology, 38, 5458–5464.

- 26. Millward, R.N., Bridges, T.S., Ghosh, U., Zimmerman, J.R., and Luthy R.G. (2005). Addition of Activated Carbon to Sediments to Reduce PCB Bioaccumulation by a Polychaete (Neanthes arenaceodentata) and an Amphipod (Leptocheirus plumulosus). Environmental Science and Technology, 39, 2880–2887.
- 27. Wang, Jiann-Ming, Maier, R.M and Brusseau. M. L. (2005). Influence of hydroxypropyl-b-cyclodextrin (HPCD) on the bioavailability and biodegradation of pyrene. Chemosphere, 60,725-728.
- 28. Putman B.J., and Neptune, A.I. (2011) Comparison of test specimen preparation techniques for pervious concrete pavements. Construction and Building Materials, 25, 3480–348.
- 29. Tennis, P.D., Leming, M.L., and Akers, D.J. (2004). Pervious Concrete Pavements, EB302.02. Portland cement Association, Skokie, Illinois, and National Ready Mixed Concrete Association, Silver Spring, Maryland, USA.
- 30. Das, B.M. (2009). Soil Mechanics Laboratory Manual. 7th. New York: Oxford University Press, 17-36.
- 31. NAVFAC, (1986) NAVFAC Soil Mechanics. Design Manual 7.01. Naval Facilities Engineering Command, Alexandria, USA.
- 32. Boyd, S.A., Mortland M.M., and Chiou C.T. (1988). Sorption characteristics of organic compounds on hexadecyltrimethylammonium-smectite. Soil Science Society of America Journal, 52,652-657.
- 33. Breakwell, I.K., Homer, J., Lawrence, M., and McWhinnie. (1995). Studies of Organophilic Clays: The Distribution of Quaternary Ammonium Compounds on Clay Surfaces and the Role of Impurities. Polyhedron, 14, 2511-2518
- 34. Wright, W., and Sautter, E. (1988). Soils of Rhode Island Landscapes. Agricultural Experiment Station Bulletin, 492.
- 35. Bayard, R., Barna, L., Mahjoub, B., (2000). Influence of the presence of PAHs and coal tar on naphthalene sorption in soils .Journal of Contaminant Hydrology, 46, 61-80.
- 36. Reible D.D., Lu, X., Jasmine, G., Qi, Y., (2010). CETCO Oilfield Services. PM-199 Sorbent Technical Fact Sheet.
- 37. Appert-Collin, J.C., S. Driri-Dhaouadi, M.O. Simonnot, and Sardin, M. (1999). Nonlinear Sorption of Naphthalene and Phenanthrene during Saturated Transport in Porous Media. Physics and Chemistry of the Earth, 24, 543-548.
- 38. Smith, J.A., Jaffe, P.R., Chiou, C.T. (1990). Effect of Ten Quaternary Ammonium Cations on Tetrachloromethane Sorption to Clay from Water. Environmental Science and Technology, 24, 1167-1171.
- 39. Toride, N., Leij, F. J. and. van Genuchten, M.T. (1995). The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments. Version 2.0, Research Report No. 137, U. S. Salinity Laboratory, USDA, ARS, Riverside, CA.
- 40. Maraqa, M.A., Zhao, X., Wallace, R.B., Voice, T.C. (1998). Retardation coefficients of nonionic organic compounds determined by batch and column techniques. Soil. Science Society of America Journal, 62,142–152.

41. Lee, J., Hundal, L.S., Horton, R., and Michael L. (2002). Thompson Sorption and Transport Behavior of Naphthalene in an Aggregated Soil. Journal of Environmental Quality, 31, 1716–1721.

7 APPENDICES

Conferences proceedings and publications

Conference presentations

- Lee, K-W, Oyanedel-Craver, V., and Kohm, S. (2010) Cool Pavements as Sustainable Approaches for Green Streets and Highways. ASCE Transportation and Development Institute. Green Streets and Highways Conference. Denver, Colorado.
- Varun Kasaraneni, Vinka Craver, (2011). Porous Concrete Research Facility: Performance and Enhancement of the Pollutants Removal. 24th Rhode Island Transportation Forum. University of Rhode Island

Master Thesis:

• Steven Kohm, (2011). Sustainable Parking Lots; Organic Modification of Porous Concrete Base Course for Enhanced Removal of Polycyclic Aromatic Hydrocarbons

Publication

V. Kasaraneni, S. Kohm, D. Ebere, T. Boving and V. Oyanedel-Craver (2013).
 Enhanced containment of polycyclic aromatic hydrocarbons (PAH) through organic modification of soils. Environmental Progress and Sustainable Energy. DOI 10.1002/ep.11749