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USING ACTIVATED CARBON TO ENHANCE THE VOCS AND HEAVY METALS REMOVAL OF A POROUS ASPHALT PAVEMENT SYSTEM

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USING ACTIVATED CARBON TO ENHANCE THE

VOCS AND HEAVY METALS REMOVAL OF A

POROUS ASPHALT PAVEMENT SYSTEM

BY

HUI CHEN

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE

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DOCTOR OF PHILOSOPHY THESIS

OF

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2014

ABSTRACT

Two different porous asphalt pavement systems (PAPS) were designed to enhance the removal of VOCs (dichloromethane and toluene) and heavy metals (cadmium, copper and lead) from roadway runoff. These two PAPS utilized granular activated carbon (GAC) additions to the conventional PAPS. One PAPS, the CPP system (carbon in porous pavement), had GAC added directly to the top porous asphalt mix, and the other PAPS, the CCA system (carbon in coarse aggregates), had GAC added to the sub-base filter course below the porous asphalt layer. The removal of selected VOCs and heavy metals through the CPP and the CCA systems was measured and compared to a conventional PAPS.

The results show that the addition of GAC into the top porous asphalt layer and the sub-base filter course layer enhanced the overall porous asphalt pavement contaminants removal capability. The addition of GAC to the sub-base filter course layer resulted in higher removal efficiencies for all of the constituents tested in this study. The CPP system is capable of removing on average 83% of dichloromethane, 95% of toluene, 71% of cadmium, 66% of copper, and 73% of lead. The CCA system resulted in the average removal of 99% of dichloromethane, 100% of toluene, 95% of cadmium, 76% of copper, and 75% of lead from a synthetic roadway runoff.

The CCA system was able to control the effluent concentrations of all of the contaminants (dichloromethane, toluene, cadmium, copper and lead) to meet the US EPA MCLs (Maximum Contaminant Levels). Even though the same amount of GAC was added into the two systems some of the GAC in the CPP system could have been coated by the asphalt binder during the construction process which would reduce the

effective GAC surface area available for adsorption and thus reduce the effectiveness

of contaminant removal.

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PREFACE

This dissertation described the design and testing of the porous asphalt pavement systems with an enhanced contaminant removal efficiency as compared to the conventional porous asphalt pavement system which are currently installed in the USA. It is an article which is going to be submitted to a peer-reviewed journal. The manuscript format is in use.

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by

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Is going to be submitted to Journal of Environmental Engineering (ASCE)

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Using Activated Carbon to Enhance the VOCs and Heavy Metals Removal of a

Porous Asphalt Pavement System

Abstract

Two different porous asphalt pavement systems (PAPS) were designed to enhance the removal of VOCs (dichloromethane and toluene) and heavy metals (cadmium, copper and lead) from roadway runoff. These two PAPS utilized granular activated carbon (GAC) additions to the conventional PAPS. One PAPS, the CPP system (carbon in porous pavement), had GAC added directly to the top porous asphalt mix, and the other PAPS, the CCA system (carbon in coarse aggregates), had GAC added to the sub-base filter course below the porous asphalt layer. The removal of selected VOCs and heavy metals through the CPP and the CCA systems was measured and compared to a conventional PAPS.

The results show that the addition of GAC into the top porous asphalt layer and the sub-base filter course layer enhanced the overall porous asphalt pavement contaminants removal capability. The addition of GAC to the sub-base filter course layer resulted in higher removal efficiencies for all of the constituents tested in this study. The CPP system is capable of removing on average 83% of dichloromethane, 95% of toluene, 71% of cadmium, 66% of copper, and 73% of lead. The CCA system resulted in the average removal of 99% of dichloromethane, 100% of toluene, 95% of cadmium, 76% of copper, and 75% of lead from a synthetic roadway runoff.

The CCA system was able to control the effluent concentrations of all of the contaminants (dichloromethane, toluene, cadmium, copper and lead) to meet the US EPA MCLs. Even though the same amount of GAC was added into the two systems

some of the GAC in the CPP system could have been coated by the asphalt binder during the construction process which would reduce the effective GAC surface area available for adsorption and thus reduce the effectiveness of contaminant removal.

Introduction

Runoff from roadway and other impervious surfaces in urbanized areas has been recognized as a leading source of water quality impairments to national water resources (EPA 2004). Major contaminants carried by roadway runoff include volatile organic compounds (VOCs) and heavy metals. VOCs (dichloromethane and toluene) and heavy metals (cadmium, copper and lead) were found in roadway runoff at concentrations which could impair the quality of drinking-water. Many VOCs and heavy metals will not degrade before reaching the groundwater and they can persist in the groundwater for decades (Borchardt and Sperling, 1997, and Zogoraki, et al.).

Volatile Organic Compounds

The EPA's National Urban Roadway Runoff Program (NURP) and National Pollutant Discharge Elimination System (NPDES) were two large scale national surveys of VOCs which provided information on VOCs occurrence in the roadway runoff in most regions of the United States. The most frequently detected VOCs in the NURP study were dichloromethane, naphthalene, and chloroform (Cole et al., 1984). Dichloromethane was detected in 10% of the samples with a maximum detected dichloromethane concentration of 14.5μg/L, and toluene was detected in 2% of the samples with the maximum concentration of 9μg/L (Cole et al., 1984). The most frequently detected VOCs for the NPDES studies were toluene, xylenes, chloroform, and trimethylbenzene (Delzer et al., 1996). The measured toluene concentration was in

the range of 0.2-6.6μg/L which was the concentration range found in 23% of the samples. Dichloromethane was found in 6% of the samples in this research with concentration in the range of 0.2-13μg/L (Delzer et al., 1996). Since dichloromethane and toluene were the most frequently detected VOCs in these studies, they were selected as the two major VOC pollutants of roadway runoff to be investigated in this study. Table 1 lists the concentrations of dichloromethane and toluene found in roadway runoff from several researchers and their maximum contaminant levels (MCL) set by the US EPA (EPA, 2012).

Table 1. VOCs Concentration in Roadway Runoff and the Comparison of VOCs in Roadway Runoff to Drinking Water Standards

VOC	Concentration in Previous Studies	Locations	MCL in μg/L (EPA, 2012)
Dichloromethane	5-14.5μg/L (Cole, 1984)	Nationwide (U.S.)	5
	0.2-13μg/L (Delzer et. al., 1996)	Nationwide (U.S.)	
	0.5μg/L (Asaf, et al., 2004)	Ashdod, Israel	
Toluene	9μg/L (Cole, 1984)	Nationwide (U.S.)	1000
	0.2-6.6μg/L (Delzer et. al., 1996)	Nationwide (U.S.)	
	0.05-0.17μg/L (Torres, 2010)	Omaha, Nebraska	
	0.2-4 μg/L (Baldys, et al., 1997)	Texas, U.S.	

VOCs have low concentration aquatic toxicities (Rowe and others, 1997) and primarily are a threat to drinking-water supplies. Makepeace and others found that dichloromethane is one of the compounds that could be a concern if roadway runoff entered drinking-water supplies (Makepeace, et al., 1995). The national assessment of VOCs in ground water aquifers found that dichloromethane and toluene were among the most frequently detected VOCs. The occurrence of dichloromethane was 3.6% and

9.9% for toluene with concentrations over 0.02μg/L from the samples collected from aquifers. The median concentration**s** of dichloromethane and toluene samples with measurable levels were 0.04μg/L and 0.032μg/L respectively. Dichloromethane was found at concentrations high enough to cause human-health concerns (Zogorski, et al., 2006). For example, in drinking water tested in Zogorski's study, concentrations of dichloromethane were 5.01μg/L which was slightly higher than the MCL standard of 5μg/L. (Zogorski, et al., 2006).

Heavy Metals

The heavy metals that are present in the roadway runoff are either dissolved or are bound to particulates. This distribution between the particulate-bound and dissolved phases was studied by many researchers. Morrison and others (Morrison et al., 1984) found that between 5% and 50% of cadmium, copper and lead were in the dissolved phase. Cadmium was most often found in the dissolved ionic forms and lead was most highly associated with particles. Washington State Department of Transportation (Herrera, 2007) reported both the total and dissolved concentrations of copper in roadway runoff and found that 29 percent of the total copper was in the dissolved form, which is generally the most toxic form of the metals (Herrera, 2007). Other studies found that in urban runoff, copper primarily was found in the dissolved form (Flores-Rodriguez et al., 1994 and Morrison et al., 1990) and lead can be either particle bound or dissolved depending on prevailing conditions (Lienden, et al., 2010). Heavy metals were often detected in more than 98 percent of the collected road way runoff samples. The typical concentrations of cadmium, copper, and lead found in dissolved and particulate phase from several researchers are presented in Table 2.

Table 2 Typical Concentrations of Copper, Lead, and Cadmium in Dissolved
and Particles Phases

Metal	Concentration		References
	Total, µg/L	Dissolved, µg/L	
Cu	4.6 to 72	3.1-18.1	Herrera, (2007)
	24 to 1,065	NM	Herrera, (2007)
	<3-210	<3-33	Bannerman, et al. (1996)
	1.3-874.5	1.5-45.5	Werf, et al. (2007)
	1-45	1-21	Harrision, et al. (1997)
	<1-250	<1-110	Strecker, et al. (1997)
	0.0157, 0.041	0.0110, 0.0063	Muthukrishnan (2010)
Pb	24 to 61	3.2	Herrera, (2007)
	0.0307	NM	Muthukrishnan (2010)
	60-112	NM	McQueen (2010)
Cd	0.1-14	NM	NURP (1984)
	0.9 to 2.8	NM	Herrera, (2007)
	ND-40	NM	Driscoll et al. (1990); Barrett et al. (1995)
	4-5	NM	McQueen (2010)

NM: not measured

The heavy metals that are present in roadway runoff could impact the aquatic system. Table 3 shows the comparison of metals in roadway runoff to the USEPA Drinking Water Standards and Aquatic Life Criteria. The cadmium and lead present in the roadway runoff were all found to have concentrations exceeding the drinking water and aquatic life standards. Copper concentrations exceed both of the aquatic life criteria and the national secondary drinking water regulations. Washington State DOT also found that concentrations of dissolved copper measured at the edge of the pavement often exceed acute and chronic water quality standards for receiving waters in western Washington (Herrera, 2007). Cole reported that cadmium, copper, and lead are among the most detected pollutants in runoff and exceed freshwater ambient 24-hour average criterion ("chronic" criterion) in 55%, 87% and 96% of the samples respectively. The highest detected values for these metals were 2 to 8 times higher than their related criteria (Cole, 1984). Consequently, these pollutants could cause

harm to aquatic life (Cole 1984). Some contaminants with lower concentration than the aquatic life criteria could still pose risks to some species. For example, Sandahl et al. has shown that even low concentrations (2-5µg/L) of dissolved Cu^{2+} can impair the olfactory system of juvenile coho salmon which is one of the species listed under the Endangered Species Act (ESA) (Sandahl et al., 2007).

Table 3 Comparison of Metals in Roadway Runoff to Drinking Water
Standards and Aquatic Life Criteria

Metal	CAS number	Concentration Range (µg/L) (Summary from Table 2.1)	Standard (µg/L)	Type of standard
Cu	7440-50-8	0.0157-1065 (Total) 0.0110 -110 (Dissolved)	1300	MCL
			1000	NSDWR
			13[a]	CMC
			9[a]	CCC
Pb	7439-92-1	0.0307 to 460 (Total) 3.2 (Dissolved)	15	MCL
			0	MCLG
			65	CMC
			2.5	CCC
Cd	7440-43-9	0.1-40 (Total)	5	MCL
			2	CMC
			0.25	CCC

(µg/L, micrograms per liter; mg/L, milligrams per liter; CAS, Chemical Abstracts; MCL, maximum contaminant level; MCLG, maximum contaminant level goals; NSDWR, national secondary drinking water regulations; CMC, Aquatic Life Criteria-- acute 1hr; CCC, Aquatic Life Criteria-- chronic 96hr)
[a]. The U.S. Environmental Protection Agency (EPA) has established hardness dependent water quality criteria for acute (1hr) and chronic (96hr) exposure to Cu^{2+} dissolved. With an assumed hardness of 100 mg/L as $CaCO_3$, the acute criteria is 13µg/L, and chronic criteria is 9µg/L for freshwater (USEPA, 2008).

Porous Asphalt Pavement System

To protect the quality of receiving waters, regulations have been established to treat runoff prior to discharging or to reduce pollutants at the source (EU Directive, 2011; Hanley et al., 2006; USEPA, 2011). Typically, roadway runoff is managed through best management practice (BMP) such as porous asphalt pavement system

(PAPS). PAPS is one of the most effective BMPs to control pollution from roadway runoff (Hansen, 2008, Ahiablame et al., 2013). The porous asphalt pavement systems (PAPS) constructed to date were designed mostly to carry light traffic load which is defined as a road which carries traffic volumes less than 2,000 vehicles per day and with gross vehicle weight rating (GVWR) not larger than 14,000lb.

Many contaminants can be removed as the roadway runoff passes through the PAPS. Numerous studies have reported that the PAPS has a high removal efficiency for total suspended solids (TSS), metals, and oil and grease (Cahill et al.,2005; Jeff, 2008; Roseen, 2009). PAPS had also been reported to be capable of removing 82% of the total organic carbon. In addition to the ability to protect receiving water quality by removing contaminants, PAPS is able to significantly reduce the quantity of contaminants in roadway runoff that would normally enter downstream water bodies (Ahiablame et al., 2012, Dreelin et al., 2006, Tota-Maharaj and Scholz, 2010). PAPS is typically able to allow for infiltration of 80% of the annual roadway runoff volume (Hansen, 2008).

Currently, most stormwater BMPs for treating roadway runoff focus on removing suspended solids and their associated contaminant loads. However, even when a significant portion of the contaminant is in a particle bound form, dissolved contaminant including dissolved metals in highway runoff may still exceed ambient water quality standards, and these dissolved contaminants are more toxic to aquatic organisms (Barber et al. 2006).

Granular Activated Carbon

One method to enhance the traditional PAPS would be through the addition of granular activated carbon (GAC). GAC is a good choice because of the fact that GAC is an effective sorbent to remove contaminants in roadway runoff (Liu, 2005; Al-Anbari, et al., 2008; Grebel, et al., 2013). Adsorption onto GAC has been shown to effectively remove dissolved VOCs and heavy metals from aqueous solutions (Chen and Lin, 2001; Machida et al., 2005; Lienden, et al., 2010, adding references of using GAC to remove VOCs).

The adsorption process depends on the properties of the contaminants, the contact time, and the GAC's internal surface area. In Zeinali's study, GAC was effective in removing dichloromethane and toluene from water, and the experimental results fit the Langmuir and BET-Langmuir model. The adsorption processes were fast during the first 30 minutes, after that, they became very slow, and they reached equilibrium in their adsorption experiments at about 2 hours (Zeinali et al., 2011). Lienden studied GAC adsorption of copper and found that the Freundlich equation provided the best fit for copper GAC adsorption (Lienden, 2010). Trace metal adsorption by GAC was also studied by Abudaia. Under the same conditions, copper was found to have a higher adsorption than lead (Abudaia, et al., 2013).

Objectives

PAPS is capable of removing the particulate fraction of contaminants from roadway by filtration, but the capability of removing the dissolved contaminants has not been investigated. Based on the fact that adsorption has been recognized as an effective and economic method for heavy metal removal, and more specifically GAC

adsorption has been studied and is widely used in removing heavy metals for drinking water and wastewater treatment, there exists a high potential for success in treating roadway runoff by GAC adsorption (Fu and Wang, 2011). So in this study, enhanced PAPS with GAC added were created, which has the potential to control some of the total suspended solids (TSS) in roadway runoff, but also to be able to reduce the environmental load of dissolved compounds, including VOCs and heavy metals.

The goal of study is to construct enhanced PAPS and test their removal efficiency for removing VOCs and heavy metals from roadway runoff. More specifically, the goal of designing these enhanced PAPS was to treat runoff with varying concentration of VOCs and heavy metals to achieve an effluent below the USEPA MCLs set for these contaminants. The enhanced PAPS can offer site planners and public works officials more opportunities to manage roadway runoff with higher contaminant removal efficiencies.

Methodology

A typical PAPS structure is shown in Figure 1. From the top to the bottom, the layers that comprise the PAPS are the porous asphalt pavement layer, the filter layer, the reservoir course, a nonwoven geotextile filter fabric, and native existing soil. These layers are described below:

The porous asphalt pavement layer is placed on the top. This permeable asphalt pavement surface is 2 to 4 inches in thickness (EPA, 2009a) and is a standard hot mix asphalt layer with reduced sand or fines. It allows roadway runoff flow through the pavement, and at the same time, it traps some of the particles from the roadway runoff.

The layer right below the surface porous asphalt pavement layer is the filter layer. This layer of aggregates is typically 3 to 12 inches thick (UNHSC, and EPA, 2009a) and consists of crushed stones typically 3/16 to 3/4 inch (EPA, 2009a). Besides storing water, this high infiltration rate layer provides a transition between the bedding and sub-base layers (EPA, 2009a).

Then next layer is the reservoir course. The stone sizes for this layer are larger than the filter course, typically 3/4 to 2 ½ inch stone (EPA, 2009a). This reservoir course is typically between 12 and 36 inches in depth. The 40 percent voids ratio in the stones is capable of storing the roadway runoff before infiltrating into the sub native soil (Hansen, 2008). This reservoir course may not be required in pedestrian or residential driveway applications (EPA, 2009a).

The nonwoven geotextile filter fabric is an optional layer and can be used to prevent the migration of the native soil into the aggregate layers above it (UNHSC, 2009)

At the bottom of the PAPS structure is the existing native soil. The infiltration capacity of the native soil determines how much water can exfiltrate from the aggregate into the surrounding soils. This native soil is generally not compacted. (EPA, 2009a)
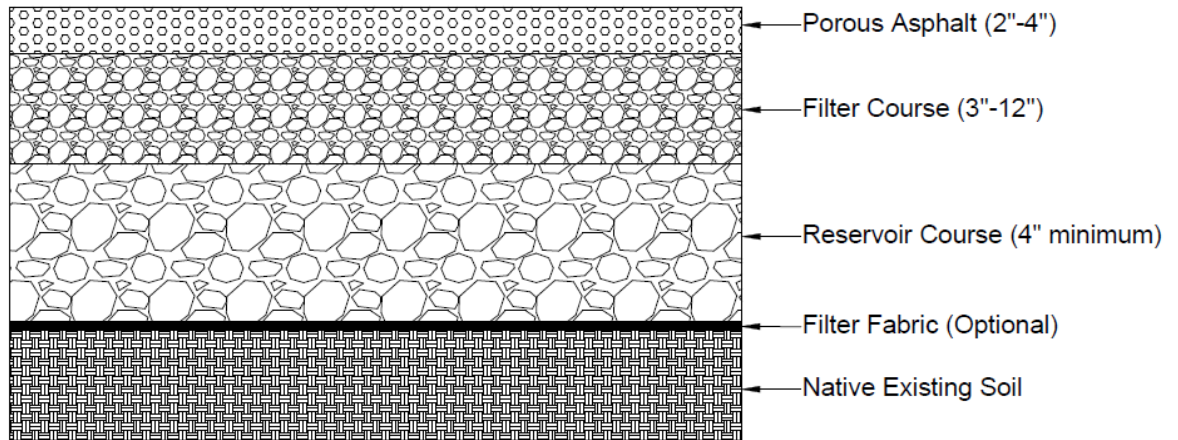
Figure 1. Typical PAPS Structure and Their Thickness Requirements

Sources: 1. EPA, 2009a. EPA Porous Asphalt Pavement Fact Sheet.
        2. UNHSC, 2009. UNHSC Design Specifications for Porous Asphalt
           Pavement and Infiltration Beds.
        3. Hansen, 2008. Porous Asphalt Pavements for Stormwater Management:
           Design, Construction and Maintenance Guide

The layers where the contaminant removal mainly occurs are the top porous asphalt pavement layer and the filter course layer, and as a result the constructed PAPS contained only these two layers.

Column Construction

Three columns with different PAPS structures were set up in the lab (Figure 2). Each of the PAPS was dimensionally similar with a diameter of 6 inches. The control column (CC column), which holds a PAPS, had no GAC added; the CPP column is an enhanced PAPS that has GAC added into the top porous asphalt layer; and the CCA column is another enhanced PAPS that has GAC only added into the sub-base filter course layer.
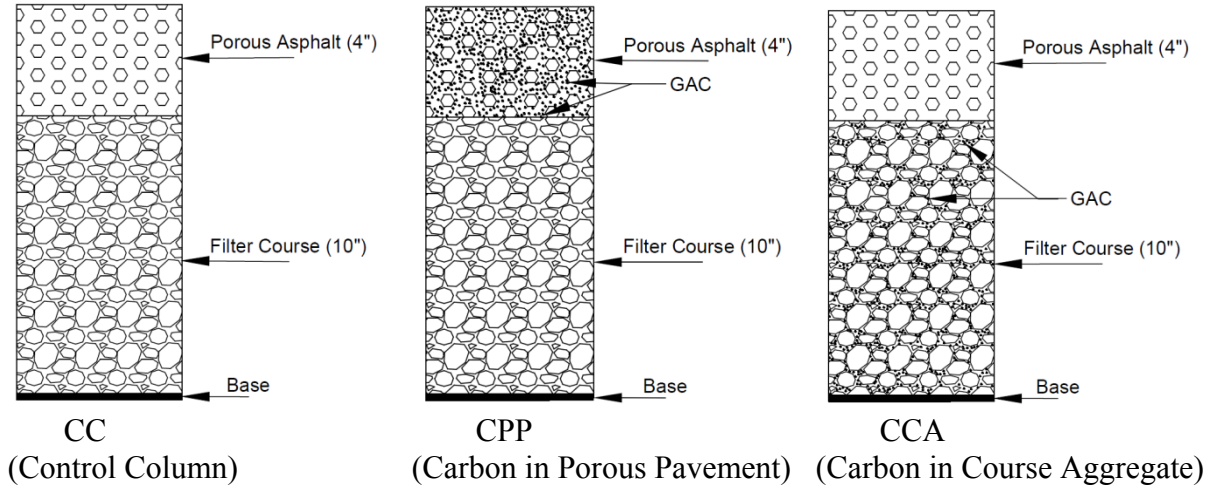
Figure 2 Test Column Construction Details

1. The CC Column Structure

A photo of the CC column is in Figure 3. The mix aggregates, weight of 4000g, for making the top porous asphalt pavement layer for the CC column consisted of coarse and fine aggregates are listed in Table 4. A 255g mass of asphalt binder mixed with styrene butadiene rubber (SBR) was added to the aggregates (6% of the total weight of the porous pavement), which includes 244g mass of asphalt binder and 11g of SBR (67% solids) at 0.18% by dry weight of the porous asphalt pavement.

Table 4 Porous Asphalt Mix for the CC Column

Mixing Particle Size		Weight	Weight
Sieve Size	Diameter (mm)	(g)	Percentage (%)
3/4"	19	0	0
1/2"	12.5	400	9
3/8"	9.5	1000	23
#4	4.75	2000	47
#8	2.36	280	7
#200	0.075	200	5
#-200	0.075	120	3
Asphalt Binder		244	6
SBR (67% solids)		11 (dry weight,7g)	0.3
Total		4255	100

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The calculation process of the weight of the styrene butadiene rubber (SBR) is shown in the equations below:

MAB = 6% MPAP = 6% (MAB + MAG), when MAG = 4000g, MAB = 255g

DMSBR = 3% (MAB + MSBR), when MAB = 255g, DMSBR = 67% MSBR,

MSBR = 11g

Where: MAB, Mass of asphalt binder

DMSBR, Dry weight of SBR

MSBR, Mass of SBR

MPAP, Mass of porous asphalt pavement (PAP)

MAG, Mass of aggregates

When making the sub-base filter course layer mix, aggregates sizes distribution were listed in Table 5.

Table 5 Filter Course Mix for the CC Column

Mixing Particle Size		Weight (g)	Weight Percentage (%)
Sieve Size	Diameter (mm)		
3/4"	19	0	0
1/2"	12.5	3297	50
3/8"	9.5	3297	50
Total		6594	100
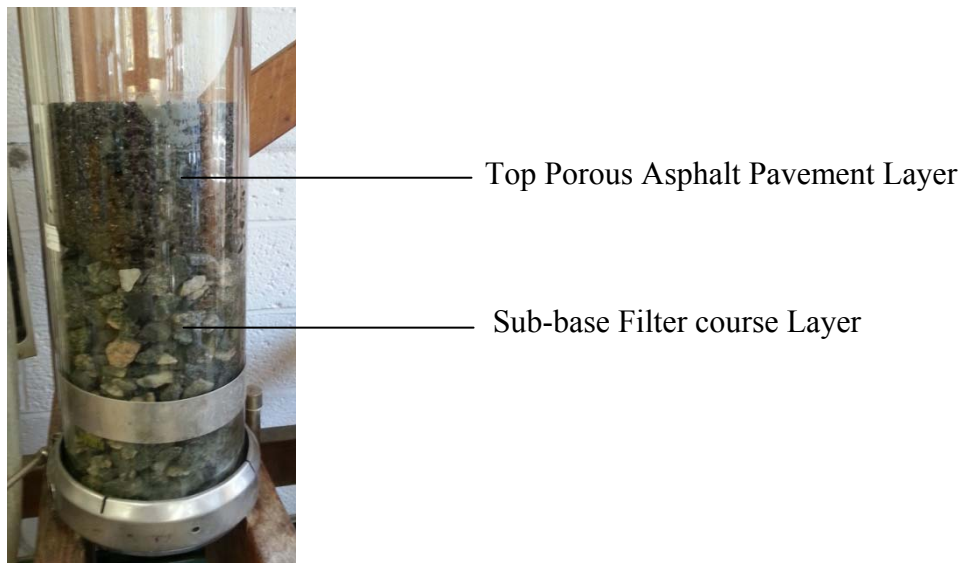
Figure 3 Photo of the CC Column

2. The CPP Column Structure

When making the CPP column, GAC was added into the top porous asphalt pavement layer (Table 6). The amount of the GAC used in this column is 182g which was calculated as the weight for the same total apparent volume of the fine particles (+200 and -200) of the standard asphalt mixture. This was to produce a PAPS which was structurally similar to one without GAC added. A review of the size gradations recommended by various highway authorities and the Franklin Institute Research Laboratories for composition of the aggregate in porous pavement indicates that a minimum of two percent passing the Number 200 sieve was required to provide stabilization of the filter course fraction. So 2% by weight of the fines that passed the Number 200 sieve were added back into the mixture. The CPP column had the same mix design for the sub-base filter coarse layer as for the CC column.

Table 6. Porous Asphalt Mix Gradation of the CPP Column

| Mixing Particle Size | | Weight | Weight |
Sieve Size	Diameter (mm)	(g)	Percentage (%)
3/4"	19	0	0
1/2"	12.5	400	10
3/8"	9.5	1000	24
#4	4.75	2000	48
#8	2.36	280	7
#200	0.075	0	0
#-200	0.075	80	2
GAC #12-#40	0.42-1.68	182	4
Asphalt Binder		244	6
SBR (67% solids)		11 (dry weight,7g)	0.3
Total		4186	100

3. The CCA Column Structure

The top porous asphalt pavement layer of the CCA column is the same as the layer in the CC column. The only difference was that 182g of GAC were added into the sub-base filter course aggregates mix.

Materials

The VOCs used in this study were dichloromethane (BJ brand) having mass fraction of 99.995% purity and toluene (Fisher Scientific brand) having mass fraction of 99.9% purity. The dichloromethane and toluene were used as received. After the stock solution was prepared, the dichloromethane and toluene's concentrations were tested using gas chromatography–mass spectrometry.

The trace metals used in this study were copper, cadmium, and lead.

The GAC that was used was a coal-based granular activated carbon (Calgon Carbon Corporation, Filtrasorb 400) with a size range of 0.55-0.75 mm and an apparent density of 0.52g/ cm^3. Prior to the start of the experiment, activated carbon was dried in an oven at 115°C for 6 hours to remove any adsorbed gases and moisture.

Synthetic Roadway Runoff

For the VOCs removal, DI water containing only dichloromethane and only toluene was used for the influent. For the heavy metal removal, DI water containing three metals (cadmium, copper and lead) together was used as the influent. A 0.2N sodium hydroxide solution was added to the stock solution as necessary to adjust pH to 6.6.

A pH slightly lower than 7 of the runoff will lead to an increase in the dissolved fraction and an increased mobility of the trace metals. Since a decrease in pH leads to more metals existing in a bioavailable free ionic form, the lower pH can cause an increase in toxicity (Hall and Anderson, 1998). Metal adsorption on GAC also depends on the pH of the water (Dabioch, et al., 2013). So in this study, the pH was kept constant for each experiment. The pH value of 6.6 was selected because it was the most often occurring pH value of the roadway runoff found in literature (USGS, 2009).

Researchers found that the GAC adsorption of cadmium increased with the increased pH of the solution within a pH range of 5 to 8 (Disnati and Ali, 2014). Abudaia reported that adsorption of copper and lead was very low in strong acidic solutions and the adsorption capacity increased with increasing pH values and reached its maximum at pH 6.5 (Abudaia et al., 2013). The heavy metal removal study was run with a runoff pH of 6.6 which was a natural occurring pH value of roadway runoff and is close to the pH value of 6.5 where the GAC adsorption of copper and lead reached its maximum adsorption capacity.

Porous Asphalt Pavement Manufacture

The process of the PAPS construction followed the procedure given in the University of New Hampshire Design Specifications for Porous Asphalt Pavement and Infiltration Beds (UNHSC, 2009) and the National Asphalt Pavement Association published Porous Asphalt Pavements for Stormwater Management: Design, Construction, and Maintenance Guide (Hansen, 2008).

The procedure was as follows: all aggregates (except +/-200 fines) were soaked and washed by DI water and put in the oven for 12 hours at a constant temperature of 350°F and cooled; aggregates and asphalt binder PG 64-22 were put in the oven at 300 °F for 1 hour, then discharged into the mixer bucket to be mixed; the mixture went back into the oven at 300 °F for 1 hour for asphalt binder absorption. The SBR was added into the mixing bucket and mixed again; the cylindered mold was heated to 300 °F for 15 min. The asphalt mixture was added to the cylindrical mold in the Superpave Gyratory Compactor, and the compactor was set to a compacting pressure of 600KPa and compacted for 100 gyrations. The finished sample was unmolded and cooled.

Air Void Content Test

The air void content of the top porous asphalt layer is required to be within the range of 16.0-22.0% as described in the UNHSC Design Specifications for Porous Asphalt Pavement and Infiltration Beds (UNHSC, 2009). The theoretical maximum specific gravity, G_{mm} was tested using the AASHTO T209 standard. The Bulk Specific Gravity, G_{mb} was tested using the AASHRO T275 standard.

Saturated Hydraulic Conductivity Test

Hydraulic conductivity tests of the top porous asphalt pavement layer were conducted following the methods described in EPA Method 9100. A layer of model clay was used to cover the sides of the pavement samples to prevent sidewall leakage. The thickness of the pavement sample was 10.2cm, and the test was conducted using a constant hydraulic gradient of 0.48 (4.9cm/10.2cm) which is in the recommend range of 0.2 to 0.5 to prevent turbulent flow from occurring. Prior to testing, samples were water soaked in the water for 2 hours. Water was allowed to flow through the porous asphalt pavement samples for three times, and hence, three hydraulic conductivity readings were measured. The average value of the three hydraulic conductivity readings was then reported.

Experimental Apparatus
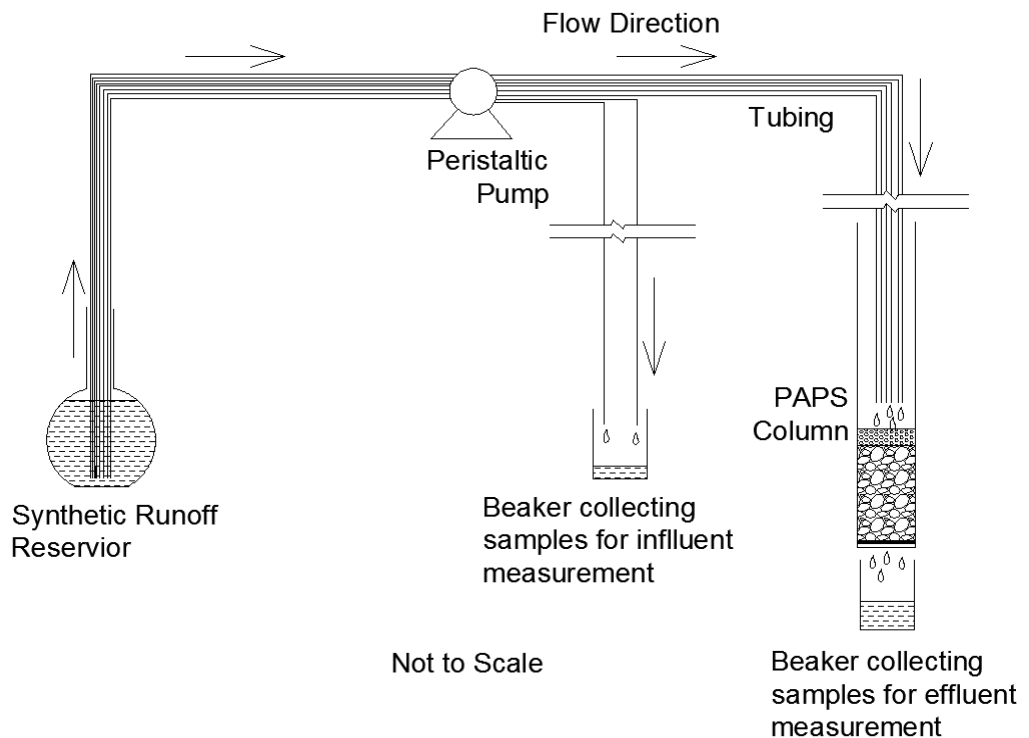
Figure 4 Hydraulic Flow Diagram

Figure 4 is the hydraulic flow diagram for the experiments. The synthetic roadway runoff was pumped using a peristaltic pump with 8 tube capability to transport roadway runoff to the surface of the pavement inside the columns. Among the 8 tubes, 6 tubes discharged to the top of the surface of the PAPS inside the columns to distribute the lab synthetic roadway runoff. Containers under the columns collected the water which flowed out of the columns. This treated water was tested for contaminants. Water samples from the other 2 tubes were collected and analyzed for the influent water quality.

The pump flow rate was set at 0.7ml/min for each tube (which was calculated based on the Kingston, RI area's 1 year 2 hours rainfall intensity of 0.58in/hr). For each experiment, the pump ran for 2 hours. For a period of 2 hours the water samples which flowed through the columns were collected and analyzed as effluent. Flow through the other 2 tubes were collected and analyzed as influent. There were at least 48 hours between each experiment to mimic typical rainfall intervals.

Contaminant Analysis

The concentrations of toluene and dichloromethane were analyzed by Gas Chromatography – Mass Spectrometry (GCMS) using a Purge and Trap apparatus. EPA method 502.2 was followed.

For the heavy metal analysis, after the samples were collected, they passed through a plastic syringe filter. Nitric acid was added as a preservative to make a 4% nitric acid solution. The heavy metal concentrations were measured by a PERKIN ELMER Optima 3100 XL Inductively Coupled Plasma instrument (ICP).

Removal Efficiencies

The removal efficiency method typically used by investigators to determine the contaminants removal by a BMP device was utilized in data analysis (National Cooperative Highway Research Program, 2006; Horwatich and Bannerman, 2011). This method uses data from the influent and effluent to produce a single number that is designed to represent removal efficiency of the system for each experiment. For the BMP studies, the most common and typically most cost-effective method when collecting samples is flow-weighted composite sampling. This method uses flow data to collect larger sample amounts during high flows, allowing for a more accurate representation of an entire roadway runoff event. The generation of a flow weighted mean or event mean concentration is the most commonly used method when assessing BMPs. But in this research, each experiment lasted two hours, and the total influent to each column for the two hours of testing was 504ml. All of the influent and effluent water during the two-hour tests was collected. The differences between the mass of influent contaminants to the mass of effluent contaminants were calculated when discussing the GAC adsorption capability.

Infiltration Rate Test

The infiltration rate can influence the GAC contact time with runoff. Even though the total mass of GAC added to the CPP and the CCA systems was equal, the GAC was added to different locations with the PAPS.

A saturated NaCl solution was run through each column and the effluent was collected with a plastic bowl under the columns. Prior to testing, the top porous asphalt layer of the CPP system and the sub-base filter course layer of the CCA system

were soaked in DI water for two hours to saturate them. Next, DI water was first run through the column with a flow rate of 4.2 ml/min for 20min. A saturated NaCl tracer solution ran through the columns. A conductivity meter was used to detect the NaCl tracer appearance in the effluent.

QA/QC

The QA/QC steps that were undertaken included: the use of non-contaminating materials, containers, and apparatus. All glassware was cleaned and put into the oven at over 110°C for 2 hours. All plastic ware for metals sampling were washed with 2% nitric acid with post DI water rinsing. Samples were preserved at 4°C. Samples were analyzed within 48 hours after the samples were collected. VOC filled containers were filled as close to the top as possible to minimize VOCs volatilization. Influent solutions were passed through pumps and tubes for 30 min prior to the beginning of the experiment. Syringe filters were rinsed with samples before they were collected. Each syringe filter was used only one time. Standards were used to calibrate the GCMS and ICP results.

DI water with an adjusted pH of 6.6 was passed through the CC, CPP and CCA systems to test if there was any metal leaching from the systems. No cadmium, copper or lead leaching was observed.

Since the collection of effluent took two hours, some volatilization of VOCs might be occurred during the experiments, so a volatilization test was conducted to measure the possible amount of VOCs volatilized during each experiment. A beaker containing dichloromethane and toluene were left open for 2 hours. Samples were collected at the beginning and two hours later. The results were listed in Table 7. The

influent and effluent concentrations of dichloromethane and toluene from the experiments were then adjusted based on these volatile testing results.

Table 7 Dichloromethane and Toluene Volatile Testing Results

VOCs	Volatile Time (hour)	VOCs Concentration (µg/L)			
		Run 1	Run 2	Run 3	Run 4
DCM	0	218.9	41.8	8.36	5.21
	2	203.75	28.15	5.28	1.71
Toluene	0	108.95	42.7	9.09	2.59
	2	97.55	32	7.17	1.65

Results and Discussion

Contaminants Removal Efficiency

In this study, the lab synthetic roadway runoff containing only dichloromethane and only toluene were prepared as lab synthetic roadway runoff for VOCs removal and tested separately. The lab synthetic roadway runoff containing cadmium, copper, and lead together with different concentrations were prepared and tested for heavy metals removal. The testing results showing the influent concentration, effluent concentration and removal efficiency of these compounds are presented below.

1. Dichloromethane Removal Efficiency

The synthetic roadway runoff containing 37µg/L to 241µg/L dichloromethane was passed through systems to conduct the tests. The maximum concentration of dichloromethane found in roadway runoff from previous studies listed in Table 1.1 was 14.5µg/L, the influent dichloromethane concentrations were in the range of 2 to 17 times the maximum concentration found in the previous studies. Four runs with

different dichloromethane concentrations were tested for each system. The results

from these runs are summarized in Table 8.

Table 8 Concentrations of Dichloromethane in the Influent (Before Flow Through the PAPS) and Effluent (After Flow Through the PAPS) and the Calculated Removal Efficiency

Systems	Dichloromethane Influent (μg/L)	Dichloromethane Effluent (μg/L)	Removal Efficiency (%)
CC	37	11	71
	52	15	72
	135	32	76
	241	41	83
CPP	46	10	79
	52	11	79
	141	23	84
	234	23	90
CCA	48	ND	100
	52	ND	100
	135	ND	100
	240	12	95

ND: Not Detected, detection limit is 1.4μg/L

When the influent concentrations went from 37μg/L to 241μg/L in the CC

system, the effluent concentrations went from 11μg/L to 41μg/L. The effluent

concentration increased when the influent concentration increased. The contaminant

removal efficiencies ranged from 71% to 83%.

For the CPP system, which has GAC embedded into the top porous asphalt

layer, when the influent concentrations of dichloromethane were at 46μg/L and

52μg/L, the contaminant removal efficiency was 79%, which is higher than the

contaminant removal efficiency of the CC system of 72% under similar condition.

When the influent concentrations increased to 141μg/L and 234μg/L, the effluent

concentration was 23μg/L, and the contaminant removal efficiencies were 84% and

90%. A comparison with the CPP results to those of the CC system showed that the CPP system achieved lower effluent concentrations for the same influent concentration.

For the CCA system which has GAC added into the sub-base filter course layer, even higher contaminant removal efficiencies were observed. When the influent dichloromethane concentrations were 48μg/L and 52μg/L, the removal efficiency of the CCA system reached 100%. The 100% dichloromethane removal also occurred when the influent concentration increased to 135μg/L. When the initial concentration went up to 240μg/L, the CCA system's dichloromethane removal efficiency was 95%. By comparison with the other two systems, the CCA system has the highest dichloromethane removal efficiency for all of the influents that were tested.

Figures 5 shows the dichloromethane removal efficiency of the three systems. The removal efficiency of the CC system and the CPP system increased with an increase in the influent dichloromethane concentration.

Figure 6 shows the influent vs. effluent of the three systems. The CCA system greatly improved the effluent water quality with non-detectable dichloromethane when the influent concentrations did not exceed 135μg/L. Curves were created to illustrate the removal behavior of the systems.

The curve fitting equations for the CC and the CPP systems are similar to the Freundlich isotherm adsorption curve equation. The same curve fitting equations were created for the other contaminant influent vs. effluent figures. The Freundlich isotherm equation is defined as:

$$\frac{x}{m} = K_f C_e^{1/n}$$

Where, x/m = weight of adsorbed substance per unit weight of active carbon

C_e = concentration in fluid, mg/L

K_f, n = specific constants

The Freundlich adsorption isotherm equation is an equilibrium expression. The contacting time of the synthetic roadway runoff with the GAC particles in the PAPS systems in this study were not long enough to reach equilibrium. Even though the similar trends to Freundlich isotherm curves were observed, the constants K_f and n are not able to be determined. Further studies are needed to develop the adsorption isotherm equation constants.
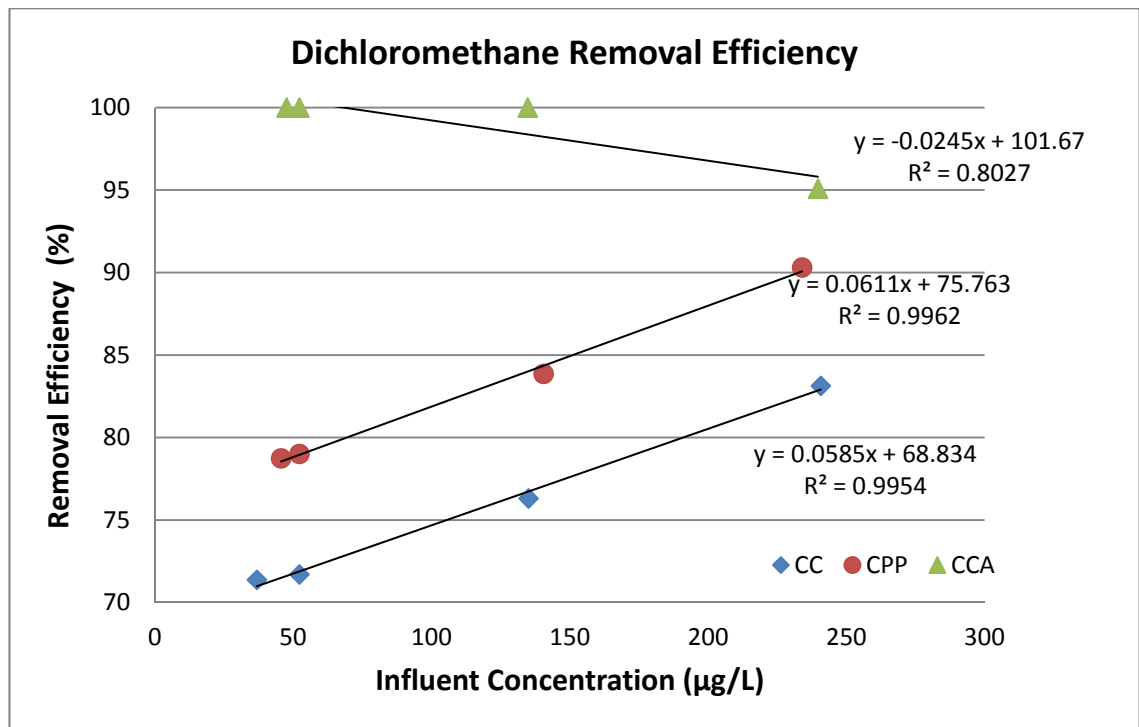
Figure 5 Dichloromethane Removal Efficiency
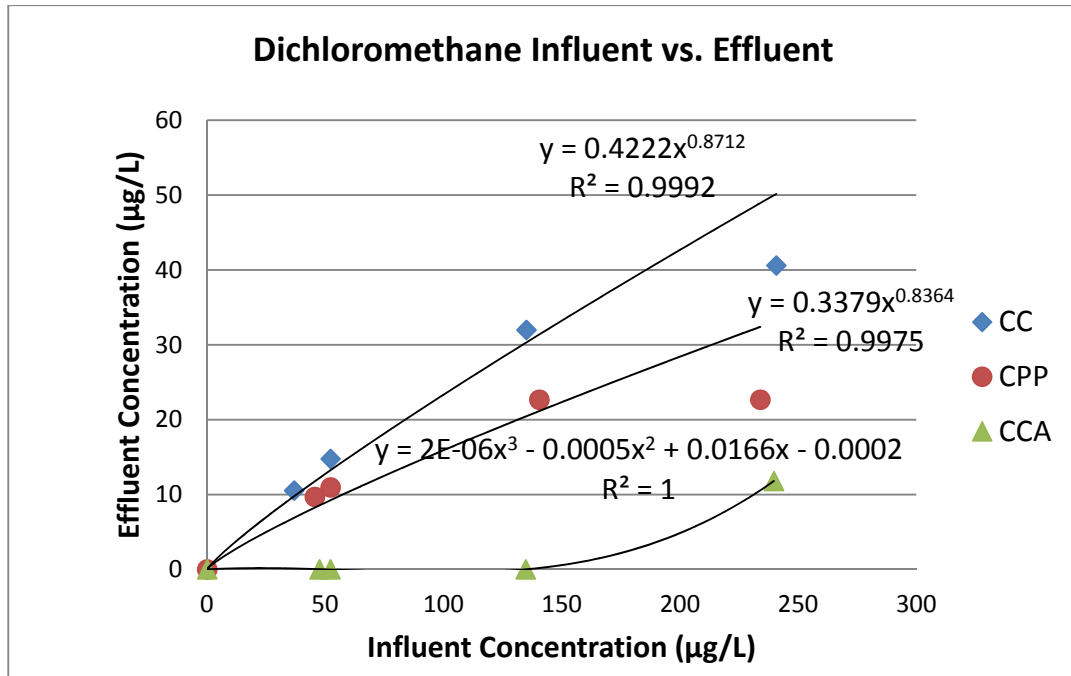
Figure 6 Dichloromethane Influent vs. Effluent Concentration

2. Toluene Removal Efficiency

The synthetic roadway runoff containing toluene with concentrations in the range of 22μg/L to 283μg/L was passed through each system to conduct the testing. The maximum concentration of toluene found in roadway runoff from previous studies listed in Table 1.1 was 9μg/L, thus the toluene concentrations that were tested were in the range of 2 to 31 times the maximum concentration found in the previous studies. Four runs with a different influent toluene concentration for each system were tested. The results from these tests are summarized in Table 9.

Table 9 Concentrations of Toluene in the Influent (Before Flow Through the PAPS) and Effluent (After Flow Through the PAPS) and the Removal Efficiency

Systems	Toluene Influent (μg/L)	Toluene Effluent (μg/L)	Removal Efficiency (%)
CC	22	2	90
	24	2	90
	48	4	92
	173	31	82
CPP	24	1	96
	27	2	95
	37	2	95
	271	8	97
CCA	23	ND	100
	24	ND	100
	27	ND	100
	284	1	100

ND: Not Detected, detection limit is 0.6μg/L

For the CC system, when the influent concentrations were 22μg/L and 24μg/L, the effluent concentration was 2μg/L with removal efficiency of 90%. When the influent concentration was 48μg/L and 173μg/L, the effluent concentration were 4μg/L and 31μg/L with removal efficiency of 92% and 82%, respectively.

For the CPP system, which has GAC added into the top porous asphalt layer, the effluent concentrations were in the range of 1μg/L to 8μg/L with the influent toluene concentrations in the range of 24μg/L to 271μg/L.

For the CCA system which has GAC added into the sub-base filter course layer, an even higher contaminant removal efficiency was observed. When the influent toluene concentration was in the range of 23μg/L to 284μg/L, the effluent concentrations did not exceed 1μg/L. Compared with the other two systems, the CCA system achieved the highest contaminant removal efficiency among the three systems.

Figure 7 and Figure 8 show the toluene removal efficiency of the three test systems and their influent vs. effluent concentrations. When the influent toluene concentration was lower than 48μg/L, all of these three systems have toluene removal concentrations no less than 90%. As the influent concentration increased to 173μg/L, the CC system removal efficiency decreased to 82%, but the removal efficiencies of the CPP and CCA systems kept increasing to 97% and 100%, respectively.

Toluene Removal Efficiency

$y = -0.0016x + 100.02$
$R^2 = 0.9851$

$y = 0.0085x + 94.62$
$R^2 = 0.8209$

$y = -0.0563x + 92.38$
$R^2 = 0.8804$
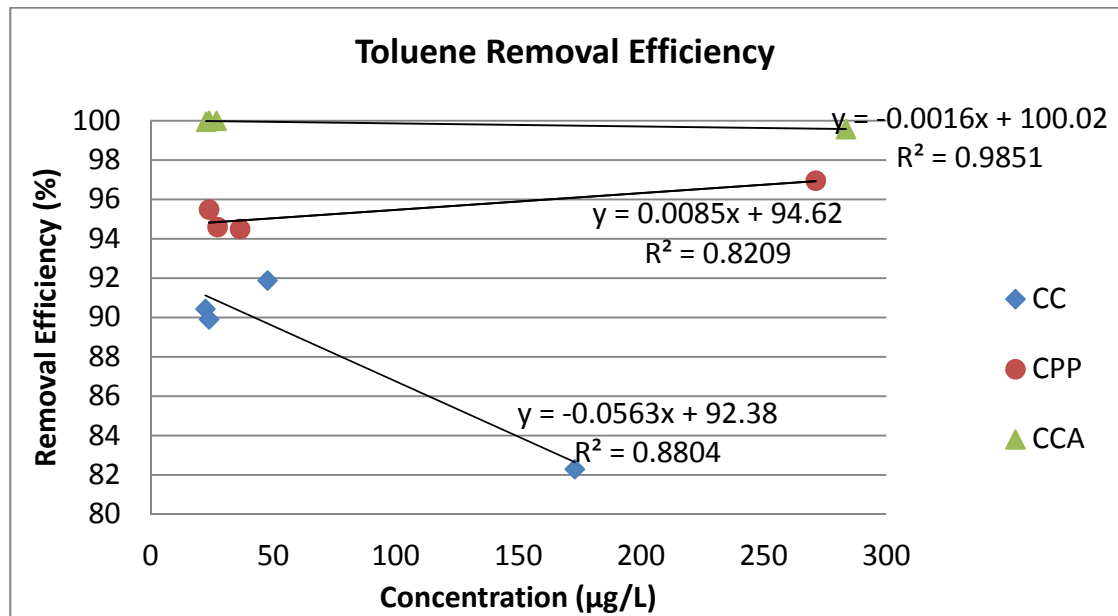
Figure 7 Toluene removal efficiency

Toluene Influent vs. Effluent Concentration

$y = 0.2339x^{0.8072}$
$R^2 = 0.9878$

$y = 0.1376x^{0.7163}$
$R^2 = 0.9987$

$y = 2E\text{-}05x^2 - 0.0003x + 0.0019$
$R^2 = 0.9999$
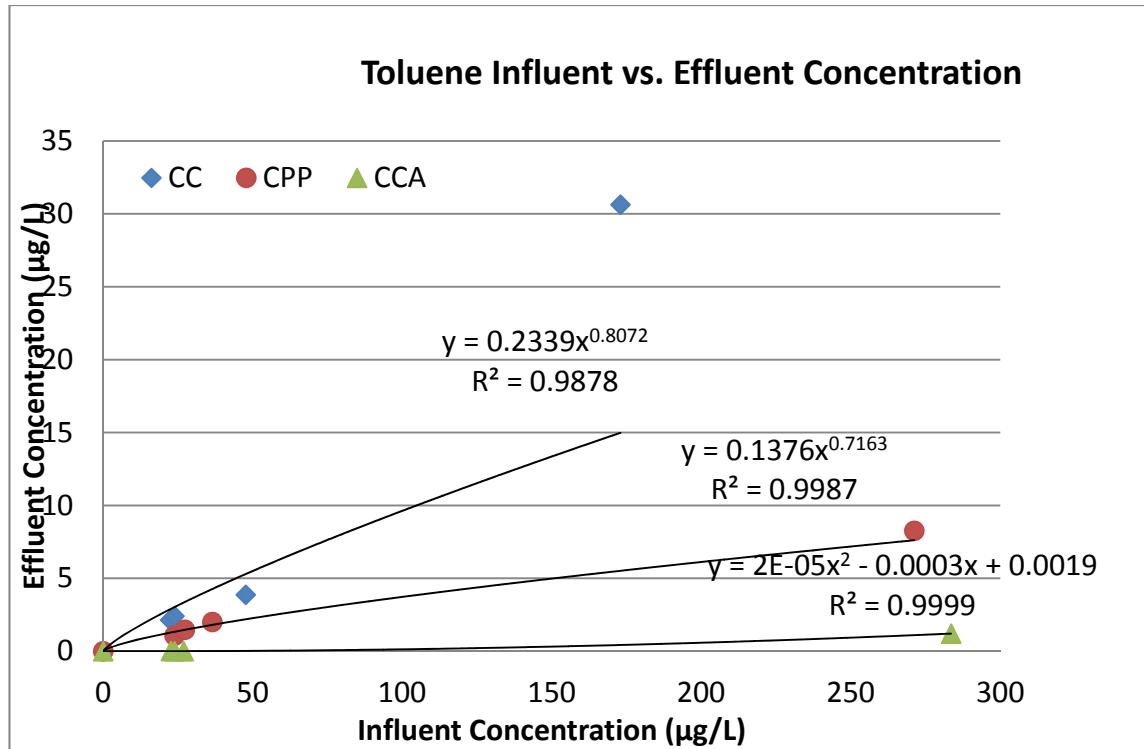
Figure 8 Toluene Influent vs. Effluent Concentration

3. Cadmium Removal Efficiency

Most of the literature reported total cadmium concentrations found in roadway runoff were lower than the detection limit of the ICP used in this study. Thus, the lab synthetic roadway runoff utilized in this study contained cadmium concentrations higher than the literature runoff concentrations. The lab synthetic roadway runoff used for the system influent contained dissolved cadmium in the concentration range of 21μg/L to 88μg/L. The results of cadmium concentrations before and after flowing through the three PAPS are summarized in Table 10.

Table 10 Concentrations of Cadmium in the Influent (Before Flow Through the PAPS) and Effluent (After Flow Through the PAPS) and the Removal Efficiency

Systems	Cadmium Influent (μg/L)	Cadmium Effluent (μg/L)	Cadmium Removal Efficiency (%)
CC	21	13	40
	42	17	59
	44	21	53
	50	22	57
	74	27	64
	82	37	55
CPP	21	9	55
	43	11	74
	44	12	72
	50	13	75
	74	16	79
	79	22	73
	89	28	69
CCA	21	ND	88
	40	ND	94
	45	ND	94
	49	ND	95
	74	ND	97
	81	ND	97
	88	ND	97

ND: Not Detected, detection limit is 5μg/L, using 2.5μg/L as effluent concentration when calculating the cadmium removal efficiency

For the CC system, when the influent concentrations went from 21μg/L to 82μg/L, the effluent concentrations went from 13μg/L to 37μg/L. The cadmium removal efficiencies were in the range of 40% to 65%.

For the CPP system, which has GAC embedded into the top porous asphalt layer, when the influent concentrations went from 21μg/L to 89μg/L, the effluent concentrations went from 9μg/L to 28μg/L. The cadmium removal efficiencies were in the range from 55% to 79%.

The removal of cadmium in the CCA system which has GAC added into the sub-base filter course layer was measured. When the influent cadmium concentrations

went from 21µg/L to 88µg/L, the effluent concentrations were all below the detection limit of 5µg/L.

Figure 9 shows the cadmium removal efficiency of the three systems. The CPP and CCA systems all have higher cadmium removal efficiencies compared with the CC system. The CCA system achieved the highest cadmium removal efficiency for all influent cadmium concentrations.
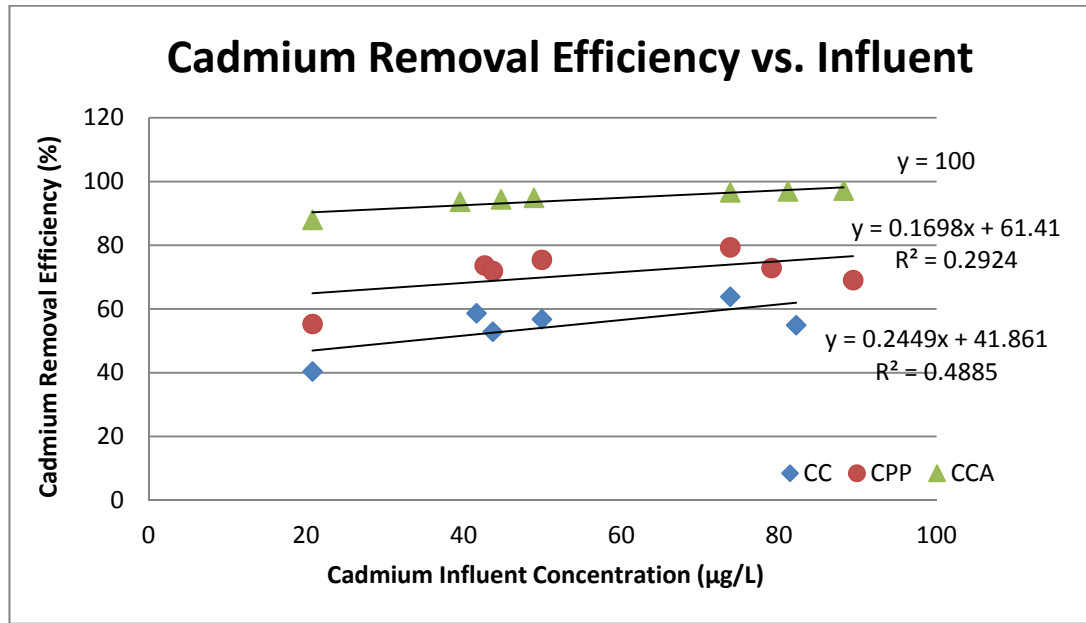

Figure 9 Cadmium Removal Efficiency

Figures 10 shows the influent vs. effluent concentration for cadmium. For the CC and the CPP systems, the effluent concentration increased with an increasing influent cadmium concentration. The CCA system removed nearly all of the cadmium applied in the influent.

Cadmium Effluent vs. Influent

Y-axis: Cadmium Effluent Concentration (µg/L)
X-axis: Cadmium Influent Concentration (µg/L)

$y = 0.575x^{0.9379}$
$R^2 = 0.9992$

$y = 0.4192x^{0.9029}$
$R^2 = 0.998$

$y = 0.1225x^{0.7623}$
$R^2 = 0.9899$
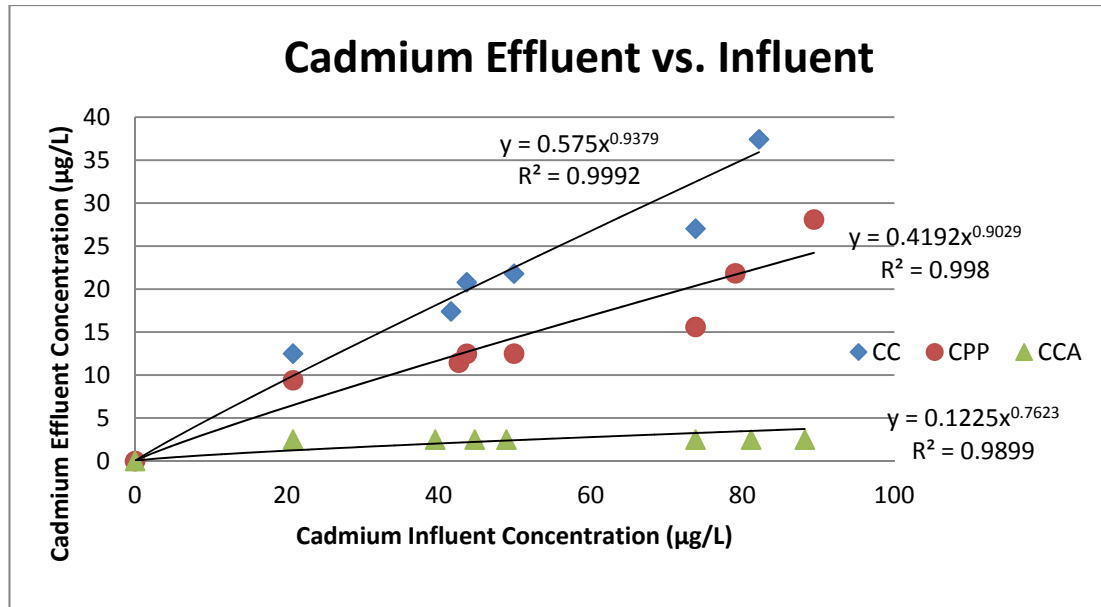
Legend: ◆ CC   ● CPP   ▲ CCA

Figure 10 Cadmium Influent vs. Effluent

4. Copper Removal Efficiency

The lab synthetic roadway runoff used for the system influent contained dissolved copper in the concentration range of 35µg/L to 77µg/L. The results of the initial copper concentrations before and after flowing through the pavements are summarized in Table 11.

Table 11 Concentrations of Copper in the Influent (Before Flow Through the PAPS) and Effluent (After Flow Through the PAPS) and the Removal Efficiency

Systems	Copper Influent (μg/L)	Copper Effluent (μg/L)	Copper Removal Efficiency (%)
CC	37	18	53
	40	20	50
	41	22	46
	63	24	62
	75	24	68
	77	29	62
CPP	35	15	59
	42	17	60
	45	17	63
	56	18	69
	61	19	70
	74	20	73
	75	22	71
CCA	35	9	74
	41	11	72
	45	11	74
	59	14	77
	67	15	78
	71	15	79
	75	17	78

For the CC system, when the influent copper concentrations went from 37μg/L to 77μg/L, the effluent copper concentrations went from 18μg/L to 29μg/L. The copper removal efficiencies were in the range of 46% to 68%.

For the CPP system, which has GAC embedded into the top porous asphalt layer, when the influent copper concentrations went from 35μg/L to 75μg/L, the effluent concentrations went from 15μg/L to 22μg/L. The removal efficiencies of copper were in the range from 59% to 73%.

The CCA system contained GAC which was added into the sub-base filter course layer. When the influent concentration went from 35 to 75μg/L, the effluent

concentrations were increased from 9 to 17µg/L and the removal efficiencies of the CCA system were in the range of 72 to 79%.

Figure 11 shows the copper removal efficiency of the three systems. The best fit lines were created and shown in the figure. The CPP and CCA systems all have higher copper removal efficiencies compared with the CC system. The CCA system achieved the highest copper removal efficiency for all conditions.
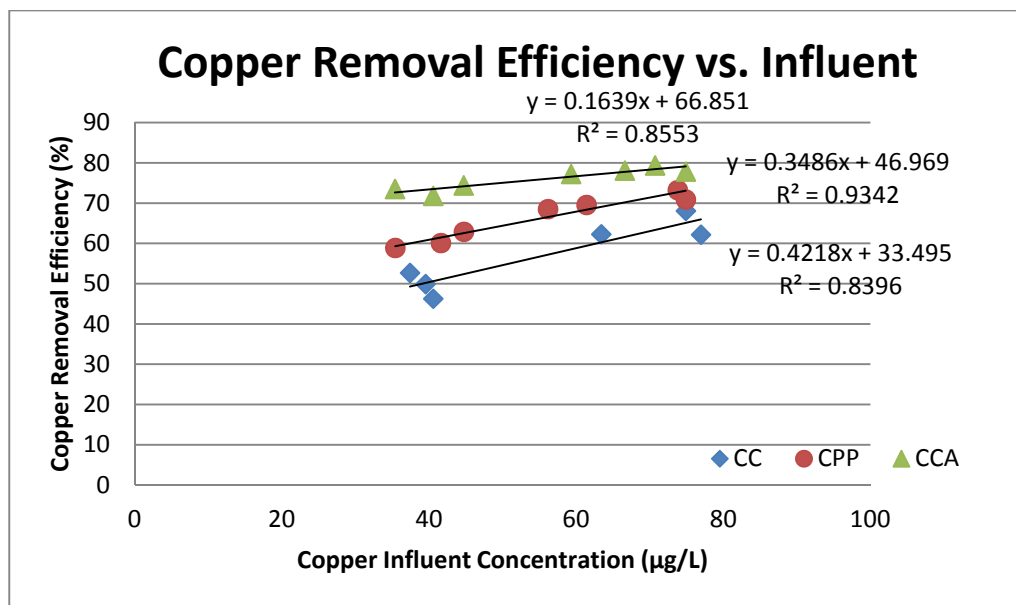

Figure 11 Copper Removal Efficiency

Figures 12 shows the influent vs. effluent concentration for copper removal through the systems. For the three systems, the effluent concentration increased with the increased influent copper concentration within the testing range. The CCA system had an effluent water quality of 9 to 17µg/L.

Copper Effluent vs. Influent

$y = 0.5511x^{0.9331}$
$R^2 = 0.9987$

$y = 0.4658x^{0.9151}$
$R^2 = 0.999$

$y = 0.3683x^{0.8905}$
$R^2 = 0.9996$

X-axis: Copper Influent Concentration (µg/L)
Y-axis: Copper Effluent Concentration (µg/L)
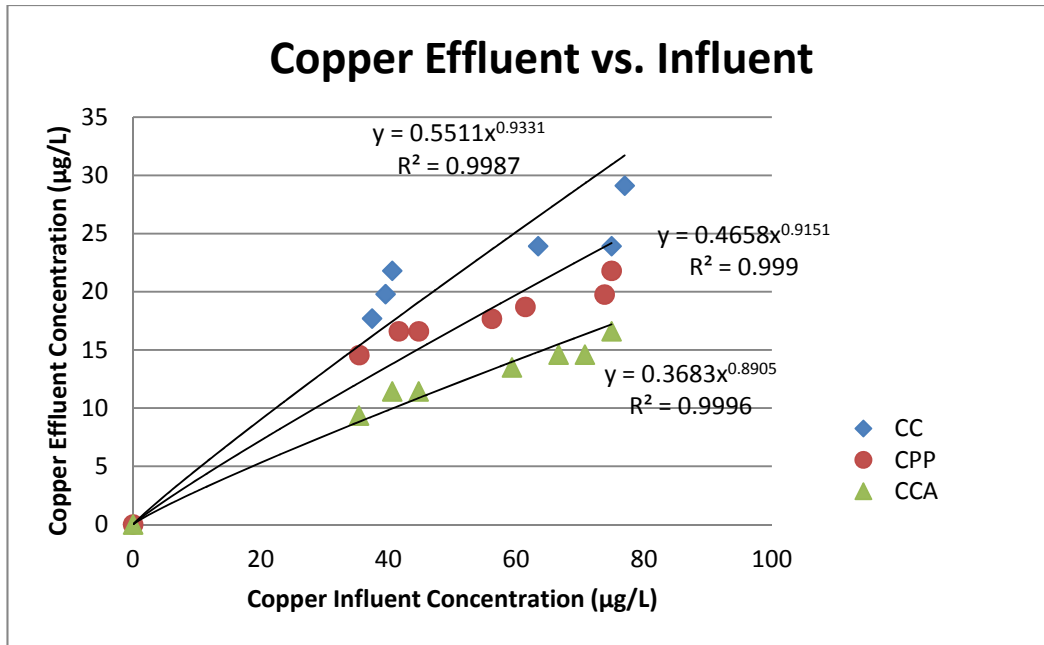
Legend: CC, CPP, CCA

Figure 12 Copper Influent vs. Effluent

5. Lead Removal Efficiency

The lab synthetic roadway runoff used for the system influent contained dissolved lead in the concentration range of 23µg/L to 67µg/L. The results of the initial lead concentrations before and after flowing through the pavements are summarized in Table 12.

Table 12 Concentrations of Lead in the Influent (Before Flow Through the PAPS) and Effluent (After Flow Through the PAPS) and the Removal Efficiency

Systems	Lead Influent (μg/L)	Lead Effluent (μg/L)	Lead Removal Efficiency (%)
CC	23	10	54
	26	11	56
	33	11	66
	50	13	75
	56	13	78
	67	19	72
CPP	26	8	68
	31	9	70
	33	10	69
	36	10	71
	49	11	77
	50	11	77
	65	13	81
CCA	24	8	65
	30	9	69
	33	9	72
	47	10	78
	52	10	80
	66	10	84

In the CC system, the influent lead concentrations went from 23μg/L to 67μg/L, and the effluent lead concentrations went from 10μg/L to 19μg/L. The lead removal efficiencies were in the range of 54% to 78%.

For the CPP system which has GAC embedded into the top porous asphalt layer, when the influent lead concentrations went from 26μg/L to 65μg/L, the effluent concentrations went from 8μg/L to 13μg/L. The removal efficiencies of lead in the CPP system were in the range of 68% to 81%.

For the CCA system, which has GAC added into the sub-base filter course layer, the influent concentrations range from 24μg/L to 66μg/L, the effluent concentrations went from 8μg/L to 10μg/L, and the removal efficiencies of the CCA system were in the range of 65% to 84%.

Figures 13 shows the lead removal efficiency of the three systems. The GAC increased the removal efficiency of the CPP system and CCA system compared with the CC system. At influent concentration around 20μg/L, the CCA system only achieved slightly higher removal efficiency as compared with the CPP system. The removal efficiency then became greater with the increased influent concentration.
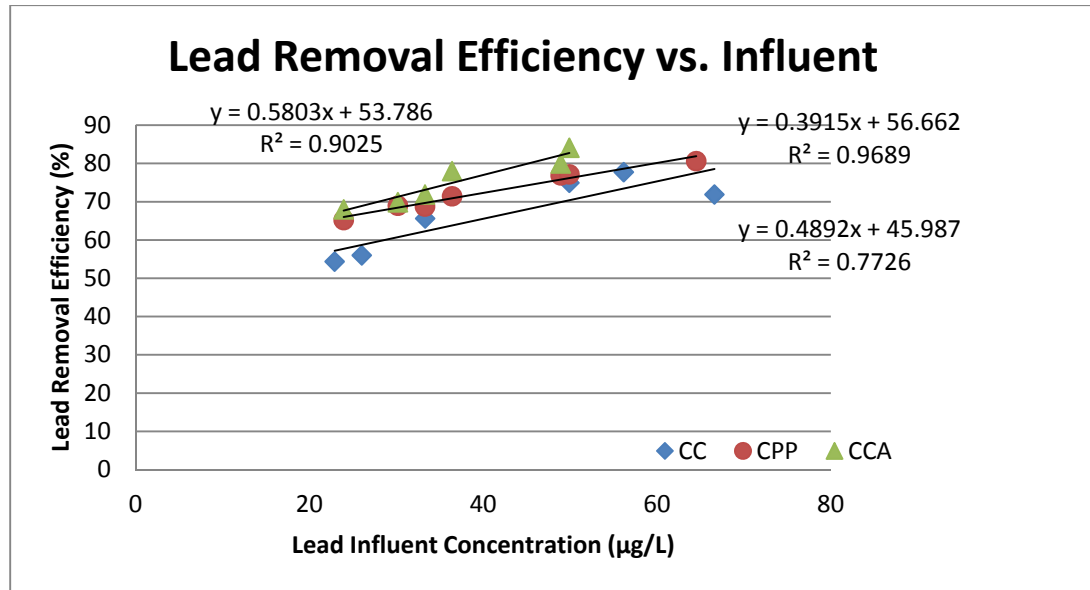

Figure 13 Lead Removal Efficiency

Figures 14 shows the influent vs. effluent concentrations for all three systems. For the three systems, the effluent concentration increased with the increased influent copper concentration. The CCA system produced the best effluent water quality with an effluent lead concentration in the range of 8μg/L to 10μg/L.
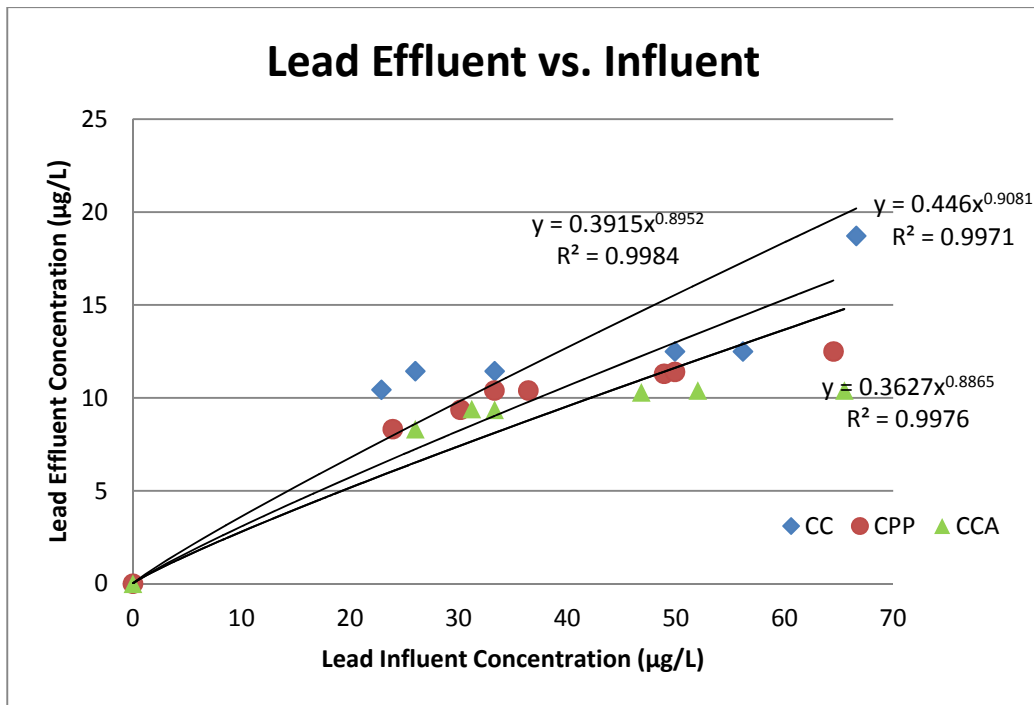
Figure 14 Lead Influent vs. Effluent

Improved Removal Efficiency Differences

The average removal efficiency of the CC, CPP and CCA system for VOCs were shown in Figure 15. For dichloromethane, the average removal efficiency of CC system was calculated by averaging the removal efficiencies achieved from all experiments. The same method was used to calculate the average removal efficiency for other systems and other compounds. The CCA system achieved the highest average contaminant removal for both dichloromethane and toluene.

To illustrate the increase in the VOCs removal due to the addition of GAC into the CPP and CCA systems, the differences in the VOC average removal efficiency of these two PAPS over the CC system average removal efficiency were plotted in Figure 16.
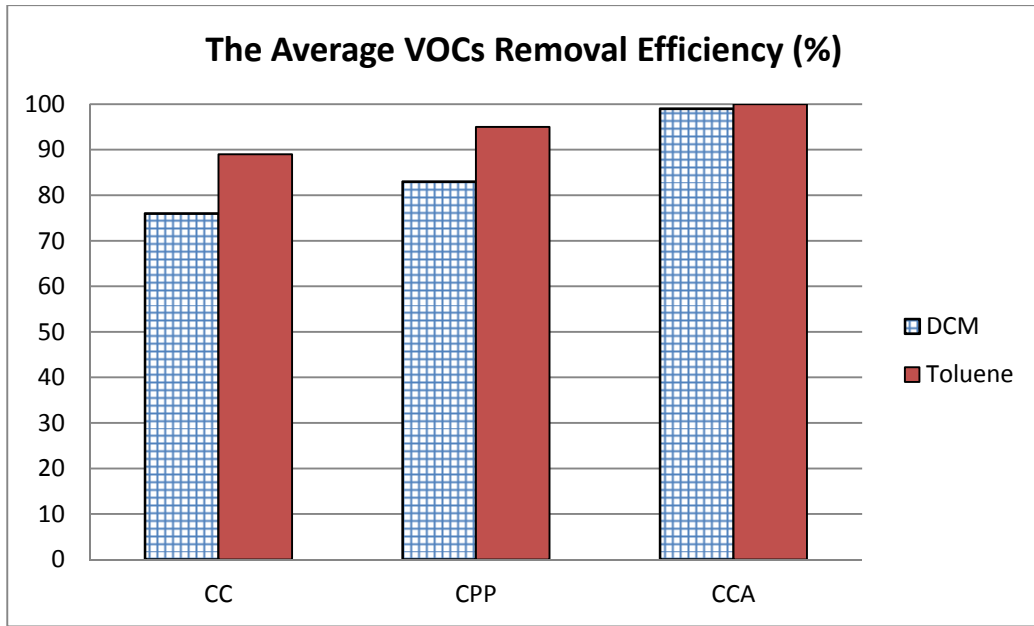
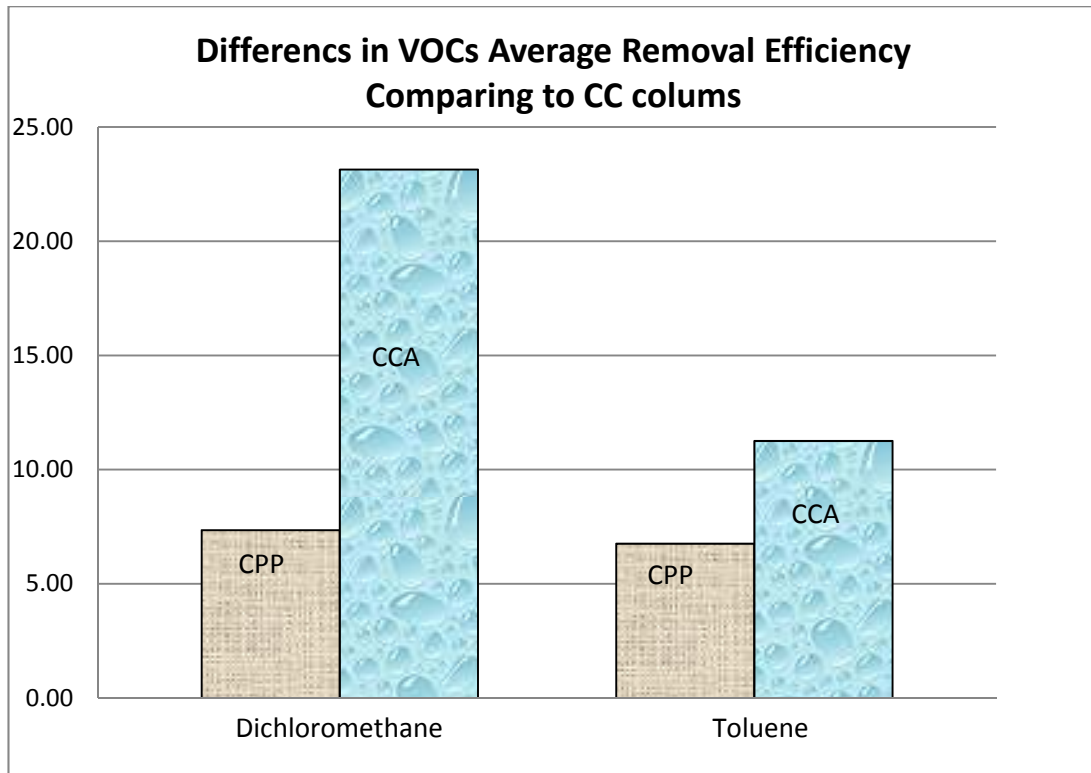Figure 15 The average VOCs Removal Efficiency by the CC, CPP and CCA Systems

Figure 16 Impact of GAC Addition on VOCs Removal
[CPP System Percent Removal − CC System Percent Removal]
[CCA System Percent Removal − CC System Percent Removal]

Zeinali's study found that for the same conditions, GAC has a higher adsorption capability for dichloromethane than for toluene given a short contacting time (Zeinali, 2012). This coincides with the results found in this study, that the removal efficiency of the CCA system had a higher increase in removal for dichloromethane than for toluene.

Figure 17 shows the average heavy metals removals of three systems and Figure 18 shows the differences in metals removal efficiency between the CPP and CCA systems over the CC system. For the CPP and CCA system, the differences between the metal removal efficiency compared to the CC system was plotted for cadmium, copper and lead. The same data were plotted for the CCA system. Cadmium showed the highest difference in removal efficiency from the GAC addition and lead showed the lowest increase.
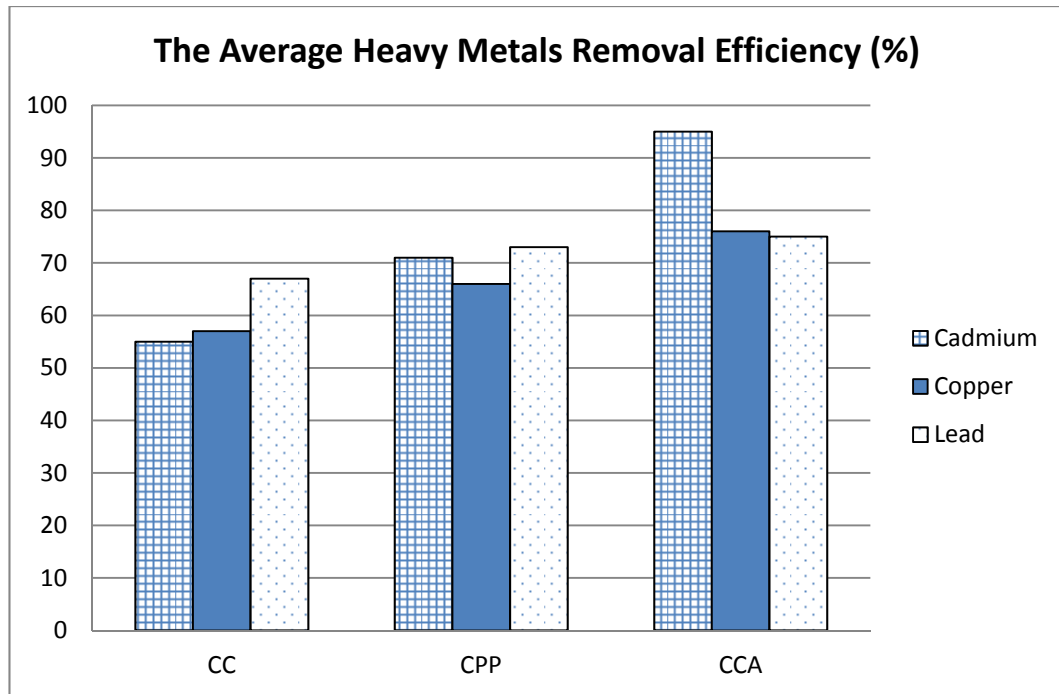

Figure 17 The Average Metals Removal Efficiency by the CC, CPP and CCA Systems
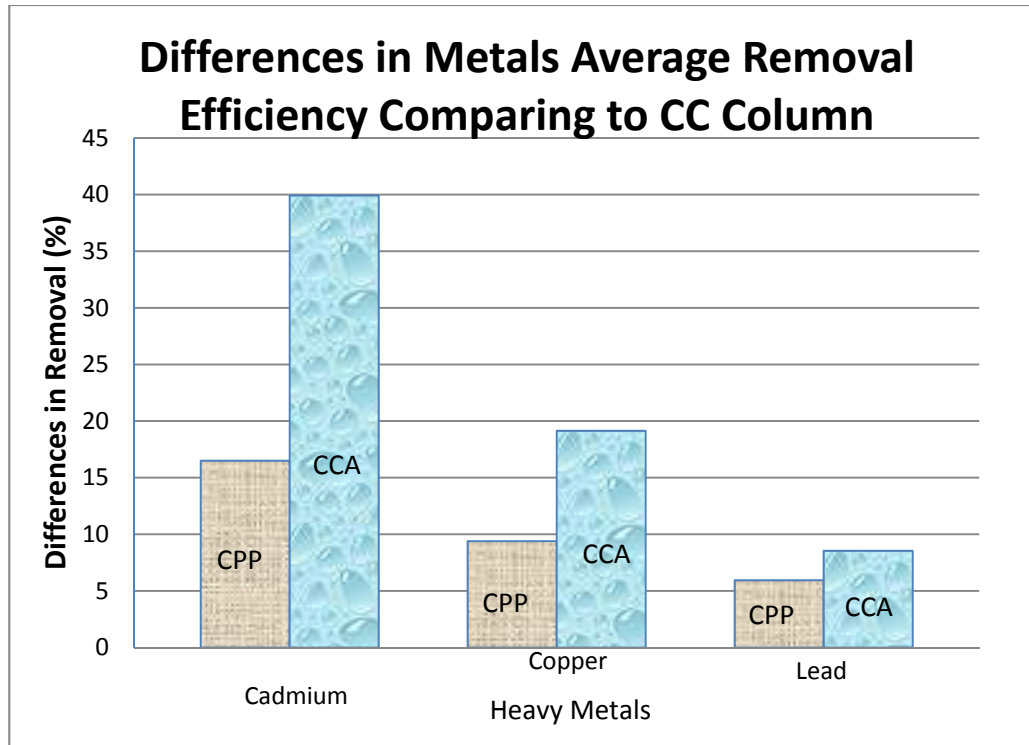
Figure 18 Impact of GAC Addition on Metals Removal
[CPP System Percent Removal – CC System Percent Removal]
[CCA System Percent Removal – CC System Percent Removal]

The metal removal increases resulted from the addition of GAC. Abudaia found that under similar conditions, GAC had a higher adsorption of copper than lead (Abudaia, et al., 2013). Zayat and Smith found the same metal removal trend for copper and lead, but in their research, cadmium removal was the least compared with copper and lead (Zayat and Smith, 2013a and 2013b). Heavy metals removal by GAC is controlled by several processes including adsorption, precipitation and surface interaction (Smith et al., 1996, and Zayat and Smith, 2013a).

Comparison with MCL

The US EPA MCL for dichloromethane is 5μg/L. In this study, the effluent dichloromethane was below the detection limit until the influent concentration went up

42

to 135µg/L which is higher than the highest dichloromethane influent concentration found from roadway runoff.

The concentrations of toluene found from roadway runoff were lower than the MCL of 1mg/L, so the comparison of effluent toluene with its MCL is not necessary.

The US EPA MCL for cadmium is set at 5µg/L. For the cadmium removal from the CCA system, when the influent concentration was set at the concentration of the highest total cadmium concentration reported from roadway runoff, 40 µg/L (Table 2), no cadmium was detected in the effluent from the CCA system.

For copper, the US EPA MCL is 1,300µg/L. The copper concentrations found from the roadway runoff were all lower than its MCL.

The US EPA MCL set for lead is 15µg/L. The reported total lead concentration was in the range of 0.03µg/L to 112µg/L (Table 2). Between 5% and 50% of lead in roadway runoff was found to be in the dissolved phase (Morrison et al., 1984). The maximum dissolved lead concentration would be half of their total concentration of 56µg/L. For the CCA system, when the influent concentration was set at 66µg/L, the effluent concentration was 10µg/L which is lower than the MCL of 15µg/L.

The best fit equations of the influent vs. effluent of dichloromethane and toluene for the PAPS systems were developed based on the data in Figure 6 and 8. These equations were used to predict the effluent dichloromethane and toluene concentrations from the CCA system when the highest field measured influent concentration was 14.5µg/L of dichloromethane and 9µg/L of toluene (Cole, 1984).

The results are shown in Table 13. The effluent metal concentrations were also

predicted and compared to their MCLs in Table 13.

Table 13 Predicted Field Effluent VOCs and Heavy Metals Concentrations as Compared to the EPA MCLs

Contaminants	Influent (µg/L)	Effluent (µg/L)	EPA MCL (µg/L)
Dichloromethane	14.5	0	5
Toluene	9	0	1000
Cadmium	40	0	5
Copper	56*	13	1300
Lead	20*	5.2	15

Note: *Half of the highest total concentrations reported in the literatures were used.

The CCA system produced an effluent concentration which met the MCL for

dichloromethane, toluene, cadmium, copper and lead.

Porous Pavement Physical and Hydraulic Properties

The results from the air void content and hydraulic conductivity of the

pavement samples are shown in Table 14. The air void content was in the range of

16% to 22% which met the requirements as advised by the University of New

Hampshire Design Specifications (University of New Hampshire, 2009)

Table 14 Hydraulic Conductivity and Air Void Content Testing Results of The Top Porous Asphalt Pavement Layer

	Traditional PAPS	CPP System	Kanitpong, 2011		Mallick, 2000	
G_{mm}	2.481	2.279	NM	NM	NM	NM
G_{mb}	2.077	1.902	NM	NM	NM	NM
Air Void (%)	16.28%	16.54%	4%	8%	16.2	16.7
K (cm/s)	0.006	0.03	8.5×10^{-7}	1.2×10^{-4}	0.09	0.03

G_{mm}: Maximum specific gravity of mixture;
G_{mb}: Bulk specific gravity;
K: Hydraulic conductivity
NM: Not measured

The porous asphalt pavement sample with the GAC added has a higher air void

percentage and also a higher hydraulic conductivity. Very few studies could be found

to compare the porous asphalt pavement hydraulic conductivity. There were two studies which investigated the relationship between hydraulic conductivity and air void content, and researchers found the data followed two different simple power functions (Kanitpong et al., 2003; Kutay, 2006). Both researchers suggested that air voids could explain a large component of the variation in hydraulic conductivity (Kanitpong, et al., 2003; Kutay, 2006). Because only one sample was tested in this study (Table 1.8), no air void vs. hydraulic conductivity function can be estimated. By comparing the results from the porous asphalt pavement samples of the CPP system to the CC system, air voids increased from 16.28% to 16.54% by the replacement of part of the fine particles in the porous asphalt pavement sample by GAC. The hydraulic conductivity increased from 0.006cm/s to 0.03cm/s. The same trend of higher hydraulic conductivity with larger air void content occurred. The samples used in this study did not fit in any of the equations established from previous studies (Kanitpong et al., 2003; Kutay, 2006), since the previous studies were done for pavement with lower air voids (4%-5%), and their hydraulic conductivities are lower than 10^{-4} cm/s.

The hydraulic conductivity depends on not only the air void content, but also on how the air spaces are connected. When the mixing design changes, the channel connections may change accordingly. In one study, 18 samples with different mixing designs were tested for both the permeability and air voids (Mallick et al., 2000). The results showed that the air voids were between 13.9% and 19.2%, and the sample's permeability ranged from 0.02cm/s to 0.09cm/s. For samples having similar air voids 16.2% and 16.7% to the air voids in this study (Table 1.8), the permeability values vary from 0.03cm/s to 0.09cm/s respectively (Mallick et al., 2000).

Infiltration Rate

The time spent for the saturated NaCl solution flowing through the systems and their infiltration rates were in Table 15. The top asphalt layer in the CPP system has an infiltration rate of 4.9cm/min, and the sub-base filter course layer of the CCA system has an infiltration rate of 4.1cm/min. So for the same amount of GAC, the runoff took longer contacting time with GAC in the CCA system than in the CPP system.

Table 15 Infiltration Rate of the top Porous Asphalt Layer of the CPP System and the sub-base Filter Course Layer of the CCA System

Systems	Average Infiltration Time (min)	Thickness (in)	Infiltration Rate (cm/min)
CPP top asphalt layer	2.07	4	4.9
CCA filter course layer	6.23	10	4.1

Discussion

After adding GAC into the traditional PAPS, the CPP and CCA systems showed increased removal of VOCs and heavy as compared to the CC system. The increased VOCs and heavy metals removal by the two enhanced PAPS will depend on the surface area of the GAC, the GAC contact time and the pH of solutions (Zayat and Smith, 2013b). Since the pH was constant throughout the test, only the surface area of the GAC and the contacting time of the GAC remained to affect contaminants removal.

The CC system and the CPP system had the same sub-base filter course layer configuration. In a comparison between these two systems, the only difference is the top asphalt pavement layer composition. The top porous asphalt layer of CPP system had a hydraulic conductivity of 0.03cm/s which is higher than the 0.006m/s measured

in the CC system, the top porous asphalt pavement layer without the addition of GAC (Table 15). The contact time of roadway runoff flow through the CPP system, which had a higher hydraulic conductivity, was shorter as compared to the contacting time of the CC system. Since the adsorption process depends on the surface area of the sorbent and the contact time, given a shorter contacting time, the CPP system would be expected to remove less contaminant if the limiting step was contact time. The testing results showed that the CPP system had a higher contaminant removal efficiency than the CC system. So it can be concluded that GAC added into the CPP system plays the role of enhancing removal of the contaminants. The GAC added to the CPP system was not completely covered by the asphalt binder during the construction process. Since enhanced removals were measured, the hypothesis would be that the GAC was not completely coated by the asphalt binder.

For the CCA system, the GAC that was added into the sub-base filter course layer removed more contaminants than the CPP system. The reason is that the GAC added into the CCA system sub-base filter course was loose and not had been coated by asphalt binder which increased the size of the surface area of the GAC that was exposed for the same amount of the GAC added. In addition to this lager surface area, the infiltration rate of the sub-base filter course layer of the CCA system was 4.1cm/min which is lower than the infiltration rate of the top asphalt pavement layer of the CPP system (4.9cm/min) (Table 16). The decreased infiltration rate resulted in an increase in contact time.

VOCs Removal Capacity of the CCA System

The volume of roadway runoff containing dichloromethane or toluene applied to the three systems over a period of 2 hours was 504ml. Table 16 lists the difference between the total mass of dichloromethane and toluene contained in the influent and the effluent of the CCA system based on their measured concentrations. The mass differences between the influent and effluent indicated the amount of the VOCs removed from the roadway runoff by the systems. For the CCA system, the maximum difference of the total amount of VOCs of the influent and the effluent was 115μg for dichloromethane and 142μg for toluene. This means that 115μg of dichloromethane and 142μg of toluene were able to be sorbed by the CCA system.

Table 16 The Mass of VOCs Removal From the CCA System

Compounds	Influent Mass (μg)	Effluent Mass (μg)	Mass Removed (μg)
Dichloromethane	24	0	24
	26	0	26
	73	0	73
	121	6	115
Toluene	11	0	11
	12	0	12
	14	0	14
	143	0.6	142

The reported maximum dichloromethane and toluene concentrations in the roadway runoff that were found from previous studies were 14.5μg/L and 9μg/L respectively (Cole, 1984; and Delzer et. al., 1996). When the equilibrium concentrations were set at 14.5 μg/L of dichloromethane and 9 μg/L of toluene for aGAC adsorption, the calculated GAC removal capacity was 2mg/kg for dichloromethane and 5mg/kg for toluene (Zeinali, 2011). Thus the 182g of GAC

contained in the CCA system had a removal capacity of 360μg of dichloromethane and 910μg of toluene.

Given a one inch rainfall (0.46L of roadway runoff added to each system), when the contaminant concentrations were 14.5μg/L of dichloromethane and 9 μg/L of toluene, the roadway runoff contained a mass of 7μg dichloromethane and 4μg of toluene. The average yearly rainfall in Rhode Island is 42 inches, the year loads of dichloromethane would be 280μg, and 174μg of toluene.

In the CCA system, the contaminants were removed by the regular PAPS composition and the GAC particles working together. The regular PAPS system has the same structure as the CC system. So in this study, the amount of contaminants removed from the CC system was assumed to be the same as the contaminants removed by the regular PAPS part in the CCA system. Thus, given an influent dichloromethane concentration of 14.5μg/L, the traditional PAPS components removed 10.2μg/L (Table 13) and the GAC removed the remaining 4.3μg/L. So the GAC removed 30% of the total dichloromethane. For the toluene removal, when the influent toluene concentration was 9μg/L, the traditional PAPS components of the CCA system removed 7.6μg/L, and the GAC removed the remaining 1.4μg/L based on the same assumption. The GAC removed 16% of the total toluene influent.

For dichloromethane removal, when the influent concentration is 14.5μg/L, the yearly load is 280μg for each system. The proportional loads for the GAC inside the CCA system is 84μg. Since the GAC of each system has a removal capacity of 360μg, based on this calculation, the GAC will last 4.5 years.

For toluene removal, when the influent concentration is 9μg/L, the yearly load is 174μg/L for each system. The proportional loads for the GAC inside the CCA system is 44.8μg/L. Since the GAC of the CCA system has removal capacity of 910μg of toluene, the GAC is able to last about 20 years

These are estimates and environmental conditions could change the ultimate removal capacity of the system.

Conclusions

The addition of GAC into the top porous asphalt layer and the sub-base filter course layer are all able to enhance the porous asphalt pavement contaminants removal capability for VOCs and heavy metals. Adding GAC to the sub-base filter course layer resulted in higher removal efficiencies than adding the GAC directly to the top porous asphalt mix layer. With the influent contaminant set at the concentrations typically found in the roadway runoff, the effluent concentrations from the CCA system had non-detectable concentrations for dichloromethane, toluene, and cadmium. The CCA system lowered the effluent concentration of copper to 13μg/L and lead to 5μg/L which meet the EPA MCL for these metals.

Further Studies

This study proved that adding GAC into the PAPS could enhance the contaminants (VOCs and heavy metals) removal from roadway runoff. In order to better understand the contaminant removal process before applying these PAPS to serve the real stomwater management projects, further studies were suggested including perform longer time testing with constant inflow flowrate to create breakthrough curves to determine the ultimate capacity of the CCA system; expand

the number of contaminants studied both separate and combined for the removal tests;

and utilize existing roadway runoff to better represent existing contaminant conditions.

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