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Introduction

Rooftop stormwater runoff has been shown to be a major source and pathway of heavy metals and bacterial load into local surface waters (Lye, 2009; Van Metre and Mahler, 2003). Polycyclic aromatic hydrocarbons (PAHs), contaminants of emerging concern known to cause carcinogenic and mutagenic effects in humans and biota, have been found in stormwater runoff due to atmospheric deposition on rooftops, especially in urban areas (Forster, 1999; Van Metre and Mahler, 2003). Polybrominated diphenyl ethers (PBDEs), which are used as flame retardants, are also being found in water, surface sediments, and marine biota (Oros et al., 2005). PBDEs are of concern as research has shown that they bioaccumulate and have potential endocrine disrupting properties (Rahman et al., 2001).

Rainwater harvesting (RWH) is a low impact development (LID) stormwater best management practice (BMP) that involves the capture, diversion and storage of rainwater for later non-potable and sometimes potable use while also helping reduce stormwater runoff volume. The majority of a rooftop’s dust and debris is thought to be washed away during the initial periods of a rainfall event, a phenomenon known as the “first flush” (Martinson and Thomas, 2005). If it occurs in the classical sense, the removal of the first flush in RWH can dramatically increase the collected water’s quality (Lye, 2009). Research has shown varied conclusions in how much runoff should be diverted in the first flush in order to have satisfactory water quality in the RWH system. Yaziz et al. (1989) suggested diverting five liters for galvanized-iron and concrete tile roofs with catchment areas of 18 m² from the RWH system. Martinson and Thomas (2005) proposed that contamination will be halved for each mm of rainwater that is diverted from the RWH system. The Texas Manual on Rainwater Harvesting recommends diverting one to two gallons of the first flush for every 9.29 m² of catchment area (TWDB, 2005). While research has shown that diverting the first flush does play a significant role in harvested rainwater quality, there has yet to be a universal consensus on what exactly constitutes a first flush (Lye, 2009; Martinson and Thomas, 2005).

There are many variables that play a role in the water quality of roof runoff. For example, the roofing material, catchment parameters, precipitation events, local weather, chemical properties of the pollutants, and geographical location of the RWH system all need to be taken into consideration when designing a first flush device (Forster, 1996; Forster, 1999). This paper focuses on the research materials and methodology utilized in testing the hypothesis that a more site-specific first flush can be quantified based on the roofing material, roof orientation, and geographical location by continuous monitoring and analysis of contaminants, including PAHs and PBDEs, found in the rooftop runoff throughout a storm event in the state of Oklahoma.

Materials and Methods

This study was conducted at two different locations in Oklahoma: the Oklahoma State University Oklahoma City campus (OSU-OKC) and the OSU Agronomy Farm, located in Stillwater. The OSU-OKC campus is located west of Interstate 44 (I – 44) and the OSU Agronomy Farm is...
located north of Highway 51. The sites’ close proximity to the two highways allows for a more accurate representation of the environmental occurrence of PAHS and other contaminants from anthropogenic sources (i.e. motor vehicles) as dust from the highway is expected to become atmospherically deposited onto the buildings and roof structures.

**OSU – OKC**

Three different roof types were analyzed for contaminants in the rooftop runoff at the OSU – OKC site. Runoff samples were collected from two commercial buildings, the Horticulture Pavilion and the Maintenance Shop, representing metal and built-up (tar and gravel) roof types, respectively, as well as from a constructed asphalt-shingle roof structure located next to the Maintenance Shop. A single downspout on both the Horticulture Pavilion and the Maintenance Shop have been replaced and modified with a PVC pipe configuration in order to allow for continuous water quality readings and auto sampling with a Hach® Hydrolab MS5 Water Quality Multiprobe and Teledyne Isco 6712 portable sampler. The same PVC downspout configuration was also placed on the constructed asphalt shingle structure. In addition, a 90° V-notch weir box was placed at the outlet of each downspout configuration in order to measure stormwater runoff flow in conjunction with a Teledyne Isco 720 Submerged Probe Flow Module.

In order to help quantify the first flush occurrence, the OSU – OKC site had continuous monitoring of specific conductance and turbidity as well as auto sampling for total suspended solids (TSS), PAHs, PBDEs, bacteria, metals and nitrate throughout the duration of the storm event. Each roof had 24 1000 mL water samples collected by the sampler during each sampled storm event. The sampler will be set to take samples at irregular time intervals, with the majority of the samples programmed to be collected during the rising limb of the storm. Six grab samples were collected from the 24 1000 mL water samples based on the storm hydrograph. Samples were collected from 10 storms between the months of March and June 2012.

**OSU Agronomy Farm**

Eighteen simulated roof structures were constructed and placed at the Agronomy Farm in Stillwater, OK, for evaluation of first flush occurrence from simulated rainfall events for new TAMKO® Elite Glass-Seal® three tab asphalt shingles, new MasterRib® acrylic coated Galvalume® sheeting, and 60 year-old clay tile roofing materials. Each roofing material is replicated six times. Nine roofs, consisting of three replicates of each roofing material, are oriented north-south while the remaining nine roofs are oriented east-west in order to determine if roof orientation in relation to the sun and prevailing wind direction have a significant impact on rooftop runoff water quality.

A rainfall simulator will be used to simulate a high, medium and low intensity storm on the roofs, resulting in a total of three experimental runs on each roof throughout the duration of the study. Water used in the simulations will pass through a reverse osmosis (RO) filter before passing through the simulator nozzle in order to mimic rainwater quality. Six samples, five individual and one composite, will be manually collected from each roof during the three simulated rainfall events. Collected samples will then be analyzed for specific conductance, turbidity, TSS, PAHs, PBDEs, metals and nitrate. In addition to the water samples, the surface temperature will be recorded on each of the simulated structures at each rainfall simulation. Weathering of the roofing materials will also be evaluated throughout the duration of the study.

**Analytical Methods**

Water samples from both sites were analyzed for PAHs and PBDEs using solid-phase extraction of whole water samples and then frozen until analysis can be completed. Of the six
water samples collected from each roof, the first sample and the composite sample were initially analyzed for PAHs and PBDEs; if there is no detection in these samples, the remaining four samples were not analyzed. Analysis of extracts was conducted using gas chromatography coupled with mass spectrometry detection. Electron ionization was used for detection of the PAHs while negative chemical ionization will be used for PBDE detection. Detection was performed using select ion-monitoring using three-ions per analyte.

Samples were analyzed for the following PAHs listed in Table 1, of which 16 are designated by the Environmental Protection Agency (EPA) as Priority Pollutants. PBDEs selected for detection analysis are listed in Table 2.

Table 1. PAHs highlighted in research study.

<table>
<thead>
<tr>
<th>Polycyclic Aromatic Hydrocarbons (PAHs)</th>
<th>Acenaphthene</th>
<th>Acenaphthylene</th>
<th>Anthracene</th>
<th>Benzo(a)anthracene</th>
<th>Benzo(a)pyrene</th>
<th>Benzo(b)fluoranthene</th>
<th>Benzo(ghi)perylene</th>
<th>Benzo(k) fluoranthene</th>
<th>Chrysene</th>
<th>Dibenzo(a,h)anthracene</th>
<th>Fluoranthene</th>
<th>Fluorine</th>
<th>Ideno(1,2,3-cd)pyrene</th>
<th>1-methylnapthalene</th>
<th>2-methylnapthalene</th>
<th>Naphthalene</th>
<th>Phenanthrene</th>
<th>Pyrene</th>
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Probable Human Carcinogen
Probable Human Carcinogen
Possible Human Carcinogen
Probable Human Carcinogen
Probable Human Carcinogen
Probable Human Carcinogen
Probable Human Carcinogen
Possible Human Carcinogen

Table 2. Select congeners of PBDEs highlighted in research study.

<table>
<thead>
<tr>
<th>Polybrominated Diphenyl Ethers (PBDEs) – Select Congeners</th>
<th>28</th>
<th>47</th>
<th>99</th>
<th>100</th>
<th>153</th>
<th>154</th>
<th>183</th>
<th>209</th>
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QA/QC

Replicate and field blank samples were collected at a rate of 10% of the environmental sample count for quality assurance/quality control of the results. Prior to analyzing samples for PAHs and PBDEs, accuracy and precision studies, as well as method detection limit studies, were performed. Laboratory blanks and spikes were run at a frequency of 10% the number of samples.
**Objectives and Hypotheses**

The objective of this research are to investigate two questions that remain regarding the widespread implementation of rainwater harvesting as a solution for decreasing demand on water systems from water used for urban irrigation. These two questions are:

1. Does the runoff from the beginning part of a storm, also referred to as the “first flush” contribute a substantial portion of contaminants in rooftop runoff, and, if it does, can design of the rainfall harvesting system decrease the concentration and bioaccumulation potential of contaminants in harvested rainfall?

2. Do PAHs, PBDEs, and pyrethroid insecticides occur in rooftop runoff, and what is the bioaccumulation potential of these compounds in lawns if the water is used for urban irrigation?

This objective is being investigated by testing two hypotheses: (1) a site specific first flush can be quantified based on the roofing material, roof orientation, and geographical location by continuous monitoring and analysis of contaminants found in the rooftop runoff throughout a storm event, and (2) PAHs, PBDEs, and selected pyrethroid insecticides have the potential for long-term accumulation in soils from harvested rainfall used as urban irrigation.

The hypotheses to be tested are being investigated discrete monitoring of simulated rainfall from 18 smaller structures to be constructed near Stillwater, Oklahoma; by a combination of continuous and discrete monitoring of harvested rainfall from three buildings with different roof types in central Oklahoma; a field survey of accumulation concentrations of PAHs, PBDEs, and selected pyrethroid insecticides in soils below downspouts from 30 buildings (representing 3 roof types) in central Oklahoma; and, a leaching test on the parent roofing material to determine leaching potential.

**Results**

Full results from all four tasks are not currently interpreted and/or completed because my graduate student is currently completing a Fulbright project in Sierra Leone that was not anticipated at the time this grant was received. A full project report will be completed by December 31, 2013.

**Simulated Harvested Rainfall from Different Roofs and Intensities.** Between July 2011 and January 2012 three separate rainfall simulations were performed on 18 roofs. In general, the results indicate that the poorest water quality comes from asphalt roofs compared to clay tile and metal roofs. The first flush was prevalent and dependent on rainfall intensity and roof type. It appears that PAH’s are being transported in from roof as shown by a decrease in concentration during the storm. Example results for turbidity, specific conductance, and benzo(a)pyrene are shown in Figures 1, 2, and 3. Full results will be presented in the final project report.
Figure 1. Average turbidity measurements for rooftop runoff at different intensities and roof types.
Figure 2. Average specific conductance measurements for rooftop runoff at different intensities and roof types.
Figure 3. Average benzo(a)pyrene concentration for rooftop runoff at different intensities and roof types.
Oklahoma City Harvested Rainfall. Between April and July 2012, water samples were collected from the rooftop runoff during 10 storms. These samples have been analyzed in the laboratory, but interpretation of the results has not yet been completed. Full analysis is completed in the final report that will be submitted in December 2013.

Soil sampling below downspouts. Between April and July 2012, soil samples were collected from below downspouts and in nearby areas not affected by rooftop runoff from 30 different buildings—10 buildings with three different types of roofing materials. These samples have been analyzed in the laboratory, but interpretation of the results has not yet been completed. Full analysis is completed in the final report that will be submitted in December 2013.

Leaching studies. These studies are currently in progress, with final results expected in fall 2013. The results of these studies will be included in the final report.