PASSIVE STORMWATER SAMPLERS FOR SAMPLING HIGHWAY RUNOFF FROM BMPS: FEASIBILITY STUDIES

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13. Abstract

Pollution from highway stormwater runoff has been a concern within the environmental field. To reduce contamination within highway runoff, many structural Best Management Practices (BMPs) have been implemented. One challenge for BMPs is monitoring their effectiveness along with determining effluent concentrations. The objectives of this research were to develop passive samplers to monitor the pollutants in roadway runoff BMPs. Passive samplers with Amberlite IRC748 ion exchange resin as sorbent were tested for monitoring heavy metals and samplers with polyurethane foam (PUF) as sorbent were tested for polycyclic aromatic hydrocarbons (PAHs). Results from batch kinetic studies, and lab- and field-scale BMP (bioretention cell) tests indicate that the passive samplers developed can be used for monitoring BMPs under the given conditions. In order to obtain representative data for determination of removal efficiency of BMPs, the influent and effluent passive samplers must be placed in two different flow paths, and the quantity of stormwater contacting the passive samplers needs to be known.

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Executive Summary

Pollution from highway stormwater runoff has been an increasing area of concern within the environmental field. To respond to the need for reduced contamination within highway runoff, many structural Best Management Practices (BMPs) have been implemented. One challenge for BMPs is monitoring their effectiveness along with determining effluent concentrations. The current methods for stormwater sampling include sending technicians or installing auto-samplers to collect either grab or composite samples. These methods become costly, cumbersome and, in many cases, infeasible due to the potentially large number of BMPs across a region and the irregularity and difficulty of predicting storms. Passive samplers have proven to be reliable and cost-effective for monitoring groundwater, seawater and air pollution; but a greater understanding is needed for using passive samplers for monitoring stormwater and BMP performance.

The objective of this research is to develop passive samplers that will operate under roadside BMP conditions and to test their feasibility for BMP stormwater sampling. More than twenty existing groundwater or air pollution passive samplers have been reviewed for possible use in stormwater scenarios. Amberlite IRC748 ion exchange resin has been selected for developing passive samplers for monitoring heavy metals (with Cu, Zn, and Pb being the representatives), and polyurethane foam (PUF) for polycyclic aromatic hydrocarbons (PAHs) with phenanthrene (PHE) as a representative. The feasibility of the passive samplers developed were tested via kinetic studies in batch reactors, tests in lab-scale BMPs loaded with differing synthetic storms and field-scale BMPs under real-world situations.

For heavy metal passive samplers, batch test results reveal ion exchange resin as a potential sorbent unhindered by stormwater matrix effects (i.e., the addition of sediments) and able to have fast contaminant uptake. Lab-scale BMPs were designed and constructed to expose ion exchange resin passive samplers to various flow scenarios. These controlled scenarios included the

application of synthetic stormwater at rates expected for storm durations of 0.5, 3, and 12 hours. A field test was also conducted by placing the samplers in deployment units upstream and downstream of pilot BMPs and utilizing velocity sensor data for the site to characterize the storm event. Results indicate that the influent and effluent passive samplers must be placed in two different flow paths in order to obtain representative data for calculation of claimed removal efficiency. The average influent uptake percentages by the influent samplers for three respective storm durations (0.5, 3, and 12 h) were 49.26%, 15.17%, and 40.59% for copper, lead, and zinc, respectively, and that by the effluent samplers were 35.57%, 66.31%, and 43.25% for copper, lead, and zinc, respectively. The removal percentages of heavy metals by the BMPs predicted by passive samplers were very similar to the actual treatment efficiencies calculated from control reactors, with errors between the claimed and actual values ranged from -4.99% to 2.15%. The results indicated that the ion exchange resin passive sampler can be used for monitoring both heavy metals in highway runoff and the performance of bioretention cells for heavy metal removal.

For PUF passive samplers, batch test results reveal that when the PUF plug was 2.5-in-long and weighed 1.32 g, more than 90% PHE in the synthetic storm water could be sorbed by properly installed PUF passive samplers under different stormwater runoff conditions. Sorption for PHE by PUF mainly happened in the first 15 min, and the high sorption capacity allows the PUF passive sampler to monitor stormwater events for extended periods. The PUF passive samplers could be embedded in BMPs for monitoring influent and effluent PHE concentrations. The predicted removal efficiencies of BMPs were close to the real values with errors ranging between -8.46–1.52%. Therefore, it is possible to make PUF passive samplers for sampling stormwater and monitoring the performance of stormwater BMPs.

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Chapter 1 Introduction

1.1 Background

Increasing regulations pertaining to the environment and the quality of our nation's waters & waterways have resulted in a renewed interest in stormwater discharges. The Clean Water Act (CWA) passed in 1972and amended in 1977 established the basic legislation that led to the formation of the National Pollutant Discharge Elimination System (NPDES). The NPDES enforces pollutant elimination by issuing permits to facilities detailing monitoring, operation and maintenance plans, bypass provisions, inspections and record keeping (Vacha 2012).

Currently, NPDES only requires permitting for highway runoff that discharges into urban receiving waters which are regulated by the Municipal Separate Storm Sewer System (MS4). MS4 permits include Stormwater Management Plans requiring 6 minimum Best Management Practice (BMP) programs (NDOR 2012). These six programs are public education & outreach, public participation & involvement, illicit discharge detection & elimination, construction site runoff control, post-construction site runoff control, and pollution prevention & good housekeeping. BMPs can otherwise be categorized as structural and non-structural, with non-structural focusing on source reduction and structural providing physical treatment of polluted discharges.

As part of the MS4 permitting requirements, transportation agencies like the Nebraska Department of Roads (NDOR), are required to fulfill certain requirements. NDOR has funded a series of research studies looking into primary Nebraska highway discharge constituents, assembling a set of design guides of effective highway BMPs, and testing the feasibility of certain roadside BMPs & plant establishment (Torres 2010; Jones 2012; Vacha 2012). These studies in conjunction with the current study fulfill part of the MS4 permit requirements for NDOR.

Although current permits do not require specific BMP effectiveness or effluent discharge concentrations, it is anticipated that these will be required in the future. A variety of BMPs have been constructed and assessed in the lab and in the field, but their life-cycle performance is not yet well understood (Flynn and Traver 2013). In addition, the EPA has encouraged the use of BMPs as parts of systems rather than stand-alone processes to prevent water pollution (USEPA 2014).

Current stormwater monitoring procedures rely on spot, grab or automatic sampling. Because of the varying concentrations within a hydrograph, each of these methods collects a single window of the storm and do not accurately represent the entire event. Also, these methods usually require collection of a large volume of water because the contaminants of interest are present at trace levels (Vrana et al. 2005a).

Spot and grab samples require someone to be present during the storm and collect bottles of stormwater at certain intervals in order to get a representative sample. This is costly and dangerous as many storms are accompanied by violent weather. It is also unreliable, due to the sporadic nature of storms and the common occurrence of night storms. Auto-samplers remove the human aspect, but remain expensive to purchase and complex to operate. It is difficult to arrange the equipment to catch the entire storm and effectively look at small windows into the whole event. For an entity such as NDOR that may have hundreds of roadside BMPs to monitor for multiple storms each year, the current methods of stormwater sampling are not economical.

Passive samplers collect the target constituent *in situ* while leaving the bulk flows and concentrations undisturbed. This method of sampling has been effectively applied to groundwater and marine pollutant monitoring (Magaritz et al. 1989; Gustafson and Dickhut 1997; Vroblesky and Hyde 1997; Persson et al. 2001; Vroblesky and Pravecek 2002; Harter and Talozi 2004; Allan et al. 2007). These samplers rely on contaminant uptake in a predictable manner based on diffusion, adsorption and/or other transport mechanisms. They reflect either a time-weighted average

concentration or an equilibrium concentration with the surrounding environment. They are simple, robust and economical.

Passive sampling technologies have proven their effectiveness in monitoring situations that have relatively consistent pollutant concentrations. Roadway pollution occurs from natural vehicle wear as well as occasional automotive fluid spills. These common pollutants include heavy metals, volatile organic compounds (VOCs), and polycyclic aromatic hydrocarbons (PAHs) (Keblin et al. 1997; Kayhanian et al. 2012).This combined with inconsistent storm timing, results in the presence of upwards of eighty percent of pollutant mass loads within the first half inch of runoff, called the Water Quality Volume (WQV). The feasibility and potential applications of passive samplers under varying concentrations are not well understood.

It is the intent of this study to identify current passive sampling technologies used in other environmental monitoring scenarios and assess their feasibility within stormwater applications. Specifically, the assessment of existing and/or novel samplers for heavy metals and polycyclic aromatic hydrocarbons (PAHs) will be assessed under highway runoff BMP scenarios. Potential passive samplers will be deployed within a series of increasingly complex conditions to identify the important factors upon uptake and mimic field application scenarios.

1.2 Objectives

The goal of this study is to develop a cost-effective stormwater passive sampler for sampling highway runoff from BMPs under roadside conditions. Specifically to:

1. Select and/or develop passive samplers for capture of heavy metals or phenanthrene in stormwater.
2. Test the feasibility of their use for BMP stormwater sampling.

1.3 Report Organization

This report contains seven chapter. The first chapter is an introduction to the study conducted. It provides a background for applicable regulations, research motivation and objectives. The second chapter provides a literature review of existing samplers and discusses their feasibility under highway runoff BMP conditions. This chapter explains the basic components of a passive sampler and some of the particular mechanisms which provide contaminant transport into the sampler. This chapter then explains the reasoning behind selecting an existing passive sampler (regenerated cellulose membrane filled with DI water) and the development of i) a novel device (Amberlite IRC748 encased in a polyester mesh) for capture of heavy metals and ii) a polyurethane foam (PUF) sampler for capture of phenanthrene. Chapter three is titled Batch Tests for Heavy Metal Passive Sampler. It details a series of laboratory kinetics and calibration experiments on the selected samplers. This chapter presents the results of these experiments, and it explains why the regenerated cellulose sampler is eliminated from further testing. The fourth chapter, Lab Scale and Field BMP Tests for Heavy Metal Passive Sampler, explains the bench-scale BMPs constructed in the lab, the field deployment cells used to house the ion exchange resin samplers in the field, and their results. A discussion is included detailing difficulties and issues encountered and attempts to overcome them, and supplementary tests are described to demonstrate the feasibility of heavy metal passive samplers. In parallel with chapters 3 and 4, the fifth and sixth chapters are about batch tests and column studies of PUF passive samplers for monitoring PAHs in stormwater and BMPs. The seventh chapter is titled Summary, Conclusions and Recommendations. This chapter reiterates the conclusions drawn from each previous chapter and provides recommendations for future work. Appendices include analytical methods, quality control and quality assessment, and further data.

Chapter 2 Selection of Passive Samplers for Stormwater Monitoring

2.1 Introduction

Growing environmental concerns have spurred increasingly strict regulations pertaining to stormwater runoff. Many transportation agencies like the Nebraska Department of Roads (NDOR) have been incorporating Best Management Practices (BMPs) to treat the first half inch of runoff. The current method of monitoring BMPs for effectiveness or management purposes includes either the use of auto-samplers or sending technicians to collect grab or composite samples during storm events. Both of these methods are expensive and often infeasible (hundreds of BMPs throughout the state for multiple storms per year). Each of these methods collects a single window of the storm and, because of the varying concentrations within a hydrograph, do not accurately represent the entire event. Also, these methods usually require a large volume of water to be collected because the contaminants of interest are present at trace levels (Vrana et al. 2005a).

Spot and grab samples require someone to be present during the storm and collect bottles of stormwater at certain intervals in order to get a representative sample. This is costly and dangerous as many storms are accompanied by violent weather. It is also unreliable, due to the sporadic nature of storms and the common occurrence of night storms. Auto-samplers remove the human aspect, but remain expensive to purchase and complex to operate. It is difficult to arrange equipment to catch the entire storm. These methods effectively look at small instances into the whole storm. Also, pumping may cause inaccuracy of volatile organic compound (VOC) concentrations as well as issues with sediment interference (Powell and Puls 1997).

Passive samplers commonly acquire a representative sample (as opposed to instantaneous) discretely and without active media transport. They are currently used to determine a variety of pollutant levels within groundwater, rivers/streams, and air. Contaminant uptake occurs in a predictable manner based on diffusion, adsorption or other transport mechanisms. They reflect

either a time-weighted average concentration or an equilibrium concentration with the surrounding environment (Vrana et al. 2005a). Some passive samplers physically collect contaminants. Various types of these samplers are discussed in this section as well.

Currently, passive samplers are commonly used for groundwater, river/stream, air, and industry wastewater monitoring. Few samplers have been utilized for stormwater flows. This application is unique because of varying concentrations that occur within the stormwater flows.

This section provides a non-exhaustive review of existing passive samplers used in other monitoring scenarios and assesses their feasibility for stormwater highway BMP monitoring. More than twenty existing samplers and four potential sorbents are reviewed and discussed. As a result of this review, a regenerated cellulose (dialysis) membrane sampler, a chelating ion exchange sorbent (Amberlite IRC748) and a polyurethane foam (PUF) sampler were chosen for batch, lab- and field-scale BMP testing.

2.2 Passive Sampler Principles

In a general sense, a passive sampler can be defined as a sampling technique that relies on the transport of the target molecules from the environmental medium to a receiving phase in a sampling device. This is the result of the difference between the chemical analyte in both the sampler and surrounding media (Vrana et al. 2005a). Passive samplers simply rely on chemical potential differences to collect a sample, which means significant cost reduction compared to other sampling techniques.

Samplers consist of a barrier phase and a receiving phase. The barrier phase is a liquid or solid layer that allows the passing of the target analyte into the receiving phase. The receiving phase consists of a medium that contains the pollutant of the sampler. Depending on the sampler, this is either ultrapure water or a chemical sorbent that attracts the pollutant and holds it within the sampler (Ehlke et al. 2004; Allan et al. 2007).

Diffusion based samplers follow the common pattern of contaminant uptake detailed in Figure 2-1. The limiting analyte transport mechanism is a diffusive barrier phase. Typically the initial uptake into the sampler occurs rapidly at a linear rate. This uptake then slows asymptotically eventually reaching equilibrium with the surrounding environment. Some samplers rely on reaching equilibrium; this calibration is straight forward and makes for simple assessment of the surrounding media. The main stipulation is that these samplers be deployed long enough to reach equilibrium, which ranges from seconds to months depending on the sampler (Ouyang and Pawliszyn 2007). This type of sampling is ideal for monitoring pollutants at relatively constant concentrations.

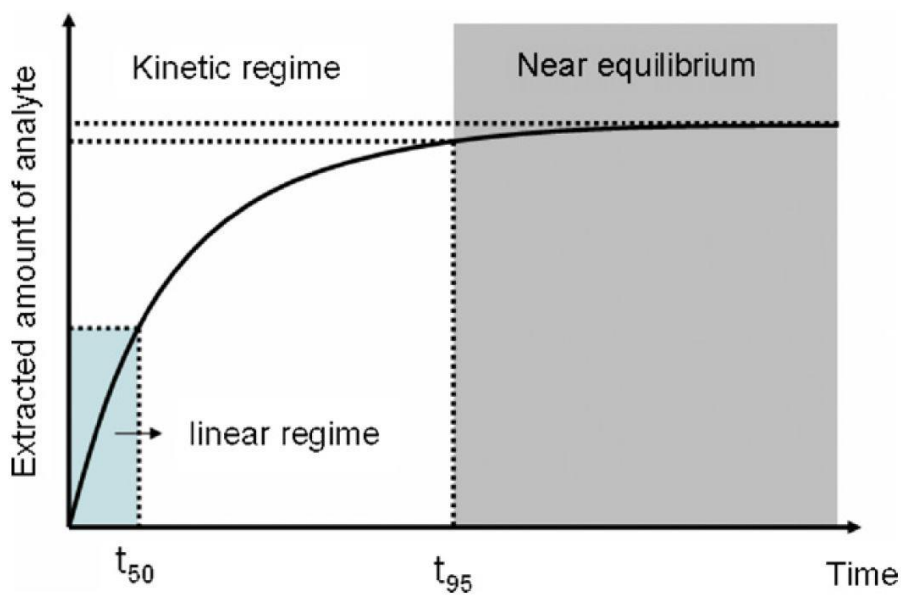

Figure 2-1 kinetic and equilibrium uptake regimes (Ouyang and Pawliszyn 2007)

Samplers that operate within the liner regime of the typical kinetics curve (Figure 2-1) generally require the sampling time to be less than half the total time to equilibrium (Ouyang and Pawliszyn 2007). Calculation of the surrounding pollutant concentration relies on a rate constant, the time of sampler deployment, and the mass contained within the sampler (Vrana et al. 2005a). These samplers can be used where water concentrations vary.

2.3 Passive Sampler Technologies

Currently most passive samplers are utilized in environmental monitoring applications other than stormwater flows. More than twenty of these samplers have been reviewed and assessed for their highway runoff monitoring feasibility including diffusion, diffusion & adsorption, and physical recovery devices. Three heavy metal sorbents commonly used in environmental applications and several materials used for sampling PAHs were also reviewed and assessed as possible passive sampler devices. Sampler construction, materials, relevant studies, target analytes, and other factors are discussed if information was available.

Because few passive samplers have been applied to stormwater sampling, anticipated sampler requirements are discussed in section 2.4.1 (Requirements for Highway Runoff BMP Monitoring). A table (Table 2-2) evaluating all reviewed samplers & sorbents is provided in section 2.4.2 (Comparison of Reviewed Passive Samplers).

2.3.1 Diffusion Devices

Diffusion devices consist of a diffusive barrier phase filled with ultrapure water. Contaminants diffuse through the barrier phase until equilibrium is reached between inside and outside the sampler. Upon collection the water within the sampler can be analyzed and the concentrations should be representative of the surrounding environment.

2.3.1.1 Regenerated Cellulose (Dialysis) Membrane Sampler

This device consists of deionized (DI) water contained within a regenerated cellulose membrane. Cotton linters are dissolved in a solvent to produce regenerated cellulose, which has great compatibility with most environmental applications. Dialysis samplers regulate the passage of molecules by having a set molecular weight cutoff. Size, shape, charge, concentration gradient, and other molecule parameters determine if a given molecule can diffuse across the membrane (Ehlke et al. 2004).

Figure 2-2 regenerated cellulose (dialysis) membrane sampler (Imbrigiotta et al. 2007)

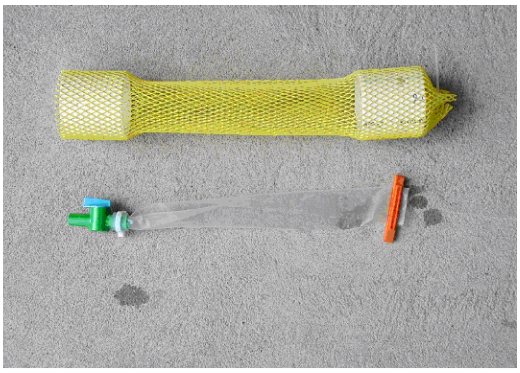

Figure 2-3 Components of dialysis membrane sampler (Imbrigiotta et al. 2007)

The sampler is often placed inside a low density polyethylene (LDPE) mesh (Figures 2-2 & 2-3), which provides protection during deployment and collection. To overcome buoyancy, a weight is attached while deployed within the well. Sampler membrane diameters are typically 1.25 to 2.5 inches. These samplers are commonly utilized in groundwater applications.

Studies have proven the effectiveness of dialysis samplers for monitoring inorganic ionic and organic constituents (Vroblesky and Pravecek 2002; Ehlke et al. 2004; Harter and Talozi 2004; Imbrigiotta et al. 2007). This sampler was developed as an alternative to the Passive Diffusion Bag (PDB) sampler, which cannot accurately test for very soluble VOCs or inorganic pollutants (Imbrigiotta et al. 2007). Recommended sampler deployment time is two weeks (ITRC 2006).

2.3.1.2 Nylon-screen Passive Diffusion Sampler (NSPDS)

The Nylon-screen passive diffusion sampler (NSPDs) consists of a wide mouth bottle filled with DI water and enclosed with a nylon screen. The bottle dimensions are typically 62 mm diameter at the top and 58mm diameter at the bottom with a total height of 58mm (ITRC 2006). The nylon screen consists of 125µm-mesh that is held in place by a cap with an opening of approximately 58mm in diameter. This sampler style is depicted in Figure 2-4.

Figure 2-4 Nylon-screen passive diffusion sampler (ITRC 2006)

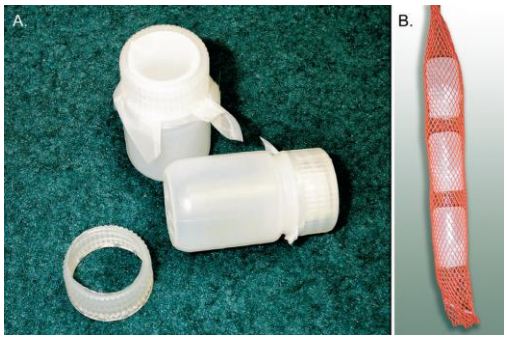

Figure 2-5 NSPD samplers in series (Vroblesky et al. 2002)

The sizes of this sampler have varied depending on the study or volume of sample needed. Figure 2-5 shows a series of NSPD samplers were deployed vertically within a low density polyethylene (LDPE) mesh for looking at inorganic constituents (Vroblesky et al. 2002).Other sampler variations include a nylon screen opening size of 48µm with similar bottles (Vroblesky et al. 2003).

The NSPD sampler has been used to target organic & inorganic pollutants as well as dissolved oxygen levels. A study performed at an Air-Force base in Guam showed that chloride values were underestimated by the NSPD samplers (Vroblesky et al. 2003). NSPD samplers were used to detect metals in sediment pore water and found reasonable results other than high concentration biases for barium and zinc (Zimmerman et al. 2005). Results from field tests reveal close concentrations of dissolved oxygen, calcium, chloride and other inorganic to low flow samples (Vroblesky et al. 2002). Some issues have been noted with sampling redox-sensitive metals in anaerobic scenarios (O'Neill 2006).

2.3.1.3 Passive Vapor Diffusion (PVD) Sampler

Passive vapor diffusion (PVD) samplers consist of an uncapped glass vial sealed within a layer of polyethylene. The outer polyethylene layer consists of either heat sealed polyethylene

tubing or a sealed polyethylene sandwich bag. These samplers are typically attached to a surveyor flag for easier location upon collection. Figure 2-6 shows multiple variations of the polyethylene layer for the PVD sampler.

Figure 2-6 Passive vapor diffusion samplers (Church et al. 2002)

PVD samplers are primarily used on hazardous waste sites to detect locations of VOC contaminated groundwater discharging into surface water (ITRC 2006). A study assessing VOC presence in bottom sediments showed their effectiveness in tracing the migration of VOCs near hazardous sites (Church et al. 2002).A similar study showed that PVD samplers are advantageous for the analysis of vapor-phase VOC monitoring within wells compared to other established approaches (Adamson et al. 2012).

2.3.1.4 Peeper Sampler

The basic principle of a peeper sampler is a rigid body that contains holes fitted with a membrane or mesh diffusive material. Millable materials such as Lexan, acrylic, Teflon, steel provide the structure for the sampler. This structure is then encompassed in a diffusive layer, typically a dialysis membrane. A box corer design is illustrated in Figure 2-7.

Figure 2-7 Box corer design of the peeper sampler (ITRC 2006)

Peeper samplers are used to determine the aqueous concentration of the saturated sediments. These samplers have been deployed in saline environments within sand resulting in disproportionate initial pollutant concentrations within the samplers (Grigg et al. 1999). Once the density difference between the DI water within the sampler and the surrounding water is equilibrated, then diffusion becomes the ruling mechanism of contaminant flow and the sample is representative.

2.3.1.5 Polyethylene Diffusion Bag Sampler (PDB)

Polyethylene diffusion bag (PDB) samplers consist of DI water within low density polyethylene (LDPE) tubing (Figure 2-8). The tubing is heat sealed on both ends and attached to a weight during deployment. For wells with vertical differences in flow or concentrations, a series of samplers is recommended for comprehensive monitoring. Typical sampler lengths are 18 to 24 inches at a tubing diameter of 1.25 to 1.75 inches which provides sample volumes of 200 to 350 ml (ITRC 2006).

PDB samplers regulate the passage of certain molecules by allowing the transport of most chlorinated VOCs into the sampler (Vrana et al. 2005b). PBD samplers enable the quantification of VOC without significant volatilization of the sample, which is common with pumping techniques. Diffusion and appropriate sample retrieval from the sampler allows this to occur. These samplers are commonly accepted by state and local regulatory agencies as reliable methods of attaining VOC concentrations for sites of concern (ITRC 2006). Two weeks is the recommended deployment time.

Figure 2-8 Passive diffusion bag sampler (b) with protective mesh (a) & (c) (Vroblesky 2001a)

Toluene and benzene have been sampled successfully in a study of groundwater observation wells (Vroblesky and Hyde 1997). PBD samplers have been extensively evaluated in six governmental agency case studies of contaminated bases throughout the country (Vroblesky 2001b). A comparative study of PDBs to regenerated cellulose (dialysis) samplers showed that iron and bromide were incapable of diffusing through the LDPE membrane, rendering the sampler ineffective for inorganic contaminant monitoring (Ehlke et al. 2004). A comparison of PDB, NSPD, and regenerated cellulose (dialysis) samplers proved PDB sampler the most reliable for VOC measurements, but emphasized the importance of correct depth placement within the well (Vroblesky et al. 2003).Another study determined the partitioning coefficients of 14 organochloride pesticides and three PAHs for two LDPE membrane types (Hale et al. 2010).

2.3.2 Diffusion and Absorption Devices

Diffusion and absorption devices consist of a diffusive barrier phase filled with a sorptive material which acts as a contaminant sink. Contaminants diffuse through the barrier phase at a linear rate and then adsorb/absorb into the receiving phase until capacity is reached. Upon collection, the receiving phase typically requires some sort of extraction prior to analysis. Uptake rates are considered so that surrounding contaminant concentrations can be calculated based on the mass present within the sampler.

2.3.2.1 Semi-Permeable Membrane Device (SPMD)

The semi-permeable membrane device (SPMD) is a passive sampler that consists of lay-flat tubing made of low density polyethylene (LDPE). This tubing contains a high-molecular weight lipid, usually high-purity synthetic triolein, to attract and hold hydrophobic pollutants (Figure 2-10). The LDPE membrane consists of a pore size that prevents large molecules, colloid adsorbed molecules, or humic acids. Passage into the sampler is only available to truly dissolved pollutants (Vrana et al. 2005a).

The lay-flat tubing is about one meterlong and about 2.5 centimeters wide, which contains approximately 1 ml of triolein. Figure 2-10 depicts tubing wrapped in a ‘Spider Carrier’ deployment device and combined with multiple other SPMDs within a stainless steel deployment canister (Johnson 2007). Deployment times range from a few days to months, depending on the application. This sampler can be combined with performance reference compounds (PRCs) to adjust for additional factors beyond what is predictable from the laboratory setting (ITRC 2006). PRCs are chemicals that leave the sampler based on flow, temperature, biofouling etc. in a predictable manner. The application of PRCs within the semipermeable membrane device (SPMD) sampler reduced the inaccuracy of the sampler due to facial velocities from tenfold to twofold (Huckins et al. 2002).

Figure 2-9 Semi-permeable membrane device in deployment apparatus

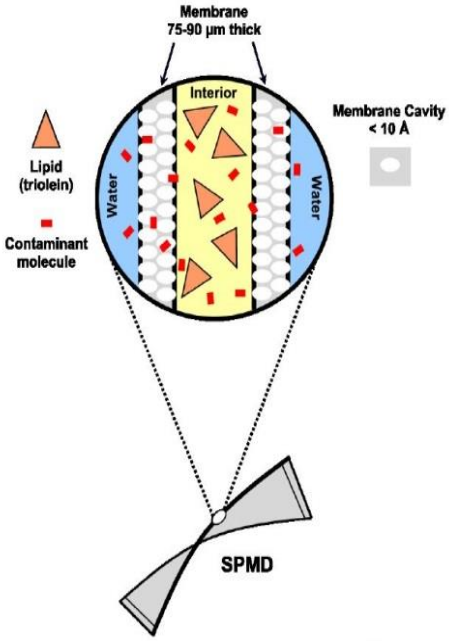

Figure 2-10 Interior of SPMD (ITRC 2006)

SPMDs are capable of sampling air, groundwater, rivers & streams. The development occurred in 1990 and was initially used as a compliment to biomonitoring for organic pollutants (Huckins et al. 1990). This device is the most mature method of passive sampling for organic pollutants (Vrana et al. 2005a). Kinetics has been looked at extensively for polychlorinated biphenyls (PCBs) and PAHs and uptake rates developed (Booij et al. 1998). Another study looks at the effects of hydrodynamics and offers a PRC approach to correct for non-uniform flows within the field (Vrana and Schuurmann 2002)

A study assessing SMPD samplers in stormwater scenarios was conducted over deployment times of 28 days. Results pointed to accurate PAH concentrations determined by SPMD samplers which were too low to be detectable via grab samples (Komarova et al. 2006).This study assessed concentrations within drainage wells in urban catchments, which could provide for a relatively even concentration throughout deployment. Performance reference compounds were utilized to help with calibration.

2.3.2.2 GORE Sorber Module

Gore Sorber samplers consist of four Sorber packets, 25 mm in length and 3 mm in diameter. Each packet contains approximately 40 mg of sorbent material within a microporous expanded Polytetraflouroethylene (ePTFE). This membrane is hydrophobic, which enables vapor transportation to the sorbent material, while preventing passage of sediments and water. As described by Henry's Law, VOCs and Semi-VOCs dissolved within the water partition to the membrane and pass into the sampler (ITRC 2006).

Potential analytes are a wide variety of VOCs, Semi-VOCs, PAHs, pesticides, herbicides and PCBs (ITRC 2006).Sorbent material varies depending on the targeted contaminant. Sorbent material analysis is required to be performed at the W. L. Gore & Associates, Inc. laboratory in Elkton, MD. A typical deployment arrangement for the Gore Sorber sampler is depicted in Figure 2-11. The Gore Sorber sampler detects vapor presence of the aforementioned analytes within sediment-type monitoring.

2.3.2.3 Polar Organic Chemical Integrative Sampler (POCIS)

The polar organic chemical integrative sampler (POCIS) consists of a solid-phase absorbent material sandwiched between two semi-permeable disk-shaped polyethersulphone membranes. These membranes allow dissolved constituents and water to pass through the sampler but prevent the passage of sediments. The sorbent disk is combined with two membranes (each side) all sandwiched between two compression rings, typically made of stainless steel or polyvinyl chloride (PVC). This arrangement is displayed in Figure 2-12.

POCIS samplers have the capability to monitor a variety of polar (hydrophilic) organic compounds. Two typical sorbents are the 'generic' configuration and the 'pharmaceutical' configuration. The 'generic' sorbent is a combination of three sorbents and is used for targeting pesticides, hormones, and water soluble organic chemicals. The 'pharmaceutical' configuration is

geared towards the class of chemicals typical of the pharmaceutical industry (Vrana et al. 2005a). Multiple samplers can be deployed in an array; it is common to combine various sorbents to monitor a greater range of constituents, as shown in Figure 2-13.

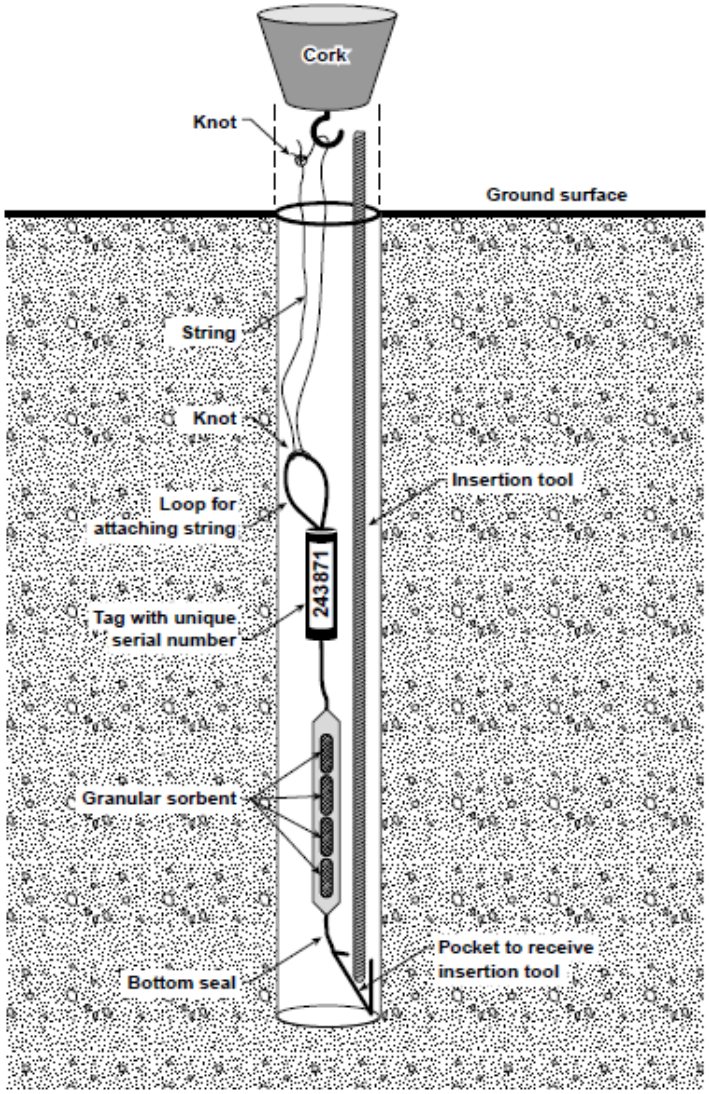

Figure 2-11 Gore sorber deployment apparatus (Vonder Haar and Gregory 2000)

Sampling times range from multiple weeks to months, and the sampler results are time weighted average concentrations (Vrana et al. 2005a). One study compared this technology to the traditional water column sampling technique for measuring 96 emerging contaminants within a stream (Alvarez et al. 2005). It was found that the passive sampler was more apt at detecting the

pollutants at low levels compared to the direct testing; analytical detection limits did not interfere due to the prolonged collection of pollutants. Uptake rates for 65 compounds were determined in another study (Bartelt-Hunt et al. 2011). The use of this sampler for the detection of drug and other trace contaminants within municipal waste-water treatment plants has been assessed also (Jones-Lepp et al. 2004).

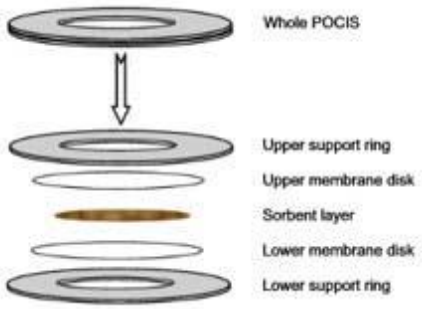

Figure 2-12 Polar organic chemical integrative sampler (ITRC 2006)

Figure 2-13 POCIS deployment array (ITRC 2006)

2.3.2.4 Passive in situ Concentration Extraction Sampler (PISCES)

The passive in situ concentration extraction sampler (PISCES) is made of a metal (brass) vessel and a polyethylene membrane. This assembly is filled with a sorbent, typically hexane or isooctane. The sampler is metal-backed with a membrane face that regulates analyte uptake into the sorbent filled cavity. Figure 2-14 illustrates the sampler's robust and rugged design. This sampler is primarily used for surface water applications; it is not suitable for air monitoring as the sorbents volatilize in air scenarios. Target analytes include nonionic organic compounds dissolved within the water.

Sampling rates remain consistent across contaminants, thus relative concentrations within the sampler represent the distribution within the sampled media (ITRC 2006). This sampler allows for easy sorbent retrieval through a cap located in the sampler rear; this cap also contains a small vent filter which allows for the release of gas that may accumulate within the sampler. Due to the

large volume of sorbent contained in the sampler, the deployment times can vary from weeks to months.

Figure 2-14 Passive in situ concentration extraction sampler (ITRC 2006)

2.3.2.5 Dialysis with Receiving Resins Sampler

A regenerated cellulose membrane encasing is filled with ion exchange receiving resins and deployed within stormwater scenarios to monitor metals (Morrison 1987; Morrison 1989; Tao and Liang 1997). Figure 2-15 displays this sampler's configuration. This dialysis with receiving resins sampler has multiple mechanisms of contaminant capture at work: diffusion through the membrane and adsorption onto the internal resins. This prevents the simplicity of a liner uptake by diffusion only, one of the more desirable characteristics of the dialysis sampler.

This sampler targets aqueous concentrations of metals. Studies on this type of sampler have only been able to identify the rate of contaminant uptake by taking the total amount adsorbed to the resin or membrane divided by the time of sampler deployment (Morrison 1987; Morrison 1989; Tao and Liang 1997). A study assessing this samplers' potential for long term copper monitoring within stormwater scenarios proved them ineffective but showed potential for single event

monitoring (Tao and Liang 1997).This study also reveals that the use of dialysis membranes prevents non-dissolved metals from being collected by the sampler.

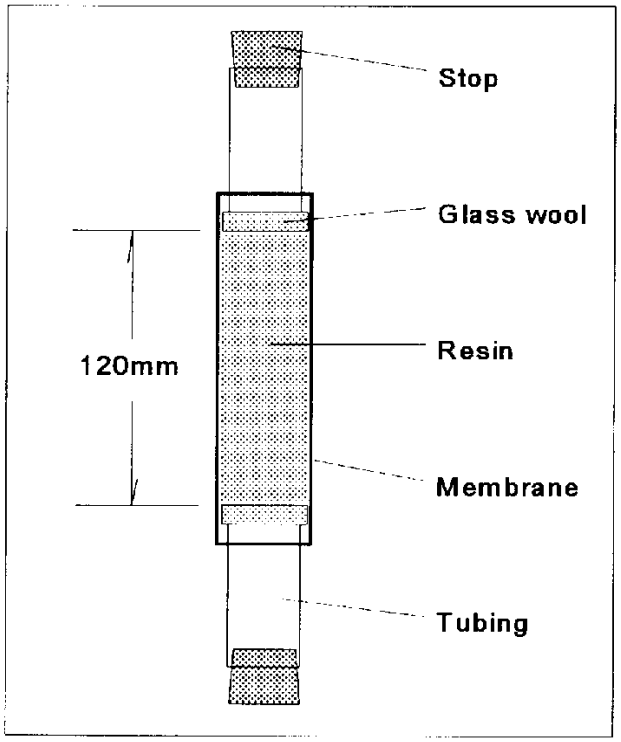

Figure 2-15 Dialysis with receiving resins sampler (Tao and Liang 1997)

2.3.2.6 Chemcatcher (Inorganic & Organic)

The chemcatcher passive sampler assembly consists of a rigid inert polytetrafluoroethylene (PTFE) housing which contains a sorbent Empore disk and membrane (Figure 2-16). The membrane provides a diffusion-limited uptake as well as selectivity for only targeted analytes. Empore disks consist of sorbent particles within a PTFE matrix resulting in a solid disk. The type of sorbent disk can be chosen to target specific analytes and does have some effect on the sampler uptake rate (Vrana et al. 2006).

Chemcatcher configurations include a variety of membranes and Empore disks, which enables the monitoring of both organic and inorganic constituents. A typical assembly for PAH and other organic contaminant monitoring includes a LDPE membrane combined with a C_{18} Empore

Disk (Kingston et al. 2000; Vrana et al. 2005a; Lobpreis et al. 2008). A styrenedivinylbenzene-reverse phase sulfonated (SDB-RPD) Empore disk was successfully used without a membrane to assess the removal of diuron, simazine, and atrazine within constructed wetlands (Page et al. 2010). Metal sampling can be attained by combining a nafion-coated cellulose acetate membrane with an Empore chelating disk (Vrana et al. 2005a).

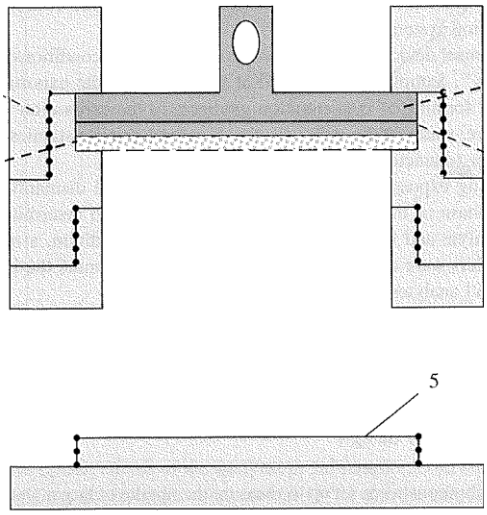

Figure 2-16 Chemcatcher sampling device and lid (Vrana et al. 2006)

This sampler is relatively mature in its development and has been modified to improve pollutant uptake consistency by adjusting the housing unit and adding PRCs (Vrana et al. 2007; Lobpreis et al. 2008). Theoptimization of sampler uptake for PAHs was achieved by adding an internal medium of *n*-octonal between the Empore disk and membrane (Vrana et al. 2005b).

Metal concentrations have been assessed using the chemcatcher within environmental applications. A study found that the membrane limited the diffusion of metals significantly (Persson et al. 2001). The addition of a nafion coating onto the cellulose acetate membrane proved to increase sampler selectivity by preventing the passage of metals bound to natural organic matter (Blom et al. 2003). Studies looking at the effectiveness of these samplers in fluctuating concentrations showed that first-order modeling was accurate for monitoring herbicide concentrations and

reasonable predictability for metals (Allan et al. 2007; Shaw and Mueller 2009). This sampler has been assessed in a storm detention pond for metal concentrations over time periods ranging from 5 to 8 days. Results showed reasonable time weighted averages (Blom et al. 2002).

2.3.2.7 Solid-Phase Microextraction (SPME)

The solid-phase microextraction (SPME) sampler consists of a small coated fiber that is mounted within a steel rod or syringe handling device (Greenwood et al. 2007). This device, shown in Figure 2-17, houses the fiber, keeping it from pre-contamination prior to sampling. It then exposes the fiber during contaminant assessment and again houses the fiber following exposure, keeping it from post-contamination (Pawliszyn et al. 1997).

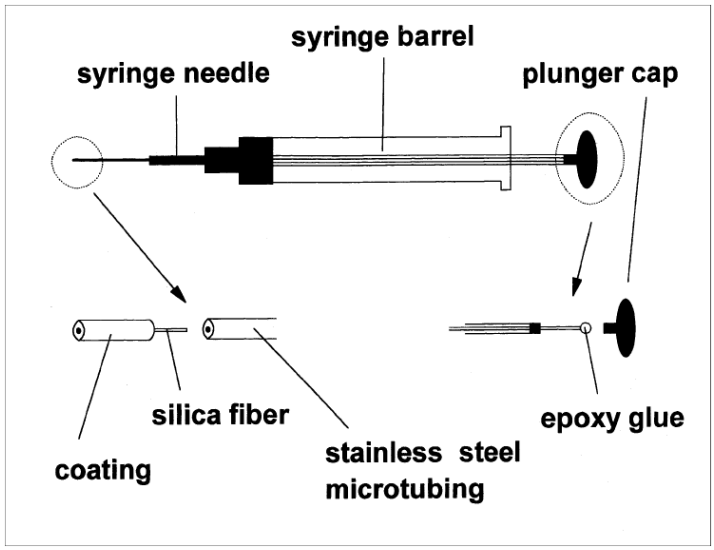

Figure 2-17 Solid phase microextraction (SPME) sampler (Pawliszyn et al. 1997)

SPME samplers can analyze contaminant concentrations within water, air, sludge and soil. Various arrangements and coatings are used to detect VOCs, semi-volatile organic compounds (SVOCs), PAHs as well as inorganic compounds within environmental, agricultural, industrial, culinary, and clinical settings (Pawliszyn et al. 1997). Exposure of the fiber is needed until contaminant equilibrium is reached with its surroundings; due to the small fiber and coating volume this is a relatively short time.

This sampler is unique in that it can be directly inserted into a liquid or gas chromatograph (LC or GC) which eliminates errors or sample contamination during analysis preparation. The thermal desorption mechanism of the chromatograph removes the contaminant from the fiber and directly analyzes the concentrations (Hinshaw 2003).

Carboxen/PDMS 75 µm fiber was used to measure short chain volatile fatty acids (VFAs) at swine facilities (Alexander et al. 2005). Results show that dynamic air sampling introduces significant air flow, temperature, humidity and time of exposure effects on the total mass uptakes. Increased temperature increased adsorption, yet increased humidity slowed adsorption. A study assessed the SPME sampler's ability to monitor nine different hydrophobic organic compounds both in laboratory and field settings (Sayre et al. 2010). Results showed that SPME samplers were able to reproduce reliable dissolved hydrophobic organic compound concentrations.

2.3.2.8 Polyurethane Foam (PUF)

The PUF sampler has been used as passive air sampler for semi-volatile organic compounds (Klánová et al. 2008; Ahrens et al. 2013). Usually, PUF air samplers contain pumps or vanes, glass fiber filters, and a PUF plug as sampling media. The PUF sampler is often shaped into a disk or a column and put into a steel container. Figure 2-18 shows a flow-through PUF air sampler. The sampler mainly consists of a steel flow tube mounted on a post with a PUF plug. In general, the uptake of chemical in air (or water) by PUF depends on the chemical's diffusivity in air (or water) and the partition coefficient of the chemical in passive sampler medium and air (or water), which depend on the passive sampler and characteristics of the chemicals. Usually, the sampling rate of the chemical is also influenced by environmental conditions (e.g., meteorological conditions like wind speed and temperature). To compensate for varying conditions, PRCs are used to determine the site-specific sampling rate by assessing their loss during the deployment period. However, to make uptake rates of the chemical of interest equal to the loss of the PRC is always challenge due to heterogeneities in diffusivities within the PUF passive sampler.

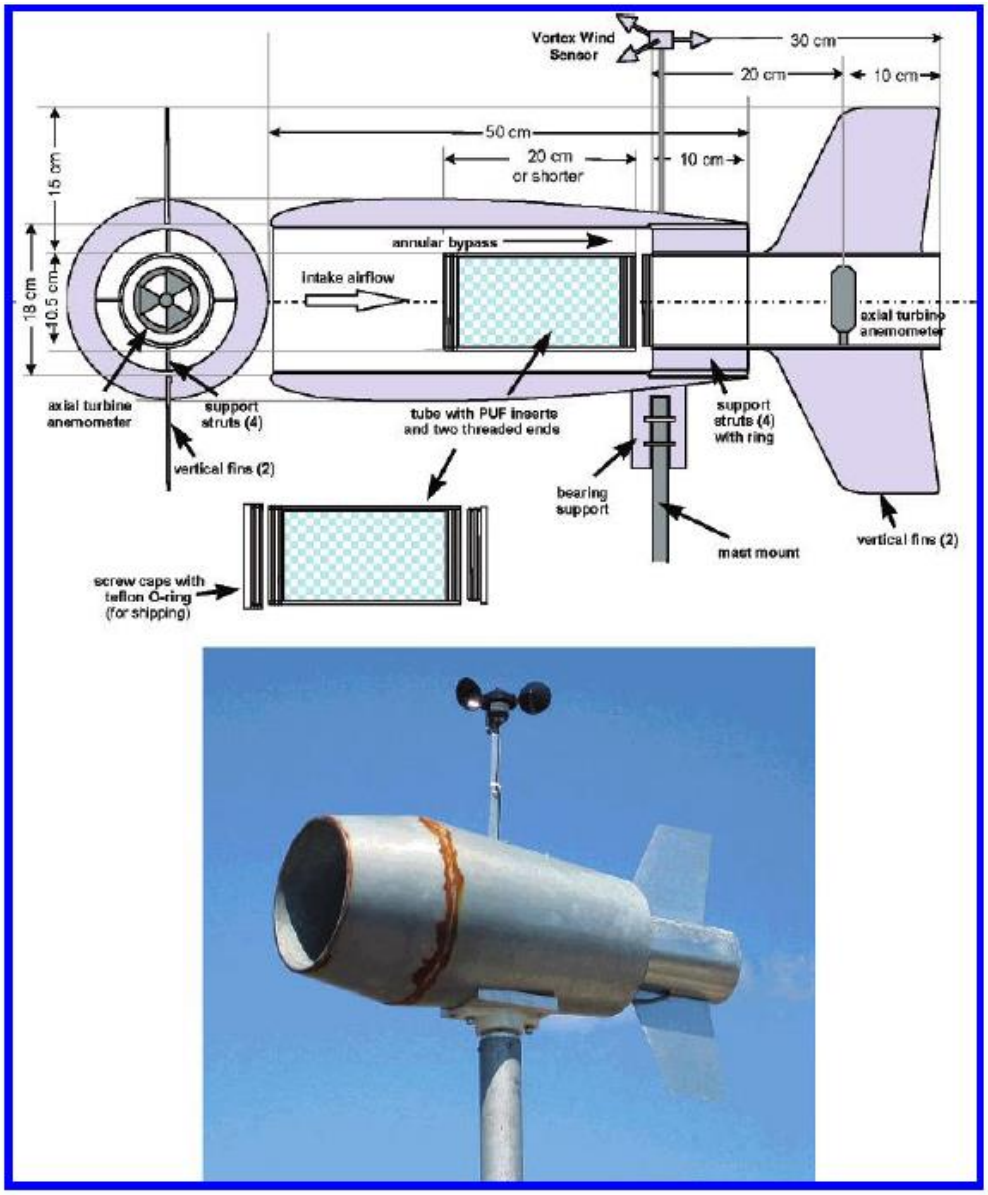

Figure 2-18 Flow through PUF air sampler (Xiao et al. 2007)

2.3.3 Physical Recovery Devices

Some samplers are passive in that they do not use pumping and purging to collect a sample. These samplers accumulate a sample physically by allowing the sampled media (e.g., air or water) to directly contact the sampler in the flow path of the media. Samples attained are representations of actual concentrations of the surrounding media.

2.3.3.1 HydraSleeve Sampler

The HydraSleeve passive sampler enables an instantaneous sample to be collected without the typical purging and pumping techniques used to collect well samples. This prevents unnecessary turbidity and sample mixing which may alter sample results. This sampler consists of a polyethylene sleeve, a self-sealing valve and a reusable weight as shown in Figure 2-18. The sampler volume is 350 ml and the target contaminants include metals, VOCs, pesticides and explosives. The sampler is lowered to the desired depth and then retrieved at least 24 hours later. The design enables the sampler to be lowered below the sampling range while minimally disturbing the well. The upward motion of the sampler opens the sleeve and effectively collects the sample. Multiple samplers enable contaminant strata to be collected. Other collection techniques enable composite or specific depths to be sampled (ITRC 2006). The HydraSleeve was compared with other discrete groundwater passive samplers and resulted in generally representative samples (Parker and Clark 2004). This device did, however, cause undesired bubbling during sampling as well as increased turbidity within the test well.

2.3.3.2 Snap Sampler

The Snap Sampler is designed for groundwater testing within wells. The sampler consists of a double-ended glass vial that has Teflon end closure caps attached to an internal spring. This spring is stainless steel coated with perfluoroalkoxy Teflon, preventing interaction with the sample (ITRC 2006). Samplers are mounted with a trigger device that enables the sampler to be set at the desired depth within the well and closed from the well opening. Multiple samplers can be triggered at once, enabling sampling of various depths within the well.

Sizes range from 40 ml glass bottles to 125 ml and 350 ml plastic bottles. Sample analytes include VOCs, SVOCs, metals, anions, explosives, oxygenates and perchlorates. Figure 2-19

displays a closed Snap Sampler system. A comparison of six sites that utilized Snap Samplers proved their viability as a passive sampler with minimal sample distortions (Britt et al. 2010).

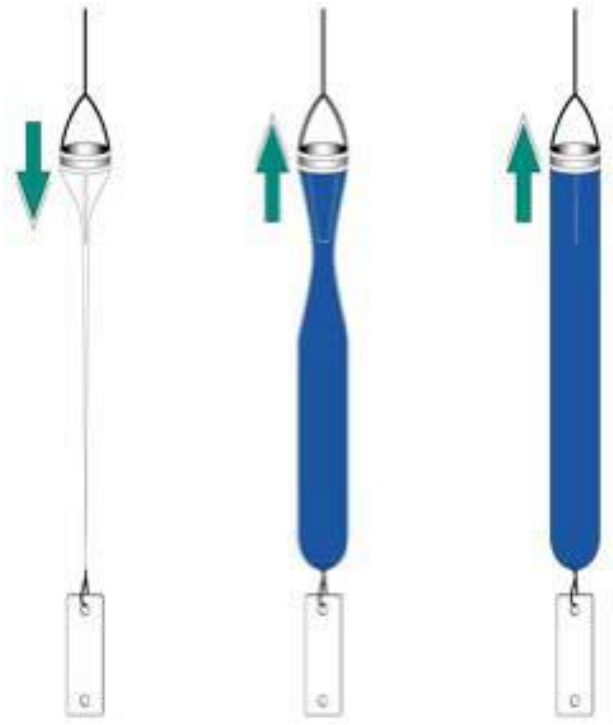

Figure 2-18 HydraSleeve sampler (ITRC 2006)

2.3.3.3 Gravity Flow Sampler

The gravity flow sampler is designed to collect stormwater runoff. The basic design of this sampler is the collection of stormwater flow as it passes over the sampler inlet. These samplers are set so that the inlet sits even to the sampling surface (Brodie and Porter 2004). Flow passing through the inlet is retained within the collection bottle or reservoir.

Versions of this sampler have been embedded within the roadway to collect runoff (Waschbush et al. 1999). This version of the sampler is displayed in Figure 2-20. This second version has been designed to collect sheet flow from roadway shoulders. Sometimes this sampler's capacity is reached prior to the completion of the storm flow, because of this, gravity flow samplers are primarily used to sample the first flush of storm events.

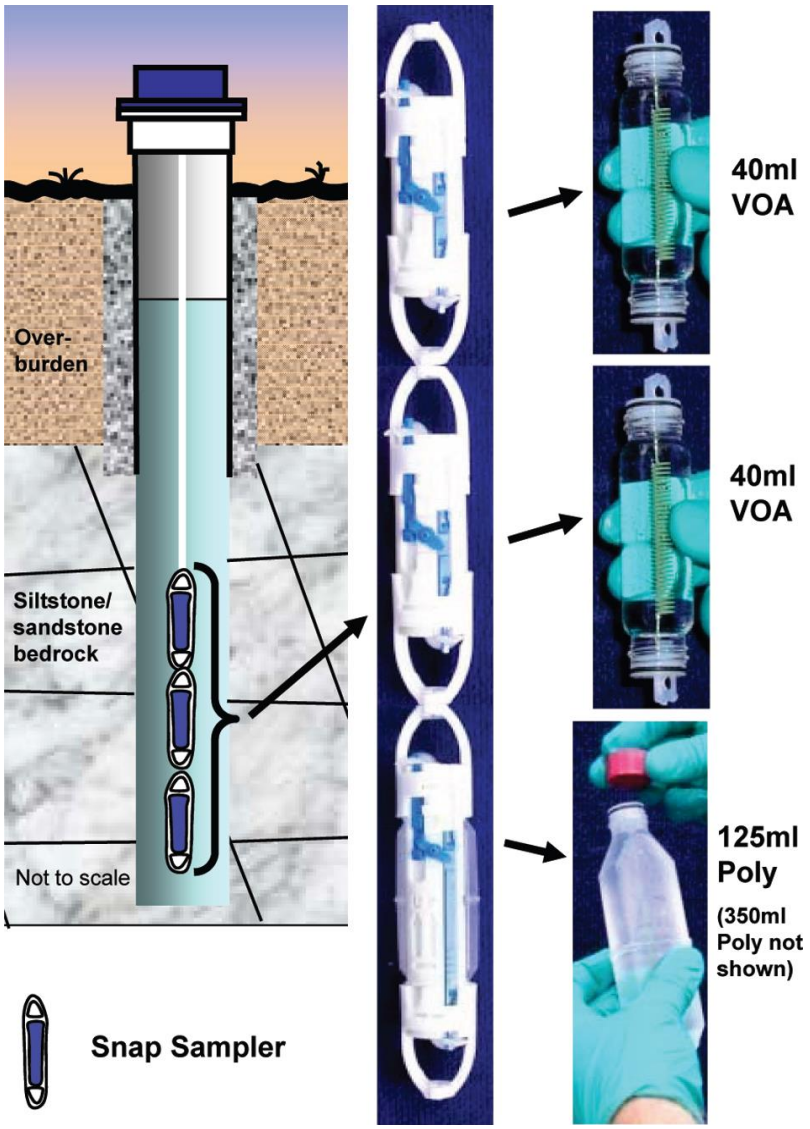

Figure 2-19 Snap sampler system (Britt et al. 2010)

Other versions of this sampler are equipped with buoyant inlet valves that seal off the sampler once capacity is reached (Young et al. 1998). This sampler is also called a first flush sampler. First flush samplers have a sampler capacity of 5 liters, making it ideal for the collection of the initial flush of the storm event. These samplers were used to assess the effects of a permeable friction course asphalt system on runoff quantity and quality (Barrett and Stanard 2008).

This sampler can be retrofitted with a PVC collection pipe to sample roadside slopes where sheet flow occurs. They consist of an 8 inch PVC pipe with a section removed from the side along

the entire length of the pipe. This is inset into the slope, perpendicular to the direction of the sheet flow. The open section of the pipe is attached to a strip of galvanized metal flashing to direct water into the pipe as shown in Figure 2-21. This system has been used to assess the effectiveness of vegetated side slopes in removing runoff contaminants (Kearfott et al. 2005; Li et al. 2008).

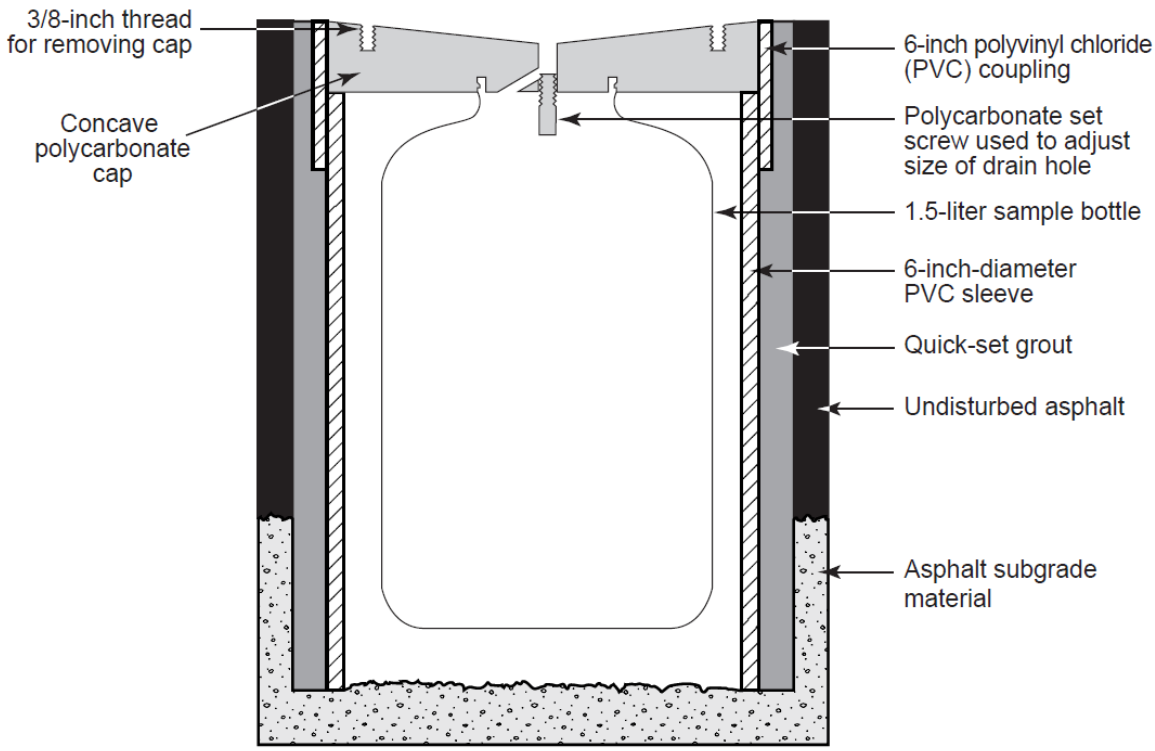

Figure 2-20 Gravity flow sampler (Waschbush et al. 1999)

2.3.3.1 Siphon Flow Sampler

Siphon flow samplers utilize the formation of a siphon action to collect a sample. These samplers are placed in flows that rise during storm events. As the flow level rises, the siphon forms and a sample is collected. Multiple samplers can be combined within one housing structure to enable sampling at various stages of the flow event, as shown in Figure 2-22 (Brodie and Porter 2004). The unit collects a sample until it is filled. The sampler is not capable of collecting sample while the stream stage is decreasing.

Figure 2-21 Collection pipe assembly for first flush sampler (Kearfott et al. 2005)

Water inlet and air outlet tubes are connected to the sampling bottle and enable the siphon to take place. A comparison of the siphon flow sampler and automatic methods of sample collection resulted in similar results (Graczyk et al. 2000). A recent study assessed the feasibility of this sampler to attain metal concentrations in Australian dry land river sand results proved reliable (Mackay and Taylor 2012). Horizontal siphon samplers proved to be a viable method of sampling shallow water during storm events, but sediment concentrations were not accurate (Diehl 2008). Single stage siphon samplers were combined with sediment traps were used to analyze sediment loads within tidal flows in a Delaware marsh (Moskalski and Sommerfield 2012). The siphon sampler's inability to accurately collect larger sediments resulted in a slight bias.

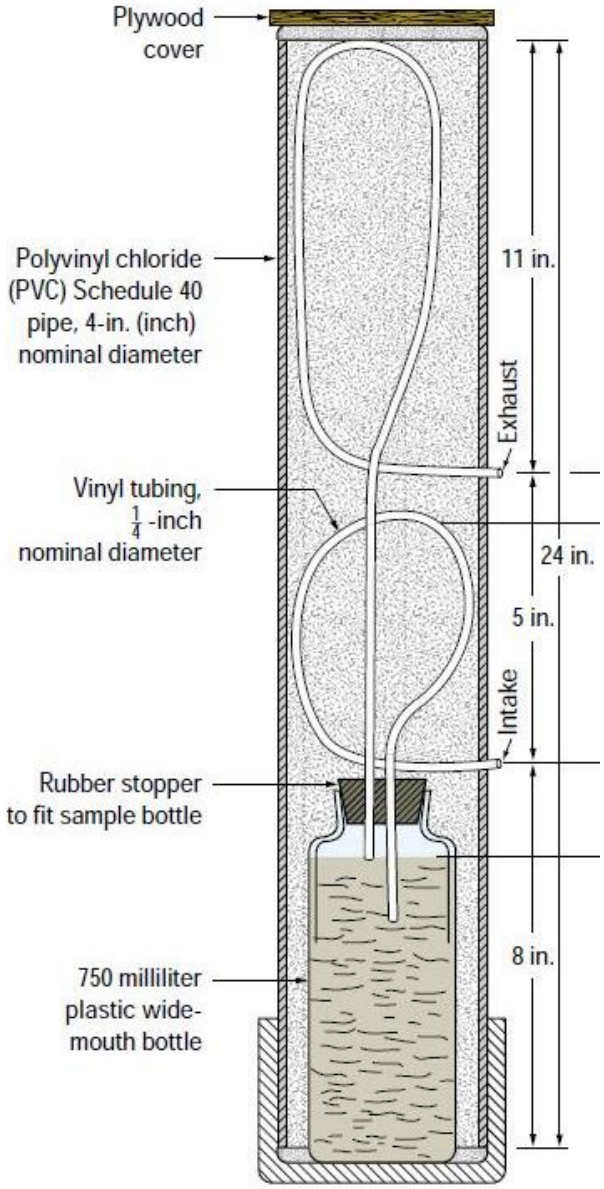

Figure 2-22 siphon flow sampler (Graczyk et al. 2000)

2.3.3.2 Rotational Flow Sampler

The rotational flow sampler consists of a flume which discharges into a Coshocton wheel. This sampler was originally developed for agricultural runoff sampling (Brakensiek et al. 1979). The flume is located slightly above the wheel and the water flow causes rotation (Figure 2-23). On the wheel, an elevated sampling slot collects a portion of the water when it rotates directly under the flow. The collected water passes below the wheel and into the storage tank.

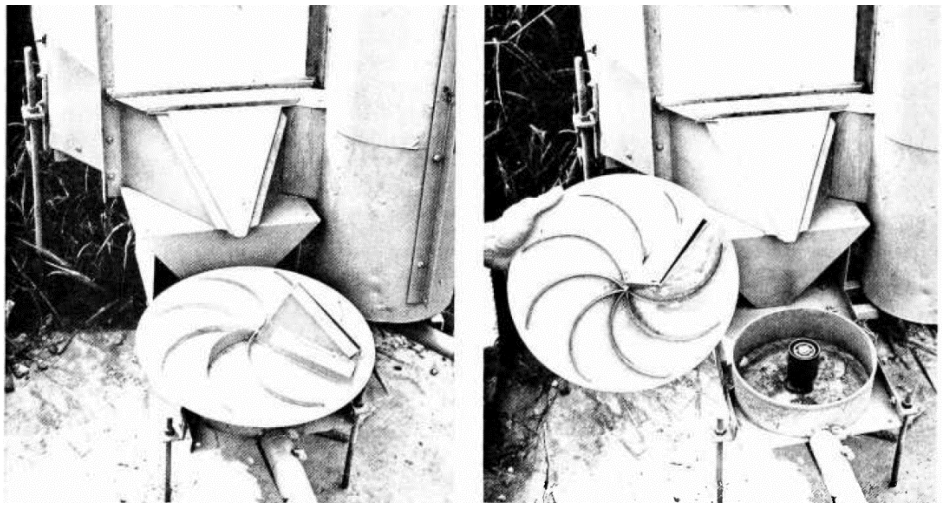

Figure 2-23 Rotational flow sampler completely assembled (left) and with wheel removed (right) (Brakensiek et al. 1979)

The sample is composite and flow-weighted, which is representative of the entire storm flow (Brodie and Porter 2004). This sampler is commonly used for agricultural sediment measurements (Owens et al. 2001). A study focusing on this sampler's optimization noted that wheel rotation above 35 rpm resulted in stalling and irregular rotation, effectively skewing sample collection. A limitation of this sampler is the requirement of a vertical drop.

2.3.3.3 Flow Splitting Sampler

The flow splitting sampler separates and diverts a percentage of the total flow into a collection device. It is similar to the rotational flow sampler in that the sample is proportional to the total volume of water. The sampler uses baffles to separate portion of the flow, multiple variations of this style of the sampler have been developed. This sampler also requires a vertical slope for proper application. A modification of this sampler has been tested and sediment concentrations including large particles were able to be collected accurately (Bonta 1999).

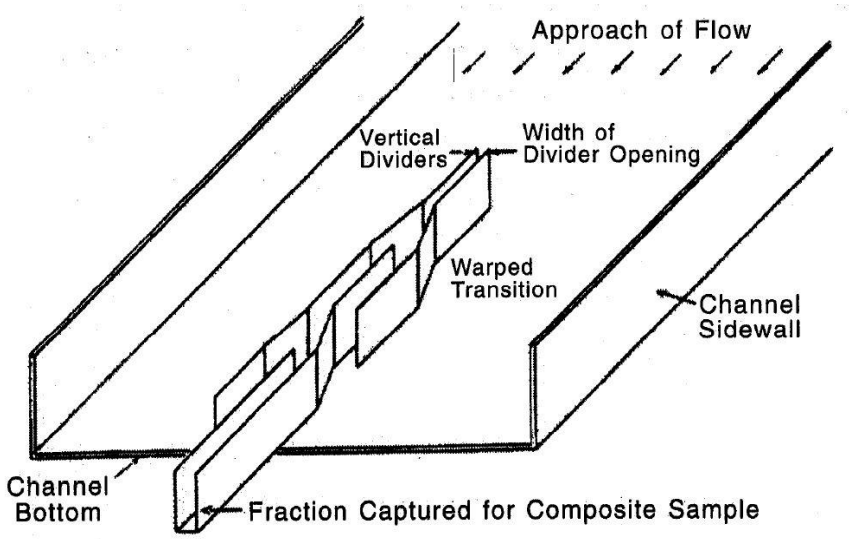

Figure 2-24 Flow splitting sampler (Powell et al. 1996)

The sampler described by Brodie and Porter requires the flow to be super critical, thus the chute needs to be at a gradient of 9% (Brodie and Porter 2004). A variation of this previous sampler which drops the sampled flow beneath the main channel was also developed (Brodie 2005). This sampler is significantly long. Figure 2-24 displays a different flow splitting design which incorporates baffles within the main channel, thus reducing the total footprint needed (Powell et al. 1996). A flow splitting sampler has been combined with modern data collection technologies for the monitoring of sediments and pollutants within agricultural runoff (Bonilla et al. 2006).

2.3.3.4 Direct Sieving Sampler

The direct sieving sampler (Figure 2-25) is designed to assess sediment loadings within stormwater flows. This sampler consists of a series of mesh screens which the flow travels through. The screen pore sizes decrease successively so that the larger material is separated from the flow first and smaller particles are separated out as the flow progresses.

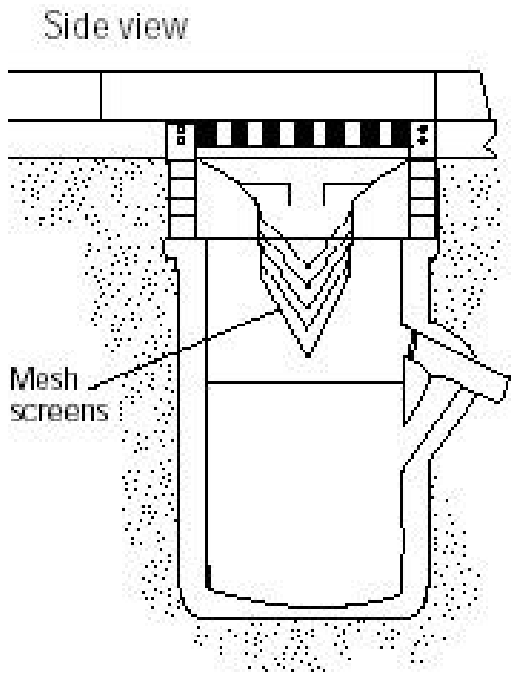

Figure 2-25 Direct sieving sampler (Brodie and Porter 2004)

This sampler inlet is level with the surrounding flow, requiring the sieves and additional structure to be installed below. Unlike previously discussed samplers, this sampler does not collect any water samples. This sampler requires an estimate/measurement of the total flow the sieves were exposed to (Brodie and Porter 2004).

2.3.4 Novel Sampler Sorbents

Along with analyzing current passive sampling technologies, a few novel sampler ideas were considered. The following two sorbents were looked at in detail for their ability to remove target analytes from water. Both of these sorbents have a high sorption capacity and thus merited a closer look. Each sorbent would need to have the analytes removed in a laboratory following deployment.

2.3.4.1 Granular Activated Carbon

Granular activated carbon consists of a carbonaceous solid that has been superheated in the absence of oxygen. This procedure results in an extremely low density, high surface area material.

Activated carbon is commonly used for its large sportive properties in a variety of water treatment applications. Granular activated carbon has been assessed for its ability to adsorb metals; trace metal uptake onto activated carbon was looked at and combining a chelating agent (8-hydroxyquinoline) within the aqueous solution was found to significantly improve the adsorption onto the carbon (Vanderborght and Vangrieken 1977). It is impractical to add a chemical into the sample in an environmental scenario, so alternatives were considered.

Activated carbon without pretreatment was noted to have sorptive uptakes of 12.2 to 29.1% for most metals (Daorattanachai et al. 2005). This study compared these uptakes to that of activated carbon impregnated with the chelating agent Ammonium pyrrolidinedithiocarbamate (APDC), which yielded over 99% uptake for all metals tested. Another study looked at the uptake of trace metals onto N, N'-diacetyl-4-bromo-2, 6-di (aminomethyl) phenol (DBDP) and found that eluent recoveries were all above 97% (Ahmadi et al. 2009). One thing to note about this study is that all organic matter was removed from the river samples used, which removes competition for adsorption sites. Activated carbon impregnated with three separate ligands (5,5-diphenylimidazolidine-2,4-dione (phenytoin) (DFTD), 5,5-diphenylimidazolidine-2-thione-,4-one (thiophenytoin), (DFID) &2-(4'-methoxy-benzylidenimine) thiophenole (MBIP)) were assessed for copper and lead uptakes from river, wastewater, spinach and blood samples (Ghaedi et al. 2008). Results proved satisfactory, with eluent recovery rates consistently over 95%.

2.3.4.2 Ion Exchange Resins

Ion exchange resins consist of a structural matrix with a functional group embedded onto the surface. The sorptive sites are preconditioned with a weakly charged ion. The desired sorbate attaches to the functional site and exchanges with the weaker ion, releasing it from the resin. Ion exchange resins are employed in a variety of applications including the removal of hardness in water treatment.

The majority of resins, however, reveal poor performance for selecting metal ions. To overcome this, metal-specific ligands were incorporated, resulting in chelating technologies (Eccles and Greenwood 1992). These improved technologies have good selectivity. They also have sorptive capacities that can be applied in large scale treatment scenarios. Industrial wastewater treatment has been able to capitalize on these large scale selective applications (Dabrowski et al. 2004). Agricultural and environmental soil applications have also been developed and extensively studied (Qian and Schoenau 2002). Ion exchanges resins have even been incorporated into stormwater BMPs to improve heavy metal removals from shipyard runoff (Burgos 1997).

Iminodiacetic acid (IDA) has proven itself as a moderately inexpensive chelating ligand that performs well for the collection of heavy metals (typically divalent cations) due to high capacity, selectivity, fast kinetics and high mechanical strength (Eccles and Greenwood 1992). One plus of this functional group is that it has preference for copper, lead, and zinc over more prevalent divalent cations within environmental samples like calcium or magnesium (Rohm and Haas 2006). IDA can have binding forces for alkaline earth metals that can be 5,000 times greater than alkali metals (Lin and Juang 2005).

Two types of chelating ion exchange resins with IDA as the functional group are compared below. They were chosen because of their relatively low costs, performance and accessibility; both are manufactured on a large scale.

Chelex 100

Chelex 100 is manufactured by Sigma Co. and is a laboratory grade IDA chelating ion exchange resin. The solid matrix is composed of Styrene-divynlbenzene and has a dry resin particle size of 0.15-0.30 mm. Chelex 100 exchange capacity is 0.7 equivalents/cubic decimeter of resin (Lin and Juang 2005). A study looked into Chelex 100 and what forms of marine trace metals it could effectively adsorb (Abdullah et al. 1976). Results show that species of metals bound with

organic and colloidal species are not affected by the resin; thus only the free forms of copper, lead, cadmium and zinc were adsorbed. Another study loaded Chelex 100 and a different IDA ion exchange resin (Lewatit TP-207) under stream and marine water scenarios (Alvarez et al. 2004). Chelex 100 proved to be a viable method for adsorbing free metals, and was unaffected by other cationic compounds.

Amberlite IRC748

Amberlite IRC748 is manufactured by Rohm & Haas Co. and is an industrial grade IDA chelating ion exchange resin. Styrene-divynlbenzene is the type of solid matrix, and it has a dry resin particle size of 0. 05-0.65 mm. Amberlite IRC748 exchange capacity is 1.25 equivalents/cubic decimeter of resin (Lin and Juang 2005). Researchers looked at using Amberlite IRC748 to pre-concentrate mine stream water samples for portable analysis (Heiden et al. 2010). This step is required because portable monitoring equipment has detection limits within the mg/l range while regulations call for trace metals to be below the µg/l range. Nickel, copper, lead and zinc were found to accumulate onto the resin relatively unaffected by other constituents within the water. Australian researchers assessed this resin's ability to adsorb copper and ammonium and compared it to a natural zeolite material (Mumford et al. 2008). This study provides an extensive assessment of copper uptake under various conditions. Exchange equilibrium was found to occur within three days, and the maximum exchange capacity was found to be 5.4 millequivalents/gram of dry resin at 4, 20 and 40°C. Cationic preference of this resin is as follows:

$$Na^{+} << Ca^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Cd^{2+} < Zn^{2+} < Ni^{2+} < Pb^{2+} < Cu^{2+} < Hg^{2+} < Fe^{3+}$$

PUF

The PUF plug is made from a PUF sheet, which is manufactured several companies (e.g., ITW Co.). It has100 pore-per-inch and density of 0.03g/cm3, and the character is similar with the PUF used in air passive sampler (Klánová et al. 2008). Currently, there is a widely acknowledged

limitation of passive sampling designs for SVOCs (ITRC 2006). Nevertheless, PUF has been used in passive samplers and has been shown to achieve rapid uptake and reliable quantitative information if the wind is forced to blow through the sampling medium (Xiao et al. 2007).

2.4 Results and Discussion

2.4.1 Requirements for Highway Runoff BMP Monitoring

Stormwater contaminants include a wide range of pollutant types. Highway runoff characteristics have been assessed in various studies (Keblin et al. 1997; Kayhanian et al. 2012). Table 2-1displays the results of a previous study assessing highway runoff contaminants and compares those results to other studies (Torres 2010). Three main pollutant types are of concern within stormwater runoff: VOCs, PAHs, and heavy metals. VOCs originate from fuel emissions, PAHs result from incomplete combustion, and heavy metals result from vehicle wear. Due to the inherent difference in molecular structure and chemical behavior in the environment, different samplers are needed to monitor each class of highway runoff pollutant.

Table 2-1 Highway runoff pollutants comparison (Torres 2010)

Analyte		NDOR Study						Wu et al. (1998)			Kayhanian et al. (2007)			Barret et al. (1998)			Driscoll et al. (1990)		
		West Pipe (EMC)			East Pipe (EMC)			Monitoring Site I (EMC)			Range	Median	Mean	35th Street (EMC)			National Highway Runoff Report		
		Range	Median	Mean	Range	Median	Mean	Range	Median	Mean				Range	Median	Mean	Range	Median	Mean
Cu	(µg/L)	2.5 - 24	6.0	9.4	1.26 – 17.5	5.5	7.9	9.0 - 52	15	24.2	1.1 - 130	14.9	10.2	2.0 – 120	34	38	5 - 155	52	39
Cd	(µg/L)	0.3 – 1.8	0.5	0.58	0.28 – 1.6	0.5	0.56	<DL	<DL	<DL	0.2 - 8.4	0.24	0.13	-	-	-	-	-	-
Cr	(µg/L)	0.02 – 5.8	0.72	1.5	0.02 – 7.3	0.65	1.5	5.0 - 20	6.5	8.1	1.0 - 23	3.3	2.2	-	-	-	-	-	-
Pb	(µg/L)	0.2 – 6.0	0.67	1.5	0.2 – 8.7	0.65	1.7	7.0 - 56	15	21	1.0 - 480	7.6	1.2	7 – 440	50	99	11 - 1457	525	234
Fe	(µg/L)	0.5 - 125	42.6	55.8	2.9 – 1233	7.5	226	-	-	-	32 - 3310	378	150	300 – 10000	2606	3537	-	-	-
Ni	(µg/L)	0.6 – 9.0	1.3	2.5	0.6 – 13.9	7.4	2.6	9.0 - 17	9	8.1	1.1 - 40	4.9	3.4	-	-	-	-	-	-
Zn	(µg/L)	0.05 – 162	16.6	30.6	0.05 – 186	15.0	32.0	-	-	-	3 - 1017	68.8	40.4	34 – 590	208	237	40 - 2892	368	217
TDS	(mg/L)	5 – 3236	106	423	10 – 1334	146	306	61 - 577	107	157	3.7 - 1800	87.3	60.3	-	-		-	-	-
TSS	(mg/L)	47 – 1040	116	235	5 - 419	80	125	32 - 771	215	283	1. - 2988	112.7	59.1	33 – 914	131	202	9 - 406	143	93
COD	(mg/L)	2.5 – 276	46	86	2.5 – 200	30.6	50.6	4 - 177	48	70	-	-	-	18 – 464	126	149	41 - 291	103	84
$NO_3^- + NO_2^-$	(mg/L)	0.2 - 2.4	0.5	0.8	0.1 - 1.8	0.6	0.72	0.08 - 13.37	0.38	2.25	0.01 - 4.8	1.07	0.6	0.0 – 3.66	1.03	1.25	0.19 - 3.32	0.84	0.66
TKN	(mg/L)	0.64 - 9.04	1.62	2.50	0.4 - 3.86	1.2	1.6	0.76 - 2.45	1	1.42	0.1 - 17.7	2.06	1.4	-	-	-	0.38 - 3.51	1.79	1.48
Ortho P	(mg/L)	0.09 – 0.41	0.1	0.15	0.025 – 0.24	0.085	0.103	0.01 - 0.74	0.08	0.15	0.01 - 2.4	0.11	0.06	-	-	-	-	-	-
Total P	(mg/L)	0.05 - 0.83	0.23	0.30	0.07 - 0.67	0.18	0.25	0.04 - 1.54	0.2	0.43	0.03 - 4.69	0.29	0.18	0.07 - 1.09	0.33	0.42	-	-	-
O&G	(mg/L)	0.025 - 14	1.81	2.4	0.025 – 9.6	1.52	1.95	1.0 - 11-1	3.3	4.4	1. - 20	6.6	6	0.8 - 35.1	4.1	6.5	-	-	-

Passive samplers used for BMP stormwater monitoring will be limited to less than two days of exposures. A BMP design manual recommends flow to leave bioretention cells within 2 days (ISMM 2009). A comparison study of BMP performance noted most flow occurred within six hours (Maniquiz et al. 2012). Thus, typical exposure times should range within hours. Combined with fast, predictable contaminant uptake, these passive samplers will also need to be able to retain contaminant mass during dry periods prior to and after the storm flows.

2.4.2 Comparison of Reviewed Passive Samplers

The reviewed passive samplers were compared (Table 2-2) for their ability to monitor stormwater highway BMPs. Samplers are compared by seven criteria, each displayed within its own column. The sampler's current applications are included as well as the sampler's ability to monitor VOCs, PAHs, and heavy metals. The sampler's ability to handle dry and wet periods is provided alongside the sampler's typical deployment time. If a cost was available, it was included for general estimation. Finally, pertinent sources were included for reference.

Regenerated cellulose (dialysis) membrane samplers, a chelating ion exchange sorbent (Amberlite IRC748), and a PUF sampler were chosen for batch, lab-scale BMP, and field testing. A thorough explanation of the sampler selection process is detailed in the following section (2.4.3 Sampler Discussion). In general, the physical recovery devices for groundwater sampling were not chosen because they either i) require a technician present to collect the sample, or ii) need significant space for installation, or iii) only collected part of the storm event, or iv) only assessed sediment loads. Few diffusion devices are still available and can monitor heavy metals, only regenerated cellulose was selected from this group. As for the diffusion and adsorption devices, the inability to measure heavy metals or cost was the reason for not being selected. Of the novel samplers, Amberlite IRC748 was chosen due to its preference for heavy metals, high adsorptive capacity and low cost. For PAH samplers, PUF sampler was selected because of their simplicity, efficiency and being cost effective.

Table 2-2 Evaluation of reviewed passive samplers for highway runoff sampling and monitoring

Sampler	Current Applications	Contaminants VOCs[a]	PAHs[b]	HMs[c]	Dry/Wet[d]	Deployment	Cost	Source(s)
Diffusion Devices								
Regenerated Cellulose (Dialysis) Sampler	Groundwater	Y[e]	Y	Y	Slight loss of water though membrane	2 weeks	Pre-assembled:~$40 /sampler self-assembled: ~$8/sampler	(Ehlke et al. 2004; Harter and Talozi 2004; Vrana et al. 2005a; ITRC 2006; Imbrigiotta et al. 2007)
Nylon-screen Passive Diffusion Sampler (NSPDS)	Groundwater& Sediment pore water	Y	Y	Y	NA[f]	3 days to 3weeks	~$40/sampler	(Vroblesky et al. 2002; Vroblesky et al. 2003; Zimmerman et al. 2005; ITRC 2006)
Passive Vapor Diffusion Sampler (PVD)	Vapor-phase Groundwater &Sediment pore water	Y	N[g]	N	Sampler needs to remain submerged	12 hours to 1 week	<$10/sampler	(Church et al. 2002; Vrana et al. 2005a; ITRC 2006; Adamson et al. 2012)
Peeper Sampler	Aqueous-phase Sediment pore water	Y	Y	Y	Sampler needs to remain submerged	1 to 2 weeks	$312/sampler	(Grigg et al. 1999; ITRC 2006)
Polyethylene Diffusion Bag Sampler (PDB)	Groundwater	Y	Y	N	Slight loss of water though membrane	2 weeks	Pre-assembled: ~$25/sampler Self-assembled: <$5/sampler	(Vroblesky and Hyde 1997; Vroblesky 2001a; Vroblesky 2001b; Ehlke et al. 2004; Parker and Clark 2004; Vrana et al. 2005a; ITRC 2006; Hale et al. 2010)
Diffusion and Adsorption Devices								
Semi-Permeable Membrane Device (SPMD)	Air, Groundwater & Rivers/Streams	Y	Y	N	Sampler needs to remain dry or wet	1 month	$50/sampler Deployment Unit: $250	(Huckins et al. 1990; Gustafson and Dickhut 1997; Vrana and Schuurmann 2002; Vrana et al. 2005a; Komarova et al. 2006; Johnson 2007)

[a]VOCs = Volatile Organic Compounds *(continued on next page)*

[b]PAHs = Polycyclic Aromatic Hydrocarbons; [c]HMs = Heavy Metals; [d]Dry/Wet = Sampler's ability to handle periods of drying & wetting during deployment

[efg]Y/N/NA = Yes/No – sampler's ability to monitor class of contaminants; NA – Information not available or doesn't apply to particular sampler

Table 2-2 Evaluation of reviewed passive samplers for highway runoff sampling and monitoring (continued)

Sampler	Current Applications	Contaminants VOCs	PAHs	HMs	Dry/Wet	Deployment	Cost	Source(s)
GORE Sorber Module	Vapor-phase Groundwater	Y	Y	N	Sampler needs to remain dry or wet	2 weeks	$185 - $285 includes analysis	(Vonder Haar and Gregory 2000; Vrana et al. 2005a; ITRC 2006)
Polar Organic Chemical Integrative Sampler (POCIS)	Aqueous-phase Wastewater, Rivers/Streams, Lakes & Marine	Y	Y	N	Sampler needs to remain submerged	Up to 2 months	$60/sampler Deployment Unit: $265	(Jones-Lepp et al. 2004; Alvarez et al. 2005; Vrana et al. 2005a; ITRC 2006; Bartelt-Hunt et al. 2011)
Passive in situ Concentration Extraction Sampler (PISCES)	Aqueous-phase Surface water	NA	Y	N	Sampler needs to remain submerged	2 weeks	$70 - $100	(Vrana et al. 2005a; ITRC 2006)
Dialysis with Receiving Resins Sampler	Stormwater	N	N	Y	Sampler can handle wet & dry periods	NA	NA	(Morrison 1987; Morrison 1989; Tao and Liang 1997; Vrana et al. 2005)
Chemcatcher (Inorganic & Organic)	Aqueous-phase Stormwater, Rivers/Streams, Industrial, Wastewater & other aquatic applications	N	Y	Y	Sampler needs to remain dry or wet	Up to 1 month	Housing: ~$40 Sorbent Disks & membrane: ~$15/sampler	(Kingston et al. 2000; Persson et al. 2001; Blom et al. 2002; Blom et al. 2003; Vrana et al. 2005a; Vrana et al. 2005b; Vrana et al. 2006; Allan et al. 2007; Vrana et al. 2007; Lobpreis et al. 2008; Shaw and Mueller 2009; Page et al. 2010)
Solid-Phase Microextraction (SPME)	Air, Wastewater, Sludge, & Soil	Y	Y	Y	Sampler needs to remain dry or wet	15 minutes to a few hours	Sampler Holder: ~$750 Fibers: ~$300-$500/pack	(Pawliszyn et al. 1997; Hinshaw 2003; Alexander et al. 2005; Vrana et al. 2005a; ITRC 2006; Greenwood et al. 2007; Sayre et al. 2010)

(continued on next page)

Table 2-2 Evaluation of reviewed passive samplers for highway runoff sampling and monitoring (continued)

Sampler	Current Applications	Contaminants VOCs	PAHs	HMs	Dry/Wet	Deployment	Cost	Source(s)
PUF	Air, Aqueous-phase	N	Y	N	Sampler needs to remain dry or wet	weeks	NA	Pozo et al. 2006; Lee et al 2007; Zhang et al. 2011
HydraSleeve Sampler	Groundwater	Y	Y	N	NA	Instant collection	~$25/sampler	(Parker and Clark 2004; ITRC 2006)
Snap Sampler	Groundwater	Y	Y	Y	NA	Instantaneous collection	$165/bottle Deployment materials: ~$70	(ITRC 2006; Britt et al. 2010)
Gravity Flow Sampler	Runoff	N	Y	Y	NA	Permanent; sample collects first flush	NA	(Young et al. 1998; Waschbush et al. 1999; Brodie and Porter 2004; Kearfott et al. 2005; Barrett and Stanard 2008; Li and Barrett 2008; Li et al. 2008)
Siphon Flow Sampler	Streams, Runoff & Tidal Flows	NA	NA	Y	NA	Permanent; samples attained water level increasing	~$65/sampler	(Graczyk et al. 2000; Newham et al. 2001; Brodie and Porter 2004; Diehl 2008; Mackay and Taylor 2012; Moskalski and Sommerfield 2012)
Rotational Flow Sampler	Runoff	NA	Y	Y	NA	Permanent: collects composite of total flow	Sampler: $4470 - $4790 Wheel: $785 - $955	(Brakensiek et al. 1979; Owens et al. 2001; Bonta 2002; Brodie and Porter 2004)
Flow Splitting Sampler	Runoff	Y	NA	Y	NA	Permanent: collects composite of total flow	~$1200 total	(Powell et al. 1996; Bonta 1999; Brodie and Porter 2004; Brodie 2005; Bonilla et al. 2006)

*Granular Activated Carbon requires ligand or anion impregnation to adsorb Heavy Metals effectively

(continued on next page)

Table 2-2 Evaluation of reviewed passive samplers for highway runoff sampling and monitoring (continued)

Sampler	Current Applications	Contaminants VOCs	PAHs	HMs	Dry/Wet	Deployment	Cost	Source(s)
Direct Sieving Sampler	Runoff	N	N	N	NA	Permanent: Sediment	NA	(Brodie and Porter 2004)
Novel Sampler Sorbents								
Granular Activated Carbon	Water & Wastewater Treatment	Y	Y	Y*	Sorbent may lose VOCs when dry	NA	GAC: ~$20/lb Sorbent: NA	(Vanderborght and Vangrieken 1977; Daorattanachai et al. 2005; Ghaedi et al. 2008; Ahmadi et al. 2009)
Amberlite IRC748 Ion Exchange Resin	Wastewater &Industrial Treatment	N	N	Y	Unaffected by dry& wet periods	NA	~$93/lb	(Lin and Juang 2005; Rohm, and Haas, 2006; Mumford et al. 2008; Heiden et al. 2010)
Chelex 100 Ion Exchange Resin	Wastewater & Industrial Treatment	N	N	Y	NA	NA	~$659/lb	(Abdullah et al. 1976; Alvarez et al. 2004; Lin and Juang 2005)
PUF	Air	N	Y	N	Unaffected by dry& wet periods	NA	5~$100/lb	Armitage et al. 2005; Armitage et al. 2013; Petrich et al. 2013

2.4.3 Discussion

Regenerated cellulose samplers, Amberlite IRC748 ion exchange resin contained within mesh, and PUF samplers were selected for further testing in this study. The subsequent section describes the selection process concerning which passive samplers are to be used for batch, lab-scale BMP, and finally field tests. In general, diffusion as well as diffusion with adsorption devices are more feasible due to their smaller size and ability to be incorporated within Highway BMP flows. Each sampler not chosen is mentioned along with the reason for ruling it out. Regenerated cellulose, ion exchange, and PUF samplers are also discussed in further detail.

2.4.3.1 Diffusion Devices

Nylon-screen Passive Diffusion Sampler (NSPDS).

The nylon-screen diffusion sampler was deemed infeasible due to follow-up conversations with researchers (O'Neill 2012). Issues with finding the correct screen mesh size to keep water in and allow analytes to diffuse occurred as well as major inconsistencies with uptake depending on sampler orientation. Both of these factors lead to the termination of research and production of this sampler. This sampler is no longer produced, thus it was not selected for this study.

Passive Vapor Diffusion (PVD) Sampler

The passive vapor diffusion sampler only measures vapor-phase VOCs. This poses an issue for BMP use, where the sampler may be exposed to both water and air during deployment. Due to the limited analyte capabilities, this sampler was not selected for this study.

Peeper Sampler

The peeper sampler has the ability to analyze VOCs, PAHs, and heavy metals, but it is designed and calibrated for sediment pore water concentrations. This sampler consists of a rigid

structure and a diffusion limiting membrane which isn't predictable prior to equilibrium (Grigg et al. 1999). Because of this, the peeper sampler was not selected for this study.

Polyethylene Diffusion Bag Sampler (PDB)

The polyethylene diffusion bag sampler is significantly cheap, simple and easy to self-assemble. The LDPE membrane however, does not allow the passage of heavy metals into the sampler (Ehlke et al. 2004). Due to the inability to monitor heavy metals, this sampler was not selected for this study.

2.4.3.2 Diffusion and Adsorption Devices

Semi-Permeable Membrane Device (SPMD)

The semi-permeable membrane device has been proven effective for VOC and PAH analysis within air, rivers/streams, and groundwater. It, however, is incapable of monitoring metals due to its LDPE membrane and cannot be exposed to air. Combined with the high cost per sampler and deployment unit, this sampler was not chosen for this study.

GORE Sorber Module

The Gore Sorber sampler requires analysis to be conducted through the laboratory of W.L. Gore & Associates, Inc. in Elkton, MD (ITRC 2006). This sampler has the ability to test VOCs, PAHs, and heavy metals and could handle wet and dry periods. Due to the high cost of this sampler and the inability to analyze the samplers outside of the Elkton, MD facility, this sampler was not selected for this study.

Polar Organic Chemical Integrative Sampler (POCIS)

The polar organic chemical integrative sampler requires significant preparation prior to deployment and cannot be exposed to air. This sampler also does not have the capabilities to measure heavy metals. Because of these reasons, the POCIS has not been chosen for this study.

Passive in situ Concentration Extraction Sampler (PISCES)

The passive in situ concentration extraction sampler can monitor VOCs and PAHs, but not heavy metals. This sampler is not capable of being exposed to air during deployment, and is not commercially available (ITRC 2006). Because of these reasons the PISCES was not selected for this study.

Dialysis with Receiving Resins Sampler

The dialysis with receiving resins sampler has been applied to stormwater monitoring with some success (Morrison 1987; Morrison 1989). This sampler has been deemed ineffective for long-term stormwater monitoring (Tao and Liang 1997). This sampler has the ability to measure metals, but multiple mechanisms affect the transport and collection of metals in the sampler. These interactions are not well documented and lead to this sampler not being selected for this study.

Chemcatcher (Inorganic & Organic)

The Chemcatcher has membrane and sorbent disk combinations which enable the monitoring of VOCs, PAHs, and heavy metals (Vrana et al. 2005a). The Empore disk technology has enabled a variety of solid-state sorbents to be utilized within this arrangement. The Chemcatcher's ability to handle wet and dry periods is unlikely (Mills 2012).This sampler is moderately expensive and decided against for these reasons.

Solid Phase Microextraction (SPME) Sampler

The solid phase microextraction sampler has a very short deployment time compared to the rest of the samplers, so much so that it would require a technician to be present to deploy and collect it during the storm. This sampler is brittle and should only be deployed in either water or air (Shulte 2012). This sampler is very expensive and was not chosen for this study.

2.4.3.3 Physical Recovery Devices

HydraSleeve Sampler

The HydraSleeve sampler cannot collect heavy metals and it requires a technician to be present during sample collection. This sampler only collects an instantaneous sample, which would not be representative of the storm event. For these reasons, this sampler was not selected.

Snap Sampler

The Snap sampler can attain accurate concentrations of VOCs, PAHs, and heavy metals. It is undesirable in that it only captures an instantaneous sample, which requires a technician present to collect. This sampler was not chosen for this study.

Gravity Flow Sampler

This sampler only collects the first flush, which could be useful. It does, however require significant installation efforts and only provides a composite of a set volume (typically 5 liters) of rain. This sample volume is independent of the storm hydrograph and may not be representative of the storm. This sampler was not selected for this study.

Siphon Flow Sampler

The siphon flow sampler is only capable of sampling in flows that rise above the sampler. It can only collect samples while the flow level is rising. This means the entire section of the storm following the peak flow is neglected. These samplers are not capable of measuring shallow flows; thus they were not chosen for this study.

Rotational Flow Sampler

The rotational flow sampler collects a set proportion of the entire flow. This sampler, however, is very expensive and requires a drop in elevation for installation. It is somewhat large and may be difficult to integrate into a highway BMP. It was not chosen for this study.

Flow Splitting Sampler

The flow splitting sampler also collects a set proportion of the entire storm flow. This sampler requires a large amount of space and a fairly large drop in elevation from the beginning to the end of the sampler. This sampler is also too expensive for the scope of this study, and therefore, it was not selected.

Direct Sieving Sampler

The direct sieving sampler only collects sediments from runoff flows. This does not help achieve the goals of this study and thus it was not chosen for further testing.

2.4.3.4 Novel Sampler Sorbents

Granular Activated Carbon

Granular activated carbon requires pretreatment, including the impregnation of ligands or anions to effectively adsorb heavy metals. This adds complexity to sampler preparation. In addition, sample volumes of the reviewed literature were relatively small and have not been applied at a large scale unlike some industrial ion exchange resins. Moreover, cationic preference was not found. It is ideal that sorbents prefer copper, lead and zinc over other prevalent cations within stormwater (i.e. calcium or magnesium). For these reasons granular activated carbon was not selected for this study.

Chelex 100 Ion Exchange Resin

Chelex 100 ion exchange resin utilizes Iminodiacetic Acid (IDA), a chelating agent that targets heavy metals above more prevalent cations within the environment like calcium and magnesium. Chelex 100, however, was outperformed in copper and zinc uptake and the total exchange capacity by Amberlite IRC748 in a comparative study (Lin and Juang 2005). Chelex 100

ion exchange resin is used primarily for laboratory functions and is thus significantly more expensive. This sorbent was not chosen for this study.

2.4.3.5 Selected Samplers

Regenerated Cellulose (Dialysis) Samplers

Regenerated cellulose samplers were chosen for a multitude of reasons. The sampler is simple in design and diffusion is the only mechanism affecting sampler transport. This sampler is inexpensive (~$8/sampler), easy to construct, and has the capabilities to analyze metals, VOCs, and PAHs. Regenerated cellulose tubing can be cut to a shorter length that is appropriate for highway BMP flows. Although recommended deployment for this sampler is two weeks, the initial uptake is expected to be linear because diffusion is the only transport mechanism at work. Figure 2-26 displays this sampler.

Figure 2-26 Regenerated cellulose (dialysis) membrane sampler

Dialysis samplers consist of various cellulose membranes ranging from cellulose acetate to regenerated cellulose filled with high purity water. The cellulose acetate versions lack durability compared to the regenerated cellulose membrane (Ehlke et al. 2004). Cotton linters are dissolved in a solvent to produce regenerated cellulose membrane, which has great compatibility with most

environmental applications. Diffusion is the main mechanism of contaminant transport across the membrane. Dialysis samplers regulate the passage of molecules by having a set molecular weight cutoff. Size, shape, charge, concentration gradient, and other molecule parameters determine if a given molecule can diffuse across the membrane.

Amberlite IRC748 Ion Exchange Resin

Amberlite IRC748 ion exchange resin was chosen as a sorbent for a novel sampler. This is due to a variety of factors including the preference Amberlite IRC748 has for heavy metals over other prevalent cations within environmental waters including calcium and magnesium. This sorbent is inexpensive. It costs about $4 dollars per sampler. Amberlite IRC 748 has a very large exchange capacity (5.4 millequivalents/gram of dry resin) which could enable a small amount of resin to absorb trace metals from a large volume of water. This resin can be wrapped in mesh to any desired shape and size.

For this study, a woven polyester monofilament mesh with a 0.008-inch-hole size was chosen to encase the Amberlite IRC748 resin. 15 g of resin was used for each sampler. This enables the sampler to remain small in size while absorbing the metals from large volumes of stormwater. This chelating ion exchange resin has been shown to be superior to Chelex 100 ion exchange resin in a comparative study (Lin and Juang 2005).Figure 2-29 displays the sampler arrangement.

Figure 2-27 Ion exchange resin sampler

PUF samplers

Because of being low-cost and versatility, PUF is a commonly used as a passive air sampler for semi-volatile organic compounds, especially for SVOCs, such as PAHs and polychlorinated biphenyls (PCBs). In this study, a PVC column containing a PUF plug with the size of 1/2 inch diameter by 1.5 to 3 inch long was made as the SVOC sampler. Figure 2-28 displays the arrangement of the PUF sampler.

Figure 2-28 PUF sampler

2.5 Conclusion

A non-exhaustive review of existing passive samplers and three potential sorbents was conducted. Some passive samplers have been used for stormwater monitoring, others in similar scenarios. All were evaluated for their ability to effectively monitor highway runoff BMPs and two were selected for further testing and analysis. A regenerated cellulose (dialysis) membrane sampler, a chelating ion exchange sorbent, and a PUF sampler were chosen for batch, lab-scale BMP, and field testing in this study.

Chapter 3 Batch Tests for Heavy Metal Passive Sampler

3.1 Introduction

Two passive samplers have been identified as potentially feasible for monitoring trace metals within highway stormwater BMPs (detailed in Section 2), that is i) the regenerated cellulose (dialysis) bag filled with DI water and ii) a mesh sampler containing a chelating Ion Exchange resin. Both samplers were chosen for their compatibility with heavy metals, reproducibility and cost-effectiveness (Ehlke et al. 2004; Lin and Juang 2005; Vrana et al. 2005a; ITRC 2006).

Dialysis samplers have proven effective and economical for groundwater monitoring of multiple types of constituents including VOCs, fertilizers, chloride, sulfate, iron, alkalinity, arsenic, methane and trace metals(Magaritz et al. 1989; Vroblesky and Pravecek 2002; Ehlke et al. 2004; Harter and Talozi 2004). These applications consist of deployment times of 4 to 30 days and depend on the sampler reaching equilibrium with the surrounding solution. The use of the dialysis sampler for stormwater would depend on the diffusive linear uptake into the sampler that occurs early in the kinetics curve detailed in Figure 3-1.

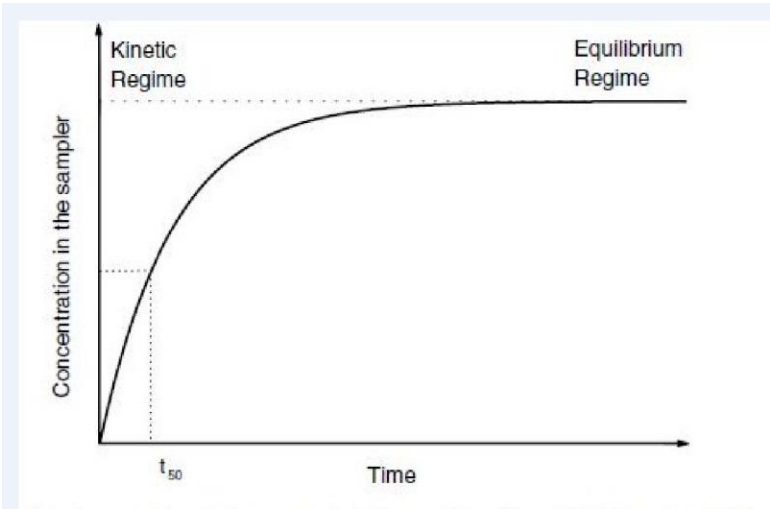

Figure 3-1 Schematic of kinetic and equilibrium regimes (Vrana et al. 2005a)

Regenerated cellulose membrane has also been filled with ion exchange receiving resins and deployed within stormwater scenarios to monitor metals (Morrison 1987; Morrison 1989; Tao and Liang 1997). This sampler has multiple mechanisms of contaminant capture at work: diffusion through the membrane and adsorption onto the internal resins. This prevents the simplicity of a liner uptake by diffusion only, one of the more desirable characteristics of the dialysis sampler. The uptake rates of metals onto the membrane have been examined and reported (Morrison 1987; Morrison 1989). These studies only detail the rate of mass attaching to the membrane itself.

Short term kinetics is required to better understand the uptake capabilities of the dialysis sampler under stormwater conditions. The series of batch tests performed in this study attempted to provide this missing data and give greater insight to the feasibility of using dialysis samplers for stormwater monitoring, particularly for monitoring highway BMP effectiveness.

Chelating ion exchange resins have been utilized to remove trace metals from industrial and environmental waters (Burgos 1997; Xiao et al. 2003; Dabrowski et al. 2004). Another application is the preconcentration of low level constituents for sampling purposes (Narin et al. 2007; Heiden et al. 2010).Ion exchange resins enable the removal of certain anions or cations from a media by replacing them with ions that have neutral effects on the environment.

Ion exchange resin adsorption sites exchange weakly charged ions (i.e. Na^{+} or H^{+}) for molecules with greater charges (i.e. Ca^{2+} or Pb^{2+}). This alone is not ideal for the removal of trace metals because many of the sites will be filled with other cations that have neutral effects on the environment. To overcome this issue, ion exchange resins have been coupled chelation technologies. This chemical arrangement allows preference for certain metals based on molecule size and orientation (Eccles and Greenwood 1992).

Various chelating ion exchange resins are available and a variety of studies have been conducted comparing differing types (Lin and Juang 2005; Mumford et al. 2008) and characterizing

adsorption kinetics (Huang and Lin 1987; Demirbas et al. 2005; Rengaraj et al. 2007). Amberlite IRC 748 resin was chosen in this study because of its preference for copper, lead and zinc over other environmentally prevalent cations. This resin was also selected because of its relatively low cost and superior performance when compared to other chelating resins and adsorbents (Lin and Juang 2005; Mumford et al. 2008).

Amberlite IRC748 consists of iminodiacetic acid as the functional group situated on a macroporous styrene divinylbenzene matrix. Typical applications of this resin are in a column type setting, not as a passive sampler. This combined with the fact that isotherm characterization of adsorption relies on complete uptake, points to a need to better understand the uptake kinetics under highway stormwater BMP scenarios.

It is imperative to conduct preliminary experiments to better understand sampler kinetics under scenarios similar to those expected in BMP monitoring. A series of batch tests were performed to provide initial feasibility as well as calibration curves. The batch tests mimic the static exposure design utilized for semi-permeable membrane device samplers (Greenwood et al. 2007). These experiments provide an understanding of sampler performance prior to pilot and field testing as well as the feasibility of both the dialysis and ion exchange resin samplers.

3.2 Materials and Methods

3.2.1 Samplers and Materials

Dialysis bag samplers were constructed with 8,000 MWCO regenerated cellulose tubing material and 65 mm locking dialysis membrane clamps, purchased from Membrane Filtration Products Inc. (314 N. River Street, Seguin, TX 78155). The membrane used was CelluSep H1, produced in 5 m long rolls with a 50 mm flat width. The nominal volume/length ratio was 7.94 ml/cm. CelluSep H1 membrane is pretreated with an ethylenediaminetetraacetic acid (EDTA)

solution by the manufacturer to remove metals and glycerol. The membrane is shipped wet in a sodium azide and ethanol solution to prevent bacterial growth during storage.

Ion exchange resin samplers consisted of Amberlite IRC 748 chelating ion exchange resin manufactured by Rohm and Haas and purchased via Fisher Scientific from Acros Organics (500 American Road, Morris Plains, NJ 07950). Amberlite IRC 748 consists of a macroporous styrene divinylbenzene solid matrix mounted with an iminodiacetic acid functional group (Rohm and Haas 2006). Resin was wrapped within a polyester monofilament woven mesh with a 0.008-in-hole size purchased from Industrial Netting (7681 Setzler Pkwy N., Minneapolis, MN 55445).

Trace metal grade concentrated nitric, hydrochloric, and sulfuric acid were purchased from Fisher Scientific as was certified ACS grade sodium chloride. Sodium hydroxide was produced by Acros Organics and purchased via Fisher Scientific. Reagent grade copper(II) nitrate trihydrate, lead(II) nitrate, and zinc(II) nitrate hexahydrate (Acros Organics) were used. Analytical reagent grade sodium carbonate and Kaolin powder were purchased from Mallinckrodt Baker, Inc. (Phillipsburg, NJ 08865).

DI water was purified via a ThermoFisher Scientific EASYpure RoDi water purification machine. Parafilm, used to cover any temporary glassware openings and beakers during batch experiments, was manufactured by Pechiney Plastic Packaging (8770 W. Bryn Mawr Ave. Chicago, IL 60631). Aluminum foil that was used to cover batch tests, preventing biological growth, was manufactured by Reynolds and purchased at a local kitchenware store. Samples were collected and stored in16 x 125 mm polypropelyne capped tubes (19.0 ml) purchased from Evergreen Scientific (2254 East 49th St. P.O. Box 58248 Los Angeles, CA 90058).

Pond sediment, used to simulate sediments within stormwater was collected from a local detention pond (Omaha, NE) near a section of Interstate roadside and analyzed by Mid-West Laboratories. Sediments that were used are characterized in Table 3.1. Prominent concentrations

of Zinc were present within the roadway sediment: 113.842 µg/g. Significant amounts of Iron were detected within the roadway sediment, and it was not considered during batch tests because iron is not within the scope of this study.

Table 3-1 Chemical characterization of roadway sediments (Jones 2012)

Constituent	Roadway Sediment (µg/g)	Instrument Detection Limit (µg/l)
Cr	12.148	12.362
Fe	3054.209	5.198
Ni	7.255	3.373
Cu	28.076	2.100
Zn	113.842	2.201
Ag	31.982	7.436
Cd	< DL[a]	1.228
Sb	< DL	8.404
Pb	19.076	3.794
NO^3	185	276

[a]< DL = Value below detection limit

3.2.2 Preconditioning and Assembly

Dialysis samplers were rinsed and assembled similar to the a previous method used by rinsing 4 inch of regenerated cellulose tubing with DI water three (3) times to remove sodium azide and ethanol storage solution (Ehlke et al. 2004). DI water (50ml) was placed within membrane. Clamps were used to seal tube ends. Clamps were washed with detergent, rinsed with tap water and then rinsed three (3) times with DI water.

To improve ion exchange resin performance, resin was placed in sodium form prior to use. A method was used similar to previous studies on Amberlite IRC-748(Lin and Juang 2005; Mumford et al. 2008). Preconditioning was done by rinsing 30mg of resin with three (3) 25ml aliquots of DI water followed by three (3) aliquots of the same volume of 0.5 M hydrochloric acid. This removed any other cations from the resin's exchange sites and placed resin in the hydrogen form. Then resin was rinsed with 25 ml of 0.5 M sodium hydroxide three (3) times. As a result the

resin was placed in the sodium form. Finally, three (3) rinses of DI water were used to rinse any excess chemicals from the resin.

Ion exchange samplers were assembled by taking a 4 inch by 6 inch section of washed polyester netting, folding in half lengthwise, and heat sealing along 'free' end forming a tube. One of the tube ends was sealed and 15mg of resin in sodium form was added. The final open side of the sampler is then sealed closed.

3.2.3 Methods

Due to the high variability and variety of factors that play a role within the environment, it was decided to begin with kinetics tests starting with the simplest scenario and increasing in complexity. The first tests only exposed the samplers to an individual metal (copper, lead, or zinc). Then after analysis, the samplers were exposed to all three metals in solution. Finally, the samplers were exposed to a synthetic stormwater. All conducted batch tests focused on the uptake of the samplers within a static exposure design. This method of calibration has been utilized for other passive sampler types (Greenwood et al. 2007).

3.2.3.1 Experimental Design

Dialysis and ion exchange resin samplers were suspended via string within 1 liter glass beakers and surrounded by a known solution. Solution constituents vary by the type of test (individual metal, tri-metal, or synthetic stormwater) and are detailed in Table 3.2. Constituents and concentrations of metals and synthetic stormwater were based on documented concentrations of highway runoff (Keblin et al. 1997).

No metals were added to the system during deployment, meaning mass was constant within the system. Dialysis samplers were deployed within the solution for 14 days so that equilibrium occurred. Due to a shorter equilibrium time, the ion exchange resin samplers were only exposed

for a total of 3days. Turbulence was provided by a magnetic stir-bar at 400rpm for the duration of the test.

Table 3-2 Batch test constituents and concentrations

Constituent	Concentration (mg/L)	Copper Test	Zinc Test	Lead Test	Tri-Metal Test	Stormwater Test
Copper (Cu)	0.11	x			x	x
Lead (Pb)	0.16		x		x	x
Zinc (Zn)	0.91			x	x	x
Sodium Carbonate (Na_2CO_3)	0.9					x
Sodium Chloride (NaCl)	200					x
Kaolin	60					x
Pond Sediment	500					x

To reduce the effects of evaporation, the beaker opening was sealed with Parafilm. Biological growth has been noted as a factor that can inhibit the performance of passive samplers (Vrana et al. 2005a). To prevent these effects the batch tests were wrapped in aluminum foil, eliminating light within the system.

Adsorption and glassware control tests were performed to determine the cause of some unexpected results. The copper adsorption control test consisted of a copper and DI water solution totaling 1 liter. All other parameters of the individual tests were held constant except the dialysis tubing was cut in half lengthwise to prevent any diffusion. Copper and zinc glassware and clamps control tests had the same parameters as the uptake tests, except the dialysis membrane was not present. Experiment length was three days.

Desorption control tests were performed in four different experiments. A sheet of dialysis membrane (4-inches by 4-inches) was exposed either to typical landfill leachate concentrations of copper or zinc (5,000 µg/l or 500,020 µg/l, respectively) or to stormwater concentrations of copper or zinc (110.0 µg/l or 160.0 µg/l, respectively) for one day (Keblin et al. 1997; Kjeldsen et al. 2002). Solution samples were taken to quantify the amount of adsorption. The dialysis membranes with a

metal (Cu or Zn) being adsorbed via the 1-day adsorption test were then exposed to 1 liter of DI water, and the solution concentration of the metal was tracked for fourteen days to evaluate the desorption properties of the membranes.

3.2.3.2 Solution Measurements

The external concentration of the solution was measured prior to deployment. Samples were taken prior to sampler deployment and periodically at 0 min, 15 min, 30 min, 1 hour, 5 hours, 1 day, and 3 days during deployment for dialysis samplers and ion exchange samplers. Additional measurements were taken (7 days and 14 days) during deployment for the dialysis samplers. Because of the expected exposure times within field deployment, external concentrations measurements emphasize initial uptake.

3.2.3.3 Sampler Measurements

At the completion of the experiment, internal concentrations or mass loadings were collected. The method of collection and unit of measurement varied depending on the type of passive sampler.

Internal concentrations were collected for the dialysis samplers by collecting a sample from the water within the dialysis membrane. The dialysis membrane tubing was split along the side and rinsed twice with 10 ml of 3M nitric acid followed by two rinses (5 ml each) of DI water within a separatory funnel, from which a sample was collected. This procedure was conducted for all tests except the individual copper test.

Due to the nature of the ion exchange resin, an internal concentration was not directly available. The metals collected onto the ion exchange resin adsorption sites were eluted and then a mass balance enabled a calculation of the mass loadings. Following deployment, ion exchange resin samplers were allowed to air-dry for a day. This enabled the resin beads to be easier to handle.

No standardized method for metal retrieval from Amberlite IRC748 chelating ion exchange resin was found. Therefore adjustments to the elution procedure were made throughout testing to improve retrieval efficiency. Results and analysis of the elution procedure is detailed in the section 3.3.2.4 (Ion Exchange Resin Control Test Results). For the copper individual test, three 20 minute soaking rinses off 120 ml of 0.5 M hydrochloric acid within a 250 ml beaker. A sample was collected and analyzed from each rinse of the resulting solution. The elution procedure for the lead & zinc individual tests as well as the tri-metal and synthetic stormwater tests was adjusted to include flow of the hydrochloric acid through the resin. Following the drying period, the resin was poured into a burette containing a small amount of hydrochloric acid (~15 ml) enabling the resin to expand before settling which prevented clogging of the burette during the actual elution. The elution consisted of passing 120 ml of hydrochloric acid through the resin at a flow rate of 2 ml/min. From the resulting solution a sample was collected and analyzed.

A verification of the ion exchange resin elution procedure was conducted by exposing a sampler to stormwater for three days. Samples were collected prior to sampler deployment, following three days of exposure and from the elution. This control test was conducted in triplicate.

3.2.3.4 Sample Collection, Preservation, and Analysis

Sample collection, preservation and analysis followed the recommendations for metals set forth by Standard Methods (APHA 2012). Samples (5 ml) were collected via pipette and placed in capped polypropylene test tubes. Samples were preserved immediately by adding concentrated nitric acid to achieve a 2% (v/v) ratio. Samples were stored at or below 4° C prior to analysis, which was performed within thirty days of collection. Analysis was performed via a 2004 Varian Inductively Coupled Plasma Mass Spectrometer (ICP-MS) by the University of Nebraska – Omaha Chemistry Department.

Dilutions were performed on all values above the calibrated range (250 ppb). These were conducted in a parallel manner by adding the sample to a 2% (v/v) concentrated nitric acid and DI water solution prior to analysis. Volumes were calculated to achieve the desired dilution ratios for a total volume of 5 ml for analysis. All zinc uptake measurements required either a 1:5 or 1:10 dilution. Elution samples for the ion exchange resin sampler within the tri-metal and synthetic stormwater tests required dilutions to lower each metal into range. A 1:40 dilution was conducted for zinc for both tests, while a 1:20 was used for copper and lead within the tri-metal test and a 2:5 ratio for copper and lead in the synthetic stormwater test.

3.3 Results and Discussion

3.3.1 Dialysis Samplers

The dialysis sampler results that are presented below include four main components: 14 day solution concentration results, first-hour solution concentration results, internal-sampler concentration results, and mass-balance calculations. Also, follow-up control tests are detailed and discussed.

3.3.1.1 Individual Test Results

A dialysis sampler was deployed within a solution for a set amount of time (1 hour or 14 days). Individual test external solutions consisted of only one metal added to DI water totaling 1 liter. Each of the following metals presented were conducted within a separate system, some were split into multiple systems with the same analyte (zinc & lead).Further details are included in the respective sections. Some results spurred additional control tests to determine causation. These tests are detailed in the respective section as well. Results are displayed as the concentration of constituent in the solution surrounding the sampler over time.

Copper. Copper was added to the surrounding solution to achieve a 110.0µg/l concentration (Keblin et al. 1997). The external measurements were analyzed and are displayed in Figure 3-2. As is apparent in the figure, equilibrium was reached within the first three days (4,350 min). This is consistent with the equilibrium time for iron and bromide found in a similar study (Vroblesky and Pravecek 2002).

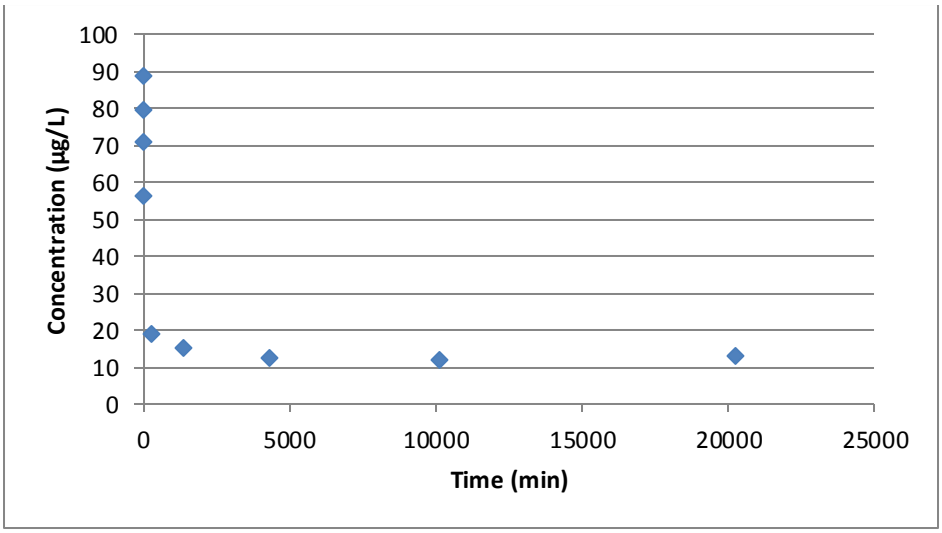

Figure 3-2 Fourteen day individual copper removal by dialysis sampler

A short equilibrium time is preferred due to the amount of time that the sampler will be exposed to the storm flows. Because of this, a closer look at the initial hour of removal is displayed in Figure 3-3. A linear best-fit equation is been included. This resulted in a coefficient of determination (R^2) of 0.9956.

The internal concentration of copper within the dialysis bag after fourteen days of deployment was 251.06 µg/l. This is much greater than the initial concentration of the surrounding solution. If diffusion is the only force at play, the concentrations both inside the dialysis bag and outside the dialysis bag should reach equilibrium at similar levels (Vroblesky and Hyde 1997). These results point to diffusion not being the only mechanism occurring within the system. This discrepancy was also noticed in a mass balance calculation detailed below.

From the mass balance calculation, a staggering 69.3% copper went missing within the system. The volume removed via sampling was 0.05 l (5%) and the mass removed totaled 2.19 µg, (only 2.0% of the total mass detected in the initial system). This led to follow-up control tests identifying adsorption onto the membrane as an influencing factor. Due to these results an elution method was developed for the dialysis samplers following deployment (detailed in section 3.2.3.3 Sampler Measurements). The elution method helped provide more accurate results.

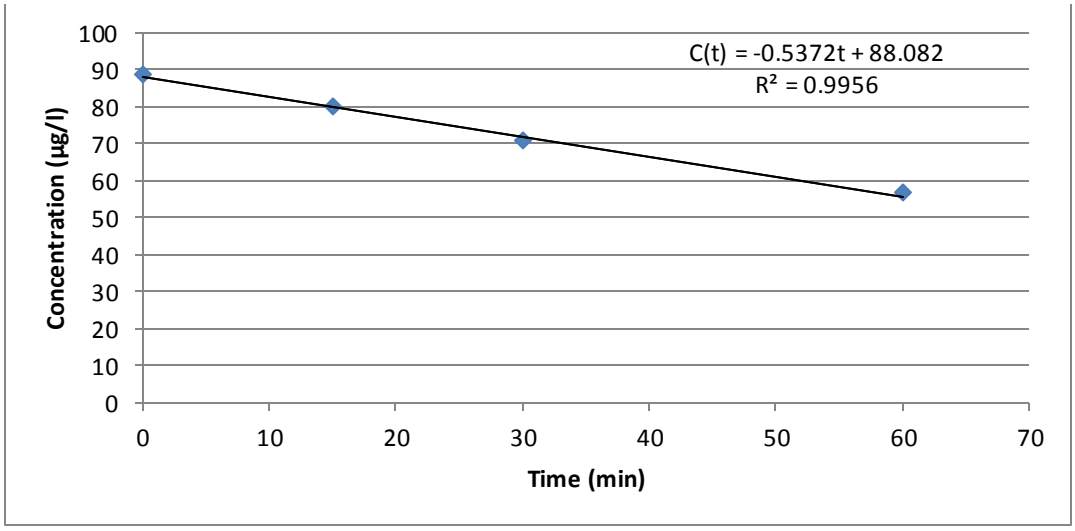

Figure 3-3 First hour individual copper removal by dialysis sampler

Lead. Lead was added to the surrounding solution to achieve a concentration of 160.0µg/l (Keblin et al. 1997). The first hour kinetics test was conducted in a separate system than the 14 day test. The 14-day test did not include the 15min, and 30 min external concentrations. External solution concentrations for the fourteen day test are displayed in Figure 3-4. Equilibrium is less apparent than the previous copper test and a slight increase occurs following an initial lead removal from the surrounding solution.

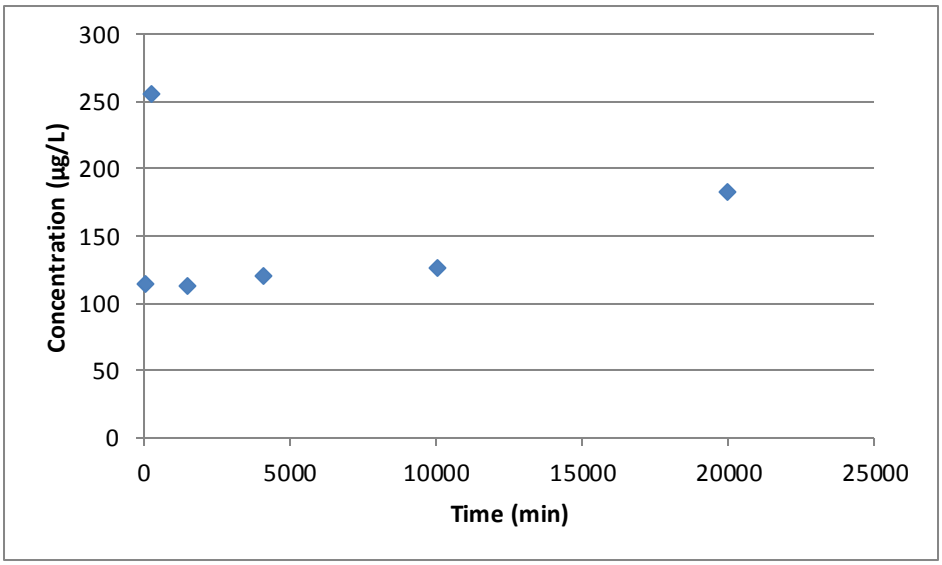

Figure 3-4 Fourteen day individual lead removal by dialysis sampler

The initial lead removal from the system is displayed in Figure 3-5 to better understand this sampler's effectiveness at collecting lead in a storm scenario. A linear best-fit equation was included and the resulting coefficient of determination was 0.8782.

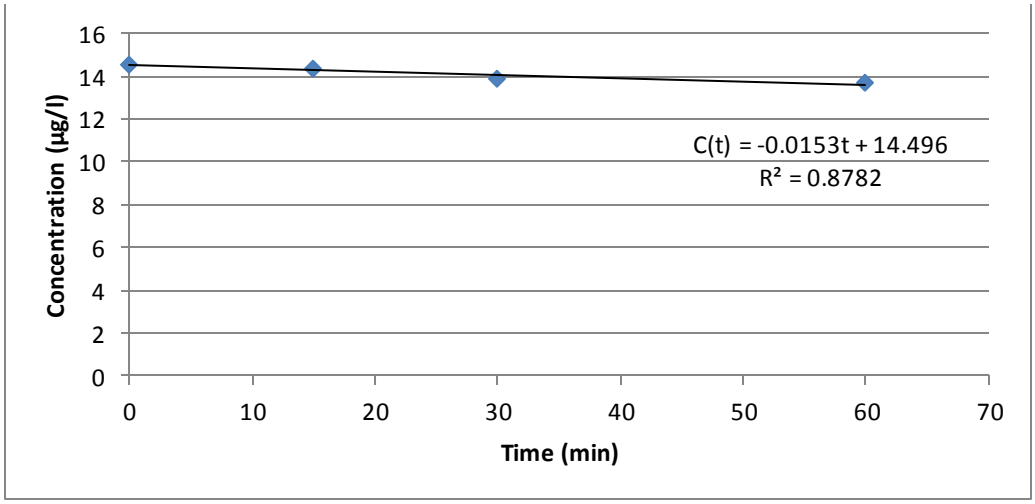

Figure 3-5 First hour individual lead removal by dialysis sampler

The internal concentration of lead within the dialysis bag after fourteen days of deployment was 128.83 µg/l. This was greater than the initial concentration of the surrounding solution, pointing to transport mechanisms other than diffusion occurring within the system (i.e. adsorption).

An elution was performed on the bag (two rinses with 10 ml of 3M nitric acid followed by two rinses (5 ml each) of DI water) and retrieved an additional 10.64 µg per bag.

Both the 14-day and 1-hour systems did not have the same issue with missing metals as did the previously described copper system. Percent losses were 2.6% and 1.5% for the 14-day and 1-hour systems respectively. Unlike Copper and Zinc, there were no instances of Lead adsorption and no follow-up control tests were performed.

Zinc. Zinc was added to the surrounding solution to arrive at the initial concentration (910.0µg/l) found in a previous study of typical stormwater pollutant levels (Keblin et al. 1997). Similar to the lead individual tests, zinc was conducted in two separate systems. The first system tested the external concentrations over 14-days and did not measure the concentrations at 15 min and 30 min. the second system focused on the first hour of uptake and include the aforementioned concentrations. The fourteen day test values are displayed in Figure 3-6. Two very high values (i.e. at 0 min &10,060 min) as well as a slight increase in zinc concentration point to minimal removal by the sampler. Equilibrium may have been met, but it cannot be determined by this data set.

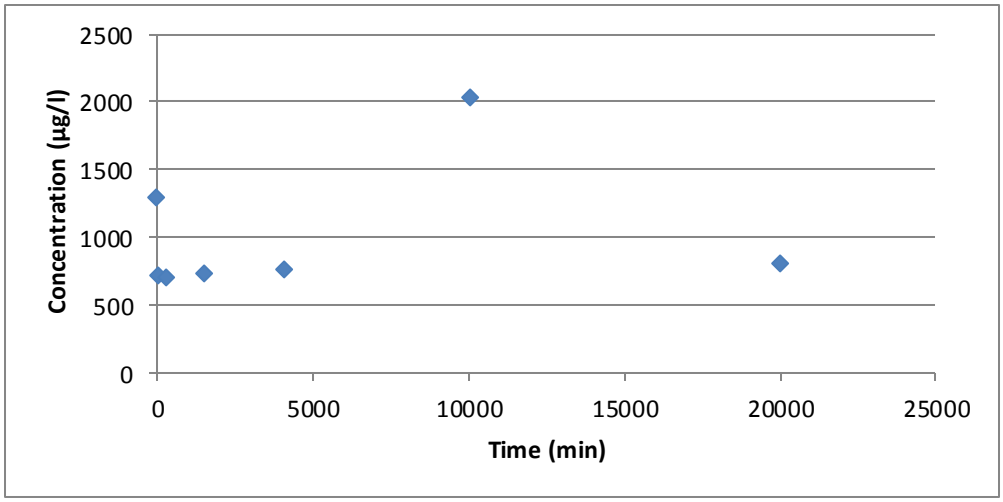

Figure 3-6 Fourteen day individual zinc removal by dialysis sampler

A look at the first hour kinetics for zinc removal by a dialysis sampler (Figure 3-7) reveals a lack of consistency in removal from the surrounding system. The best-fit equation is included within the figure. The calculated coefficient of determination is 0.0593 which reflects this inconsistency.

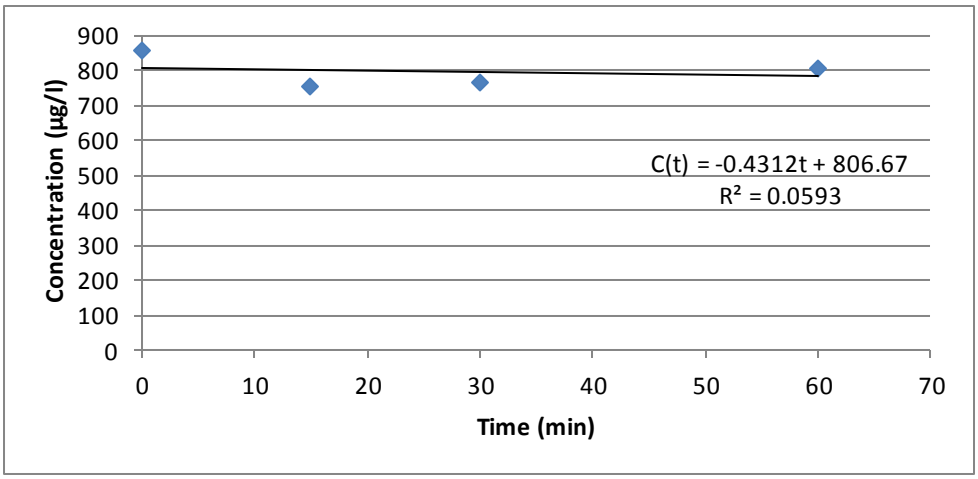

Figure 3-7 First hour individual zinc removal by dialysis sampler

The internal concentration of zinc within the dialysis bag after fourteen days of deployment was 828.41 µg/l. This is nearly the same concentration of the surrounding solution (812.14 µg/l), pointing to only diffusion occurring within the system. An elution was performed on the bag and retrieved an additional 14.05 µg. Mass balance calculations reveal the 1 hour system had no missing mass from the system, while the 14 day system was missing approximately 32.3%. Follow-up control tests were conducted to determine the cause of the missing zinc.

3.3.1.2 Tri-Metal Test Results

A dialysis sampler was deployed within a solution for a set amount of time. The tri-metal test external solution consisted of copper (110.0µg/l), lead (160.0µg/l), and zinc (910.0 µg/l) combined within DI water to total 1 liter. Results are displayed as the concentration of constituent in the solution surrounding the sampler over time. Although each metal is presented separately, metals were all analyzed from the same samples.

Copper. External copper concentrations are displayed in Figure 3-8. Copper behavior is different than the copper individual tests. As can be seen, initial removal from the surrounding solution occurred, followed by a partial increase of copper back into solution.

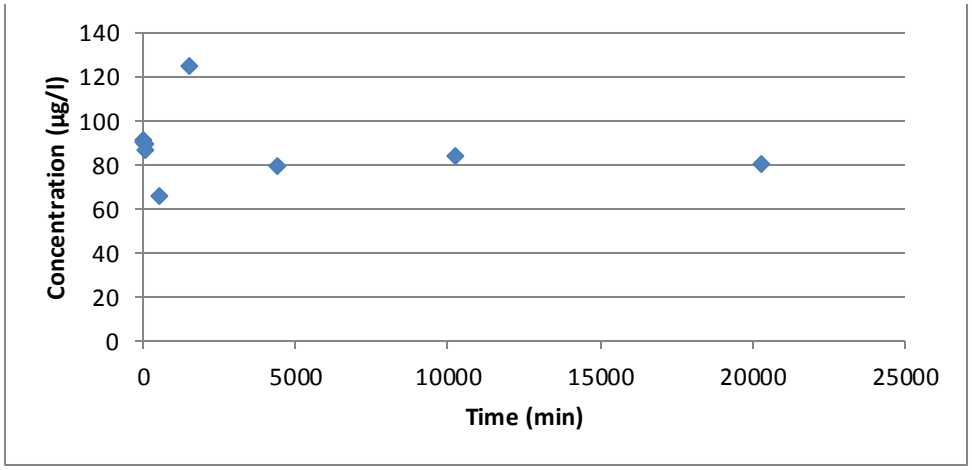

Figure 3-8 Fourteen day tri-metal copper removal by dialysis sampler

The first hour kinetics of copper within the tri-metal test is included in Figure 3-9. A best-fit liner equation is included and the trend line is displayed. The linear coefficient of determination is 0.9729 pointing to a very predictable removal of copper from the system, even with the presence of other similarly charged metals.

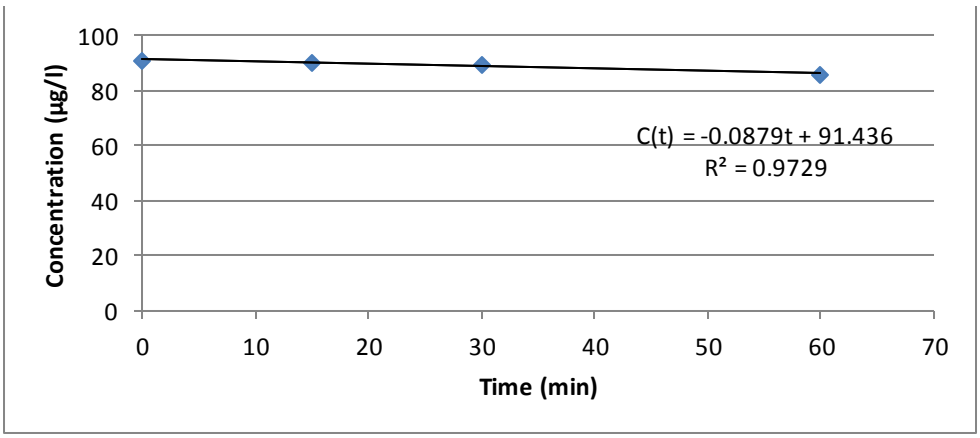

Figure 3-9 First hour tri-metal copper removal by dialysis sampler

The internal concentration of copper within the dialysis bag after fourteen days of deployment was 85.89 µg/l. This is close to the concentration of the surrounding solution when it was collected (86.48 µg/l at 14 d). The elution procedure produced a total of 2.41 µg, a relatively small amount of the total copper within the system. Unlike the individual test for copper, this points to diffusion being the main mechanism of analyte kinetics. Mass balance calculations conducted on copper within the system show that from the initial system to the final (fourteen day difference) 3.8% of copper was missing. This is significantly less than the 69.3% copper that went missing within the individual test for copper.

Lead. External lead concentrations are displayed in Figure 3-10. Lead behavior is similar to the lead individual tests in that the amount in the surrounding solution increased slightly after an initial removal. This could be due to a release of lead into the system by the membrane itself, but this is inconsistent with previous studies. Another test monitored leaching of trace metals from this same membrane and found that after seven days less than 2.1 µg/l were released (Ehlke et al. 2004).This is an order of magnitude smaller than the increase of lead noted in this test (21.78 µg/l).

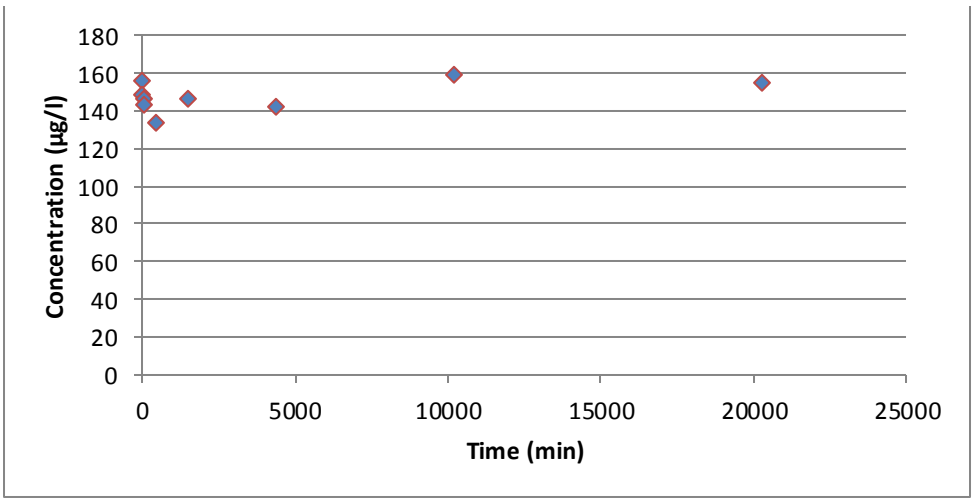

Figure 3-10 Fourteen day tri-metal lead removal by dialysis sampler

The first hour kinetics of lead within the tri-metal test is shown in Figure 3-11. A best-fit liner equation is included and the trend line is displayed. Although the coefficient of determination is 0.8381, the overall removal from the system is very slow, same to that in the individual lead test.

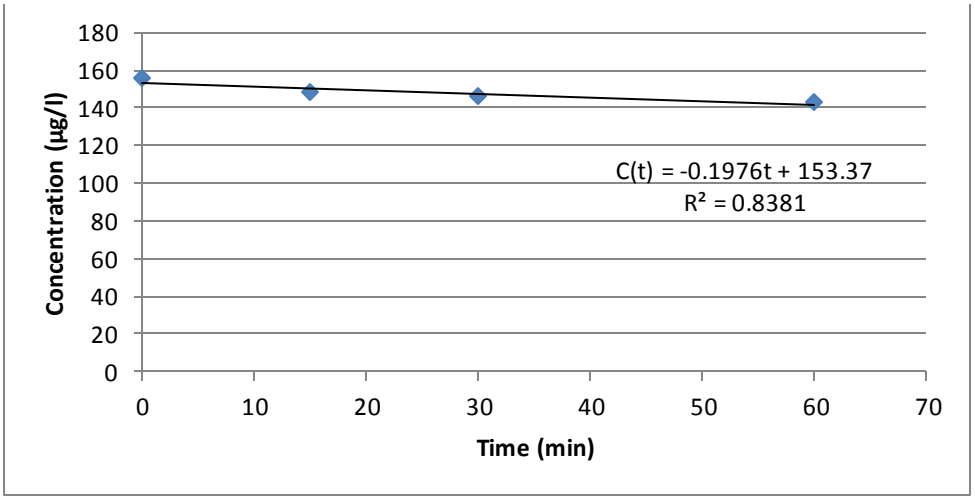

Figure 3-11 First hour tri-metal lead removal by dialysis sampler

The internal concentration of lead within the dialysis bag after fourteen days of deployment was 148.85 µg/l. This is close to the concentration of the surrounding solution when it was collected (150.83 µg/l at 14 days). The elution produced a total of 1.55 µg, much less than the 10.64 µg eluted in the individual lead test.

Mass balance calculations reveal -5.4% total lead missing from the system. This increase of lead within the system is consistent with the kinetics values displayed in Figure3-10. This small amount of total increase/decrease within the system is consistent with the lead individual test.

Zinc. Zinc tri-metal kinetics is displayed in Figure 3-12. Zinc behavior in the tri-metal system is similar to the zinc individual tests in that the amount in the surrounding solution increased slightly. This could be due to a release of zinc into the system by the membrane itself as is listed by the membrane manufacturers. The test performed by Ehlke et al. mentions zinc leaching but does not quantify the amount (Ehlke et al. 2004).

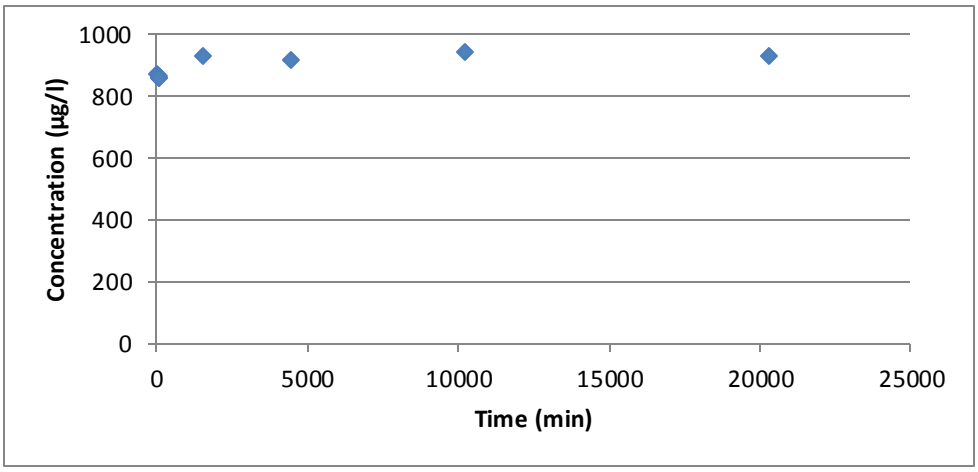

Figure 3-12 Fourteen day tri-metal zinc removal by dialysis sampler

The first hour kinetics of zinc within the tri-metal test is shown in Figure 3-13. A best-fit liner equation is included and the trend line is displayed. Although the coefficient of determination is 0.9011, the overall removal from the system is low, same to that in the individual lead test.

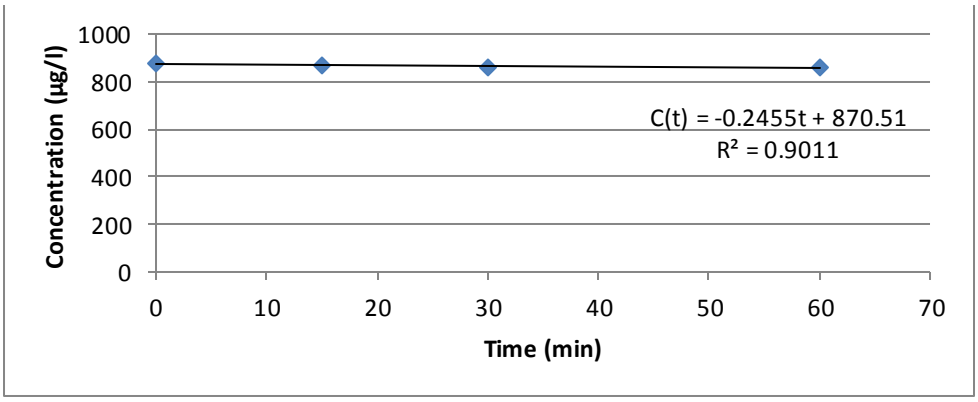

Figure 3-13 First hour tri-metal zinc removal by dialysis sampler

The internal concentration of zinc within the dialysis bag after fourteen days of deployment was 880.42 µg/l. This is close to the concentration of the surrounding solution when it was collected (933.87 µg/l at 14 d). The elution produced a total of 2.41 µg, much less than the 14.05 µg eluted in the individual zinc test.

Mass balance calculations reveal -12.8% total lead missing from the system. This increase of lead within the system is consistent with the kinetics values displayed in Figure 3-12. This amount of total increase within the system varies from the 33.2% zinc missing from the individual zinc test.

3.3.1.3 Stormwater Test Results

A dialysis sampler was deployed within a solution of synthetic stormwater for a set amount of time based on previous stormwater constituents and their concentrations (Keblin et al. 1997). The synthetic stormwater test external solution consisted of copper (0.11 mg/l), lead (0.16 mg/l), and zinc (0.91mg/l) as well as sodium carbonate (0.9 mg/l), sodium chloride (200 mg/l), kaolin (60 mg/l), and pond sediment (500 mg/l) combined within DI water to total 1 liter. Metal results were analyzed and are displayed as the concentration of constituent in the solution surrounding the sampler over time. Although each metal is presented separately, metals were analyzed from the same samples.

Copper. External copper concentrations are displayed in Figure 3-14. Copper behaved differently than the copper individual and tri-metal tests. As can be seen, initial removal from the surrounding solution occurred, followed by a steady increase of copper back into solution. Due to this unexpected result, follow-ups to determine if desorption was occurring were conducted.

The first hour kinetics of copper within the stormwater test is shown in Figure 3-15. The best-fit liner equation is included and the trend line is displayed. The coefficient of determination is 0.8117. The rate of copper removal is slower than the individual and faster than the tri-metal tests. The internal concentration of copper within the sampler after fourteen days of deployment was 97.92 μg/l. The surrounding solution concentration was 97.13 μg/l, almost identical. The elution produced a mass of 4.11 μg, approximately 4.0% of the total mass. These statistics point to minimal copper adsorption occurring by the end of the experiment. From the mass balance

calculation, 2.0% copper went missing within the system. This is comparable to the tri-metal test (3.8%) but not the individual copper test (69.3%).

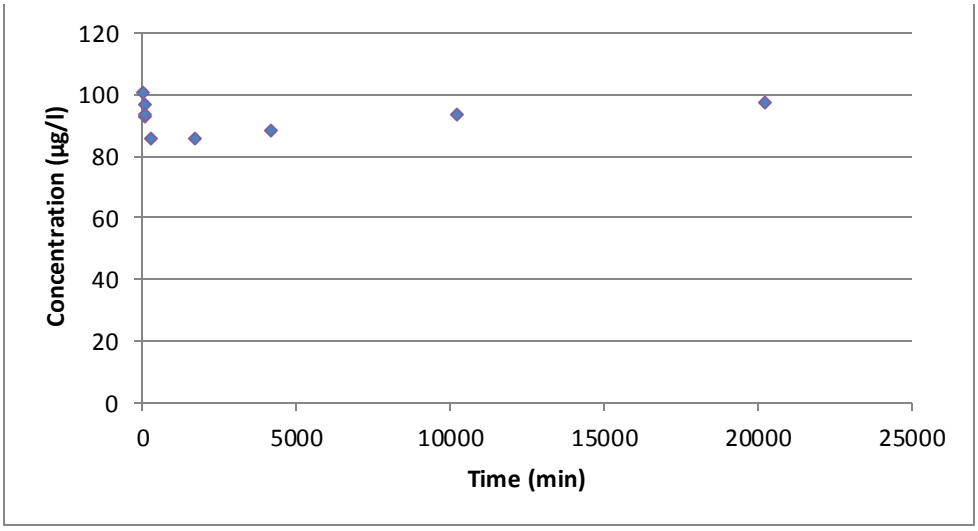

Figure 3-14 Fourteen day stormwater copper removal by dialysis sampler

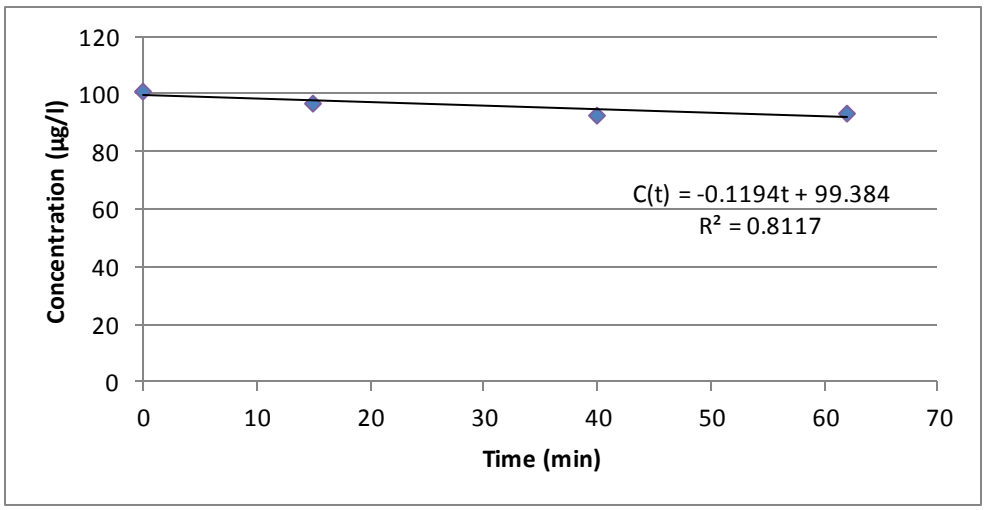

Figure 3-15 First hour stormwater copper removal by dialysis sampler

Lead. Lead concentrations in the surrounding stormwater solution are displayed in Figure 3-16. Unlike the individual and tri-metal tests, lead removal was as expected for a diffusion system. This is shown by the fast initial removal and then a gradual shift towards an equilibrium concentration.

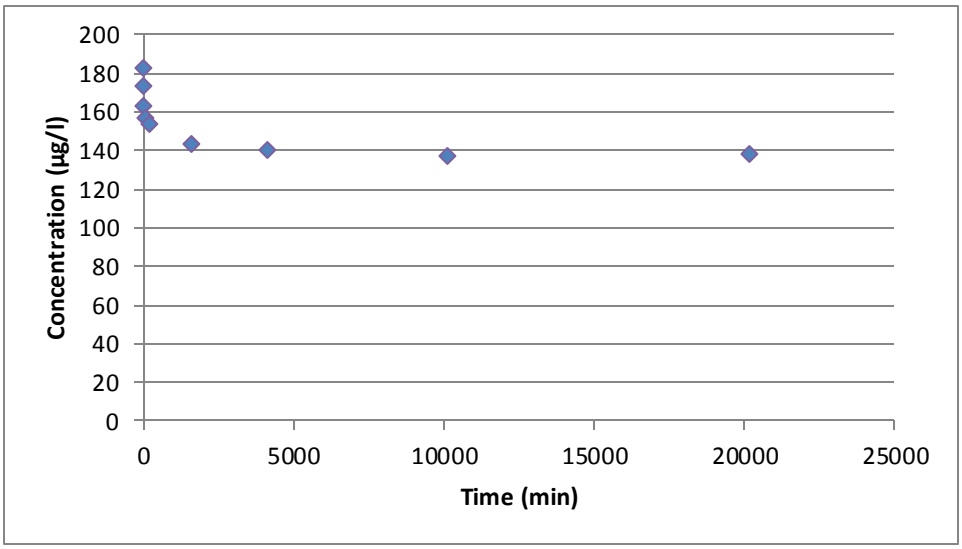

Figure 3-16 Fourteen day stormwater lead removal by dialysis sampler

Lead removal from the surrounding stormwater solution within the first hour is shown in Figure 3-17. The coefficient of determination is 0.9794. The best-fit liner equation is included and the trend line is displayed. The rate of lead removal is faster than both the individual and tri-metal tests.

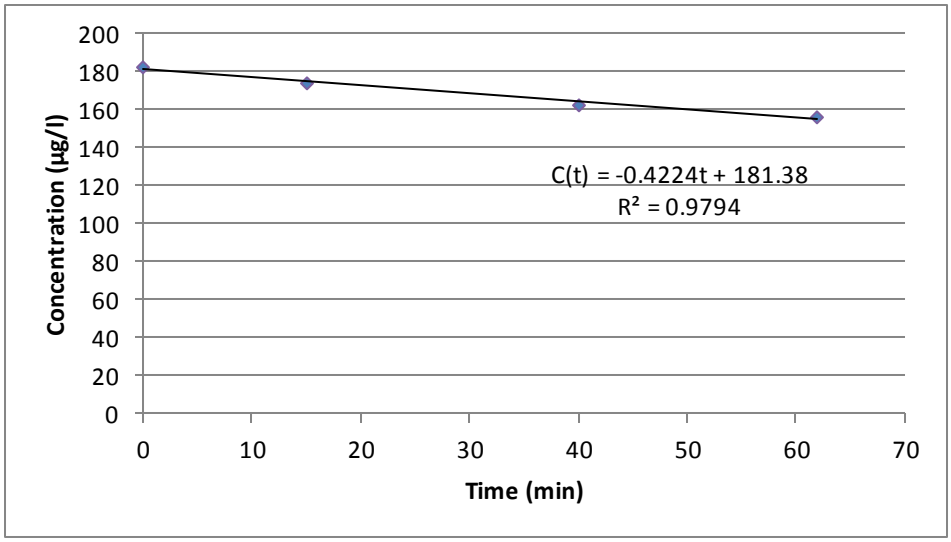

Figure 3-17 First hour stormwater lead removal by dialysis sampler

Internal lead concentration within the sampler following deployment was 140.67 µg/l. The surrounding solution concentration was 138.9 µg/l, almost identical. The elution produced a mass

of 2.83 µg, approximately 1.5% of the total mass. Internal calculations, in combination with the fourteen-day removal kinetics (Figure 3-16), point to diffusion as the main mechanism at work.

Missing lead in the system was 21.8%, however. Compared to the individual (2.6% & 1.5%) and tri-metal (-5.4%) experiments, this is a much larger mass missing.

Zinc. External zinc concentrations are displayed in Figure 3-18. Individual, tri-metal and stormwater tests showed zinc behaving in a similar manner, decreasing initially then increasing. Follow-up experiments were conducted to look into this behavior.

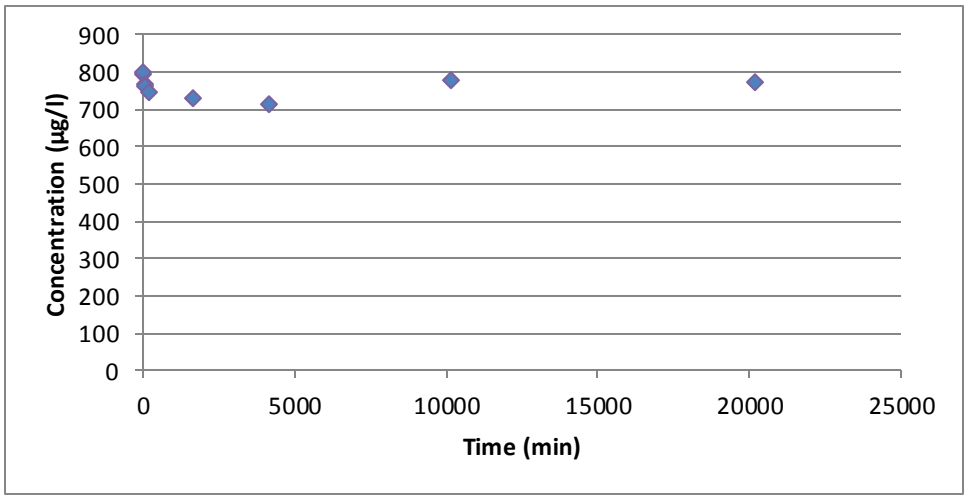

Figure 3-18 Fourteen day stormwater zinc removal by dialysis sampler

First hour removal of zinc from the surrounding stormwater solution is shown in Figure 3-19. The best-fit liner equation is included and the trend line is displayed. The coefficient of determination is 0.8132. Zinc removal rate by a dialysis sampler within synthetic stormwater is greater than the zinc-only solution and the tri-metal solution.

Internal concentration of zinc within the sampler was 781.20 µg/l while the surrounding solution contained a concentration of 772.96 µg/l. The elution produced a mass of 3.92 µg, approximately 0.5% of the total mass. Mass balance calculations were conducted. Missing zinc in

the system was 7.7%, compared to the individual (0.0% &32.3%) and tri-metal (-12.8%) experiments, this is a moderate amount missing

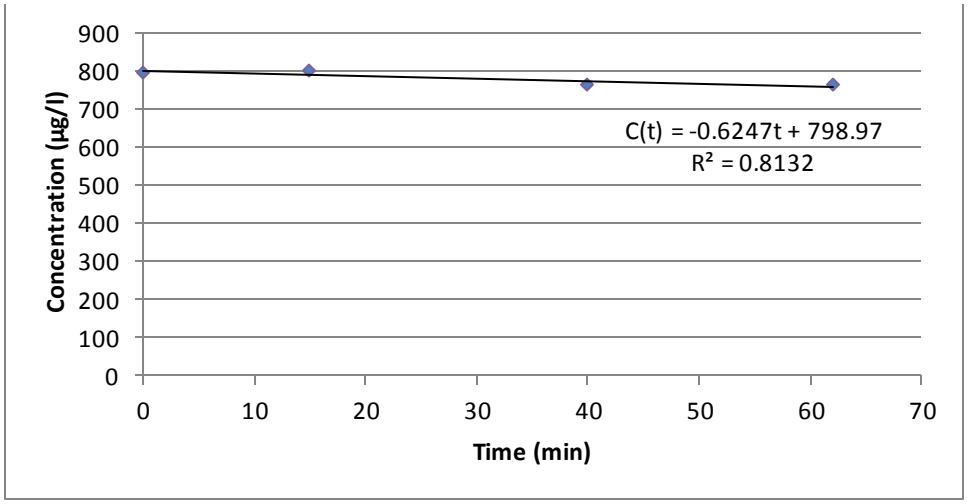

Figure 3-19 First hour stormwater zinc removal by dialysis sampler

3.3.1.4 Dialysis Control Test Results

Various control tests for the dialysis sampler were conducted to determine the cause of some unexpected results. Results for glassware, adsorption, and desorption tests are presented for zinc and copper, both metals that had kinetics results that pointed towards adsorption and desorption mechanisms occurring.

Glassware & Clamps. Both copper and zinc control tests pointed to a minimal amount of metal removal. Copper missing within the system was 4.1%, and zinc gained a slight amount of mass (-2.1%). Figures 3-20 & 3-21 display the three-day solution concentration. This shows that the clamps and glassware were not the sources of zinc or copper removal from the solution within the batch tests.

Adsorption. A simple test was conducted to show copper adsorption. Figure 3-22 presents the concentration of a copper solution surrounding a sheet of dialysis membrane (4 inches by 4

inches). 65.9% of copper within the solution went missing over the fourteen days of exposure. This explains the copper individual test missing 69.3%.

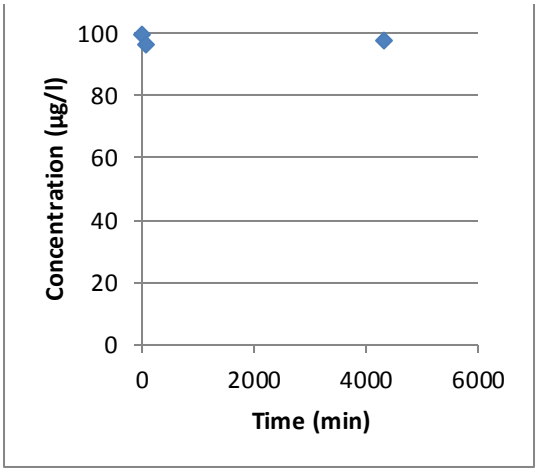

Figure 3-20 Glassware copper removal

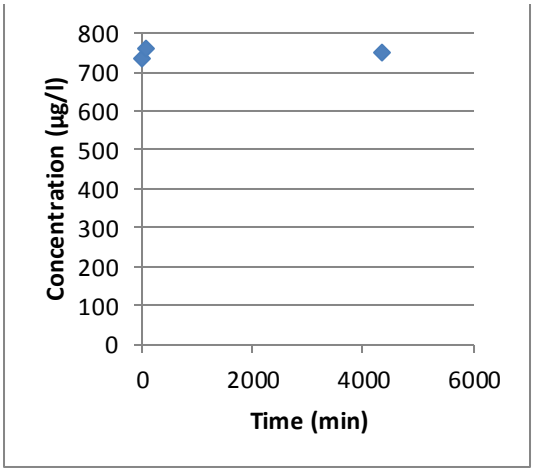

Figure 3-21 Glassware zinc removal

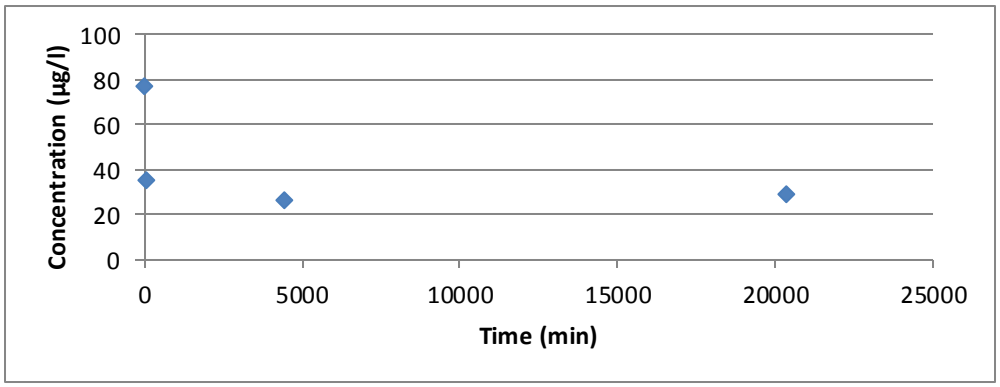

Figure 3-22 Copper removal by dialysis membrane

Desorption. Four separate systems of dialysis sheets were employed to determine the cause of zinc and copper removal and release in surrounding solutions. Figure 3-23 presents the zinc concentrations released into the surrounding solution. The percentages released from the initial exposures are 0.1% and 1.8% for landfill (500 mg/l) and stormwater (0.16 mg/l) concentrations, respectively. These are much lower than the percent of zinc released after removal in the stormwater test (6.6%).

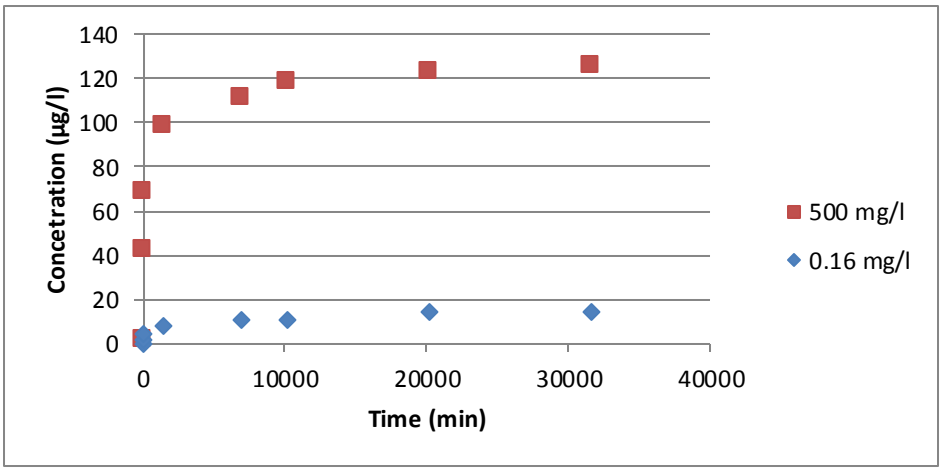

Figure 3-23 Release of zinc by dialysis membranes

Figure 3-24 presents the copper concentrations released into the surrounding solution. The percentages released from the initial exposures are 0.3% and 3.7% for the landfill (5 mg/l) and stormwater (0.11 mg/l) concentrations, respectively. These are also much lower than the percent of copper released after removal in the stormwater test: 10.6%. Also, the amount of copper adsorbed from the stormwater solution in the adsorption phase of the experiment (2.5%) was significantly less than previously noted, compared to 56.6% removal within the first hour of the copper adsorption control test. The reason for this difference is not determined within this study.

3.3.1.5 Dialysis Sampler Discussion

Regenerated cellulose dialysis membrane performed differently depending on the type of heavy metal it was exposed to. High amounts of irregularity were noted under the various chemical scenarios the membrane was deployed in. Uptake, adsorption and metal release were all noted and the causes were not determined. This may be due to the slightly negative charge which could explain varying cation concentrations surrounding and within the sampler after equilibrium is met (Ehlke et al. 2004).

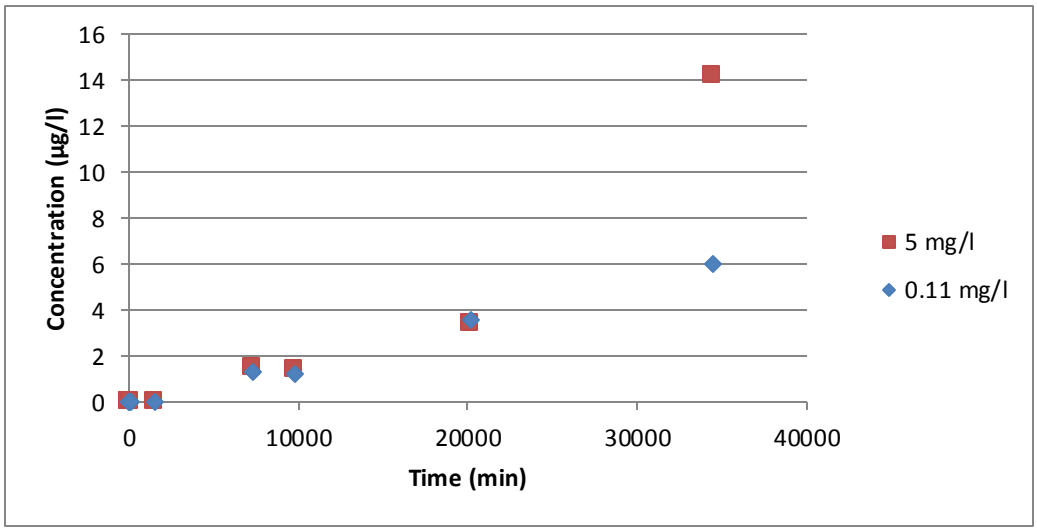

Figure 3-24 Release of copper by dialysis membranes

Zhou et al. (2004) noted a metal bio-sorption process onto cellulose beads, a similar compound as the regenerated cellulose which could shed light on the poor sampler performance within this study. The process is described as a complex forming with the heavy metal and an amine nitrogen structure within cellulose. More heavy metals adsorb near the complex, and finally hydrolysis of the complex occurs and the complex is precipitated. Adsorption and desorption tests were conducted but most adsorption and desorption occurred within the first 24 hours, a much shorter time span than the phenomenon described in previous sections of this report.

A similar sampler was developed and studied in the late 1980s by Morrison (Morrison 1987; Morrison 1989). This sampler consists of a dialysis membrane filled with ultrapure water and a chelating receiving resin and is called dialysis with receiving resins. The focus of the study was to use these passive samplers for stormwater monitoring. This sampler worked in two ways: the membrane would allow some metals to pass through and attach to the receiving resins or the metals would adsorb to the membrane itself.

Dialysis with receiving resins were placed within various sampling sites and analyzed. Metal uptake rates for both the membrane and resin were presented. Table 3.3 compares the

membrane uptake rates from these studies with the tri-metal and stormwater tests mentioned within this report.

It is important to note that the exposure time for the tri-metal and stormwater tests was fourteen days, whereas the length the dialysis with receiving resin samplers were deployed is not mentioned. The dialysis with receiving resins samplers were also exposed to flow-through conditions while the dialysis membranes in this study were deployed within a batch system with a limited amount of available metal mass. Another difference is the material used to make the dialysis membranes. Morison used Spectrapor wet cellulose tubing with a molecular cut-off of 1000 Dalton vs. the regenerated cellulose tubing with 8,000 Dalton molecular weight cut-off used in this report.

The comparison of uptake rates in Table 3.3 shows that all three metals had very similar uptake rates, whereas the Morrison studies varied between the metals. This could be due to differing available concentrations of copper, lead, and zinc. The low rate of lead uptake can be explained by the formation of complexes by dissolved organic and inorganic compounds. A high presence of these complex causing compounds in the sewage plant influent and effluent could explain the non-detectable lead rates for those sampling stations within that study.

Overall, the dialysis sampler performed much worse than anticipated under the various scenarios it was deployed in. Inconsistent uptakes for some but not all metals only decreased the feasibility as a stormwater sampler. In addition, adsorption and the release of metals after apparent uptake add complexity to what promised to be a simple calculation. Based on this series of batch tests, dialysis samplers are not recommended for passive monitoring of highway stormwater BMPs.

3.3.2 Ion Exchange Resin Sampler

Ion exchange resin sampler results are presented with three of the same main components as the dialysis sampler results: fourteen day solution concentration results, internal sampler

concentration results, and mass balance calculations. Follow-up control tests are detailed and discussed as well.

The initial ion exchange uptake kinetics fits within a first-order curve and thus the first hour was adjusted by determining the natural log of the concentration. These figures plot the natural log of the concentration on the y-axis and time on the x-axis. Equations presented are in the following form of Equation 3-1:

$$\boldsymbol{ln(C) = -kt + ln(C_0)} \tag{3-1}$$

where C = concentration of metal within solution (µg/l); k = rate constant (min^{-1}); t = time (min); and C_0 = initial metal concentration (µg/l). From the batch tests, the rate constants could be determined. Then only the time of exposure and the elution mass would be needed. For equation 3-1, C_0 is the only unknown, because the k is already determined, the elution will be found, and the time should be recorded. An analysis assessing this approach is given within section 3.3.2.5 (Ion Exchange Resin Sampler Discussion).

3.3.2.1 Individual Test Results

An Amberlite IRC748 chelating ion exchange resin sampler was deployed within a solution for a set amount of time (3 days). Individual test external solutions consisted of only one metal added to DI water totaling 1 liter. Each of the following metals presented were conducted within a separate system. Overall results are displayed as the concentration of constituent in the solution surrounding the sampler over time.

Table 3-3 Comparison of metal adsorption rates (pg mm^{-2} h^{-1}) onto dialysis membranes

	This Study			Morrison 1987						Morrison 1989			
				Ryaverket[a]									
	Tri-metal	Storm-water	Avg.[1]	Influent	Effluent	B1[b]	B2[c]	Floda[d]	Avg.	B1	B2	Floda	Avg.
Copper	1.41	2.41	1.91	3.00	3.00	2.60	22.40	1.90	6.58	2.60	23.70	1.90	9.40
Lead	1.56	1.65	1.61	nd[e]	nd	0.89	1.10	0.50	0.83	0.89	1.30	0.50	0.90
Zinc	0.91	2.29	1.60	26.80	11.20	2.90	2.40	2.20	9.10	2.90	2.70	2.20	2.60

[a]Ryaverket = Ryaverket sewage treatment plant in Goteborg, Sweden

[b]B1 = Backebolsmotet, a stormwater outfall sampling site which drains a section of the E6 motorway north of Goteburg, Sweden

[c]B2 = Bersjon, a sampling station within a residential area of Goteburg, Sweden

[d]Floda = Floda, a sampling station in northeast Goteburg, Sweden

[e]nd = not detected

[1]Avg. = Average uptake rate study for entire study

Copper. Copper individual metal tests were conducted in parallel, average results are presented. Copper was added to the surrounding solution to achieve a 110.0 µg/l concentration (Keblin et al. 1997). The external measurements were analyzed and are displayed in Figure 3-25. Equilibrium was reached within the first three days (4,280 min). This is consistent with the equilibrium time for Amberlite IRC 748 in other studies (Lin and Juang 2005; Mumford et al. 2008).

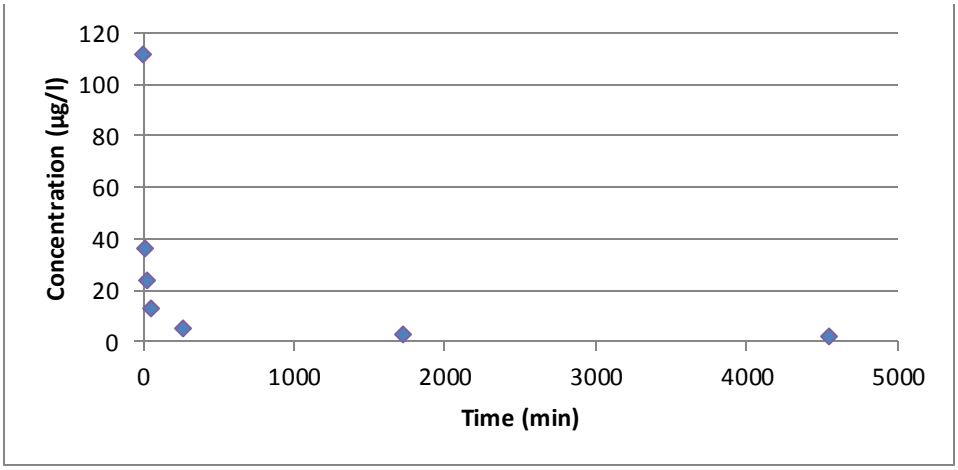

Figure 3-25 Three day individual copper removal by ion exchange resin sampler

A fast initial uptake is preferred due to the limited time that the sampler will be exposed to the storm flows. Because of this, a closer look at the initial hour of removal is displayed in Figure 3-26. The natural log of the concentration is presented on the y-axis and time on the x-axis. This resulted in a coefficient of determination of 0.8879 and the rate is significantly greater than the dialysis sampler removal. The percent mass removed from the system within the first hour was 88.5%.

Total mass removed from the system by the ion exchange resin was 108.42µg (96.9%). A rudimentary elution (described in section 3.2.3.3 Sampler Measurements) was performed on the resin following deployment and 54.41 µg were retrieved. The total mass lost from the system was 51.4%. This is a significant amount of mass missing from the system and led to a revision of the

elution procedure. Elution details are available in section 3.3.2.4 (Ion Exchange Resin Control Test Results).

Lead. Lead was added to the surrounding solution to achieve a concentration of 160.0 µg/l (Keblin et al. 1997). External solution concentrations for the three day test are displayed in Figure 3-27. Equilibrium was reached within the first three days (4,280 min).

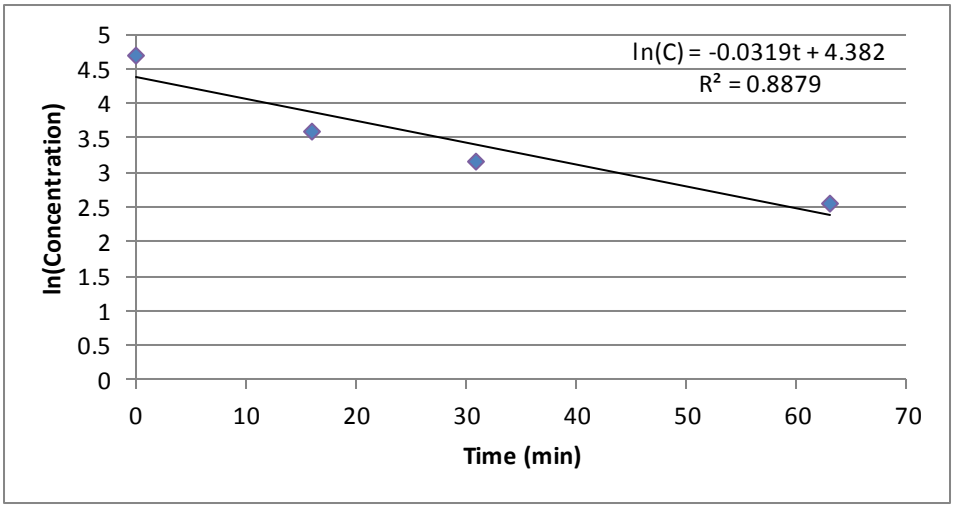

Figure 3-26 First hour individual copper removal by ion exchange resin sampler

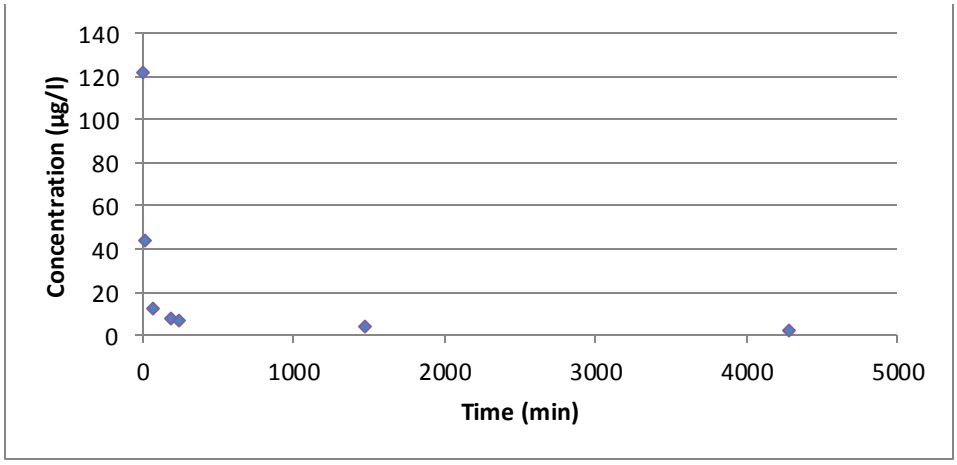

Figure 3-27 Three day individual lead removal by ion exchange resin sampler

A closer look at the initial hour of removal is displayed in Figure 3-28. The uptake follows first order uptake kinetics, thus the natural log of the concentration is presented on the y-axis and time on the x-axis. This resulted in anR^2 value of 0.9547 and the equation is included within the figure. The percent lead removed from the system within the first hour was 95.1%.

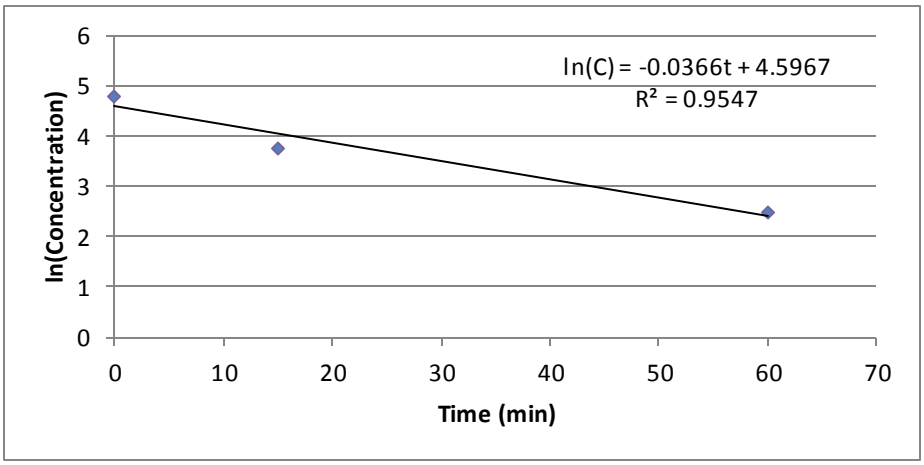

Figure 3-28 First hour individual lead removal by ion exchange resin sampler

The total lead removed from the system by the ion exchange resin was 140.86 µg (97.5%). A flow-through elution procedure (described in section 3.2.3.3 Sampler Measurements) was attempted on the resin following deployment. Elution was compromised due to clogging. As a result, no values were attained for this test

Zinc. Zinc individual kinetics is displayed in Figure 3-29. Zinc concentrations in the surrounding solution increased slightly. Equilibrium was reached within the first three days (4,280 min). The Amberlite IRC 748 uptake of zinc shown in this study is comparable to that in a separate study (Lin and Juang 2005).

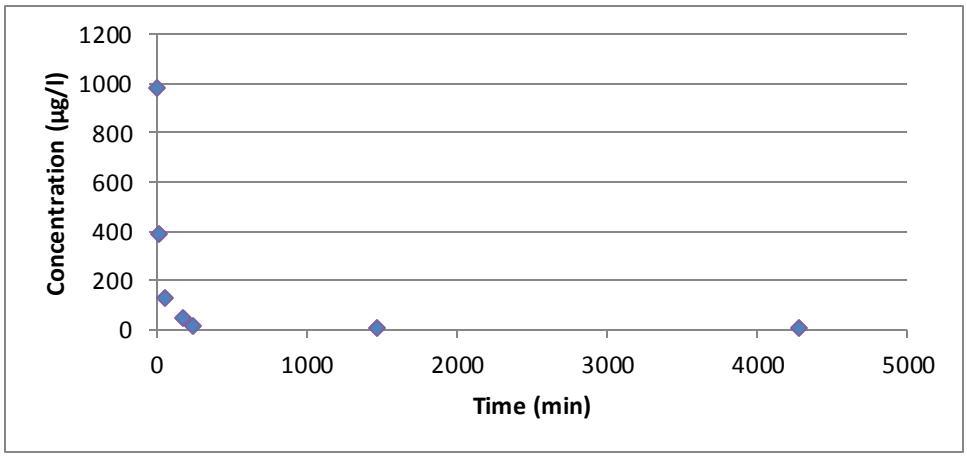

Figure 3-29 Three day individual zinc removal by ion exchange resin sampler

The initial hour of removal is displayed in Figure 3-30. The natural log of the concentration is presented on the y-axis and time on the x-axis. A linear best-fit equation is been included. This resulted in a coefficient of determination of 0.9464. The percent mass removed from the system within the first hour was 95.8%.

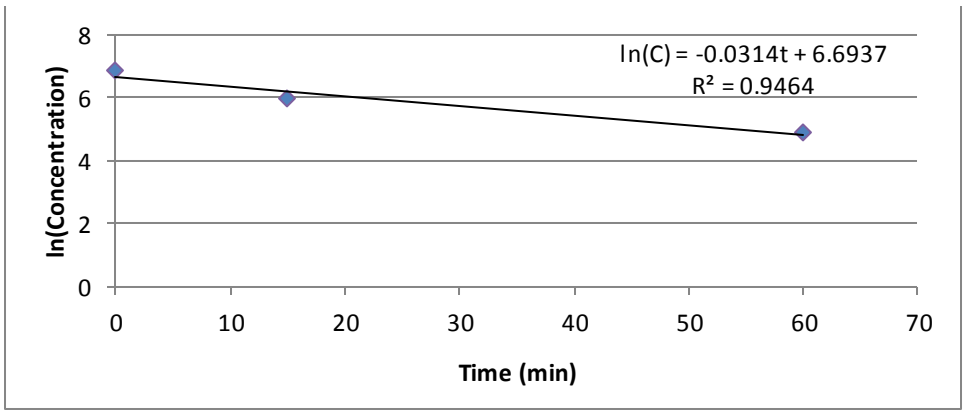

Figure 3-30 First hour individual zinc removal by ion exchange resin sampler

The total zinc removed from the system by the ion exchange resin was 1188.75 µg (98.3%). Clogging also occurred during the elution attempt for the resin within this system, similar to that which happened during the elution of the lead individual test for the ion exchange resin sampler.

3.3.2.2 Tri-Metal Test Results

Anion exchange resin sampler was deployed within a solution for three days. The external solution for the tri-metal test consisted of copper (110.0 µg/l), lead (160.0 µg/l), and zinc (910.0 µg/l) combined within DI water to total 1 liter. Results are displayed as the concentration of constituent in the solution surrounding the sampler over time. Although each metal is presented separately, metals were all analyzed from the same samples.

Copper. The external measurements of copper are displayed in Figure 3-31. Equilibrium was reached within the first three days (4,280 min). This was again consistent with the equilibrium time for Amberlite IRC 748 in other studies (Lin and Juang 2005; Mumford et al. 2008). The presence of zinc and lead within the system did not contribute a significant amount of competition for adsorption sites.

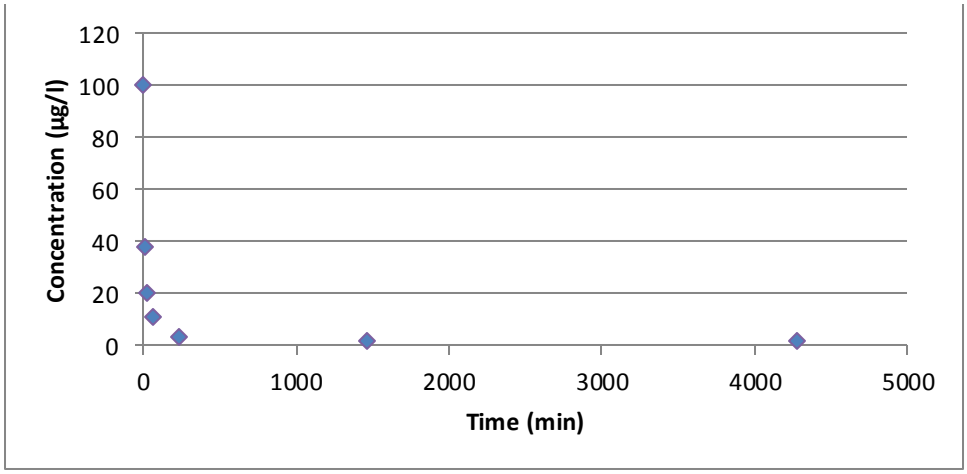

Figure 3-31 Three day tri-metal copper removal by ion exchange resin sampler

The initial hour of copper removal is displayed in Figure 3-32. The natural log of the concentration is presented on the y-axis and time on the x-axis. The coefficient of determination of the best fit line was 0.9232, the equation is included within the figure. The percent copper removed from the system within the first hour was 91.0%.

Total mass of copper removed from the system by the ion exchange resin was 115.79µg (98.5%). The finalized elution procedure (described in section 3.2.3.3 Sampler Measurements) was

performed on the resin following deployment and 105.07 µg were retrieved. The total mass lost from the system was 7.8%. This points to the elution procedure being much more effective.

Lead. The external measurements of lead are displayed in Figure 3-33. Equilibrium was reached within the first three days (4,280 min). The presence of copper and zinc within the system did not contribute a significant amount of competition for adsorption sites.

The initial hour of lead removal is displayed in Figure 3-34. The natural log of the concentration is presented on the y-axis and time on the x-axis. The coefficient of determination of the best fit line was 0.9438, the equation is included within the figure. The percent lead removed from the system within the first hour was 96.9%.

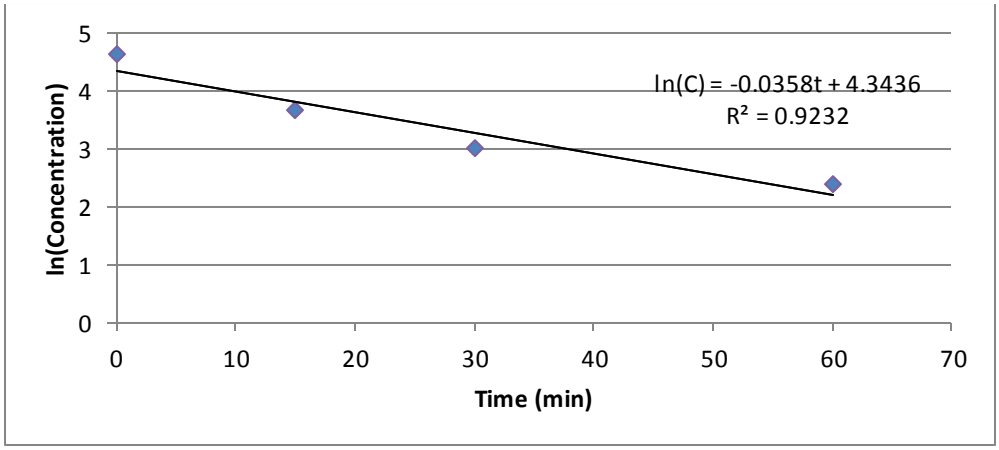

Figure 3-32 First hour tri-metal copper removal by ion exchange resin sampler

Total mass of lead removed from the system by the ion exchange resin was 147.31µg (100.0%). The finalized elution procedure (described in section 3.2.3.3 Sampler Measurements) was performed on the resin following deployment and 102.15 µg were retrieved. The total mass lost from the system was 30.33%.

Zinc. The external measurements of zinc are displayed in Figure 3-35. Equilibrium was reached within the first three days (4,280 min). The presence of copper and lead within the system did not contribute a significant amount of competition for adsorption sites.

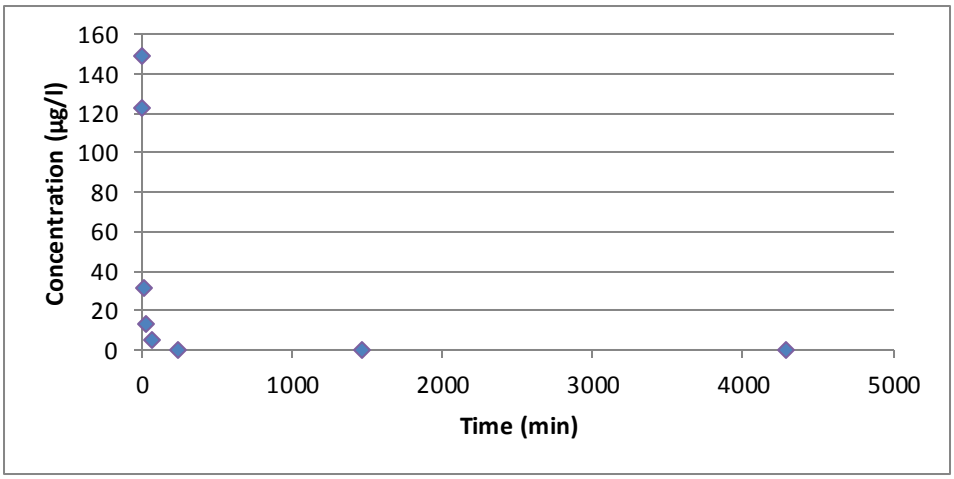

Figure 3-33 Three day tri-metal lead removal by ion exchange resin sampler

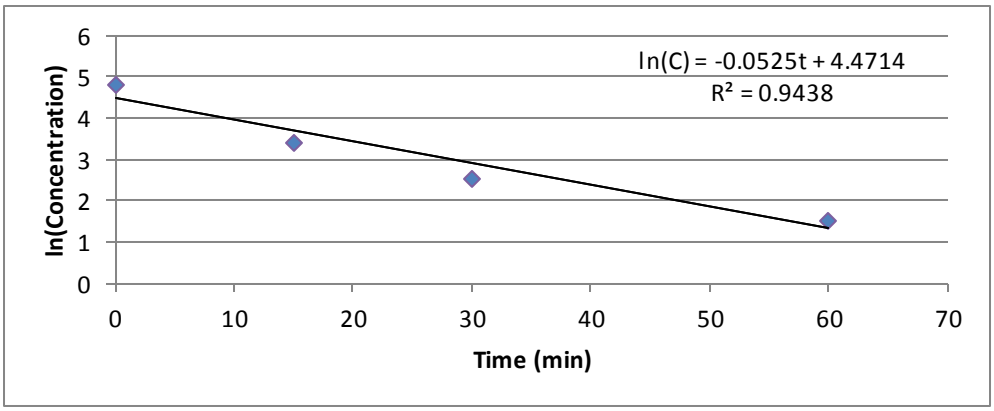

Figure 3-34 First hour tri-metal lead removal by ion exchange resin sampler

Zinc removal during the first hour of exposure is displayed in Figure 3-36. The natural log of the concentration is presented on the y-axis and time on the x-axis. The coefficient of determination of the best fit line was 0.9855, the equation is included within the figure. The percent zinc removed from the system within the first hour was 97.2%.

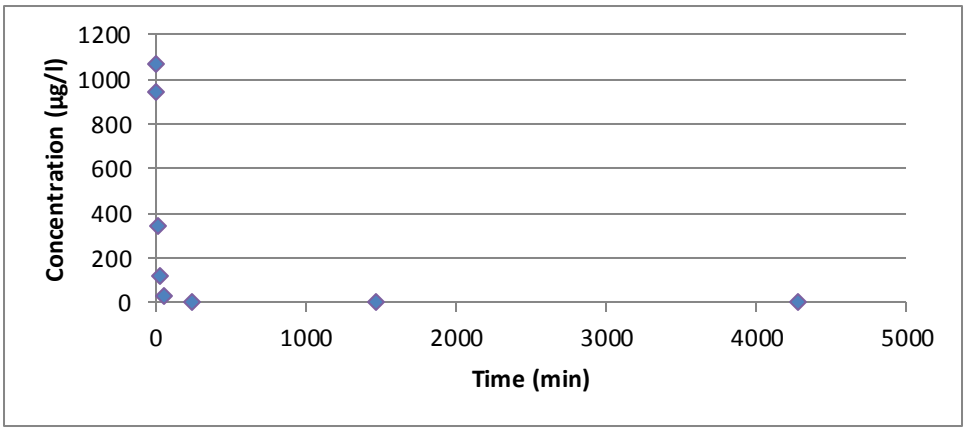

Figure 3-35 Three day tri-metal zinc removal by ion exchange resin sampler

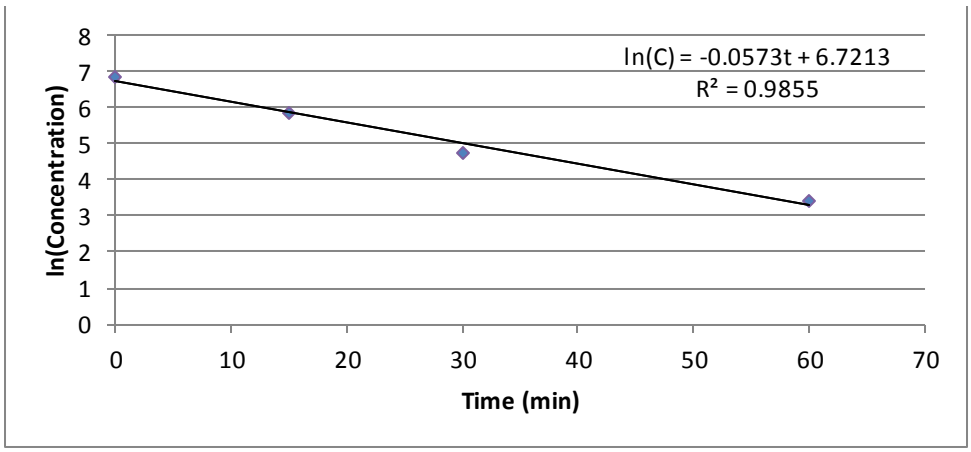

Figure 3-36 First hour tri-metal zinc removal by ion exchange resin sampler

Total mass of zinc removed from the system by the ion exchange resin was 1053.99µg (99.8%). The finalized elution procedure (described in section 3.2.3.3 Sampler Measurements) was performed on the resin following deployment and 1,175.35 µg were retrieved. The total mass lost from the system was -11.4%.

3.3.2.3 Stormwater Test Results

Anion exchange resin sampler was deployed within a solution of synthetic stormwater for a set amount of time based on previous stormwater constituents and their concentrations (Keblin et al. 1997). The synthetic stormwater test external solution consisted of copper (0.11 mg/l), lead (0.16

mg/l), and zinc (0.91 mg/l) as well as sodium carbonate (0.9 mg/l), sodium chloride (200 mg/l), kaolin (60 mg/l), and pond sediment (500 mg/l) combined within DI water to total 1 liter. Metal results were analyzed and are displayed as the concentration of constituent in the solution surrounding the sampler over time. Although each metal is presented separately, metals were analyzed from the same samples.

Copper. The external measurements of copper are displayed in Figure 3-37. Equilibrium was reached within the first three days (4,280 min). This was again consistent with the equilibrium time for Amberlite IRC 748 in other studies (Lin and Juang 2005; Mumford et al. 2008). The presence of zinc and lead within the system did not contribute a significant amount of competition for adsorption sites. Also, the matrix effect of the various other constituents seems to have a small effect. This is shown by the slower uptake over time.

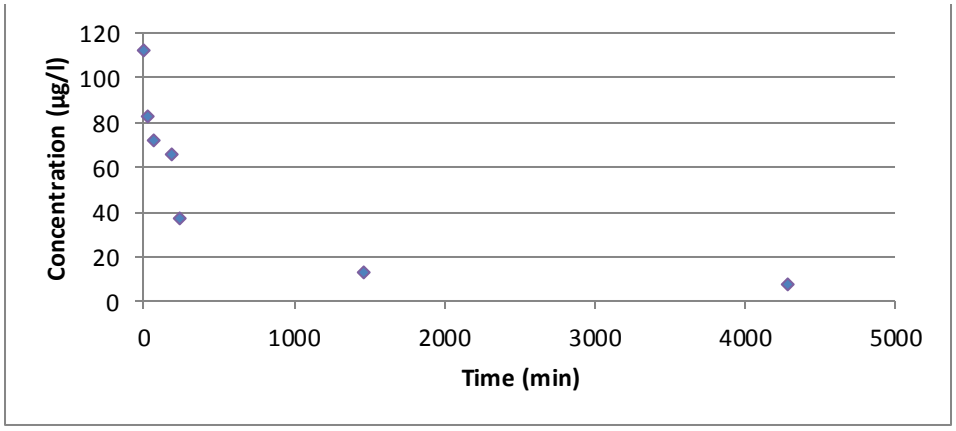

Figure 3-37 Three day stormwater copper removal by ion exchange resin sampler

A closer look at the initial hour of removal is displayed in Figure 3-38. The natural log of the concentration is presented on the y-axis and time on the x-axis. A linear best-fit equation is been included. This resulted in a coefficient of determination of 0.8311. The percent mass removed from the system within the first hour was 52.3%, much less than the 91.0% removed from the tri-metal system. This suggests a matrix effect by the additional constituents resulting in a delayed uptake.

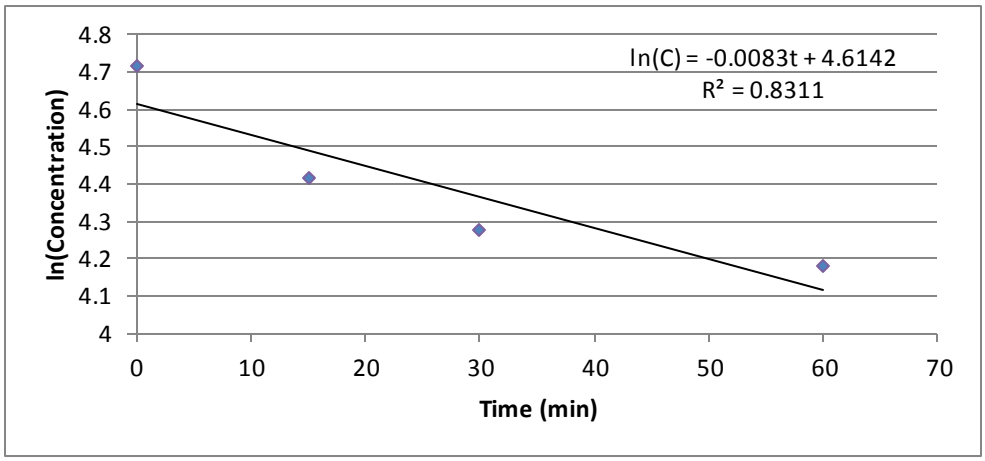

Figure 3-38 First hour stormwater copper removal by ion exchange resin sampler

Total mass of copper removed from the system by the ion exchange resin was 127.19µg (95.0%). The finalized elution procedure (described in section 3.2.3.3 Sampler Measurements) was performed on the resin following deployment and 106.55 µg were retrieved. The total mass lost from the system was 13.3%. Some delay of acid flow through the system during elution may have caused lower than expected elution values. A follow -up elution was performed exposing the resin to stormwater and results were similar. Thus, the flow issue did not seem to affect the results as otherwise thought.

Lead. The external measurements of lead are displayed in Figure 3-39. Equilibrium was reached within the first three days (4,280 min). The presence of copper and zinc within the system did not contribute a significant amount of competition for adsorption sites. But the matrix effect of the other constituents seems to have a small effect, shown by the slower uptake over time.

The initial hour of lead removal is displayed in Figure 3-40. The system kinetics are first order, so the natural log of the concentration is displayed on the y-axis and time on the x-axis. The coefficient of determination of the best fit line was 0.8854; the equation is included within the figure. The percent lead removed from the system within the first hour was 54.2%.

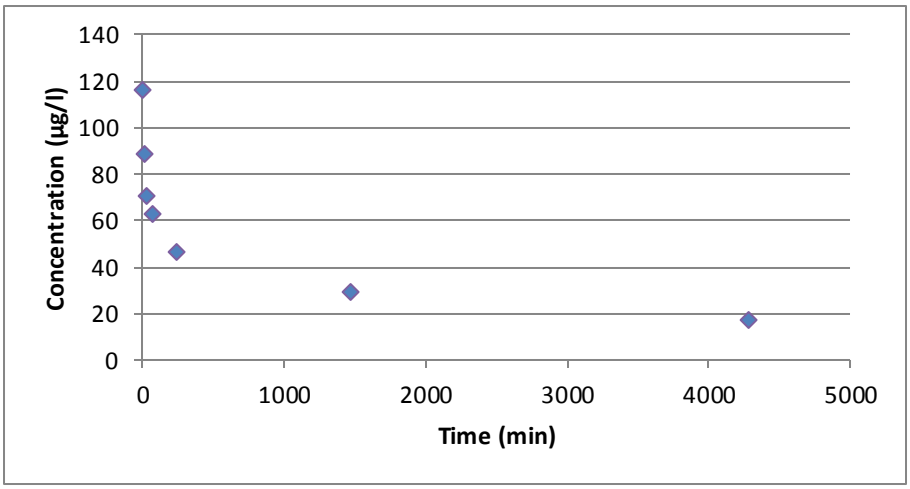

Figure 3-39 Three day stormwater lead removal by ion exchange resin sampler

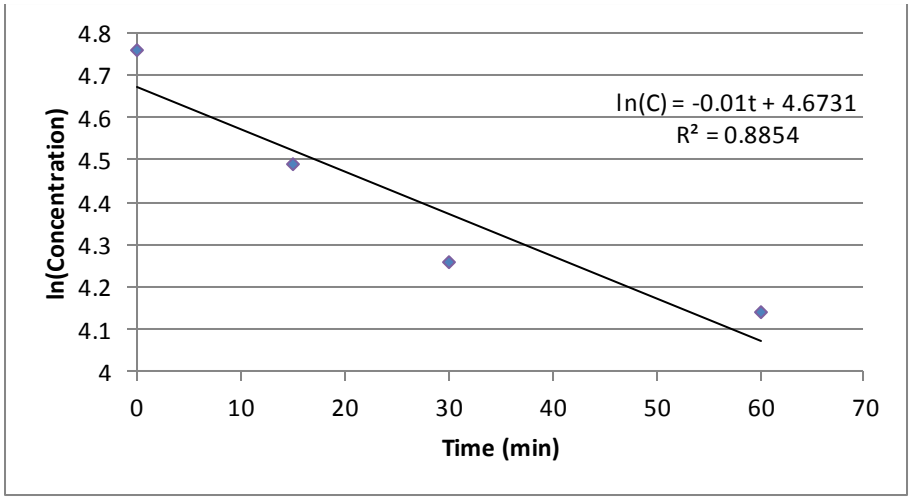

Figure 3-40 First hour stormwater lead removal by ion exchange resin sampler

Total mass of lead removed from the system by the ion exchange resin was 116.88µg (87.5%). The finalized elution procedure (described in section 3.2.3.3 Sampler Measurements) was performed on the resin following deployment, and 77.71 µg were retrieved. The total mass lost from the system was 26.8%. Some delay of acid flow through the system during elution may have caused lower than expected elution values just as reported for the copper retrieval from the stormwater solution. A follow-up elution control was performed exposing the resin to stormwater,

and results were not similar, unlike the copper kinetics. Average lead removed from the system by the sampler was 150.94 (95.4%), but the total mass lost for the system was -19.7%.

Zinc. Zinc external concentrations are displayed in Figure 3-41. Equilibrium was reached within the first three days (4,280 min). The presence of copper and lead within the system did not contribute a significant amount of competition for adsorption sites. But the matrix effect of the other constituents seems to have a small effect, shown by the slower uptake over time.

A closer look at the initial hour of removal is displayed in Figure 3-42. The system kinetics are first order, so the natural log of the concentration is displayed on the y-axis and time on the x-axis. A linear best-fit equation is been included. This resulted in a coefficient of determination of 0.8891. The percent mass removed from the system within the first hour was 69.0%, much less than the 97.2% removed from the tri-metal system. Like the Copper and Lead results, this suggests a matrix effect by the additional constituents resulting in a delayed uptake.

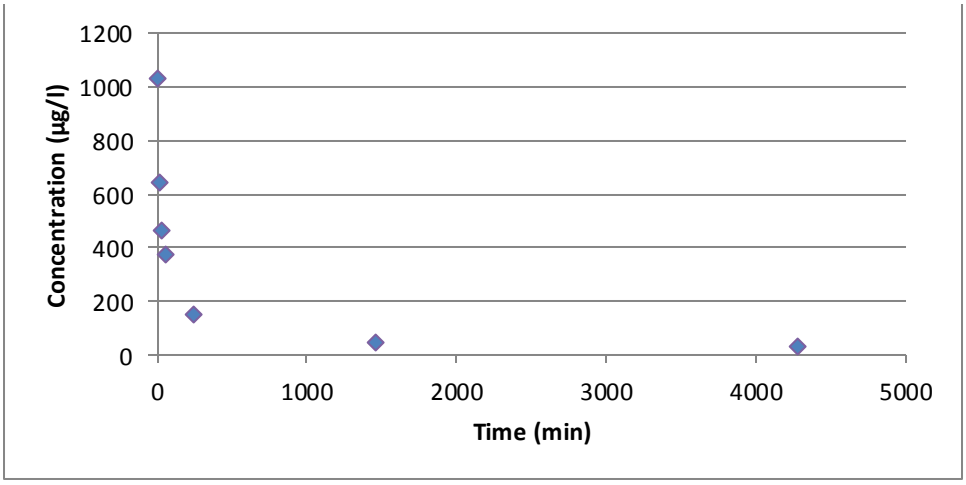

Figure 3-41 Three day stormwater zinc removal by ion exchange resin sampler

Total mass of zinc removed from the system by the ion exchange resin was 1149.21µg (97.7%). The finalized elution procedure (described in section 3.2.3.3 Sampler Measurements) was performed on the resin following deployment and 1165.34 µg were retrieved. The total mass lost from the system was 1.0%. The delay of elution flow mentioned in the copper and lead analysis did

not seem to affect zinc. Compared to the follow-up elution control, results were similar. Average zinc removed from the system was 772.94 (98.9%), and the average total mass lost was 4.7%.

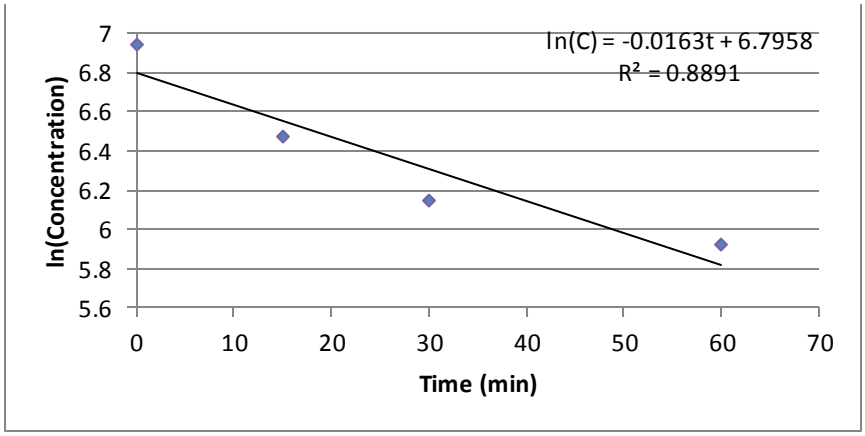

Figure 3-42 First hour stormwater zinc removal by ion exchange resin sampler

3.3.2.4 Ion Exchange Resin Control Test Results

The initial elution procedure used for the copper individual test consisted of three 20 min soaking rinses of 120 ml of 0.5 M hydrochloric acid within a 250 ml beaker. A sample was collected and analyzed from each rinse of the resulting solution, and masses of each rinse were totaled. This procedure was conducted in duplicate, and efficiencies are presented in Table 3.4. The average elution efficiency was 47.0%, spurring a new procedure to be developed.

Table 3-4 Elution rinse efficiencies

	Trial 1	**Trial 2**	**Average**
Initial Mass (µg):	117.60	106.15	111.88
Final Mass (µg):	2.03	1.87	1.95
Mass Exchanged[a]:	96.9%	96.9%	96.9%
Mass Retrieved (µg):	59.03	42.88	50.96
Elution Efficiency[b]:	51.8%	41.7%	47.0%

[a]Mass Exchanged = 1- (Initial Mass/Final Mass)
[b]Elution Efficiency = Mass Retrieved/Elution Efficiency

The modified elution procedure for the more complex tests was adjusted to include flow of hydrochloric acid through the resin. Following the 1-day drying period, the resin was poured into a burette containing a small amount of hydrochloric acid (~15 ml) enabling the resin to expand before settling, which prevented clogging of the burette during the actual elution. The elution consisted of passing 120 ml of hydrochloric acid through the resin at a flow rate of 2 ml/min. From the resulting solution a sample was collected and analyzed.

The results from the analysis are presented in Table 3.5. Average elution efficiencies for copper lead and zinc are 84.2%, 120.7%, and 95.2%, respectively. Lead values were greater than 100% for each trial. This could be due an increase in lead in the system over the course of the tests. This phenomenon did not occur, however, for the stormwater test.

Table 3-5 Modified elution procedure efficiencies

	Copper			Lead			Zinc		
	Trial 1	**Trial 2**	**Trial 3**	**Trial 1**	**Trial 2**	**Trial 3**	**Trial 1**	**Trial 2**	**Trial 3**
Initial Mass (µg):	109.55	107.06	109.55	160.66	159.03	157.54	794.71	778.76	783.56
Final Mass (µg):	3.04	3.23	3.10	7.36	7.31	7.23	9.49	8.37	8.42
Mass exchanged[a]:	96.7%	96.5%	96.7%	94.9%	94.9%	94.9%	98.3%	98.4%	98.4%
Mass retrieved (µg):	89.83	89.23	86.18	184.21	183.66	178.92	742.71	747.55	716.88
Elution efficiency[b]:	84.8%	86.4%	81.4%	120.8%	121.7%	119.7%	95.1%	97.5%	93.0%

[a]Mass Exchanged = 1- (Initial Mass/Final Mass)
[b]Elution Efficiency = Mass Retrieved/Elution Efficiency

3.3.2.5 Ion Exchange Resin Sampler Discussion

Ion exchange resin samplers performed very consistently with the increasing complexity of the surrounding solution. The addition of other cationic metals did not slow the uptake rate or limit the amount of mass to be adsorbed. The presence of other matrices expected to be present within stormwater did not pose a large change in kinetics either.

The exchange capacity was calculated for an ion exchange resin passive sampler, and the maximum mass (µg) for each metal of interest was calculated. Samplers contain approximately 15 g of dry resin or 25 g when wet. Using an equivalence per liter ratio of ≥ 1.35 recommended by the

manufacturer, the exchange capacity is 1,071 mg for copper, 3,496.5 mg for lead, and 1,103.3 mg for zinc (Rohm and Haas 2006). This means that if the ion exchange resin was able to adsorb all of the metals from stormwater at the expected conditions, the total volume of water would still be greater than 1,000 liters. Complete absorption is not likely and thus the sampling volume of these samplers is much greater than the 1,000 liter amount. This, in combination with the consistency of metal uptake under varying conditions, points to ion exchange resin samplers as being a feasible method of monitoring stormwater BMPs.

The characteristics of Amberlite IRC 748 are difficult to compare to previous studies because uptake calculations are based on isotherms (Lin and Juang 2005; Mumford et al. 2008). Applications within stormwater monitoring will not always reach equilibrium; thus isotherms don't provide an adequate method of comparison. Ion exchange resin characterizing information is for use within a column setting. This provides another difficulty in deriving necessary kinetics information for application within a stormwater passive sampler (Rohm and Haas 2006).

Initial uptake for the first hour characteristics could provide some means of quantifying the uptake within stormwater flows. In other words, the equations derived from the first order kinetics curves could give a rudimentary glimpse into metal uptake. The first assumption is that the rate constants (k) will remain the same in both the batch and reactor settings. If this holds, the amount of time and eluted mass are the only variables needed from the sampler in the field. The rate constants could be determined within the lab-scale reactors under similar conditions.

Using Equation 3-1 and assuming the C_0 is not known, it is calculated and presented in Table 3-6. The first column presents the rate constants (k) determined from the first hour stormwater tests. The second column displays the y-intercept or $\ln(C_0)$, also determined in the first hour of the stormwater tests. The third column presents a calculated initial concentration (C_0). The measured initial concentration (C_0) of the ion exchange resin stormwater test is given in the fourth column. A percent error comparison is given in the last column. Although this is a rudimentary

approach, it does give some basis to compare the batch tests with the lab-scale and field scale reactors. All calculated and actual concentrations are within 27%.

3.3.3 Dialysis vs. Ion Exchange Resin Sampler Comparison

Comparing the dialysis and ion exchange resin samplers gives an idea of relative performance. Table 3-7 presents the amount of mass removed from the system by each sampler and the percentage of removal. The ion exchange resin sampler has a significantly greater percent removal compared to the dialysis sampler within the first hour.

Table 3-6 First-order parameters for ion exchange resin samplers in stormwater

	Rate Constant, k (min^{-1})	$ln(C_0)$	Calculated C_0[a] (µg/l)	Measured C_0 (µg/l)	Percent Error (%)[b]
Copper	-0.0083	4.6142	100.91	136.46	26.05%
Lead	-0.01	4.6731	107.03	136.25	21.45%
Zinc	-0.0163	6.958	1051.53	1196.12	12.09%

[a]Calculated C_0 = e ^(ln(C0))
[b]Percent Error= 1-(Calculated C_0/Measured C_0)

Table 3-7 Sampler comparison of first hour metal removal

	Dialysis Sampler			Ion Exchange Resin Sampler		
	Individual	Tri-Metal	Stormwater	Individual	Tri-Metal	Stormwater
Copper Mass Removal[a]						
(µg)	33.22	19.78	12.09	99.18	108.41	72.45
(%)	37.4%	19.0%	11.7%	88.7%	91.1%	53.1%
Lead Mass Removal						
(µg)	1.14	16.71	32.7	137.44	144.34	74.89
(%)	7.8%	10.6%	17.9%	95.2%	96.9%	55.0%
Zinc Mass Removal						
(µg)	21.47	27.04	96.8	1138.95	1039.11	830.85
(%)	2.6%	3.1%	11.5%	95.8%	97.2%	69.5%

[a]Mass Removal = Mass removed from batch system by passive sampler

Sampler performance within the controlled batch tests reveals the dialysis sampler as having inconsistent uptake and multiple metal transport mechanisms at work. This complex collection of metals makes the dialysis sampler infeasible for use within stormwater applications.

The dialysis sampler will no longer be assessed in the column or field tests (described in Section 4) for feasibility as a stormwater sampler. The ion exchange resin, on the other hand, had consistent uptake, and it was not significantly affected by the increasing complexity of the surrounding solution. Due to these results, the ion exchange resin sampler continued to be assessed in lab-scale BMP tests as well as field experiments.

3.4 Conclusion

Batch tests mimicking stormwater scenarios were employed to assess the feasibility of two types of passive samplers. The dialysis sampler, consisting of a regenerated cellulose membrane filled with DI water, performed uncharacteristic to a diffusion only system. Metal adsorption onto the membrane was noted as well as a release of metals following uptake over time. Another issue was the small amount and slow rate of uptake within the static systems. Due to these inconsistencies the dialysis sampler was deemed infeasible for stormwater applications.

The ion exchange resin sampler consists of Amberlite IRC748 chelating resin encased in a polyester mesh. This sampler performed desirably in various stormwater scenarios, including consistent and rapid metal uptake. This sampler is considered feasible as a stormwater sampler at this point in the study and will be deployed within lab scale and field BMPs to further address its feasibility.

Chapter 4 Lab- and Field-Scale BMP Tests for Heavy Metal Passive Sampler

4.1 Introduction

An ion exchange resin has been selected from existing passive samplers and tested in static batch experiments within the lab. This sampler has shown rapid and consistent uptake of copper, lead and zinc within a synthetic stormwater solution and has been deemed feasible for further testing.

The next step in understanding the feasibility of the ion exchange resin sampler within highway BMPs is to observe how the sampler reacts to increasingly complex matrix and flow scenarios. The environmental application of these samplers for stormwater monitoring will include a lot of variables that may have conflicting effects on the sampler's uptake. It is important to add variables in a manner that the results can be interpreted and understood. The end application of the samplers within stormwater flows was considered and the anticipated factors broken into various tests to assess their implications on the sampler's performance and application results.

The objectives of this section are to 1) describe the BMPs and passive sampler deployment in both lab- and field-scale BMPs, with related methodologies being introduced, 2) test results, discussions, and implications of these results.

4.2 Materials and Methods

4.2.1 Lab-Scale BMPs

Laboratory-scale bioretention cells have been constructed for evaluating the performance of the passive samplers. Samplers were exposed to controlled flow and metal concentration conditions to assess their feasibility.

4.2.1.1 Reactor Design and Passive Sampler Deployment

Samplers, Chemicals and Materials

Ion exchange resin samplers consist of Amberlite IRC748 chelating resin encased within a woven polyester monofilament mesh (0.008-inch-hole size) as shown in Figure 4-1. They were assembled and placed within the PVC sampler housing units of the reactors. Sampler dimensions are2 inches by 4 inches. Samplers were assembled and prepared in the same manner as detailed in section 3.2.1Samplers and Materials.

Figure 4-1 Ion exchange resin sampler

Samplers were surrounded by media to encourage uniform flow through the housing units. Initial synthetic storms were conducted with the samplers surrounded by the sand/compost mixture. Due to significant sediments embedding within the samplers, acid washed Quikcrete sand was used instead.

Sand was washed by covering the bed volume of sand in 0.05 M hydrochloric acid for 24 hours. Following the acid soak, the sand was rinsed with 5 times the bed volume of DI water. This procedure was adapted from a previous study (Aronino et al. 2009).

All PVC materials were purchased at a local hardware store. PVC adjustments and manipulations were conducted within the structures laboratory at the University of Nebraska – Lincoln, Omaha Campus.

Lab-Scale Bioretention Cells

Lab-scale reactors were constructed to mimic field-scale bioretention cells located at NDOR's Salt Valley maintenance yard in Lincoln, NE. These field-scale bioretention cells were the place of deployment for the field BMP passive sampler tests, detailed later in this section. Passive samplers were placed within the lab-scale reactors and loaded with synthetic storms at varying rates to imitate common storm events. Four lab-scale bioretention cells were constructed for lab-scale BMP tests. Essentially, these lab-scale bioretention cells are made of 3 inch PVC pipe, filled with 18 inch height media (see below) and with the two passive samplers (one placed near the top and the other one near the bottom). Reactor cross section and dimensions are displayed in Figure 4-2. The media is located below the influent sampler housing unit and rests on the PVC grid and effluent acrylic sleeve as noted in the diagram. 1.5 feet of media (composition see below) was loaded within each reactor. The influent flow apparatus rests at the mouth of the column and water is allowed to free-fall and, if necessary, pond at and above the influent sampler. Details of reactor design and media are described below.

These lab-scale bioretention cells were designed based on the existing bioretention cells in the field (Jones 2012). The design process consisted of taking the existing bioretention cell and reducing the surface area of the BMP. This media core is 3 inches in diameter; all other variables are kept the same. More details of the field scale BMP design are available in section4.2.2.1BMP Design. Due to the reduction in overall size the effects of surface tension were considered. It was determined that the samplers should be placed as close to the media as possible to enable uniform flow through the column and as water passes the samplers. A design was developed that positioned the samplers adjacent to the media to prevent flow inconsistencies, while allowing the media itself to remain undisturbed. All components fit within the 3 inch PVC pipe. This design is displayed in Figures 4-2 to 4-4. The details of the itemized components are shown in Table 4-1.

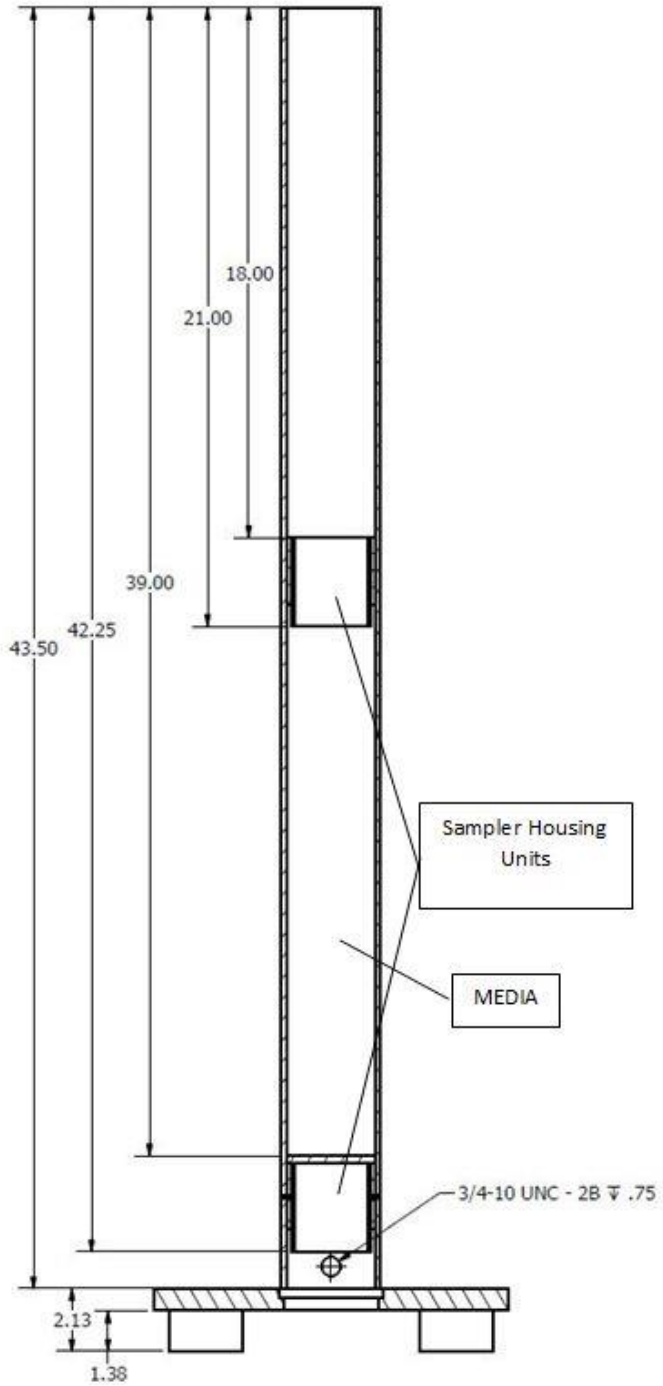

Figure 4-2 Lab-scale reactor dimensions (inches)

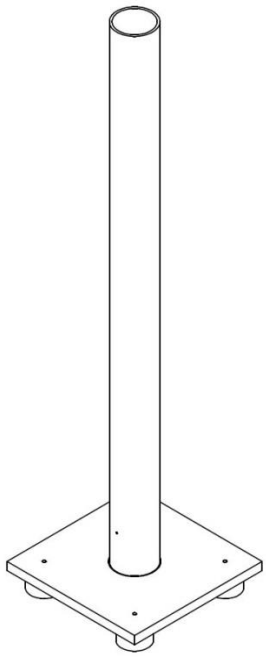

Figure 4-3 Overall view of lab-scale reactor

Table 4-1 List of parts for lab-scale reactor (Figure 4-4)

Item	Qty[a]	Description
1	1	3 inch PVC column
2		Effluent Housing Unit:
2.1	1	Acrylic Sleeve
2.2	1	PVC Grid
3		Reactor Base:
3.1	1	Square PVC Base
3.2	4	PVC Cap Risers
4		Influent Housing Unit:
4.1	1	Acrylic Sleeve
4.2	1	PVC Sampler Housing
5	1	PVC Sampler Housing
6	1	PVC Support

[a]Qty = Quantity of item

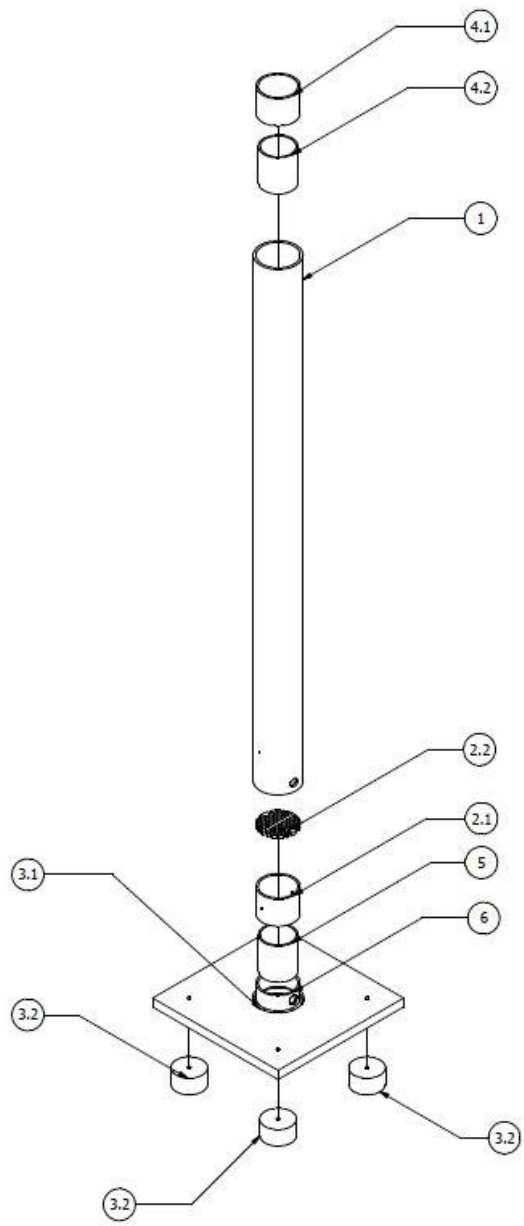

Figure 4-4 Exploded view of lab-scale reactor

Influent and effluent samplers were placed in housing units (PVC sampler housings) that enabled the free flow of water into and out of the unit. These units consisted of a 3-inch long by 2-inch diameter PVC coupler with perforated mesh soldered to the bottom. Influent units were soldered within a 2.25 inch section of 3-inch diameter acrylic pipe (acrylic sleeve) to deter flow along the sides of the column. Influent units were rested on the top of the media and were attached to a string for easy retrieval. Effluent units were not attached to the acrylic sleeve, but instead sat within this sleeve during testing. Units were inserted from beneath the reactor.

The acrylic sleeve encompassing the effluent PVC sampler housing was permanently fixed to the 3 inch PVC column via screws. This supported the PVC grid, which was covered with perforated mesh to allow flow while holding the media in place. In order to hold the effluent PVC sampler housing snug against the PVC grid a PVC support was used. This support contained an orifice to enable free flow of the effluent water out of the column. Figure 4-5 shows the removable effluent PVC sampler housing unit next to the fixed acrylic sleeve & PVC grid arrangement.

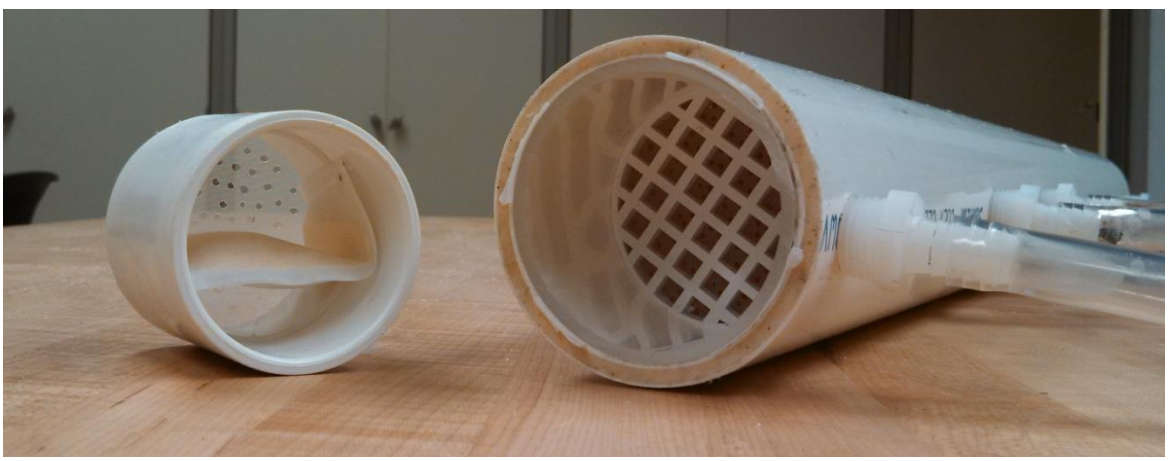

Figure 4-5 Effluent PVC sampler assembly for lab-scale reactor

The base (item 3.1 in Table 4-1 and Figure 4-4) consisted of a 1 inch by 1 foot by 1 foot PVC sheet with a circle removed from the center. This circle had a diameter less than that of the 3 inch PVC column with a ½ inch routed grove to set the column within. This arrangement resulted

in the column being able to sit securely within the base while being supported. The column and entire inner assembly were secured to the base via a removable Oatey 3 inch diameter PVC gripper which was inserted from below the base. This device, shown in Figure 4-7, held the column to the base, prevented leakage, and enabled access to the bottom of the reactor.

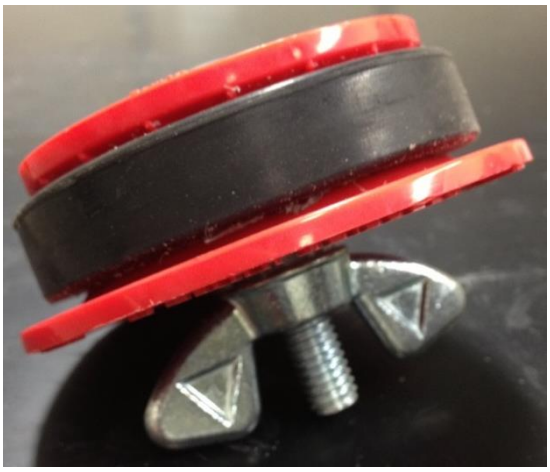

Figure 4-6 Oatey PVC gripper

Reactor Media

The media used is a 50/50 (v/v) sand and compost mixture, mimicking the bioretention media mixture used in the field. Quickrete sand was used and meets ASTM C33 standards for gradation. Oma-Gro compost was used; it is produced by the City of Omaha and consists of the city's yard waste, which is made up of primarily of grass clippings, leaves & wood mulch.

Synthetic Stormwater and Influent Distribution

Synthetic stormwater, listed in Table 4-2and used for lab-scale BMP tests, contained chemicals and concentrations similar to those found within the environment (Keblin et al. 1997). Pond sediment, a constituent of synthetic stormwater, is characterized in Table 4-2. Synthetic stormwater was continually mixed. It was pumped through the flow distribution device into the reactor. Flow was regulated by the pump and gravity from that point on. Stormwater then passed

both samplers, the media, exited the reactors, and was collected in a 1 liter glass beaker. More chemical and sediment details are available in section 3.2.1(Samplers and Materials).

Table 4-2 Chemical composition of synthetic stormwater for lab-scale reactors

Constituent	Concentration (mg/l)
Pond Sediment[a]	500
Lead (Pb)	0.16
Copper (Cu)	0.11
Zinc (Zn)	0.91
Sodium Carbonate (Na_2CO_3)	0.9
Sodium Chloride (NaCl)	200
Kaolin	60

[a]Pond Sediment Characterized in Table 4-3

Table 4-3 Characterization of pond sediment used in synthetic stormwater (Jones 2012)

Constituent	Roadway Sediment (µg/g)	Instrument Detection Limit (µg/l)
Cr	12.148	12.362
Fe	3054.209	5.198
Ni	7.255	3.373
Cu	28.076	2.100
Zn	113.842	2.201
Ag	31.982	7.436
Cd	< DL[a]	1.228
Sb	< DL	8.404
Pb	19.076	3.794
NO^3	185	276

[a]< DL = Value below Detection limit

Influent flows were applied to the system by a modified garden watering can head to enable uniform distribution across the 3 inch diameter of the PVC column. Manipulation was required because under low flows and pressure the current heads resulted in a single stream. To overcome these surface tension issues, strategic holes were enlarged and string was added to encourage the formation of droplets away from the center of the column (Figure 4-10). Effluent flows left the column just above the base via a nozzle and hose assembly (Figure 4-2). This water was directed to a 1 liter beaker located below the reactor.

Figure 4-7 Influent flow apparatus

4.2.1.2 Experimental Design

Several tests were conducted using the lab-scale bioretention cells, including: 1) initial settling tests; 2) hydraulic conductivity of the media; 3) initial leaching tests; and 4) stormwater loading tests. Details about design and conditions of these tests are as follows.

Initial Settling

To quantify the amount of settling occurring within the reactors and to reduce the effects of settling on the reactor performance, a preliminary settling test was performed. Reactors were loaded with 18 inches of media and flushed with tap water in 1 liter increments; the amount of settling between each run was recorded. This process was repeated until the amount of settling stabilized. For the sand/compost mixture settling stabilized after 3 liters.

Hydraulic Conductivity

The hydraulic conductivity of a given media plays a significant role in the BMP design and treatment effectiveness. In general, media with larger pore spaces will have a greater conductivity, while media with small pore spaces or media that swell when wet (i.e. clay) tend to restrict flow.

This was a factor in understanding the flow characterizations and treatment effectiveness of our lab-scale BMPs as well as to calculate the design water quality volume (WQV).

The saturated hydraulic conductivity was determined using a previously developed procedure (Jones 2012). This procedure was derived from the ASTM D2434 standard as well as a method employed by Thompson et al. (Thompson et al. 2008). The procedure included a consistent inflow and outflow rate with a constant head (9 inches) above the media. Once this was achieved an effluent flow measurement was made, recorded, and used to calculate the saturated hydraulic conductivity.

For the bioretention cells used in this study, the head was held constant at 18.5 inches. Tap water was applied to the top of the reactors and allowed to pond up to the overflow port. Steady flows from both the overflow and effluent ports were observed for 20 to 30 minutes before collection of effluent flow measurements. These measurements were conducted by recording the time needed to fill a 100 ml graduated cylinder with effluent flow. Measurements were conducted in triplicate for increased precision.

Saturated hydraulic conductivity was calculated using Equation 4-1:

$$K_{sat} = \frac{Q * L}{A * h * t} \tag{4-1}$$

where:

Ksat: Saturated hydraulic conductivity (cm/s)

Q: Volume of water passed through column (cm^3) (= 100 cm^3)

L: Length of soil media (cm) = 45.72 cm

A: Cross sectional area of column (cm^2) = 45.6 cm^2

h: Height of water column plus soil media (cm) = 92 cm

t: Time for Q to pass through column (s)

Initial Leaching

Due to the sensitivity of analysis and low levels of heavy metal concentrations present within stormwater, metals leaching from the media were assessed. The media was not washed to mimic the media actually used within the field. Reactors were loaded with 1 liter of local tap water and the effluent flow was collected. Influent and effluent samples were collected, preserved to 2% (v/v) nitric acid and analyzed with ICP-MS in the same manner as the batch tests, detailed in section 3.2.3.4(Sample Collection, Preservation, and Analysis). Effluent samples were filtered via 0.45 micron cellulose acetate filter prior to sample preservation and analysis. This test was conducted according to the *Standard Method*.

Stormwater Loading Tests

Most treatment BMPs are designed to treat the first half inch of runoff, which is also called the water quality volume (WQV). The initial runoff of stormwater contains the majority of pollutants. Studies have shown that the first ½ inch of runoff contains 81–86% of major contaminants while the first ¾ inch contains 89–96% of major contaminants (Flint and Davis 2007). Regardless of a storm event's precipitation, the WQV has the highest mass loadings of target contaminants.

The WQV of the 3 inch diameter lab-scale BMP was determined using an equation adjusted from the Iowa Stormwater Management Manual based on Darcy's Law. The original equation presented in the manual is displayed in Equation 4-2 (ISMM 2009).

$$\boldsymbol{A_f = \frac{WQV * d_f}{K * (H_f + d_f) * t_f}} \qquad 4\text{-}2$$

where:

WQV: water quality volume (or total volume to be captured) (ft^3)

A_f: surface area of ponding area (ft^2) = 0.04909 ft^2

d_f: filter bed depth (1.5 feet minimum) = 1.5 ft

K: hydraulic conductivity of filter media (ft/day) (use 2 ft/day for a sandy loam for the engineered soil mix; if using a natural soil profile, use 0.5 ft/day for silt-loam) = 39 feet/day (measured values for reactors)

H_f: average height of water above filter bed (ft) - (typically 3-4.5 inches (0.25-0.375 feet), which is half of the6-9 inch ponding depth) = 0.375 ft

t_f: design filter bed drain time (days); (2 days is recommended maximum) = 1 day

Equation 4-2 was re-arranged to solve for the WQV:

$$\boldsymbol{WQV} = \frac{\boldsymbol{A_F} * [\boldsymbol{K} * (\boldsymbol{H_f} + \boldsymbol{d_f}) * \boldsymbol{t_f}]}{\boldsymbol{d_f}} \qquad 4\text{-}3$$

The calculated WQV is 67.77 liters. This is the amount of runoff a lab-scale bioretention cell is designed to treat. This volume of water represents a storm event. Due to the difficulty of synthesizing such a large volume of synthetic stormwater, a scaled down approach was also developed.

The stormwater loading tests are to test how the resin uptakes the mass of metals under various flow conditions. In this study, three (3) storm events (0.5 hour, 3 hours, and 12 hours) were tested. The WQV was divided by these durations (0.5, 3, and 12 hours) to imitate the capture conditions expected in the field.

Due to the difficulty of synthesizing such a large volume of synthetic stormwater (67.77 liters), a scaled down approach was developed. One liter of synthetic stormwater was applied at the rates, listed in Table 4-4. The stormwater surface loading rate of the synthetic storms were kept the same as the surface loading rate of the total WQV for the 3 storm durations (0.5 hour, 3 hour, and 12 hour). The time for the one liter synthetic stormwater to be applied is also presented. This scaled down approach relies on the assumption that the uptake of mass onto the samplers is linear.

Table 4-4 Synthetic storms applied to lab-scale reactors

Storm Duration (hr.)	Flow Rate (l/hr.)	Surface Loading Rate (l/m^2-h)	Time of 1 liter Flow (min)
0.5	135.53	29717.52	0.44
3	22.59	4953.28	2.66
12	5.65	1238.87	10.64

Three bioretention cells were used for each storm with triplicate results. One reactor (Reactor 1) did not contain samplers and was used as a control to see if the samplers affected the treatment efficiencies.

4.2.1.3 Sampling, Measurements and Analytical Methods

Influent samples of the synthetic stormwater were collected prior to the reactors being loaded. Effluent samples were collected one hour following the loading of the stormwater. Effluent water was attained in 1 liter beakers (one for each reactor) and stirred via stir-plate and magnetic stir-bar while sample was drawn. Sample volumes were 5 ml and were filtered via 0.45 micron cellulose acetate filter paper prior to preservation and analysis, thus metal concentrations presented are dissolved metals. Samples were preserved to 2% (v/v) nitric acid and analyzed with ICP-MS in the same manner as the batch tests, detailed in section 3.2.3.4(Sample Collection, Preservation, and Analysis). Dilutions were performed in the same manner as the batch tests, but not the same ratios. Only influent zinc concentrations required a 1:10 dilution. This was the case for all lab-scale reactor tests.

Following deployment, ion exchange resin samplers were removed from the reactors and allowed to air-dry for a day for ease of handling. An elution procedure similar to that of the batch tests was performed on the resin. Following the 1 day drying period, the resin was poured into a burette containing a small amount of 10% (v/v) sulfuric acid (~15 ml) enabling the resin to expand before settling. This prevented clogging of the burette during the actual elution. The elution

consisted of passing 500 ml of sulfuric acid through the resin at a flow rate of 2 ml/min. From the resulting solution a sample was collected and analyzed.

4.2.2 Field BMPs

A set of four bioretention cells, an infiltration trench, and a filter trench were designed and constructed. These BMPs were incorporated within the Salt Valley maintenance yard for NDOR near Warlick Ave and Highway 77 in Lincoln, Nebraska. The bioretention cells and filter trench were chosen for field tests of passive samplers.

Deployment units for the samplers were designed to expose the passive samplers within the flow of the bioretention cells and the filter trench in a predictable manner. Passive samplers were deployed within these units; after retrieval, they were processed in the lab. A velocity sensor, rain gauge and grab samples were employed to help quantify the chemical concentrations and flows the samplers were exposed too. BMP design, Experimental design and deployment unit designs are described below.

4.2.2.1 BMP Design

There are a variety of BMP designs. Selection of the BMP style depends on the type of contaminants present, the volume of expected storm loadings, budget, aesthetics, and available space (Vacha 2012). Of these types, bioretention cells have proven effective for removing a variety of contaminants (Davis et al. 2003; Hsieh and Davis 2005; Li et al. 2010; Trowsdale and Simcock 2011; Hartsig and Szatko 2012; Jones 2012; Vacha 2012). These structures typically provide treatment by filtration via various media. The design draw-down time for bioretention cells ranges from one to two days (ISMM 2009).

Three roadside BMPs were constructed and their performance assessed in a sister study for NDOR (Jones 2012). The bioretention cells and filter trench were chosen for passive sampler analysis. The infiltration trench was omitted because it lacked the desired flow conditions for the

ion exchange resins samplers. Two BMP types were chosen to deploy ion exchange resin passive samplers for assessment: bioretention cells and a filter trench. Jones (2012) describes site design, storm depth, peak discharge, and WQV calculations as wells as individual BMP design plans and media characterization. Briefly, the four bioretention cells and filter trench are described below.

Bioretention Cells

Bioretention cells are designed to hold water for less than two days. These BMPs can incorporate vegetation and are versatile in that they can be designed for infiltration or filtration, depending on if under-drains are installed. The four bioretention cells utilizing different media mixtures were constructed to treat a combined WQV of 1,215 cubic feet. Using Equation 4-3, an area of 40.5 square feet was calculated for each individual cell. Flow to the bioretention cells was diverted from a nearby ditch via 4 inch diameter PVC and distributed evenly among the four cells. A photograph of these cells is shown in Figure 4-8.

Figure 4-8 Photograph of four bioretention cells (Jones 2012)

Four soil media mixtures were used: 50/50 (v/v) sand and compost, 40/60 compost and gravel, 30/50/20 loam, sand and wood mulch, and 33/66 compost and expanded shale. Sand and gravel meet ASTM C33 gradation standards. LinGro compost, produced from City of Lincoln yard

waste was used. Site soil was used for the loam requirement; wood mulch and expanded shale available from the maintenance yard was used. Any volume greater than the designed WQV would bypass the media and exit via an overflow weir. The overflow weir, a 2 by 12 inch board, was placed opposite the inlet and maintained a 9 inch maximum ponding depth.

Media depth was 18 inches beneath which an under-drain was installed. The under-drain consisted of 10 inches of ¼ inch to 3/8 inch pea gravel on top of a layer of ¾ inch gravel with a 4 inch perforated PVC pipe. This buried pipe continued past the cell at a slight downward grade until it day-lighted. Vertical observation wells constructed of 4 inch PVC pipe were installed and connected to the outflow pipes. These wells ran the depth of the media and enabled outflow cleanout if required. Figure 4-9provides a profile view of the bioretention cells and their arrangement. Flow originates in the ditch at the right side of the figure, splits into each of the cells, flows down through the media and exits via the under-drain pipe towards the reader.

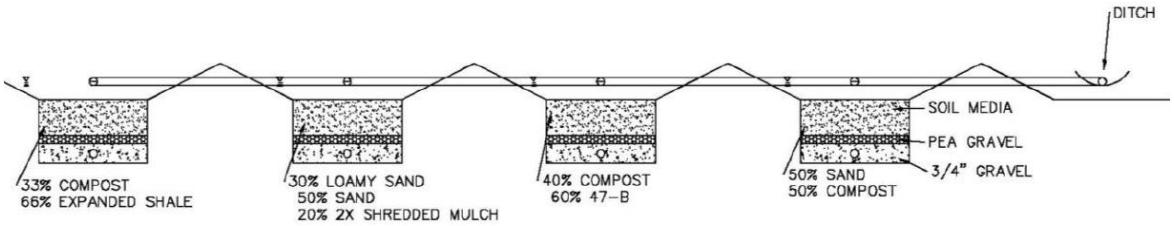

Figure 4-9 Bioretention cells profile view (Jones 2012)

Filter Trench

A filter trench, as its name suggests, relies primarily on filtration as the main form of treatment. This BMP is utilized when infiltration is not achievable due to ditch gradation. Filtration occurs because the slope encourages flows through the porous aggregate which in turn deposits sediments. Water enters the BMP at the top layer of the upstream end, flows through the pea gravel and leaves via an outlet pipe.

The filter trench is constructed on a 6.5 percent slope and is 250 feet long. The trench depth is 4 feet and the width is 3 feet. The trench consists of ¼ inch to 3/8 inch pea gravel topped with 6 inches of 3 inch armoring rock to prevent excessive scour in high flows. Seven check dams consisting of rip-rap were placed on top of the armoring rock along its length to discourage flow over the trench. The outlet pipe consists of a 4 inch PVC pipe routing flow from the bottom of the trench to ground-level. The total void volume is also the WQV: 900 cubic feet. Figure 4-10displays a profile view of the filter trench design.

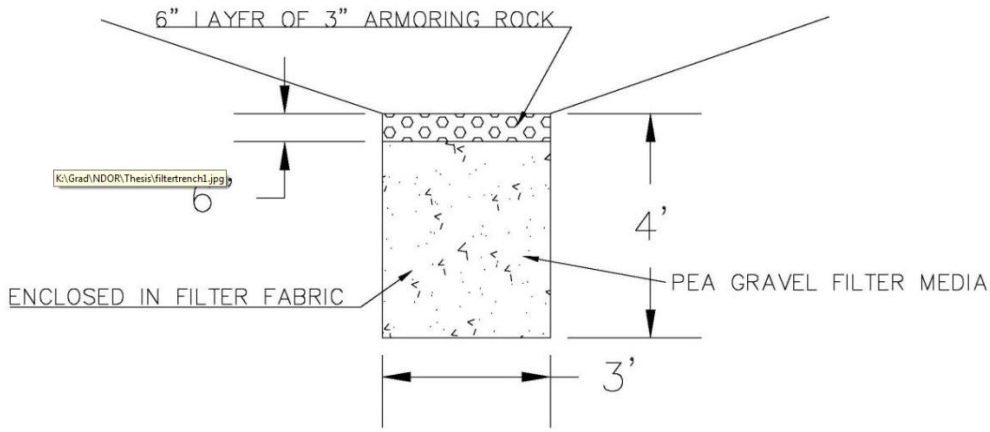

Figure 4-10 Filter trench profile view (Jones 2012)

4.2.2.2 Experimental Design

Samplers were placed within deployment units of the sand/compost bioretention cell and the filter trench between 7:00 and 7:30 p.m. June 26th, 2013. Placement occurred prior the storm. Following the storm, samplers were collected, eluted with 10% sulfuric acid, preserved to 2% nitric acid and analyzed via ICP-MS as previously detailed in section 4.2.1.3 (Sampling Measurements and Analytical Methods) except that no dilutions were used for analysis.

In order to assess the effectiveness of the samplers within field scenarios, quantification of the stormwater flows and durations was needed. Samplers were placed within the field prior to the storm event, collected afterwards and analyzed within the lab. Flow quantifying instruments were

previously installed on the site. These include an Onset automatic tipping rain gauge and an ISCO 2150 Area Velocity Flow Module and Sensor located downstream of all site BMPs. The sensor is capable of calculating flows based on the water level and velocity information it detects. With this information, it incorporates the cross-sectional area of the channel to produce flow rate and total flow calculations

A HEC-HMS model is currently being constructed for the water shed to determine flows exposed to each BMP for a given storm event, results are not included within this report.

Rainfall data and flows are available, however, for the assessed storm and were compared with the sampler results. Grab samples (400 ml) were collected in plastic bottles filtered (0.45 µm), preserved to 2% (v/v) nitric acid and analyzed via ICP-MS as were previous samples(4.2.1.3Sampling Measurements and Analytical Methods).Metal concentrations are also presented. These grab samples were collected following the majority of the storm; flow was noted at the bioretention cells only once during the time of collection, thus only one data point is available for the storm.

The resulting influent and effluent efficiencies are compared. Sediment accumulation within the samplers is noted as well as any other possible factors of the sampler's performance.

4.2.2.3 Sampler Deployment Unit Design

Ion exchange resin passive samplers can only monitor flow they come in contact with, but some stormwater flows have bursts of high volumes and large forces. In order to have this contact occur in a predictable manner while retaining the sampler in a fixed position, sampler deployment units were designed. These units vary based on the type of BMP monitored due to differing flow paths. Along with placement within influent and effluent flows, units were designed for high, predictable exposure of the samplers to the flow as well as ease of sampler deployment and retrieval.

Bioretention Cell Deployment Units

In order to expose a sampler securely within both the influent and effluent flows without providing an obstacle for debris to collect on, it was decided to mount the samplers within the bioretention cell observation wells. In order to achieve treatment between samplers, a small reactor was constructed similar to the lab-scale BMPs previously described in section 4.2.1.1 (Reactor Design and Passive Sampler Deployment). This deployment unit holds the samplers adjacent to the media in the same way the lab-scale reactors do. They also allow flow to penetrate throughout the entire area of the column, which encourages uniformity. The samplers are able to be retrieved while leaving the media undisturbed. All components are able to fit within the 4 inch PVC observation wells. This design is displayed in Figure 4-11 and Figure 4-12. The details of the itemized components are presented in Table 4-5.

Samplers were placed in housing units (PVC sampler housings) that enabled the free flow of water into and out of the unit. The influent units consisted of a 1.75 inch long 2 inch diameter PVC coupler with perforated mesh soldered to the bottom. Influent units were soldered within a 1.25 inch section of 3 inch diameter acrylic pipe (acrylic sleeve) and a section of a 3 inch to 2 inch PVC adapter to funnel flow from the 4 inch diameter pipe into the 3 inch diameter pipe. Influent housing units were rested in the top of the column; one is pictured in Figure 4-13. Samplers were covered with acid washed sand during deployment.

Figure 4-11 Overall view of bioretention deployment unit

Table 4-5 List of parts for bioretention deployment unit (Figure 4-12)

Item	Qty[a]	Description
1	1	3 inch PVC column
2		Influent Housing Unit:
2.1	1	Acrylic Sleeve
2.2	1	PVC Funnel
2.3	1	PVC Sampler Housing
3		Effluent Housing Unit:
3.1	1	Acrylic Sleeve
3.2	1	PVC Grid
4		PVC Sampler Housing
5	1	PVC Drain Grid

[a]Qty = Quantity of item

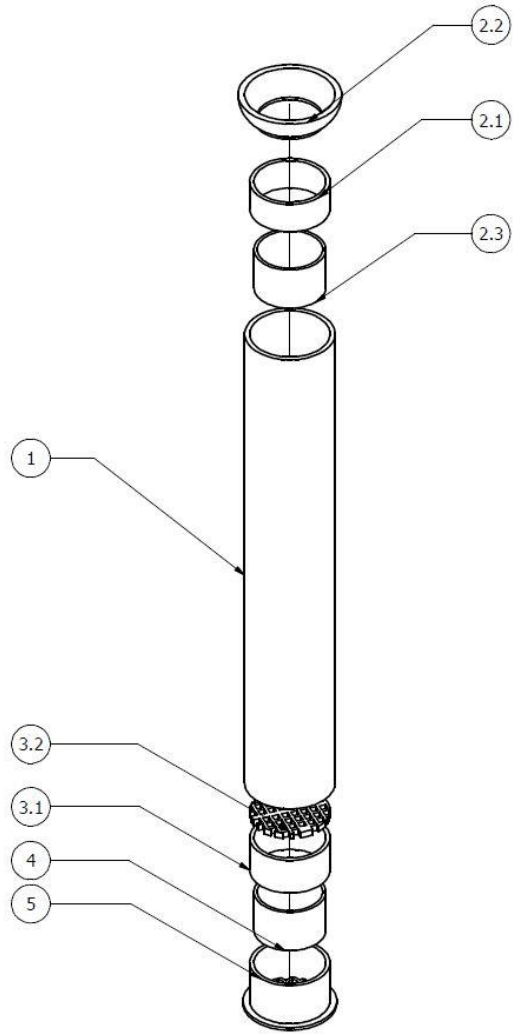

Figure 4-12 Exploded view of bioretention deployment unit

Figure 4-13 Bioretention deployment unit influent sampler housing

Effluent units were not attached to the acrylic sleeve, but instead sat within this sleeve during testing. These units were inserted from beneath the reactor. The acrylic sleeve encompassing the effluent PVC sampler housing was permanently fixed to the 3 inch PVC column via epoxy. This supported the PVC grid, which was covered with perforated mesh to allow flow while holding the media in place. A PVC drain grid held the effluent PVC sampler housing snug against the PVC grid. This PVC drain grid allowed water to pass through itself uniformly out of the column. Figure 4-14 shows the removable effluent PVC sampler housing unit to the right of the fixed acrylic sleeve & PVC grid arrangement with the PVC drain grid sitting to the left.

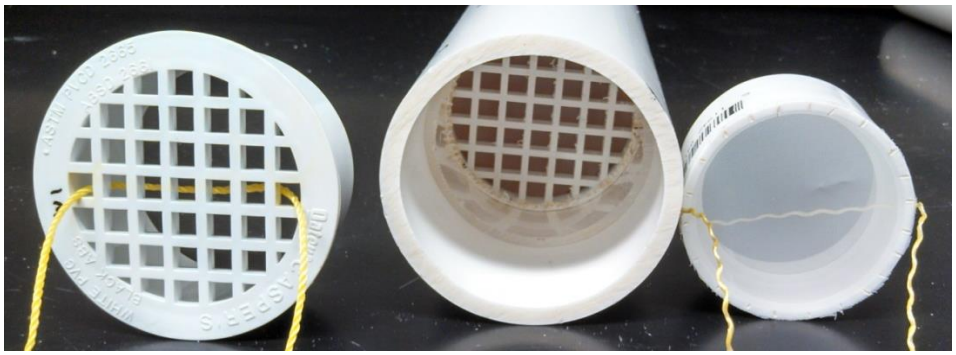

Figure 4-14 Bioretention deployment unit effluent sampler housing

The media within the bioretention deployment units was the same mixture as the cell it was deployed in. These are 50/50 (v/v) sand and compost, 40/60 compost and gravel, 30/50/20 loam, sand and wood mulch, and 33/66 compost and expanded shale. More details are listed in section4.2.2.1 (BMP Design). Only the sand/compost mixture cell was able to be quantified within this report. The units sat so that the top of the funnel was flush or slightly below the media level of the surrounding cell. Holes were drilled into the observation wells at the media level to enable water to enter the deployment unit. Once flow passed through the effluent sampler housing, it left the column and into the outlet pipe. Dimensions are shown in Figure 4-15. Overall dimensions varied on total available space within field. The media filled the entire column between the sampler housing units.

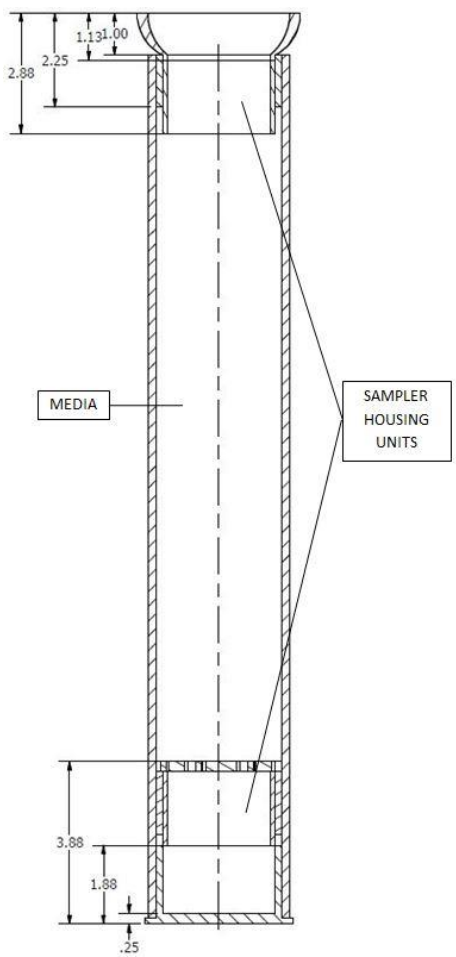

Figure 4-15 Bioretention cell deployment unit dimensions (inches)

Filter Trench Deployment Units

The filter trench is subject to high energy flows because of the steep gradation on which it was constructed. These high flows make a secure sampler deployment unit a high priority. In order to do this, two types of deployment units were developed. Influent flows are routed through a 2 foot diameter corrugated metal pipe upstream of the filter trench. Effluent flows leave the BMP through a 4 inch PVC outlet pipe.

Both influent and effluent deployment units consisted of a 6 inch section of 3 inch PVC pipe capped on both ends with a 3 inch diameter PVC grid drain, displayed in Figure 4-16. These grids allow flow to enter and leave the unit while retaining the sampler within and keeping debris out. These units were secured within the path of flow by two different mechanisms.

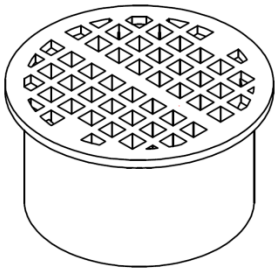

Figure 4-16 PVC grid drain

The influent sampler deployment unit was secured within the corrugated pipe. Self-tapping screws were used to secure two1-foot sections of perforated angle iron within the corrugated metal pipe 3 inches apart. Four inch diameter metal hose clamps were used to secure the PVC unit between the angle iron. This assembly is illustrated in Figure 4-17. The effluent sampler deployment unit was secured by drilling two holes in the top of the PVC pipe and running insulated wire through both. The wire was secured to two gardening ‘t’ posts on either side of the unit. This was placed directly in the flow path, so that water passes through the unit even during low flows. This apparatus is shown in Figure 4-18.

Figure 4-17 Filter trench influent sampler deployment unit

Figure 4-18 Filter trench effluent sampler deployment unit

4.3 Results and Discussion

4.3.1 Lab-Scale BMP Tests

Reactor media results (Initial Settling, Hydraulic Conductivity, and Initial Leaching) are presented according to the respective tests. Again, these tests were conducted with the unwashed media. Synthetic storm test results include reactor treatment efficiencies, influent sampler analysis, effluent sampler analysis, and influent/effluent sampler comparison.

4.3.1.1 Results from Tests of Reactor Media

Initial Settling

Initial settling is an important parameter as it gives perspective on the effects of flow through the reactors on the media. Results of the initial settling test are displayed in Table 4-6. The average percent settling for the reactors is 2.16%.

Table 4-6 Initial settling of sand/compost mixture within reactors[a]

Reactor	Volume of Water Added (L) 1	2	3	Settling Distance (in)	Percent Settling (%)
1	19	19.5	19.5	0.5	2.56%
2	-[a]	18.75	18.75	-	-
3	20	20.3	20.3	0.3	1.48%
4	20	20.5	20.5	0.5	2.44%

[a] Initial settling distance for reactor two (2) was not recorded, thus no data available.

Hydraulic Conductivity

Initial saturated hydraulic conductivities are displayed in Table 4-7. The variation in conductivities could be due to the heterogeneity of the compost mixture. The average saturated hydraulic conductivity for the reactors is 0.0148 cm/s (41.89 ft/d). This is below 127.45 ft/day, the rate of a sand/compost 50/50 mix used in a separate study (Thompson et al. 2008), but is above the rate of 6ft/day reported for vegetated bioretention cells using the 50/50 sand/compost mixture (Hartsig and Szatko 2012). The average initial saturated hydraulic conductivity was used to calculate the WQV for our laboratory BMP reactors, detailed in section 4.2.1.2 (Experimental Design).

Table 4-7 Initial saturated hydraulic conductivity of lab-scale reactors

Reactor	Time to fill 100 ml, t (s) Test 1	Test 2	Test 3	Average Time, t (s)	Hydraulic Conductivity, K (cm/s)
1	77	76	79	77.3	0.0141
2	113	110	115	112.7	0.0097
3	52	53	54	53.0	0.0206
4	74	72	75	73.7	0.0148

Initial Leaching

Initial leaching results are displayed in Table 4-8. These concentrations point to a significant amount of copper, lead and TSS being leached from the reactors. Lead, however is below detection limits for the influent tap water and the effluent water from all reactors. Lead

results are consistent with other findings indicating that lead has a high affinity to sorption onto medium matter (Morrison et al. 1984).

Table 4-8 Initial Leaching Concentrations of Lab-Scale Reactors

Sample	Copper (µg/l)	Lead (µg/l)	Zinc (µg/l)	TSS (mg/l)
Influent	34.08	< DL[a]	12.32	-[b]
Effluent				
Reactor 1	15.46	< DL	23.54	142
Reactor 2	23.97	< DL	45.38	120
Reactor 3	18.69	< DL	17.47	70
Reactor 4	28.39	< DL	29.43	85

[a]DL = Detection Limit

[b]- = Not measured

4.3.1.2 Results of Synthetic Stormwater Loading Tests

0.5 Hour Synthetic Storm Results

The 0.5 hour synthetic storm was conducted with three variations of media surrounding the samplers within the housing units. Synthetic stormwater (1 liter) was applied to the columns at a rate of 135.53 liters/hour. The first test conducted included the sand/compost mixture without the three storm wash. The second test followed the reactor wash, but still used the sand/compost mixture. The third test utilized the acid washed sand.

The 1st 0.5-h Test - Unwashed Media. Results of the test with initial unwashed media and samplers surrounded by the sand/compost mixture are presented in Table 4-9. Influent and effluent samples were collected in duplicate, average concentrations are presented. Uptake percentages and treatment efficiencies for Cu, Pb, and Zn were calculated and are also presented. A column of averages for all reactors is presented with the standard deviation for context.

Table 4-9 Results of 0.5 hour storm with unwashed media

	Reactor 1[a]	Reactor 2	Reactor 3	Reactor 4	Average	Std. Dev.
Copper						
Average Influent Mass (µg)	102.34	102.34	102.34	102.34	102.34	0.00
Average Effluent Mass (µg)	8.73	8.30	16.31	8.39	10.43	3.92
Influent Sampler Mass (µg)	-[b]	46.91	44.35	34.15	41.80	6.75
Effluent Sampler Mass (µg)	-	42.60	42.93	42.86	42.80	0.17
Influent Uptake Percentage[c]	-	45.84%	43.34%	33.37%	40.85%	0.07
Effluent Uptake Percentage[d]	-	513.25%	263.21%	510.85%	429.10%	1.44
Reactor Treatment Efficiency[e]	91.47%	91.89%	84.06%	91.80%	89.81%	0.04
Claimed Treatment Efficiency[f]	-	9.19%	3.20%	-25.51%	-4.37%	0.19
Lead						
Average Influent Mass (µg)	106.32	106.32	106.32	106.32	106.32	0.00
Average Effluent Mass (µg)	< DL[h]	< DL	< DL	< DL	< DL	-
Influent Sampler Mass (µg)	-	8.61	4.67	2.78	5.35	2.97
Effluent Sampler Mass (µg)	-	3.76	2.61	3.71	3.36	0.65
Influent Uptake Percentage	-	8.10%	4.39%	2.61%	5.04%	0.03
Effluent Uptake Percentage	-	-	-	-	-	-
Reactor Treatment Efficiency	~100%[i]	~100%	~100%	~100%	~100%	-
Claimed Treatment Efficiency	-	56.33%	44.11%	-33.45%	22.33%	0.49
Zinc						
Average Influent Mass (µg)	903.09	903.09	903.09	903.09	903.09	0.00
Average Effluent Mass (µg)	45.46	34.51	66.72	41.51	47.05	13.87
Influent Sampler Mass (µg)	-	143.37	97.04	69.19	103.20	37.47
Effluent Sampler Mass (µg)	-	105.33	78.24	72.64	85.40	17.48
Influent Uptake Percentage	-	15.88%	10.75%	7.66%	11.43%	0.04
Effluent Uptake Percentage	-	305.22%	117.27%	174.99%	199.16%	0.96
Reactor Treatment Efficiency	94.97%	96.18%	92.61%	95.40%	94.79%	0.02
Claimed Treatment Efficiency	-	26.53%	19.37%	-4.99%	13.64%	0.17

[a]Reactor 1 = Control reactor lacking passive samplers
[b]- = Data not applicable or not available
[cd]Influent/Effluent Uptake Percentages = Sampler mass divided by average mass (i.e. Reactor 2, Copper Influent: 45.84% = 46.91 µg/102.34 µg and Effluent: 513.25% = 42.60 µg/8.30µg)
[ef]Reactor/Claimed Treatment Efficiency = Unity minus effluent reactor/sampler mass divided by influent reactor/sampler mass (i.e. Reactor 2, Copper Reactor: 91.89% = 1 – [8.30 µg/102.34 µg] and Claimed: 9.19% = 1 – [42.60 µg/46.91 µg])
[g]DL = Detection Limit
[h]~100 = Treatment efficiency assumed to be 100%

Influent sampler elution masses were divided by the total mass of the influent flow for each metal. Average influent sampler uptake for the influent samplers was 40.85% for copper; this is a

significant amount of uptake for short flow conditions. Lead and zinc influent uptakes were 5.04% and 11.43% respectively, these are much less than copper.

Effluent sampler elution masses were divided by the influent mass for each metal. These calculations are estimates at best due to the fact that the effluent water is measured after it is exposed to the effluent sampler. This variability can be seen in the uptake calculations. Average uptakes of the effluent passive samplers were 429.10% for Cu, not available for Pb, and 199.16% for Zn. The copper and zinc values are much more than 100%, while lead was not detected in the effluent flows.

Reactor treatment efficiencies are calculated by taking unity minus the effluent divided by influent water masses. Reactors removed the majority of metals: 89.81% of copper, ~100% lead, and 94.79% zinc. The lead effluent mass was not detectable, thus it is assumed nearly complete removal occurred.

Claimed efficiency was calculated similarly to the reactor treatment efficiencies, but with the sampler elution masses instead of the water masses. It is the hope that these values match those of the reactor treatment efficiencies in order to accurately represent them in the field. Average claimed efficiencies for copper, lead and zinc are -4.37%, 22.33%, and 13.64% respectively. Copper efficiency was negative because the effluent sampler had collected more copper than the influent sampler. These values are much less than the actual BMP performance.

During the 1st 0.5-h Test with unwashed media, a considerable amount of fine particles accumulated within the samplers and the resins were discolored (grey). These particles were not able to be separated from the resin and were eluted with the resin. The elution would have released more than just dissolved metals, thus providing an inaccurate representation of the dissolved metals accumulated onto the sampler.

In order to circumvent the effects of fine particles, 202.2 liters of tap water were applied to the columns without passive samplers. This ‘wash’ was equivalent to the passage of three WQVs

for the reactors. Water was applied in the same manner as the synthetic stormwater, through the influent flow apparatus. The wash produced a visible difference in effluent waters, i.e. removing particles from the reactors.

The 2nd 0.5-h Test - Washed Media. Following the 1st 0.5-h test, the samplers had collected a significant amount of fines within the media. Results of the 1st 0.5-h test with unwashed media indicate that media might have released some metals, and thus, masked the intrinsic performance of passive samplers, thus a 202.2 liter wash was performed on the reactors without samplers present. Following the wash, a 2nd 0.5-h synthetic storm was conducted (samplers were present).

Reactor results after media was washed with 202.2 liters of tap water and samplers surrounded by media are presented in Table 4-10. Influent and effluent metal masses are presented as well as the influent and effluent sampler masses. Uptake estimates and treatment efficiencies were calculated and are also presented. A column of averages for all reactors is presented with the standard deviation for context. For each metal, the masses eluted from the influent passive samplers were divided by the total mass in the influent. Average uptake of the influent passive samplers was 28.17% for copper; this is a significant amount of uptake for short (0.44 min) flow conditions. Lead and zinc influent uptakes were 1.64% and 6.68%, respectively; these are much less than copper. Effluent sampler elution masses were divided by the total mass of the influent flow for each metal. These calculations are estimates at best this variability can be seen in the effluent uptake calculations. Average effluent sampler uptakes for the effluent samplers were 1216.60% of Cu, not available for Pb, and 1094.58% of Zn. The copper and zinc values are much more than 100% because the effluent sampler collected more mass than effluent water concentration. Lead was not detected in the effluent flows.

Table 4-10 Results of 0.5 hour storm with washed media

	Reactor 1[a]	Reactor 2	Reactor 3	Reactor 4	Average	Std. Dev.
Copper						
Average Influent Mass (µg)	134.70	134.70	134.70	134.70	134.70	0.00
Average Effluent Mass (µg)	2.67	2.74	4.15	3.99	3.39	0.79
Influent Sampler Mass (µg)	-[b]	39.34	37.29	37.22	37.95	1.20
Effluent Sampler Mass (µg)	-	44.07	42.49	40.60	42.39	1.74
Influent Uptake Percentage[c]	-	29.21%	27.68%	27.63%	28.17%	0.01
Effluent Uptake Percentage[d]	-	1608.39%	1023.86%	1017.54%	1216.60%	3.39
Reactor Treatment Efficiency[e]	98.02%	97.97%	96.92%	97.04%	97.49%	0.01
Claimed Treatment Efficiency[f]	-	-12.02%	-13.94%	-9.08%	-11.68%	0.02
Lead						
Average Influent Mass (µg)	63.95	63.95	63.95	63.95	63.95	0.00
Average Effluent Mass (µg)	<DL[h]	<DL	<DL	<DL	<DL	-
Influent Sampler Mass (µg)	-	1.32	0.51	1.32	1.05	0.47
Effluent Sampler Mass (µg)	-	<DL	<DL	<DL	<DL	-
Influent Uptake Percentage	-	2.06%	0.80%	2.06%	1.64%	0.01
Effluent Uptake Percentage	-	-	-	-	-	-
Reactor Treatment Efficiency	~100%[i]	~100%	~100%	~100%	~100%	-
Claimed Treatment Efficiency	-	~100%	~100%	~100%	~100%	-
Zinc						
Average Influent Mass (µg)	1137.93	1137.93	1137.93	1137.93	1137.93	0.00
Average Effluent Mass (µg)	4.58	5.20	6.13	6.19	5.525	0.78
Influent Sampler Mass (µg)	-	64.84	62.13	101.12	76.03	21.77
Effluent Sampler Mass (µg)	-	62.06	69.38	59.33	63.59	5.20
Influent Uptake Percentage	-	5.70%	5.46%	8.89%	6.68%	0.02
Effluent Uptake Percentage	-	1193.46%	1131.81%	958.48%	1094.58%	1.22
Reactor Treatment Efficiency	99.60%	99.54%	99.46%	99.46%	99.51%	0.00
Claimed Treatment Efficiency	-	4.29%	-11.67%	41.33%	11.32%	0.27

[a]Reactor 1 = Control reactor lacking passive samplers
[b]- = Data not applicable or not available
[cd]Influent/Effluent Uptake Percentages = Sampler mass divided by average mass (i.e. Reactor 2, Copper Influent: 29.21% = 39.34 µg/134.70 µg and Effluent: 1608.39% = 44.07 µg/2.74µg)
[ef]Reactor/Claimed Treatment Efficiency = Unity minus effluent reactor/sampler mass divided by influent reactor/sampler mass (i.e. Reactor 2, Copper Reactor: 97.97% = 1 – [2.74 µg/134.70 µg] and Claimed: -12.02% = 1 – [44.07 µg/39.34 µg])
[g]DL = Detection Limit
[h]~100 = Treatment efficiency assumed to be 100%

Reactor treatment efficiencies are calculated by taking unity minus the effluent divided by influent water masses. Reactors removed 97.49% of Cu, ~100% of Pb, and 99.51% of Zn; this is a

majority of metals. The lead effluent mass was not detectable, thus nearly complete removal is assumed.

Claimed efficiency was calculated similarly to the reactor treatment efficiencies, but with the sampler elution masses instead of the water masses. It is the hope that these values match those of the reactor treatment efficiencies in order to accurately represent them in the field. Average claimed efficiencies are -11.68% for Cu, ~100% for Pb, and 11.32% of Zn respectively. Copper efficiency was negative because the effluent sampler had collected more copper than the influent sampler. These values are much less than the actual BMP performance.

Passive samplers still had less fine particles, but still significant amounts were present after the 2nd 0.5-h synthetic storm. The effluent flows of Reactors 2, 3 and 4 were much more turbid than that of the control reactor. The only difference of these reactors was Reactor 1's media was not disturbed. Reactors 2, 3, and 4 had the media around the samplers disturbed in other to deploy them. In an attempt to further alleviate the accumulation of fines within the samplers, the samplers were surrounded with acid-washed sand.

The 3rd 0.5-h Test – Acid Washed Sand. Results of the 2nd 0.5-h test indicate that the media surrounding the passive samplers might have released metals that masked the true sampler performance. Therefore each of the reactors was washed with 202.2 liters of tap water, and passive samplers were surrounded by acid washed sand to reduce the effects of fines. Results are presented in Table 4-11.

Influent and effluent sample metal masses are presented as well as the influent and effluent sampler masses. Uptake estimates and treatment efficiencies were calculated and are also presented. A column of averages for all reactors is presented with the standard deviation for context. The presence of sand within the sampler housing units does not seem to have an effect on the overall treatment efficiencies.

Table 4-11 Results of 0.5 hour storm with washed media& sand

	Reactor 1[a]	Reactor 2	Reactor 3	Reactor 4	Average	Std. Dev.
Copper						
Average Influent Mass (µg)	98.23	98.23	98.23	98.23	98.23	0.00
Average Effluent Mass (µg)	2.65	2.37	2.73	3.25	2.75	0.37
Influent Sampler Mass (µg)	-[b]	36.06	40.04	33.70	36.60	3.20
Effluent Sampler Mass (µg)	-	67.59	39.88	37.51	48.33	16.72
Influent Uptake Percentage[c]	-	36.71%	40.76%	34.31%	37.26%	0.03
Effluent Uptake Percentage[d]	-	2851.90%	1460.81%	1154.15%	1822.29%	9.05
Reactor Treatment Efficiency[e]	97.30%	97.59%	97.22%	96.69%	97.20%	0.00
Claimed Treatment Efficiency[f]	-	-87.44%	0.40%	-11.31%	-32.78%	0.48
Lead						
Average Influent Mass (µg)	79.41	79.41	79.41	79.41	79.41	0.00
Average Effluent Mass (µg)	<DL[h]	<DL	<DL	<DL	<DL	-
Influent Sampler Mass (µg)	-	<DL	<DL	<DL	<DL	-
Effluent Sampler Mass (µg)	-	<DL	<DL	<DL	<DL	-
Influent Uptake Percentage	-	-	-	-	-	-
Effluent Uptake Percentage	-	-	-	-	-	-
Reactor Treatment Efficiency	~100%[i]	~100%	~100%	~100%	~100%	-
Claimed Treatment Efficiency	-	-	-	-	-	-
Zinc						
Average Influent Mass (µg)	806.48	806.48	806.48	806.48	806.48	0.00
Average Effluent Mass (µg)	6.39	4.82	3.94	3.65	4.70	1.23
Influent Sampler Mass (µg)	-	54.26	59.02	62.09	58.46	3.95
Effluent Sampler Mass (µg)	-	47.55	50.47	47.12	48.38	1.82
Influent Uptake Percentage	-	29.21%	27.68%	27.63%	28.17%	0.01
Effluent Uptake Percentage	-	1608.39%	1023.86%	1017.54%	1216.60%	3.39
Reactor Treatment Efficiency	98.02%	97.97%	96.92%	97.04%	97.49%	0.01
Claimed Treatment Efficiency	-	-12.02%	-13.94%	-9.08%	-11.68%	0.02

[a]Reactor 1 = Control reactor lacking passive samplers
[b]- = Data not applicable or not available
[cd]Influent/Effluent Uptake Percentages = Sampler mass divided by average mass (i.e. Reactor 2, Copper Influent: 36.71% = 36.06 µg/98.23 µg and Effluent: 2851.90% = 67.59 µg/2.37µg)
[ef]Reactor/Claimed Treatment Efficiency = Unity minus effluent reactor/sampler mass divided by influent reactor/sampler mass (i.e. Reactor 2, Copper Reactor: 97.59% = 1 – [2.37 µg/98.23 µg] and Claimed: -87.44% = 1 – [67.59 µg/36.06 µg])
[g]DL = Detection Limit
[h]~100 = Treatment efficiency assumed to be 100%

All lead measurements except the influent mass was below the detection limit. As a result, most lead calculations were not able to be made. Average influent sampler uptake for the influent

samplers was 37.26% for copper; this is a significant amount of uptake for short flow conditions. Average zinc influent uptake was 28.17% which is higher than previous tests.

Effluent sampler elution masses were divided by the total mass of the influent flow for each metal. These calculations are estimates at best due to the fact that the effluent water is measured after it is exposed to the effluent sampler. This variability can be seen in the uptake calculations. Average effluent sampler uptakes for the effluent samplers were 1822.29% for Cu, not available for Pb, and 1216.60% for Zn. The copper and zinc values are much more than 100% because the effluent sampler collected more mass than effluent water concentration. The copper and zinc values are much more than 100%, while lead was not detected in the effluent flows.

Reactor treatment efficiencies are calculated by taking unity minus the effluent divided by influent water masses. Reactors removed the majority of metals: 97.20% of copper, ~100% lead, and 97.49%of zinc. The lead effluent mass was not detectable, thus it is assumed nearly complete removal occurred. The removals are slightly better than previous tests. Claimed efficiency was calculated similarly to the reactor treatment efficiencies, but with the sampler elution masses instead of the water masses. It is the hope that these values match those of the reactor treatment efficiencies in order to accurately represent them in the field. Average claimed efficiencies for copper, lead and zinc are -32.78%, not available, and -11.68%respectively. Copper and zinc efficiencies were negative because the effluent sampler contained more mass than the influent sampler. These values are much less than the actual BMP performance. The effects of using acid-washed sand to surround the samplers were visible. The resin samplers had little sign of fines within them and no noticeable discoloration.

3 Hour Synthetic Storm Results

The 3 hour storm tests were conducted with washed media and sand surrounding the samplers within the housing units. Synthetic stormwater (1 liter) was applied to the columns at a

rate of 22.59 liters/hour and the time of stormwater flowing through the reactors was 2.66 min (Table 4-4). Results are shown in Table 4-12. The control reactor does not vary from the other reactors; this points to the passive samplers having minimal interference upon BMP performance.

Table 4-12 Results of 3 hour storm with washed media & sand

	Reactor 1[a]	Reactor 2	Reactor 3	Reactor 4	Average	Std. Dev.
Copper						
Average Influent Mass (µg)	72.56	72.56	72.56	72.56	72.56	0.00
Average Effluent Mass (µg)	2.39	3.90	7.30	5.30	4.72	2.09
Influent Sampler Mass (µg)	-[b]	41.07	42.14	44.29	42.50	1.64
Effluent Sampler Mass (µg)	-	40.24	39.79	39.48	39.84	0.38
Influent Uptake Percentage[c]	-	56.60%	58.08%	61.04%	58.57%	0.02
Effluent Uptake Percentage[d]	-	1031.79%	545.07%	744.91%	773.92%	2.45
Reactor Treatment Efficiency[e]	96.71%	94.63%	89.94%	92.70%	93.49%	0.03
Claimed Treatment Efficiency[f]	-	2.02%	5.58%	10.86%	6.15%	0.04
Lead						
Average Influent Mass (µg)	142.82	142.82	142.82	142.82	142.82	0.00
Average Effluent Mass (µg)	<DL[h]	<DL	<DL	<DL	<DL	-
Influent Sampler Mass (µg)	-	0.88	1.27	3.87	2.01	1.63
Effluent Sampler Mass (µg)	-	<DL	<DL	<DL	<DL	-
Influent Uptake Percentage	-	0.62%	0.89%	2.71%	1.41%	0.01
Effluent Uptake Percentage	-	-	-	-	-	-
Reactor Treatment Efficiency	~100%[i]	~100%	~100%	~100%	~100%	-
Claimed Treatment Efficiency	-	-	-	-	-	-
Zinc						
Average Influent Mass (µg)	769.53	769.53	769.53	769.53	769.53	0.00
Average Effluent Mass (µg)	7.44	5.42	14.64	5.23	8.18	4.42
Influent Sampler Mass (µg)	-	59.84	62.42	74.89	65.72	8.05
Effluent Sampler Mass (µg)	-	47.45	47.90	86.37	60.57	22.34
Influent Uptake Percentage	-	7.78%	8.11%	9.73%	8.54%	0.01
Effluent Uptake Percentage	-	875.46%	327.19%	1651.43%	951.36%	6.65
Reactor Treatment Efficiency	99.03%	99.30%	98.10%	99.32%	98.94%	0.01
Claimed Treatment Efficiency	-	20.71%	23.26%	-15.33%	9.55%	0.22

[a]Reactor 1 = Control reactor lacking passive samplers; [b]- = Data not applicable or not available

[cd]Influent/Effluent Uptake Percentages = Sampler mass divided by average mass (i.e. Reactor 2, Copper Influent: 56.60% = 41.07 µg/72.56 µg and Effluent: 1031.79% = 40.24 µg/3.90µg)

[ef]Reactor/Claimed Treatment Efficiency = Unity minus effluent reactor/sampler mass divided by influent reactor/sampler mass (i.e. Reactor 2, Copper Reactor: 94.63% = 1 – [3.90 µg/72.56 µg] and Claimed: 2.02% = 1 – [40.24 µg/41.07 µg])

[g]DL = Detection Limit; [h]~100 = Treatment efficiency assumed to be 100%

Lead effluent measurements were below the detection limit, thus effluent sampler uptake and claimed sampler efficiency lead calculations were not made. Average influent sampler uptake

for the influent samplers was 58.57% for copper; this is a significant amount of uptake for short flow conditions. Average lead and zinc influent uptakes were 1.41% and 8.54% which is similar to previous tests. Effluent sampler elution masses are estimates at best due to the fact that the effluent water is measured after it is exposed to the effluent sampler. Average effluent sampler uptakes for the effluent samplers were 773.92% for Cu, not available for Pb, and 951.36% for Zn.

Reactor treatment efficiencies are calculated by taking unity minus the effluent divided by influent water masses. Reactors removed the majority of metals: 93.49% of copper, ~100% lead, and 98.94%zinc. The lead effluent mass was not detectable, thus it is assumed nearly complete removal occurred. The removals are slightly better than previous tests. Claimed efficiency was calculated similarly to the reactor treatment efficiencies, but with the sampler elution masses instead of the water masses. Average claimed efficiencies for copper, lead and zinc are 6.15%, not available, and9.55%respectively. These values are much less than the actual BMP performance.

12 Hour Synthetic Storm Results

The 12 hour synthetic storm was conducted with washed media as well as sand surrounding the samplers within the housing units. Synthetic stormwater (1 liter) was applied to the columns at a rate of 5.65 liters/hour and the time for 1 liter of stormwater to be applied to the reactors is 10.64 min (Table 4-4).Reactor results are displayed in Table 4-13. As is the case for all previous tests, the control reactor does not vary from the other reactors, pointing to the passive samplers having minimal interference with BMP performance.

Average influent sampler uptake for the influent samplers was 45.54% for copper; this is a significant amount of uptake for short flow conditions. Average lead and zinc influent uptakes were 1.78% and 9.02% which is similar to previous tests. Lead effluent measurements were below the detection limit, thus effluent sampler uptake and claimed sampler efficiency lead calculations were not made.

Table 4-13 Results of 12 hour storm with washed media and sand

	Reactor 1[a]	Reactor 2	Reactor 3	Reactor 4	Average	Std. Dev.
Copper						
Average Influent Mass (µg)	87.16	87.16	87.16	87.16	87.16	0.00
Average Effluent Mass (µg)	2.34	3.02	3.19	3.75	3.08	0.58
Influent Sampler Mass (µg)	-[b]	43.00	39.70	36.37	39.69	3.32
Effluent Sampler Mass (µg)	-	39.98	35.29	37.77	37.68	2.35
Influent Uptake Percentage[c]	-	49.33%	45.55%	41.73%	45.54%	0.04
Effluent Uptake Percentage[d]	-	1323.84%	1106.27%	1007.20%	1145.77%	1.62
Reactor Treatment Efficiency[e]	97.32%	96.54%	96.34%	95.70%	96.47%	0.01
Claimed Treatment Efficiency[f]	-	7.02%	11.11%	-3.85%	4.76%	0.08
Lead						
Average Influent Mass (µg)	179.30	179.30	179.30	179.30	179.30	0.00
Average Effluent Mass (µg)	<DL[h]	<DL	<DL	<DL	<DL	-
Influent Sampler Mass (µg)	-	6.33	1.98	1.28	3.196667	2.74
Effluent Sampler Mass (µg)	-	<DL	<DL	<DL	<DL	-
Influent Uptake Percentage	-	3.53%	1.10%	0.71%	1.78%	0.02
Effluent Uptake Percentage	-	-	-	-	-	-
Reactor Treatment Efficiency	~100%[i]	~100%	~100%	~100%	~100%	-
Claimed Treatment Efficiency	-	-	-	-	-	-
Zinc						
Average Influent Mass (µg)	836.38	836.38	836.38	836.38	836.38	0.00
Average Effluent Mass (µg)	7.95	3.92	5.65	2.77	5.07	2.25
Influent Sampler Mass (µg)	-	98.32	69.22	58.83	75.46	20.47
Effluent Sampler Mass (µg)	-	50.90	49.55	47.78	49.41	1.56
Influent Uptake Percentage	-	11.76%	8.28%	7.03%	9.02%	0.02
Effluent Uptake Percentage	-	1298.47%	876.99%	1724.91%	1300.12%	4.24
Reactor Treatment Efficiency	99.05%	99.53%	99.32%	99.67%	99.39%	0.00
Claimed Treatment Efficiency	-	48.23%	28.42%	18.78%	31.81%	0.15

[a]Reactor 1 = Control reactor lacking passive samplers
[b]- = Data not applicable or not available
[cd]Influent/Effluent Uptake Percentages = Sampler mass divided by average mass
[ef]Reactor/Claimed Treatment Efficiency = Unity minus effluent reactor/sampler mass divided by influent reactor/sampler mass
[g]DL = Detection Limit
[h]~100 = Treatment efficiency assumed to be 100%

Effluent sampler elution masses are estimates at best due to the fact that the effluent water is measured after it is exposed to the effluent sampler. Average effluent sampler uptakes for the

effluent samplers were 1145.77%, not available, and 1300.12% for copper, lead and zinc respectively.

Reactor treatment efficiencies are calculated by taking unity minus the effluent divided by influent water masses. Reactors removed the majority of metals: 96.47% of copper, ~100% lead, and 99.39% zinc. The lead effluent mass was not detectable, thus it is assumed nearly complete removal occurred. The removals are slightly better than previous tests.

Average claimed efficiencies for copper, lead and zinc are 4.76%, not available, and 31.81% respectively. These values are much less than the actual BMP performance. Claimed efficiency was calculated similarly to the reactor treatment efficiencies, but with the sampler elution masses instead of the water masses.

4.3.1.3 Synthetic Storm Tests Discussion

Overall the samplers performed much less predictably than expected within the flow scenarios. Interactions with fine particles leached from the media (and the particles added in the synthetic stormwater) lead to modification of the media by washing with 202.2 liters of tap water. The media immediately surrounding the samplers was changed from the sand/compost mixture to acid washed sand to help alleviate the aforementioned problem.

Comparison of treatment efficiencies for the control reactor (e.g. 91.47% for Reactor 1 in the 1st0.5-h Test-Unwashed Media, Table 4-9) which lacked passive samplers, with the remaining reactors (e.g. 91.89% for Reactor 2, 84.06% for Reactor 3, and 91.80% for Reactor 4 in the 1st 0.5-h Test-Unwashed Media, Table 4-9) proved that the presence of passive samplers had little effect on BMP performance.

Reactor averages and standard deviations are presented in Table 4-14. This compilation of influent & effluent masses in the water and on the samplers as well as pertinent calculations

provides a wide spread comparison of some major factors contributing to metal mass uptake onto the samplers. These factors include the effects of media surrounding the sampler, the effects of fine particles, and the effects of flow rates.

Comparing the sampler masses in the 0.5-h Unwashed and 0.5-h Washed vs. 0.5-h Washed Sand columns in Table 4-14, can show the effect of the media type immediately surrounding the samplers under the same flow rate. In the 0.5-h Unwashed and 0.5-h Washed tests the samplers were surrounded with the sand/compost media. In the 0.5-h Washed Sand test samplers were surrounded with acid-washed sand. For example, a look at the zinc masses on the influent samplers(103.20 μg for the 0.5-h Unwashed test; 76.03 μg for the 0.5-h Washed test; and 58.46 μg for the 0.5-h Washed Sand test)and zinc masses on the effluent samplers (85.40 μg for the 0.5-h Unwashed test; 63.59 μg for the 0.5-h Washed test; and 48.38 μg for the 0.5-h Washed Sand test) reveals the media wash and sand surrounding the samplers reduced the total metals taken up onto the samplers. This was the case for all metals and samplers except for copper uptake onto the effluent samplers (42.80 μg for the 0.5-h unwashed test; 42.39 μg for the 0.5-h Washed test; and 48.33 μg for the 0.5-h Washed Sand test). This correlates with seeing decreasing amounts of fine particles within the samplers for the washed media and the sand test. Less fine particles within the sampler means less fine particles within the elution, and thus, less potential for the elution to pull more than dissolved metals from the samplers.

Table 4-14 Summary of lab-scale stormwater loading tests

	0.5-h Unwashed		0.5-h Washed		0.5-h Washed Sand		3-h Washed Sand		12-h Washed Sand	
	Average	**Std. Dev.**	**Average**	**Std. Dev.**	**Average**	**Std. Dev.**	**Average**	**Std. Dev.**	**Average**	**Std. Dev.**
Copper										
Influent Mass (μg)	102.34	0.00	134.70	0.00	98.23	0.00	72.56	0.00	87.16	0.00
Effluent Mass (μg)	10.43	3.92	3.39	0.79	2.75	0.37	4.72	2.09	3.08	0.58
Influent Sampler Mass (μg)	41.80	6.75	37.95	1.20	36.60	3.20	42.50	1.64	39.69	3.32
Effluent Sampler Mass (μg)	42.80	0.17	42.39	1.74	48.33	16.72	39.84	0.38	37.68	2.35
Influent Uptake Percentage	40.85%	0.07	28.17%	0.01	37.26%	0.03	58.57%	0.02	45.54%	0.04
Effluent Uptake Percentage	429.10%	1.44	1216.60%	3.39	1822.29%	9.05	773.92%	2.45	1145.77%	1.62
Reactor Treatment Efficiency	89.81%	0.04	97.49%	0.01	97.20%	0.00	93.49%	0.03	96.47%	0.01
Claimed Treatment Efficiency	-4.37%	0.19	-11.68%	0.02	-32.78%	0.48	6.15%	0.04	4.76%	0.08
Lead										
Influent Mass (μg)	106.32	0.00	63.95	0.00	79.41	0.00	142.82	0.00	179.30	0.00
Effluent Mass (μg)	<DL	-	<DL	-	<DL	-	<DL	-	<DL	-
Influent Sampler Mass (μg)	5.35	2.97	1.05	0.47	<DL	-	2.01	1.63	3.196667	2.74
Effluent Sampler Mass (μg)	3.36	0.65	<DL	-	<DL	-	<DL	-	<DL	-
Influent Uptake Percentage	5.04%	0.03	1.64%	0.01	-	-	1.41%	0.01	1.78%	0.02
Effluent Uptake Percentage	-	-	-	-	-	-	-	-	-	-
Reactor Treatment Efficiency	~100%	-	~100%	-	~100%	-	~100%	-	~100%	-
Claimed Treatment Efficiency	22.33%	0.49	-	-	-	-	-	-	-	-
Zinc										
Influent Mass (μg)	903.09	0.00	1137.93	0.00	806.48	0.00	769.53	0.00	836.38	0.00
Effluent Mass (μg)	47.05	13.87	5.525	0.78	4.70	1.23	8.18	4.42	5.07	2.25
Influent Sampler Mass (μg)	103.20	37.47	76.03	21.77	58.46	3.95	65.72	8.05	75.46	20.47
Effluent Sampler Mass (μg)	85.40	17.48	63.59	5.20	48.38	1.82	60.57	22.34	49.41	1.56
Influent Uptake Percentage	11.43%	0.04	6.68%	0.02	28.17%	0.01	8.54%	0.01	9.02%	0.02
Effluent Uptake Percentage	199.16%	0.96	1094.58%	1.22	1216.60%	3.39	951.36%	6.65	1300.12%	4.24
Reactor Treatment Efficiency	94.79%	0.02	99.49%	0.00	97.49%	0.01	98.94%	0.01	99.39%	0.00
Claimed Treatment Efficiency	13.64%	0.17	11.32%	0.27	-11.68%	0.02	9.55%	0.22	31.81%	0.15

Comparing the effects of the media wash can be achieved by looking at the 0.5-h Unwashed and 0.5-h Washed columns within Table 4-14. The only difference in circumstances between the 0.5-h unwashed test and the 0.5-h Washed test is the media within the reactors. A look at the influent uptake percentages for copper (40.85% for the 0.5-h Unwashed test and 28.17% for the 0.5-h Washed test), lead (5.04% for the 0.5-h Unwashed test and 1.64% for the 0.5-h Washed test), and zinc (11.43% for the 0.5-h Unwashed test and 6.68% for the 0.5-h Washed test) reveals that the media wash decreased the amount of metal uptake across the board. A look at the effluent uptake percentages for copper (429.10% for the 0.5-h Unwashed test and 1216.60% for the 0.5-h Washed test), lead (not calculable for either), and zinc (199.16% for the 0.5-h Unwashed test and 1094.58% for the 0.5-h Washed test) shows a trend the other way. The reactor treatment efficiencies for copper (89.81% for the 0.5-h Unwashed test and 97.49% for the 0.5-h Washed test), lead (assumed 100% for both), and zinc (94.79% for the 0.5-h Unwashed test and 99.49% for the 0.5-h Washed test) show marked improvement with the media wash.

The effects of flow rate can be attained by comparing the 0.5-h Washed Sand, 3-h Washed Sand, and 12-h Washed Sand tests. A look at influent sampler uptakes for copper (38.26% for the 0.5-h Washed Sand test, 58.57% for the 3-h Washed Sand test, and 45.54% for the 12-h Washed Sand Test), lead (non-detect. for the 0.5-h Washed Sand test, 1.41% for the 3-h Washed Sand test, and 1.78% for the 12-h Washed Sand Test), and zinc (28.17% for the 0.5-h Washed Sand test, 8.54% for the 3-h Washed Sand test, and 9.02% for the 12-h Washed Sand Test) points to minimal consistency for the samplers.

Another important phenomenon was the tendency for effluent samplers to accumulate more mass than was present within the effluent flows. This could be for two reasons. The first is that the sample was collected following exposure to the exchange resin. This could mean that any mass transferred to the sampler isn't present in the sample. A second, more likely possibility is that the ion exchange resins are able to accumulate more than just the dissolved fraction of metals

within the environment; metals originally associated with the media or the acid-washed sand might have been attracted by the resins, released into the aqueous phase and then absorbed by the resins. A study was able to group metals into five distinct species within the environment (Tessier et al. 1979). This has been capitalized on in other instances, as some ion exchange resins are utilized for monitoring metals within soils (Qian and Schoenau 2002).

The inconsistency of the claimed reactor treatment efficiencies based on different flows applied to the system points to an incorrect assumption of flow rates through the reactor. Time of flow or ponding into the media was measured for the rectors and it ranged from 3 to 26 minutes. This means the influent samplers were only exposed to flow for part of the exposure time of the effluent samplers. The effluent reactors were exposed for different times (48 min to 57 min) than those of the influent reactors and the direct comparison of masses is inaccurate. One way to overcome this problem is to incorporate performance reference compounds (PRCs) within the samplers.

Another approach is to adjust the presented results based on time of exposure and known concentrations within the reactors. Due to time limitations, this concept has not been allowed to mature. Initial adjustments have promising results, but lack sensitivity to accumulated sampler mass.

4.3.1.4 Comparison to Batch Test Results

In order to compare the reactor results to the batch test results, a few major assumptions must be made. The first assumption is that the rate constant remains the same in both the batch tests and the reactor tests. A second assumption is that the samplers were exposed to the flow for a full hour (60 minutes). With these assumptions, the k, which was determined in the batch tests, can be applied to the reactors. The sampler mass can be treated as the concentration because only one liter is used in all tests. This means the mass in the solution is per liter and the mass taken

onto the resin is per liter. The natural log is taken of the concentration of the solution, as is the case for the first hour of the batch experiments (3.3.2 Ion Exchange Resin Sampler). Equations from Section three (Batch Tests) are presented in the following form (Equation 3-1):

$$\boldsymbol{ln(C) = -kt + ln(C_0)} \tag{4-4}$$

Where C = concentration of metal within solution (µg/l); k = rate constant (min^{-1}); t = time (min); and C_0 = initial metal concentration (µg/l). Eq. 4-4 can be rearranged as:

$$\boldsymbol{C = C_0 e^{-kt}} \tag{4-5}$$

From the batch tests, the rate constants have been determined. Only the time of exposure and the elution mass is needed. For equation 4-5, C_0 is the only unknown, because the k is already determined, the elution will be found, and the time should be recorded. An analysis assessing this approach is given within section 3.3.2.5 (Ion Exchange Resin Sampler Discussion).

The sampler results have been assessed and are presented in Table 4-15. The first columns presents the rate constants (k) as determined from section 3.3.1.3 (Stormwater Test Results). The second column presents the sampler masses as reported within section 4.3.1.2 (Results of Synthetic Stormwater Loading Tests).The third column presents the natural log of the sampler masses (assumed to be concentrations). The fourth column presents the time of sampler exposure (assumed to be 60 minutes, the length of the test). The fifth column displays the y-intercept of Equation 4-4 using Columns 1, 3, and 4. The sixth column presents the C_0 from the fifth column. The seventh column presents the actual concentration the sampler was exposed to (influent or effluent). A percent error comparison of the actual and calculated C_0 populates the final column.

Table 4-15 First-order concentration determination lab-scale BMP reactors

	K (min^{-1})	Sampler Mass (µg)	ln(C)[a]	Time (min)	ln(C_0)[b]	Calculated C_0 (µg/l)[c]	Actual C_0 (µg/l)	Percent Error (%)[d]
0.5-h Unwashed Test (influent)								
Cu	-0.0083	41.8	3.73	60	4.23	68.77	102.34	32.79%
Pb	-0.01	5.35	1.67	60	2.27	9.74	106.32	90.83%
Zn	-0.0163	103.2	4.63	60	5.61	274.42	1196.12	77.06%
0.5-h Unwashed Test (effluent)								
Cu	-0.0083	42.8	3.75	60	4.25	70.42	10.43	-575.21%
Pb	-0.01	3.36	1.21	60	1.81	6.12	< DL	-
Zn	-0.0163	85.4	4.44	60	5.42	227.08	1196.12	81.01%
0.5-h Washed Test (influent)								
Cu	-0.0083	37.95	3.63	60	4.13	62.44	134.7	53.64%
Pb	-0.01	1.05	0.04	60	0.64	1.91	63.95	97.01%
Zn	-0.0163	76.03	4.33	60	5.30	202.17	1137.93	82.23%
0.5-h Washed Test (effluent)								
Cu	-0.0083	42.39	3.74	60	4.24	3.39	10.43	67.50%
Pb	-0.01	< DL[e]	-[f]	60	-	-	< DL	-
Zn	-0.0163	63.59	4.15	60	5.13	169.09	1137.93	85.14%
0.5-h Washed Sand Test (influent)								
Cu	-0.0083	36.6	3.60	60	4.09	60.2	98.23	38.69%
Pb	-0.01	< DL	-	60	-	-	79.41	-
Zn	-0.0163	58.46	4.06	60	5.04	155.45	806.48	80.72%
0.5-h Washed Sand Test (effluent)								
Cu	-0.0083	48.33	3.87	60	4.37	3.39	2.75	-23.27%
Pb	-0.01	< DL	-	60	-	-	< DL	-
Zn	-0.0163	48.38	3.87	60	4.85	128.64	4.7	-2637.21%
3-h Washed Sand Test (influent)								
Cu	-0.0083	42.5	3.75	60	4.24	69.93	72.56	3.62%
Pb	-0.01	2.01	0.69	60	1.29	3.66	142.82	97.44%
Zn	-0.0163	65.72	4.18	60	5.16	174.75	769.53	77.29%

[a]ln(C) = ln(Sampler mass) (i.e. 0.5-h Unwashed test (influent)Copper: ln(41.8) = 3.73) *(continued on next page)*
[b]ln(C_0) = y-intercept (i.e. 0.5-h Unwashed test (influent) Copper: ln(C_0) = 3.73 – (-0.0083)*60)
[c]Calculated C_0 = Calculated Initial Concentration (i.e. 0.5-h Unwashed test (influent) Copper: e^(4.23) = 68.78)
[d]Percent Error (%) = Unity minus Calculated C_0/Actual C_0 (i.e. 0.5-h Unwashed test (influent) Copper: 1 – (68.77/102.34))
[e]DL = Detection Limit
[f]- = Value not available

Table 4-15 First-order concentration determination lab-scale bmp reactors (continued)

	K (min^{-1})	Sampler Mass (µg)	ln(C)	Time (min)	ln(C_0)	Calculated C_0 (µg/l)	Actual C_0 (µg/l)	% Error
3-h Washed Sand Test (effluent)								
Cu	-0.0083	39.84	3.68	60	4.18	3.39	4.72	28.18%
Pb	-0.01	< DL	-	60	-	-	< DL	-
Zn	-0.0163	60.57	4.10	60	5.08	161.06	8.18	-1868.99%
12-h Washed Sand Test (influent)								
Cu	-0.0083	39.69	3.68	60	4.17	65.307	87.16	25.07%
Pb	-0.01	3.2	1.16	60	1.76	5.83	179.3	96.75%
Zn	-0.0163	75.46	4.32	60	5.30	200.65	836.38	76.01%
12-h Washed Sand Test (effluent)								
Cu	-0.0083	37.68	3.62	60	4.12	3.39	3.08	-10.06%
Pb	-0.01	< DL	-	60	-	-	< DL	-
Zn	-0.0163	49.41	3.90	60	4.87	131.38	5.07	-2491.47%

Calculating the initial concentration via the means described within this report, produces highly variable results. This means the assumptions must not be accurate, or there are other factors in metal uptake onto ion exchange resin that were not considered.

However, incorporating the mass balance, the performance of the passive samplers, the rate constants determined in section three (Batch tests), and the time of exposure could give a much more accurate claimed treatment efficiency. Efforts to adjust the data in this manner are still being evaluated.

4.3.2 Field BMP Tests

Passive samplers were deployed within the filter trench deployment units and the sand/compost mixture bioretention unit the evening of June 26th. The samplers were deployed by 7:30 pm the evening of June 26th and were collected at around 1:30pm the following afternoon (6/27). Cumulative precipitation, ditch water levels, velocities, flow rates and total flows were

collected and calculated. These results are presented below along with the results of sampler elution and analysis of the various grab samples collected.

4.3.2.1 Storm Characteristics

Rain gauge data and velocity sensor data was collected during the time of sampler deployment. Data used to generate figures within this section is presented in Appendix C (Further Data).

Rainfall began at 7:28am on June 27th until about 9:00am. A few isolated showers followed at approximately 9:30am and again around noon. No other precipitation was recorded during the time of sampler deployment. The cumulative precipitation for the deployment period is displayed in Figure 4-19.

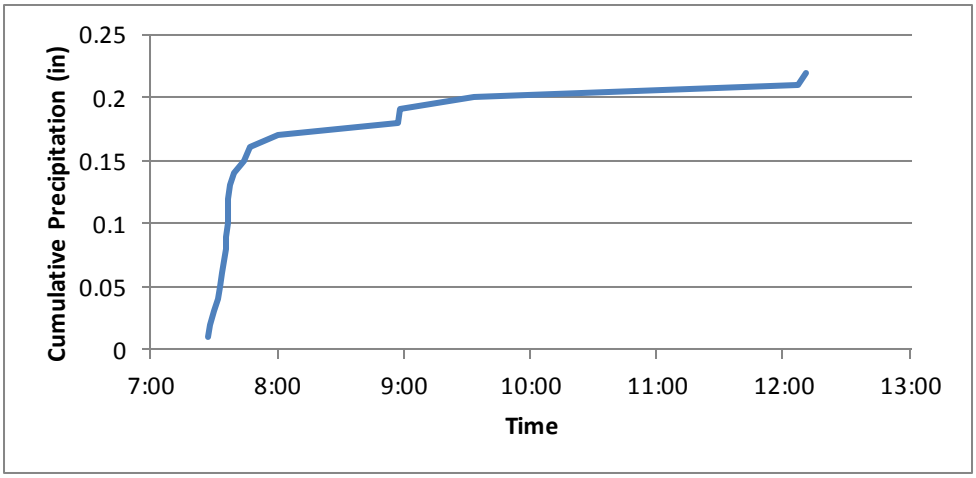

Figure 4-19 Cumulative precipitation during sampler deployment

The level of water flowing past the sensor was also recorded. The flows past the sensor were slightly delayed from the actual rainfall event. The water levels on June 27th from 7:00am until 1:30pm the samplers were removed at 1:30pm are displayed in Figure 4-20. It is important to note that some noise was detected and can be seen by the initial level at 7:00am being 0.5 inches prior to any rainfall.

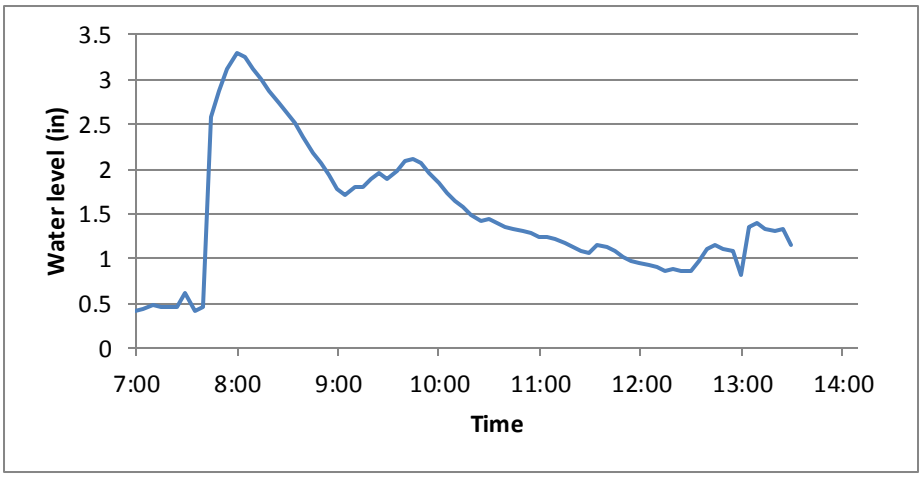

Figure 4-20 Water levels during sampler deployment

The velocity of flow was also attained by the sensor. Velocities are displayed for June 27th from 7:00am until 1:30pm in Figure 4-21. Accuracy is compromised by background noise, which can be seen by a velocity being present prior to any rainfall.

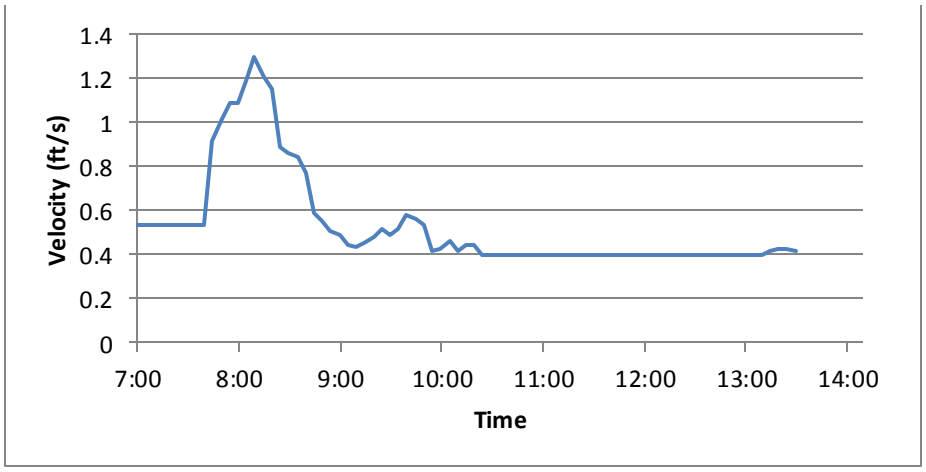

Figure 4-21 Velocity during sampler deployment

Flow rates and total flows were calculated using the detected velocities, water levels, and a basic geometry of the channel. These values are presented in Figure 4-22 and Figure 4-23. The senor module was able to eliminate background noise when only one parameter was sensing. This is seen by the fact that no flows were calculated prior to rainfall despite false water level and velocity readings.

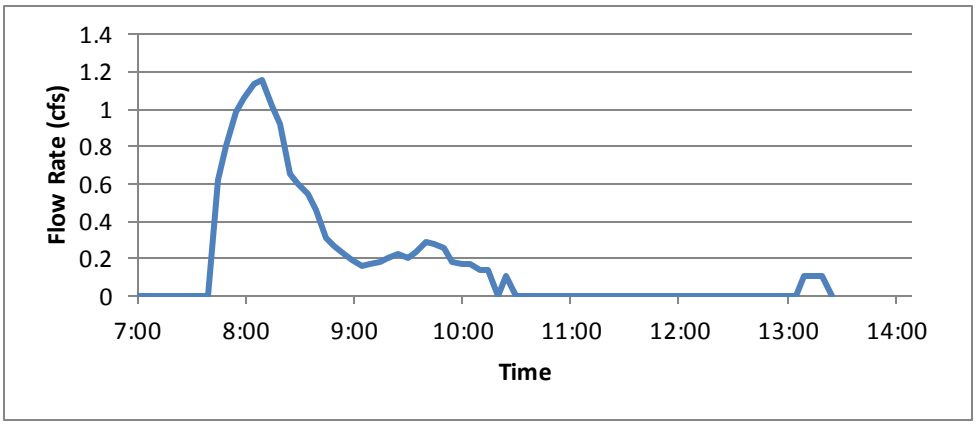

Figure 4-22 Flow rates during sampler deployment

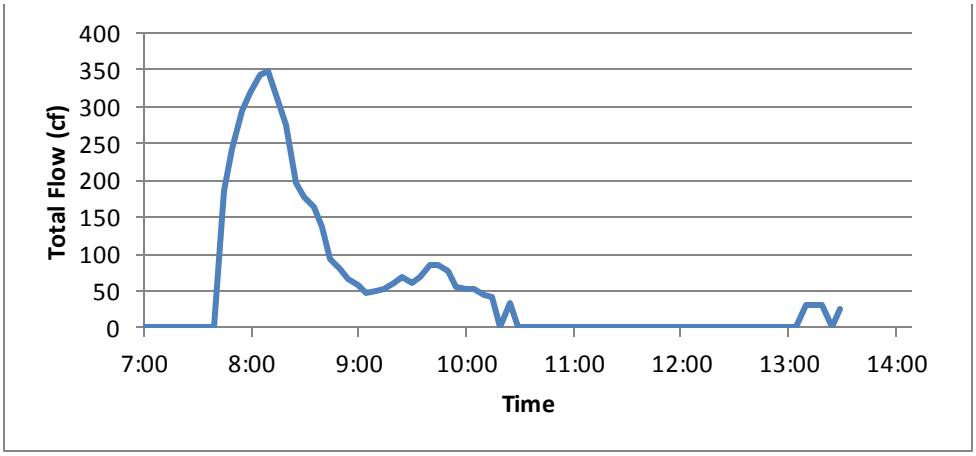

Figure 4-23 Total flows during sampler deployment

4.3.2.2 Sampler and Grab Sample Results

Samplers were analyzed within the lab along with grab samples that were collected upon sampler collection near the storm's end. Filter trench influent flows were collected four times (12:15pm, 12:30pm, 12:45pm, and 1:00pm) while effluent flows were collected five times (12:00pm, 12:15pm, 12:30pm, 12:45pm, and 1:00pm). Flow into the bioretention cells occurred only once while present (1:15pm) and no effluent flow occurred during collection. Passive samplers were collected at 1:15pm for the bioretention cell and 1:23pm and 1:27pm for the influent and effluent deployment units for the filter trench.

Sampler elution masses and grab sample concentrations are presented in **Error! eference source not found.**. The percent removal attained by the BMP according to the sampler masses is also presented. Because the amount of flow past the samplers is not quantified, percent uptake calculations were not performed.

Table 4-16 Field sampler and grab sample results

	Bioretention Cell	**Filter Trench[a]**
Copper		
Influent Conc. (µg/l)	4.66	5.65
Effluent Conc. (µg/l)	-[b]	2.99
Influent Sampler Mass (µg)	32.52	36.83
Effluent Sampler Mass (µg)	42.35	40.49
Claimed Treatment Efficiency[c]	-30.23%	-9.93%
Lead		
Influent Conc. (µg/l)	<DL[d]	<DL
Effluent Conc. (µg/l)	-	<DL
Influent Sampler Mass (µg)	<DL	<DL
Effluent Sampler Mass (µg)	0.8479	<DL
Claimed Treatment Efficiency	-	-
Zinc		
Influent Conc. (µg/l)	12.40	9.55
Effluent Conc. (µg/l)	-	1.76
Influent Sampler Mass (µg)	51.08	47.87
Effluent Sampler Mass (µg)	51.68	48.44
Claimed Treatment Efficiency	-1.19%	-1.19%

[a]FilterTrench = Inf/Eff Conc. are average of collected grab samples
[b]- = Data not applicable or not available
[c]Claimed Treatment Efficiency = Unity minus Eff Sampler Mass/Inf Sampler Mass (i.e. Bioretention Cell, Copper: -30.23% = 1 - (42.35/32.52))
[d]<DL = Value below detection limit

4.3.2.3 Field BMP Discussion

The claimed efficiencies for all metals were either non-detectable (lead) or negative, meaning more mass accumulated in the effluent sampler than the influent. This is a significant problem and should be addressed in future work.

Although the amount of data provided by the rain gauge and velocity sensor is useful, it is difficult to attain specific flows for each BMP, let alone each sampler. A HEC-HMS model has been used for the site watershed and, once calibrated, would enable the calculation of flows through each BMP based on the data attained by the sensor. This model, once complete, could give a much clearer idea of the BMP flows for each storm event, however, it will not be able to calculate the specific flows each sampler is exposed to.

4.4 Supplemental Tests

4.4.1 Motivation

Results for the column tests are summarized in Table 4-12, but we could not explain why the mass in the influent and effluent samplers in these tests are almost the same (e.g., for Cu in reactor 2, 41.07 vs. 40.24 μg). If the BMP removed 95% of the metals, the mass in the effluent sampler should be less than 10% of that in the influent sampler. After two months of intensive studies (e.g., data analysis, additional tests, and literature search), we found the two major reasons as follows:

(1) The influent and effluent passive samplers should be placed in two different flow paths in order to obtain representative data for calculation of removal efficiency.

(2) Sulfuric acid should not be used as the eluent as it will cause formation of isotopes that interfere with ICP-MS results (see Appendix B).

Therefore, supplemental tests were conducted by using three columns under each test condition to determine the feasibility of using the ion exchange passive samplers for monitoring heavy metals in bioretention cells used for highway runoff treatment. In all of the supplementary tests, trace metal grade HNO_3 was used as the eluent.

4.4.2 Materials and Methods

4.4.2.1 Reactor Design and Passive Sampler Deployment

Ion exchange resin samplers consisted of 20 g Amber IRC748 within a woven polyester monofilament mesh (i.e., the same mass and material as used in section 4.2) were used. The samplers had round shapes (diameter = 3 in) (Figure 4-24). They were placed within the PVC sampler housing unit (diameter = 3 in, height = 2 in; same as in section 4.2) such that no preferential flow along the wall would occur in the sampler unit. The sampler units were placed into the columns in the same manner as detailed in section 4.2.1.

Figure 4-24 Ion exchange resin sampler used in supplemental tests. The sampler's dimensions were the same as the housing units and BMP columns to ensure all the synthetic stormwater flowing through the sampler

For each test condition, three lab-scale bioretention cells that were the same as those used in section 4.2 (i.e., 3-in PVC pipe filled with 18-in height media) were used. The first cell had a passive sampler on the top for measuring the influent mass; the second cell had a sampler at the bottom for measuring the effluent mass; and the third was the control (without samplers) for

measuring the actual treatment efficiency of the BMP. The medium used was a 50/50 (v/v) sand and compost mixture, mimicking the bioretention media mixture used in the field.

4.4.2.2 Experimental Design, Sampling, Measurements and Analytical Methods

Three storm durations (0.5, 3, and 12 h) were tested. As in section 4.2, a scaled-down approach was developed. The constituents and concentrations of the synthetic stormwater used in this part of the study were the same as the values shown in Table 4-2. For each test, one liter of synthetic stormwater was applied at the rate listed in Table 4-4 with the same methods used in section 4.3 for the column tests.

The methods for sampling, sample treatment for elution, and sample analyses were the same as those in sections 4.2 and 4.3. Briefly, influent and effluent samplers were removed from the reactors after the bioretention cells had been loaded with synthetic stormwater for the specified storm and then allowed to air-dry for a day for ease of handing. Then the resins were poured into a burette containing a small amount of 10% (v/v) nitric acid (15 ml) enabling the resin to expand before settling. This prevents clogging of the burette during elution. The elution consisted of passing 500 ml of 10% (v/v) nitric acid over the resin at a flow rate of 2 ml/min. The elution was conducted in fume hood. From the resulting solution a sample was collected and analyzed. Sample volumes were 5 ml. For the control reactor, influent samples were collected prior to the reactors being loaded. Effluent samples were collected one hour following the loading of the stormwater. Sample volumes were also 5 ml and were filtered via 0.45 micron cellulose acetate filter paper prior to preservation and analysis, and preserved with 2% (v/v) nitric acid. All samples were analyzed with ICP-MS in the same manner detailed in section 3.2.3.4.

4.4.3 Results and Discussion

The tests results are summarized in Table 4-17. Control tests indicated that the BMPs removed the majority of the heavy metals: 94.96–97.34% of copper, 98.32–99.77% of lead,

97.44–98.43% of zinc. The removal efficiencies slightly increased with a longer duration. The average influent uptake percentages for the three respective durations (0.5, 3, and 12 h) by the influent heavy metal passive samplers were 49.26 [= (45.85 + 46.43 + 55.51)/3], 15.17, and 40.59 for copper, lead, and zinc, respectively (Table 4-17). The corresponding average effluent uptake percentages by the effluent heavy metal passive samplers were 26.16, 142.85, and 43.26% for copper, lead, and zinc, respectively (Table 4-17). The effluent lead uptake percentage in the 12 h event test was 300% (= 0.9/0.3). However, the true value of the lead concentration in the effluent of the BMP column with a sampler could be different from that in the control column effluent. Therefore, the high lead uptake percentage should not be viewed as a significant error. As a whole, the uptake percentages slightly increased with an increase in storm duration. This is likely because longer durations allow a longer contact time between the sampler and synthetic stormwater. The claimed removal percentages (i.e., as measured by passive samplers) were very similar to the actual treatment efficiencies calculated from control reactors. The errors ranged from -4.86% to 2.15%.

4.4.4 Summary of Supplemental Tests

The average influent uptake percentages by the influent samplers for three respective storm durations (0.5, 3, and 12 h) were 49.26%, 15.17%, and 40.59% for copper, lead, and zinc, respectively, and that by the effluent samplers were 35.57%, 66.31%, and 43.25% for copper, lead, and zinc, respectively. The claimed removal percentages by passive samplers were very similar to the actual treatment efficiencies calculated from control reactors. The treatment percentage errors between the claimed and actual values ranged from -4.99% to 2.15%. The results indicated that the ion exchange resin passive sampler can be used for monitoring both heavy metals in highway runoff and the performance of bioretention cells for heavy metal removal.

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Table 4-17 Results of supplemental tests

	0.5 h	3 h	12 h
Copper			
Influent Mass (μg)[a]	123.0	114.8	112.6
Effluent Mass (μg)[a]	6.2	4.9	3.0
Influent Sampler Mass (μg)	56.4	53.3	62.5
Effluent Sampler Mass (μg)	1.63	1.74	0.50
Influent Uptake Percentage[b]	45.85%	46.43%	55.51%
Effluent Uptake Percentage[b]	26.29%	35.51%	16.67%
Actual Treatment Efficiency[c]	94.96%	95.73%	97.34%
Claimed Treatment Efficiency[d]	97.11%	96.74%	99.20%
Treatment Efficiency Error[e]	2.15%	1.01%	1.86%
Lead			
Influent Mass (μg)[a]	119.4	118.0	129.4
Effluent Mass (μg)[a]	2.0	1.4	0.3
Influent Sampler Mass (μg)	15.3	18.8	21.7
Effluent Sampler Mass (μg)	1.0	1.1	0.9
Influent Uptake Percentage[b]	12.81%	15.93%	16.77%
Effluent Uptake Percentage[b]	50.00%	78.57%	300.00%
Actual Treatment Efficiency[c]	98.32%	98.81%	99.77%
Claimed Treatment Efficiency[d]	93.46%	94.15%	95.85%
Treatment Efficiency Error[e]	-4.86%	-4.66%	-3.92%
Zinc			
Influent Mass (μg)[a]	780.9	737.9	728.1
Effluent Mass (μg)[a]	20.0	12.5	11.4
Influent Sampler Mass (μg)	296	326	289
Effluent Sampler Mass (μg)	6.16	6.45	5.4
Influent Uptake Percentage[b]	37.90%	44.18%	39.69%
Effluent Uptake Percentage[b]	30.80%	51.60%	47.37%
Actual Treatment Efficiency[c]	97.44%	98.31%	98.43%
Claimed Treatment Efficiency[d]	97.92%	98.02%	98.13%
Treatment Efficiency Error[e]	0.48%	-0.29%	-0.3%

[a]Influent mass and effluent mass value were from the control reactor

[b]Influent/effluent uptake percentages = sampler mass divided by mass from control reactor (e.g., at 0.5 h, Cu influent uptake percentage: 45.85% = 56.4 /123, and effluent: 26.29% = 1.63 /6.2)

[c]Actual treatment efficiency = influent minus effluent mass divided by influent mass from control reactor (e.g., at 0.5 h, Cu actual treatment efficiency, 94.96% = (123 - 6.2)/123)

[d]Claimed treatment efficiency = influent sampler mass minus effluent sampler mass divided by influent sampler mass (e.g., at 0.5 h, Cu claimed treatment efficiency, 97.11% = (56.4 - 1.63)/56.4)

[e]Treatment efficiency error = Claimed treatment efficiency minus actual treatment efficiency (e.g., at 0.5 h, Cu treatment efficiency error, 2.15% = 97.11% - 94.96%)

4.5 Conclusions

Lab-scale BMPs were designed and constructed to expose ion exchange resin passive samplers to various flow scenarios. These controlled scenarios included the application of synthetic stormwater at rates expected for storm durations of 0.5, 3, and 12 hours. A field test was also conducted by placing the samplers in deployment units upstream and downstream of pilot BMPs and utilizing velocity sensor data for the site to characterize the storm event.

Results indicate that the influent and effluent passive samplers must be placed in two different flow paths in order to obtain representative data for calculation of claimed removal efficiency. Results of supplemental tests indicate that the samplers can be used for monitoring BMPs under the given conditions.

Chapter 5 Batch Tests for PAH Passive Sampler

5.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group organic compounds that are commonly found in highway runoff. The compounds and related metabolites are of concern because various studies have indicated some of them are carcinogenic. PAHs are usually present at trace (i.e., µg/L) or ultra-trace (i.e., ng/L) levels in stormwater (DiBlasi et al. 2009 Watts et al. 2010). Such low concentration requires extraction from 10 to 100 liters of runoff sample by routine analytical methods.

Passive sampling techniques can measure the time-integrated concentration in the environment. Komarova et al. (2006) used semi-permeable membrane devices (SPMD) to measure PAHs in stormwater. They found that SPMD could measure some types of PAHs in stormwater. However, their results indicated that the claimed PAHs data by SPMD were consistently lower than those obtained by grab water samples because the lower molar mass PAHs are not readily absorbed by SPMD from stormwater.

Because of being low-cost and versatile, PUF is commonly used as a passive air sampler for semi-volatile organic compounds, especially for SVOCs, such as PAHs and polychlorinated biphenyls (PCBs) (Petrich et al. 2013). However, to our knowledge, PUF has not been used as an absorbent in passive samplers for monitoring PAHs in stormwater runoff.

The objectives of this study were to: i) evaluate the feasibility of developing PUF passive samplers for stormwater monitoring; and ii) investigate the feasibility of monitoring the performance of BMPs for treatment of phenanthrene (PHE) (a PAH representative) in highway stormwater runoff.

5.2 Materials and Methods

5.2.1 Material

The PUF was made from 1/8-in-thick polyurethane foam sheet (6×9×1/8 in, 100 pore-per-inch, density of 0.03g/cm3), which was purchased from ITW Inc. (3600 West Lake Ave Glenview, IL 60026). ^{14}C-labled PHE (phenanthrene-9-^{14}C, specific activity = 0.1 mCi/ml) was purchased from American Radiololabeled Chemicals Inc. (101 ARC Dr., St. Louis, MO 63146). PHE standard solution (200 μg/ml in methylene chloride, analytical standard) was purchased from Supelco Inc. (595 North Harrison Road, Bellefonte, PA 16832). ACS grade methanol and HPLC grade methylene chloride were purchased from Fisher Scientific (Fair Lawn, NJ 07410).

To eliminate PHE that may accumulated in the PUF prior to any tests, the PUF was soaked in methanol for 12 h in a beaker with magnetic stirring, then rinsed with DI water three times, then put into the drying oven for 24 h at 70 °C. After that, the PUF was sealed in plastic bags and was ready for use.

Deionized (DI) water with a resistance of ~18.2 mΩ-cm was made by a Barnstead Smart2Pure System (Barnstead Easypure RoDi, Thermo scientific Inc., Waltham, MA 02454). Ten (10) μL ^{14}C-labled PHE was added to 50 ml methanol to obtain a radioactive PHE solution with a concentration of 0.013 μg PHE/ml of methanol. Unlabeled PHE stock solution was prepared by adding PHE standard solution into DI water to obtain a stock solution of 100 μg/L, which then was diluted sequentially to a series of concentrations (0.03–10 μg/L). The solutions of different concentrations were spiked with the ^{14}C-labled PHE solution and then were used in different tests. The ^{14}C changes in each solution were tracked using a Packard A2500 liquid scintillation counter (LSC). To do so, 200 μL sample was removed and placed into a 5-ml scintillation cocktail (PeakinElmer, 6013179) in a vial, and then every sample was analyzed counted in the LSC.

5.2.2 Methods

5.2.2.1 Kinetic Tests

A kinetic study was conducted to explore the PUF's sorption ability for PHE in stormwater runoff. Preconditioned PUF sheets were cut into small pieces (0.15 × 0.15 × 0.13in). About 60 pieces of PUF (total mass = 0.15 g/beaker) were added into a beaker with 30-ml ^{14}C-spiked PHE solution (Figure 5-1). Then the beakers were stirred with a magnetic stirrer at a speed of ~150 rpm, and the bulk solution was sampled periodically for analysis. In the preliminary kinetic tests, we found after 15 min, the solution concentration had changed significantly. Therefore, during the first 15 min, the solution was sampled every 5 min. After 15 min, samples were taken at 35, 60, 180 and 720 min.

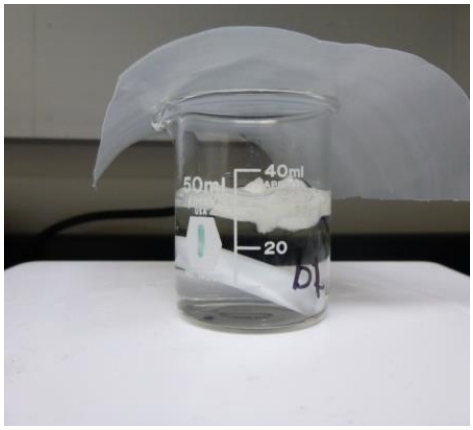

Figure 5-1 Beaker tests for evaluating sorption of PHE by PUF

5.2.2.2 Sorption Isotherm Tests

The objective of these tests was to explore the PUF's sorption capacity for PHE. Two groups of tests were conducted. The first group used six PHE concentrations (0.03, 0.3, 2.0, 5.0, 10, and 15 μg/L) to mimic the range of PAH concentration in stormwater. The second group was designed based on the solubility of PHE in water, 0.99–1.29 mg/L at 25℃ (May and Wasik 1978), and eight PHE concentrations (1.0, 10, 50, 100, 200, 400, 700, and 1000 μg/L) were utilized.

Under every concentration, PUF pieces (~0.15 g) were put into a beaker with 150-ml ^{14}C-spiked PHE solution. Based on the previous kinetic test results, the equilibrium time was set to be 60 min.

5.2.2.3 Batch Column Tests

The objective of these tests was to evaluate the performance of the PHE passive runoff sampler (PHE-PRS) for PHE sorption during individual or multiple storm events without the influence of BMPs. The passive sampler was made by rolling the PUF sheet into a plug and squeezing the plug into a glass tube (d = 0.5 in and length = 4.5 in) as shown in Fig. 5-2. To determine how long a PUF-plug is needed, two PUF plug sizes were tested, i.e., 1.5-in-long (0.85 g) and 2.5-in-long (1.32 g). There was 2–3 inches space above the PUF plug in the glass tube, which allowed water head (pressure) being built as that in column BMPs shown in chapter 4. The glass tube has an open end so that the effluent of the synthetic stormwater passing through the PHE-PRS could be collected in the Erlenmeyer flask (Fig. 5-2).

The WQV for the 0.5″ x 4.5″ lab-scale PHE-PRS BMP was calculated by Equation 4-3. The parameter A = 0.00136 ft^2; K = 9 ft/day (measured value for PUF-PRF); H_f = 0.25 ft; the others parameters values were the same as in chapter 4. The calculated WQV was 404 ml (= 28317 x 0.00136 x 9 x (0.25 + 1.5) x 1/1.5). This was the amount of runoff that a lab-scale bioretention cell with a diameter of 0.5 in was designed to treat. Because the ^{14}C-labled PHE was utilized, it was not suitable for using a large volume of radioactivity material. Therefore, a scaled-down approach was developed by applying 50 ml of ^{14}C-labled synthetic stormwater to the test columns (Table 5-1). The stormwater surface loading rate of the synthetic stormwater was kept the same as the surface loading rate of the total WQV for the 3 storm durations (0.5, 3, and 12 h). The 50-ml synthetic stormwater was split into several aliquots (with an almost-equal volume) (Table 5-1) and loaded into the glass tube reactor by hand.

For single storm events, 3 initial concentrations (i.e., 0.03, 2 and 10 µg/L PHE) were used for each storm event. To mimic individual storm durations, the PUF-PRS was loaded with 50 ml of ^{14}C-spiked PHE solution for either 3.71, 22.27, or 89.06 min to mimic loading rates of storm durations of 0.5, 3, and 12 h (Table 5-1), and for each storm duration, four concentrations (0.03, 0.3, 2.0, and 10.0 µg/L) were tested. Influent and effluent samples were taken, and results were used to calculate sorbed PHE and sorption efficiency of PHE. All the PHE concentrations were represented by ^{14}C-PHE scintillation counting (unit: DPM).

To mimic three storm events occurring in series (but with dry days between the events) during a short period of time, the PUF-PRS glass tube reactor was loaded with 50 ml of ^{14}C-spiked PHE solution (concentration = 2µg/L) for 3.71 min in day 1, then for 22.27 min in day 3, and finally for 89.06 in day 6 to mimic storm durations of 0.5, 3, and 12 h (Table 5-1).

Table 5-1 Synthetic storms applied to lab-scale reactors

Storm Duration (h)	Flow Rate (ml/h)	Time for 50 ml Flow (min)	Application interval (min)
0.5	808	3.71	0.74 (= 3.71/5 times)
3	134.67	22.27	3.18 (= 22.27/7 times)
12	33.67	89.06	8.9 (= 89/10 times)

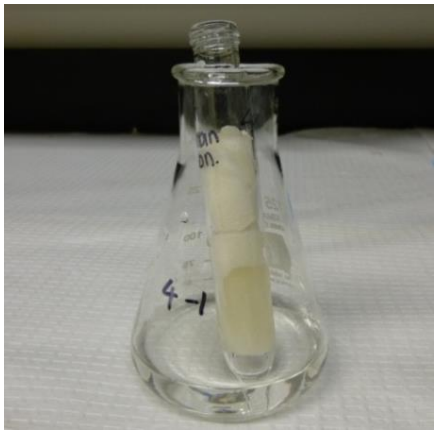

Figure 5-2 Glass tube reactor filled with a PHE-PRS with two possible PUF sizes

5.2.2.4 Desorption Tests

In the lab, the PHE mass sorbed by the PUF-PRS can be calculated by measuring the concentration difference between different times or locations. However, this method is not applicable in the field for real stormwater monitoring. Therefore, the method to elute PHE from PUF needs to be established. Desorption tests were conducted to i) find a suitable PHE desorption solvent and ii) determine desorption percentage over time.

Desorption tests were conducted in the fume hood. As per the literature (Petrich et al. 2013), methanol and methylene chloride were tested as the desorption solvents. After sorption tests, PUF plugs were taken out of the reactors (e.g., glass tubes or BMP columns), put into beakers containing 50-ml methanol or methylene chloride, and then covered with parafilm (PM-999, Pechiney Plastic Packaging Inc., Menasha, WI 54952) to reduce solvent volatilization. After that the covered beakers were stirred with a magnetic stirrer in the fume hood and sampled at different time intervals. When multiple extractions were performed, the second or third 50 ml of the solvent were added to the same PUF plug after desorption equilibrium was reached.

5.3 Results and Discussion

5.3.1 Kinetic Tests

Figure 5-3 shows the sorption percentage of PUF for PHE at 4 initial PHE concentrations. Figure 5-3 reveals that in the first 5 min, the sorption percentage ranged from 48.10 to 55.46%, and after 15 min, about 83.82–95.45% of PHE was sorbed. The initial PHE concentration had no obvious influence on the sorption kinetics. As far as we know, all of the previous studies about PUF passive samplers have been about air pollutants monitoring. The kinetic tests showed that PUF also could efficiently sorb aquatic PAHs at trace levels, which is encouraging for us to conduct the more in-depth studies.

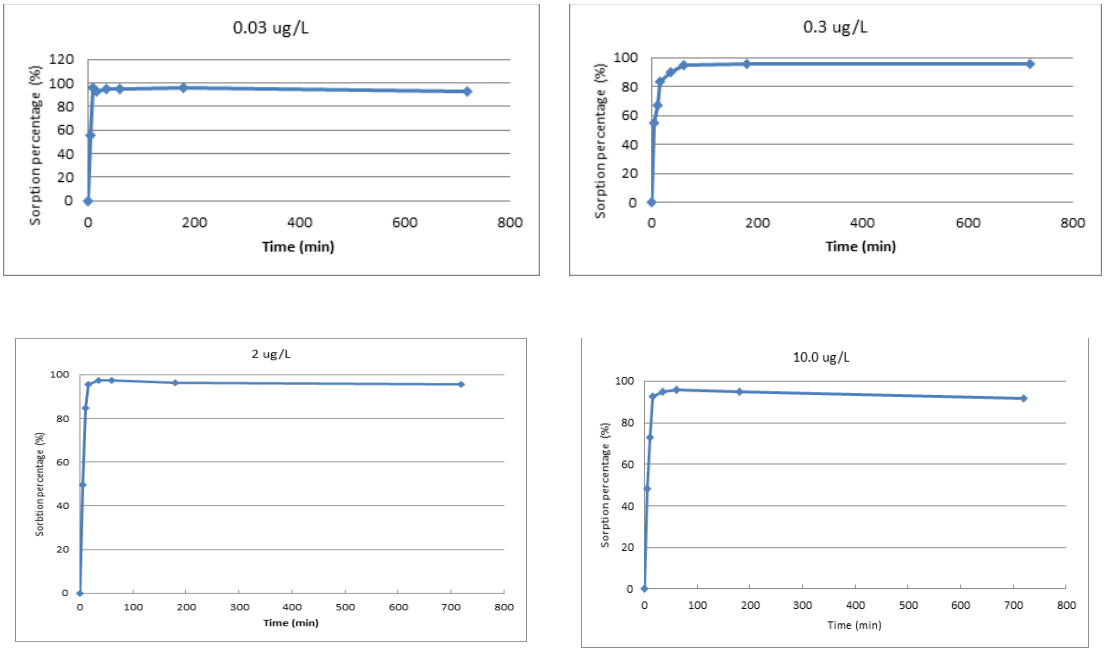

Figure 5-3 Sorption percentage for PHE under different initial PHE concentrations

5.3.2 Sorption Isotherm Curve

Results of isotherm tests indicate that the PUF sorption for PHE can be fit with a linear sorption isotherm curve for both the low and high range of PHE concentrations (Fig 5-4). The sorbing percentage ranged from 89.41% (in 1000 µg/L of solution) to 94.93% (in 1 µg/L of solution). Results of isotherm tests indicate that new test design is needed to determine the maximum sorption capacity of PUF for PHE. However, this maximum sorption capacity may not be needed for real world applications of the passive samplers.

5.3.3 Batch Column Tests

For individual storm events, the PHE sorption percentages at four initial concentrations ranged from 6.3 to 34.9% for the 1.5-in-long PHE-PRS (Figure 5-5), and from 53.25 to 93.00% for the 2.5-in-long PHE-PRS (Figure 5-6). As can be seen, the PHE sorption percentage significantly

increased when the length of the PHE-PRS increased from 1.5 to 2.5 in. Although Figure 5-6 seems to indicate that the PHE sorption percentages increased with an increase in initial PHE concentration (e.g., from 65.08–80.3% for 0.03 µg/L storm water to 79.37–93.00% for 10 µg/L storm water), examination of each PHE-PRS indicated that the PHE-PRSs were made from PUF sheet by rolling them up and jamming them into the glass tube. In some PHE-PRSs, there was tiny space between the PUF and tube wall, which would allow a very small portion of the synthetic stormwater to pass through the space directly instead of contacting the PUF plug for sorption, possibly resulting in a decrease in PHE sorption. The PHE-PRSs having more space were exactly those having lower PHE sorption percentages. Therefore, it was concluded that when the PUF plug was 2.5-in-long, more than 90% PHE could be sorbed by well-fitted PHE-PRSs under stormwater runoff concentration conditions. Therefore, 2.5″ is long enough to sorb almost all the PHE contacting the PUF with 15 to 30 min as demonstrated by the 93% sorption percentages of PHE at the 10.0 µg/L concentration and 0.5 h sorption time (Figure 5-6).

For multi-storm events, Figure 5-7 shows that the sorption for PHE was ~80% in the three events, indicating the PHE-PRSs could measure runoff PAHs for multiple storm events.

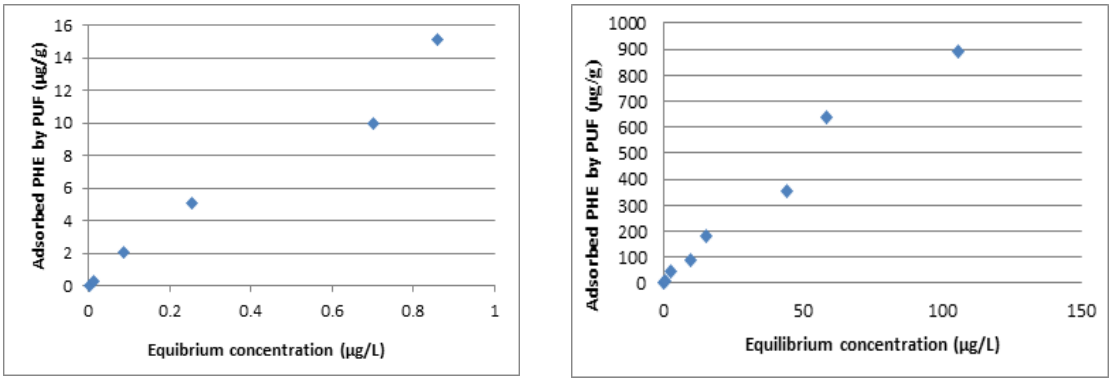

Figure 5-4 Sorption isotherm curve in the concentration range of 0.03–15 µg/L (top) and 1.0–1000 µg/L (bottom) (20 ± 1 °C)

5.3.4 Desorption Tests

Figure 5-8 shows that the PHE could be extracted very quickly from PUF in methylene chloride. The desorption ratio from the PUF was up to 82.63% at 20 min, 88.28% at 60 min, and then reach equilibrium. Figure 5-8 indicated desorption with methanol as eluting solvent was slower than methylene chloride as the solvent. The desorption percentage was 78.61% at 720 min and then approached equilibrium. The highest value was 83.02% appearing at 1200 min.

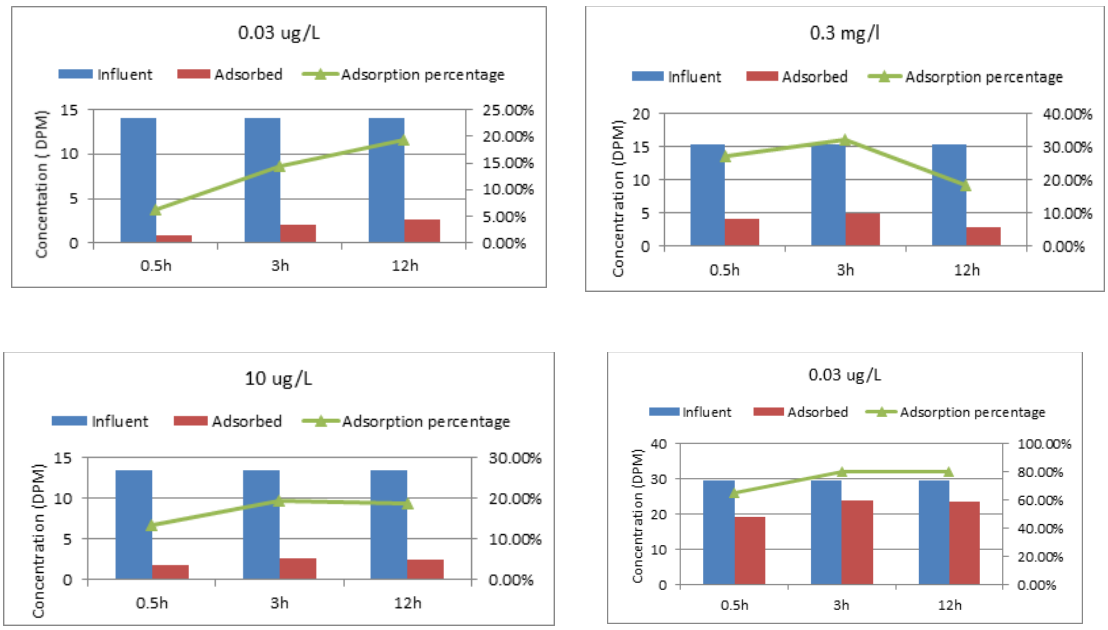

Figure 5-5 Sorption for PHE with 1.5-in PUF plug

Although it took less time reaching desorption equilibrium, methylene chloride was more volatile. After 600 min in the desorption tests, about 20% of the methylene chloride had volatilized from the beaker though it was covered with waxed paper, while the methanol volume was almost not changed. Considering that appreciable volatilization would affect calculating accuracy, methanol was selected as desorption solvent during our follow-up study.

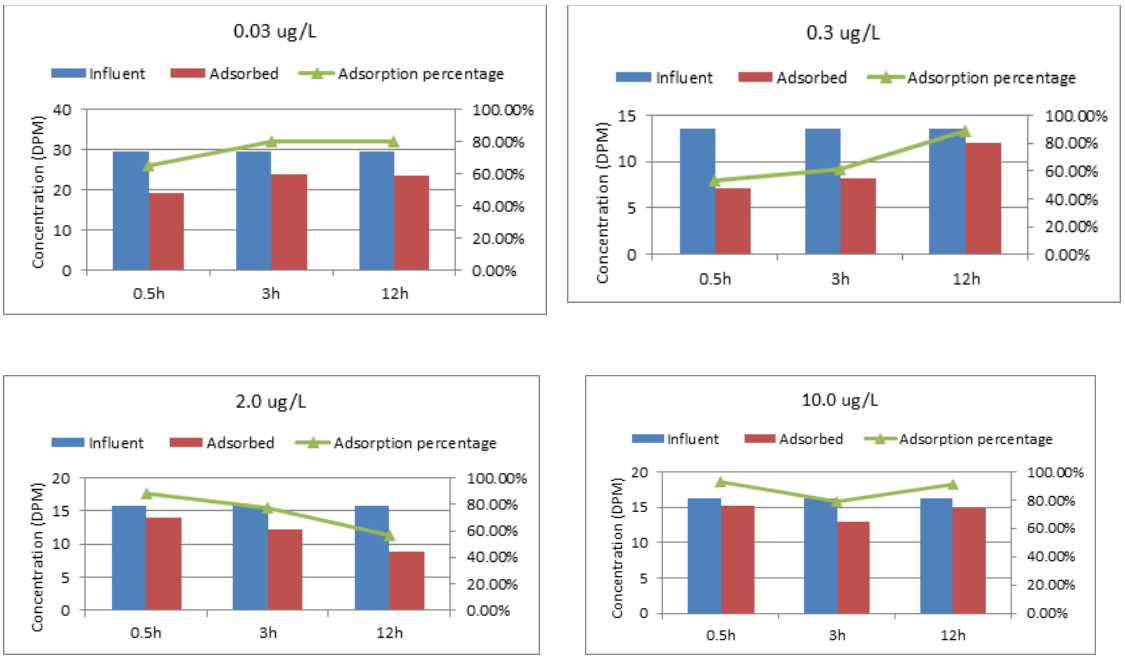

Figure 5-6 Sorption for PHE with 2.5-in PUF plug

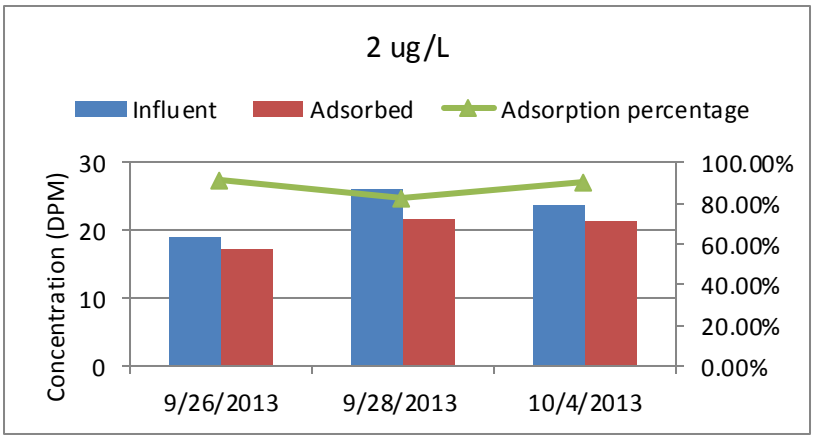

Figure 5-7 Sorption for PHE in multiple storm events

Figure 5-9 shows that after three desorption cycles, > 99% of the PHE sorbed in PUF was desorbed by methanol. Results of the desorption tests indicate that the PHE couldn't be extracted completely by one desorption cycle no matter how much PHE was in the PUF plug. Based on Figs. 5-8 and 5-9, the appropriate desorption time for methanol being a solvent was between 720–

1400 min and that 80% of the PHE was desorbed at 700 min. Therefore, for the follow-up studies, we used 700 min as eluting time, and 80% as the desorption correcting factor. For example, the actual PHE mass sorbed in the PUF plug was ~0.27 µg, which can be estimated by dividing 0.216 µg, the measured PHE mass after the first elution by 80%.

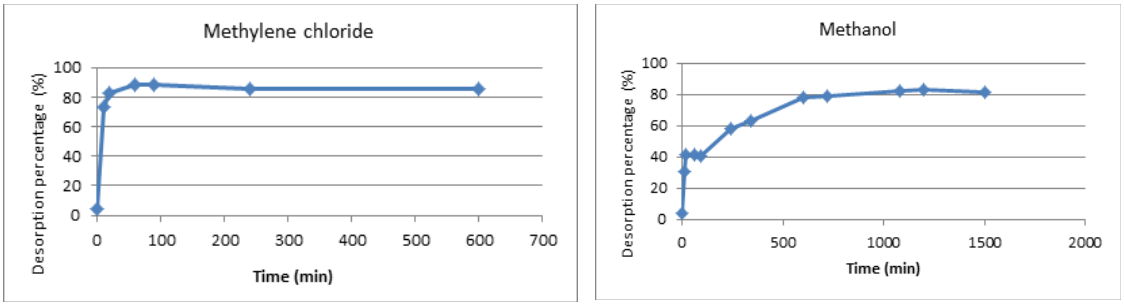

Figure 5-8 PHE desorption from PUF plug by methylene chloride (top) and methanol (bottom)

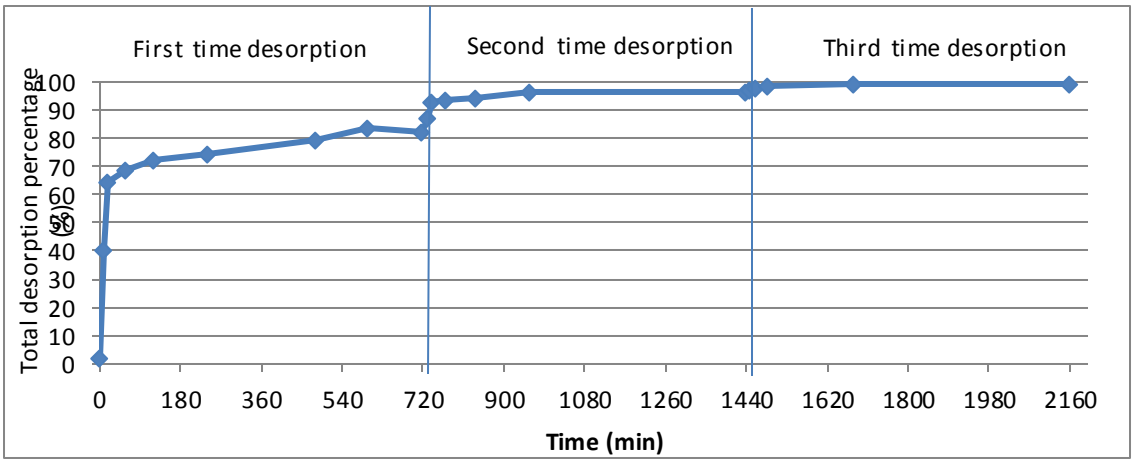

Figure 5-9 Multiple desorption of PHE from PUF plug by methanol

5.3.5 Discussion about Correction Coefficients

Based on these batch column tests and desoption tests, we would use 90% as the sorption correction coefficient and 80% as the desorption (elution) correction coefficient (elution with methanol) for calculation of the PHE in stormwater, that is,

$$C_{CS} = C_m/(0.9 \times 0.8) \quad (5\text{-}1)$$

where C_{CS} is the claimed (predicted) PHE in stormwater; C_m is the measured PHE eluted from PUF plug based on the ^{14}C activity (DPM); 0.9 is the sorption correction coefficient; and 0.8 is the desorption (elution) correction coefficient.

5.4 Conclusion

In this chapter, the feasibility of monitoring PAHs in stormwater runoff by PUF as passive sampler was studied. The major conclusions are as follows: Kinetic tests showed that after 15 min, 90 percent of the PHE that contacted the PUF was adsorbed from the liquid phase. Therefore, PUF could efficiently adsorb aquatic PAHs present at trace levels in stormwater. Batch column tests indicated that when the PUF plug was 2.5-in-long, more than 90% PHE contacting the PUF could be absorbed by well-fitted PUF-PRS under stormwater runoff concentration conditions. In three storm events during 14 days, the sorption ratios for PHE were 91%, 83%, and 90%, respectively, indicating the PHE-PRS could measure runoff PAHs of multiple storm events. Methanol and methylene chloride were utilized in the desorption tests. Although both solvents could reach a high desorption ratio, methanol was selected because of less volatilization. About 80% of the sorbed PHE was extractable in a single methanol extraction. The desorption extraction equilibrium could be reached after ~720 min. 99% PHE could be desorbed by three-time desorption in sequence.

Chapter 6 Lab-Scale Tests for PAH Passive Sampler

6.1 Introduction

After PHE-PRSs were tested in batch tests within the lab and shown to provide consistent and high uptake ratio of PHE in synthetic stormwater solutions, they were tested in the complex flow scenarios in lab-scale BMPs. Application of the sampler for stormwater monitoring will include a lot of variables that may have conflicting effects on the sampler's uptake.

The objectives of this chapter were to determine if the PHE-PRS sampler could i) monitor the PAHs in influent and effluent of the BMPs and ii) be used to estimate the removal efficiency of the BMPs under the influence of either single storm or multiple storm events.

6.2 Material and Methods

6.2.1 PUF-PRS and Lab-scale BMP Columns

The PHE-PRSs utilized in this chapter are shown in Figure 6-1. To install the PHE-PRS on top or the bottom of a BMP column (i.e., mimic the field bioretention cell), another PVC section was needed to connect the PHE-PRS with the BMP column. A nylon screen was used to separate the BMP media from the PHE-PRS.

Lab-scale column bioretention cells were constructed to mimic field-scale bioretention cells located at NDOR's Salt Valley maintenance yard in Lincoln, NE (see chapter 4 for detailed information). The lab-scale columns were made of PVC pipe (d = 3/4 in) and filled with 18-in of media (50% compost and 50% sand). To conduct the column test under one condition, three columns were needed; that is, one column with no PHE-PRS was used as control; one column with a PHE-PRS on top of the column was used to provide the PHE-PRS performance for

collecting influent information; and one column with a PHE-PRS at the bottom of the column was used to provide the PHE-PRS performance for collecting effluent information. In this study, parallel tests were conducted (Fig. 6-2). Therefore, for each condition, six columns were used.

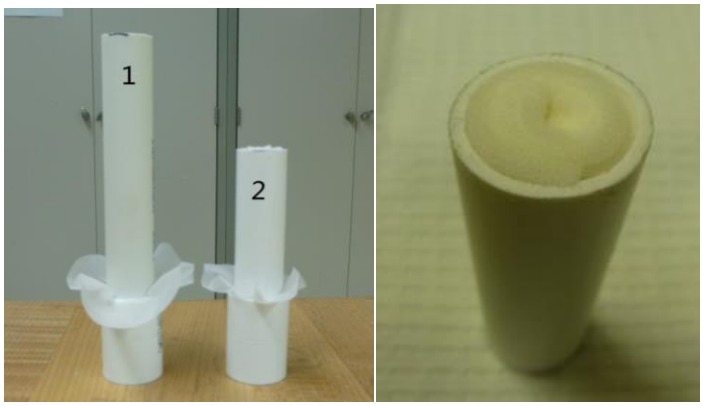

Figure 6-1 (Left) Two PHE-PRSs with connection PVC pipe and nylon screen with (1) d = 0.75 in and height = 5.5 inches filled with 1.32 g PUF and (2) d = 0.75 in, height = 3.5 in, PUF plug height = 3.0 in. (Right) top view of a PHE-PRS

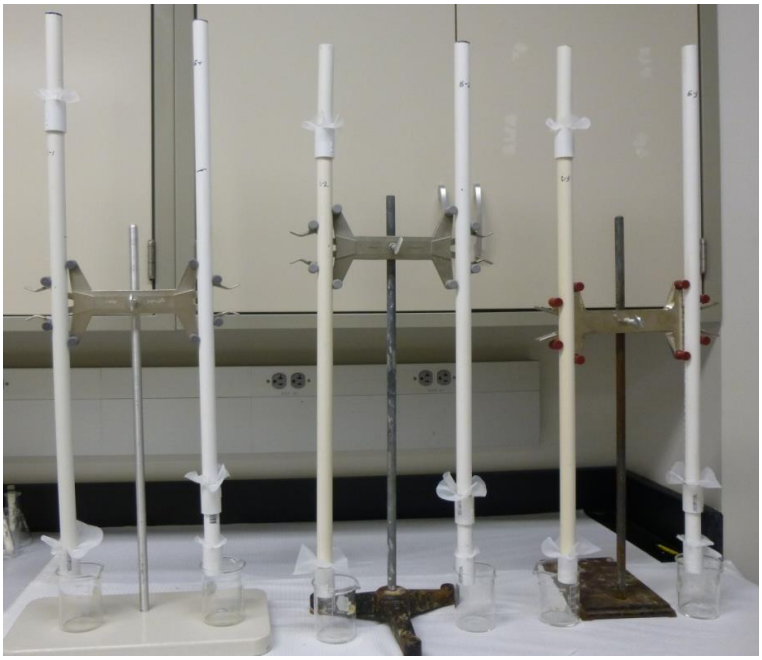

Figure 6-2 Lab-scale column bioretention cells with a PHE-PRS on top (from left 1, 3 and 5) or at bottom (2, 4, and 6) of the columns. Control columns are not shown. To hold BMP media, nylon screen at the bottom is needed for all of the columns

6.2.2 Design of Columns Tests

The column tests included tests for single-storm and multi-storm events. The WQV was calculated by Equation 4-3. The parameter A = 0.003 ft^2; K = 9 ft/day (measured value for PUF-PRF); the other parameter values were the same as in the chapter 4. The calculated WQV was 912 ml (= 28317 x 0.003 x 9 x (0.25 + 1.5) x 1/1.5). This is the amount of runoff that a lab-scale bioretention cell was designed to treat. Because the ^{14}C-labled PHE was utilized, it was not suitable for using a large volume of radioactivity material. Therefore, a scaled-down approach was developed by applying 50 ml of ^{14}C-labled synthetic stormwater to the test columns (Table 6-1). The stormwater surface loading rate of the synthetic storms were kept the same as the surface loading rate of the total WQV for the 3 storm durations (0.5, 3, and 12 h). The time for the 50-ml synthetic stormwater to be applied is also presented in Table 6-1.

Table 6-1 Synthetic storms applied to lab-scale reactors

Storm Duration (h)	Flow Rate (ml/h)	Time of 50 ml Flow (min)	Application interval (min)
0.5	1823	1.65	0.33 (= 1.65/5 times)
3	303.9	9.87	1.41 (= 9.87/7 times)
12	76.0	39.47	3.9 (= 39.47/10 times)

Control columns were loaded same as the test columns.

For single storm events, 3 initial concentrations (i.e., 0.03, 2 and 10 μg/L PHE) were used for each storm event (duration). Influent samples were taken from the synthetic stormwater before loading to the column. All effluent from each column was collected with a beaker to make a composite effluent sample. ^{14}C in influent and effluent samples were analyzed, and results were used to calculate the BMP removal efficiency of PHE. The PHE-PRS at the top and bottom of the columns were collected for eluting and then analyzing the sorbed PHE (i.e. C_m in Eq. 5-1), and results were used to calculate the claimed removal efficiency of PHE [i.e., (C_m of influent - C_m of effluent) / C_m of influent], which was then compared with the removal efficiency of the control to

determine the feasibility of using the PHE-PRS to predict the PHE removal of the BMPs. The actual mass of influent (or effluent) that was contacting with a PHE-PRS was based on the measured value of PHE (C_s) in the synthetic stormwater (or in the effluent) of the control column and sample volume (= C_s x V). The claimed mass of influent (or effluent) that was contacting with a PHE-PRS was calculated with C_{cs} x V, where C_{cs} is from Eq. 5-1 [= C_m/(0.8 x 0.9)], and V is the sample volume.

For multi-storm events, the procedure similar to the one used in section 5.2.2.3 (***Batch Column Tests***) was used. To mimic multiple storm events occurring in series (but with dry days between the events) during a short period of time, the columns were loaded with 50 ml synthetic stormwater into the column for 3.45 min to mimic 0.5 h storm event duration; 7 d later, loaded with 50 ml synthetic stormwater for 20.7 min to mimic 3 h storm event duration; 1 d later, loaded with 50-ml synthetic stormwater for 20.7 min to mimic 3 h storm event duration again; 11 d later, loaded with 50 ml synthetic stormwater for 3.15 min to mimic 0.5 h storm event duration, and 15 d later, loaded with 50 ml synthetic stormwater for 82.85 min to mimic 12 h storm event duration. This test was repeated with two concentrations (2.0 and 10.0 µg/L) with the same storm event duration arrangement. After the 5 storm events, the PHE in different samplers were analyzed and the data were interpreted in the same way as for single storm events.

The calculation methods for both single and multiple storm tests are the same. For control columns, the BMP removal efficiency is calculated with the following equation:

$$E_{Control} = [(C_{inf} - C_{eff})/C_{inf}] \times 100\% \quad (6\text{-}1)$$

where $E_{Control}$ is the control column removal efficiency; C_{inf} is the influent concentration; C_{eff} is the effluent concentration. Both C_{inf} and C_{eff} were represented by the ^{14}C activity (DPM). For the columns with a PHE-PRS, the claimed treatment efficiency is calculated by:

$$E_{CS} = [(C_{CS,\ inf} - C_{CS,\ eff})/C_{CS,\ inf}] \times 100\% \quad (6\text{-}2)$$

where E_{CS} is the sampler's claimed removal efficiency, $C_{CS,\ inf}$ and $C_{CS,\ eff}$ are the claimed (predicted) PHE in the influent and effluent, respectively (both can be calculated with Eq. 5-1). Because the correction coefficients will be cancelled with each other in Eq. 6-2, Eq. 6-3 was used actually in this study to calculate the sampler the sampler's claimed removal efficiency:

$$E_{CS} = [(C_{m,\ inf} - C_{m,\ eff})/C_{m,\ inf}] \times 100\% \qquad (6\text{-}3)$$

where $C_{m,\ inf}$ and $C_{m,\ eff}$ are the measured PHE, based on the ^{14}C activity (DPM), in the solution eluted from the PUF plug of influent and effluent, respectively. Eq. 6-3 is significant because at least to estimate the removal efficiency of a BMP, we don't need to know the correction coefficient.

6.3 Result and Discussion

6.3.1 Single Storm Event

Testing synthetic stormwater of 0.03 μg/l concentration PHE was aimed to evaluate the performance of the passive sampler for measuring low PAH concentration in storm runoff. As shown in Figure 6-3, the influent claimed mass values calculated by PHE-PRS were very similar to the actual influent mass with error in the range of ± 10%. The effluent mass error was slightly higher, ranging from -15 to 38%.

Using synthetic stormwater of 2.0 μg/l concentration was to evaluate the performance of the passive sampler for measuring the moderate PAH concentration in stormwater. In the three tests, the claimed masses by the PHE-PRS were always gently higher than the actual mass for both influent (Fig. 6-4) and effluent (Fig. 6-5). In the 12-h duration storm event, both the actual and the claimed effluent mass were not detectable by LSC as they were below the detection limit.

Using synthetic stormwater of 10.0 μg/l PHE concentration was aimed at detecting the measuring ability of the sampler for high PAHs concentrations in stormwater. Contrary to the 2.0

µg/l influent tests, all the claimed masses by PHE-PRS were lower than the actual influent mass, with error ranging from -5.7% to -13.9%.

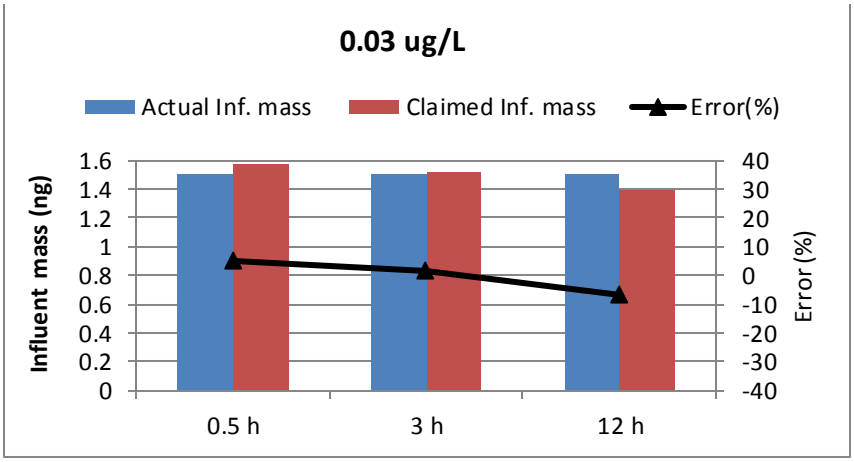

Figure 6-3 Actual and claimed influent mass under 0.03 µg/l influent concentration

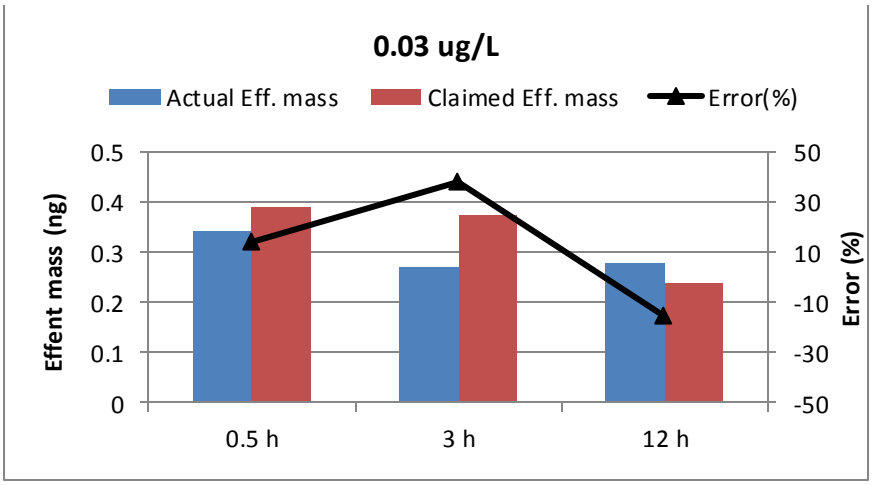

Figure 6-4 Actual and claimed effluent mass under 0.03 µg/l influent concentration

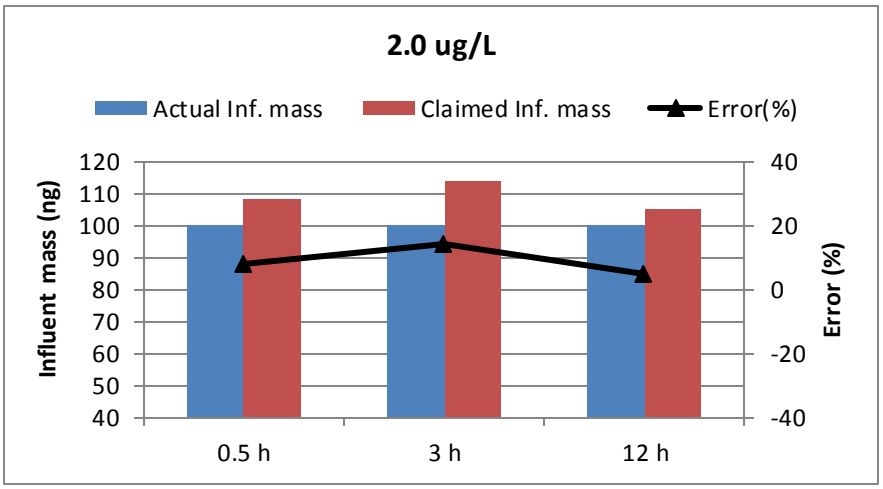

Figure 6-5 Actual and claimed influent mass under 2.0 µg/l influent concentration

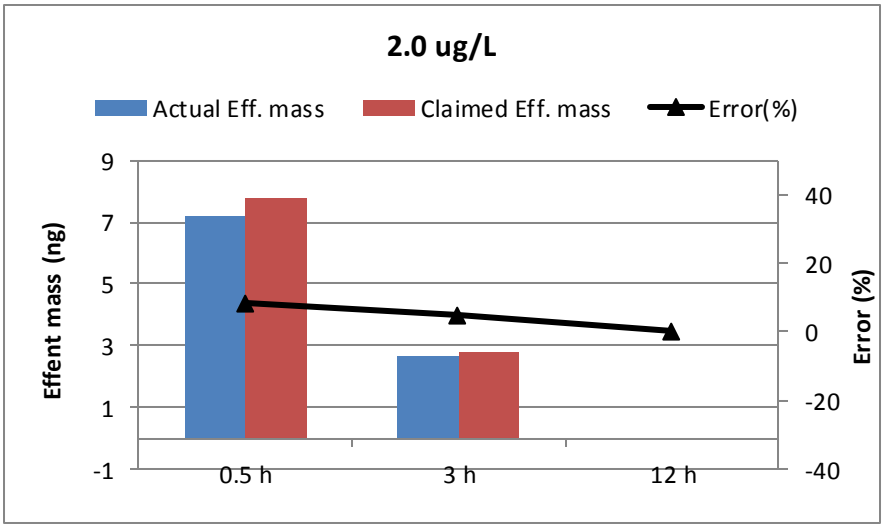

Figure 6-6 Actual and claimed effluent mass under 2.0 µg/l influent concentration. In 12 h duration cell, the activity of effluent from both the control and the cells with a PHE-PRS counted by LSC were zero (DPM)

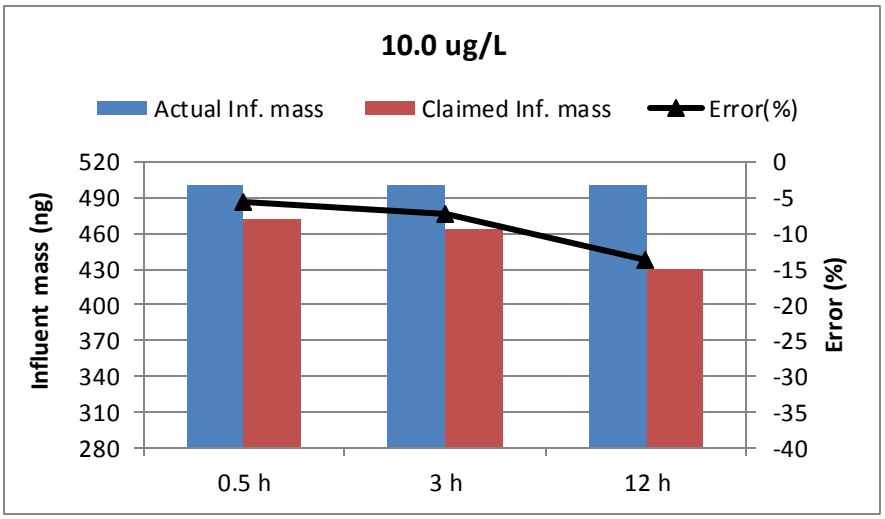

Figure 6-7 Actual and claimed influent mass under 10.0 µg/l influent concentration

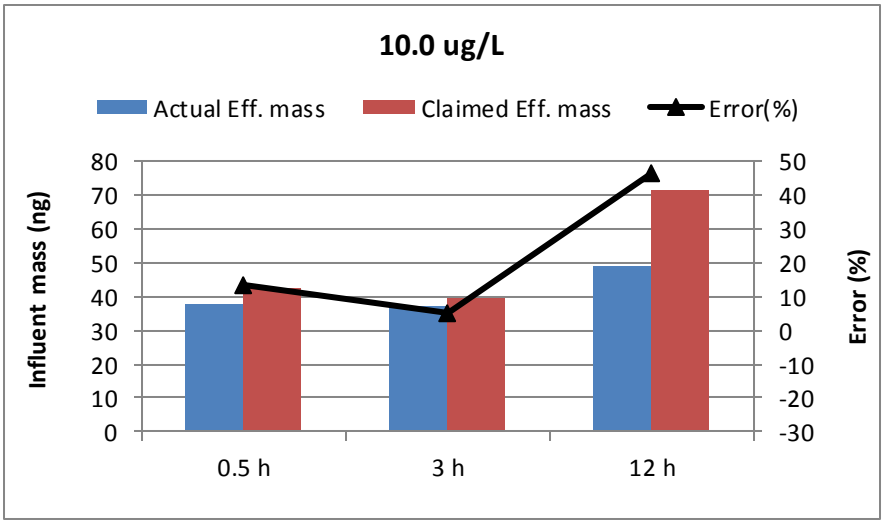

Figure 6-8 Actual and claimed effluent mass under 10.0 µg/l influent concentration

As summarized in Table 6-2, during the single storm events, on the whole, the claimed treatment efficiencies were very similar to the treatment efficiency of the control. For the influent sampler, the claimed mass was slightly higher than the actual influent mass during the low and moderate concentration tests (0.3 and 2.0 µg/L), while for the high concentration tests, the claimed mass was always

a little lower than the actual influent mass. It is possible the correction factor may be a function of the initial PHE concentration. The exact reasons for these differences are not clear at this stage, indicating detailed studies in the future may be needed.

Table 6-2 Results of single storm events

Test concentration & data category	Storm event duration (h)		
	0.5	3	12
0.03 µg/L			
Influent Mass (µg)	0.0015	0.0015	0.0015
Effluent Mass (µg)	0.000342	0.000271	0.000279
Influent Sampler mass (µg)	0.001575	0.001524	0.001393
Effluent Sampler Mass (µg)	0.00039	0.000374	0.000237
Reactor Treatment Efficiency	77.2%	81.93%	81.47%
Claimed Treatment Efficiency	75.24%	75.46%	82.99%
2.0 µg/L			
Influent Mass (µg)	0.1	0.1	0.1
Effluent Mass (µg)	0.007168	0.002688	0
Influent Sampler Mass (µg)	0.108116	0.114129	0.105169
Effluent Sampler Mass (µg)	0.007782	0.002821	0
Reactor Treatment Efficiency	92.83%	97.31%	100%
Claimed Treatment Efficiency	92.80%	97.53%	100%
10.0 µg/L			
Influent Mass (µg)	0.5	0.5	0.5
Effluent Mass (µg)	0.037658	0	0.04898
Influent Sampler Mass (µg)	0.471467	0.463126	0.430747
Effluent Sampler Mass (µg)	0.042682	0.039248	0.071628
Reactor Treatment Efficiency	92.47%	100%	90.20%
Claimed Treatment Efficiency	90.95%	91.53%	83.37%

6.3.2 Multiple Storm Events

Table 6-3 shows the test results of multiple storm events. The influent mass obtained by eluting the PUF plug was less than the real influent mass with an error of -8.58% in the 2.0 µg/L tests and -11.95% in the 10.0 µg/L tests. The reason could be mainly because that the PHE sorption correction coefficient by PHE-PRS (90%) was based on the average value gained from single batch tests. As the effluent mass values were very low for the high removal efficiency by BMPs, the calculated sorbed mass values were less than the real sorbed mass by BMPs. The claimed removal efficiencies were close to the real values because the uncertain correction factors do not affect efficiency calculations.

Table 6-3 Results of multiple storm events with synthetic stormwater of 2.0 µg/L

Date	Influent Mass (µg)	Effluent Mass (µg)	Adsorbed Mass (µg)	Reactor Treatment Efficiency (%)
2.0 µg/L				
Nov. 11 (0.5 h)	0.1	0	0.1	100
Nov. 18 (3 h)	0.1	0.002652	0.097348485	97.35
Nov. 19 (3 h)	0.1	0.016947	0.083052885	83.05
Nov. 30 (0.5 h)	0.1	0.001824	0.098175966	98.18
Dec. 15 (12 h)	0.1	0.007701	0.092298716	92.23
Total	0.5	0.029124	0.470876052	94.18
Claimed value	0.457	0.034915	0.422169569	92.36
Error (%)	-8.58	19.88	-10.34	-1.81
10.0 µg/L				
Nov. 11, (0.5 h)	0.5	0.052367	0.447633	89.53
Nov. 18, (3 h)	0.5	0.049424	0.450576	90.12
Nov. 19, (3 h)	0.5	0.080814	0.419186	83.88
Nov. 30, (0.5 h)	0.5	0.015152	0.484848	96.97
Dec. 15, (12 h)	0.5	0.016746	0.483254	92.23
Total	2.5	0.214503	2.285497	91.40
Claimed value	2.201211	0.166741	2.03447	91.42
Error (%)	-11.95	-22.27	-10.98	0.02

6.4 Conclusions

The following conclusions can be drawn based on the test results: i) for the single storm event test, the errors between claimed removal efficiencies and actual efficiencies by BMPs

ranged from -0.51 to -8.5%; ii) for the multiple storm events, the errors between claimed and actual values under two respective influent concentrations, 2.0 and 10.0μg/L were -8.58% and -11.95% for the influent mass, 19.88% and -22.27% for the effluent mass, and -1.81% and 0.02% for the removal efficiencies of the BMPs; and iii) the comparison between the claimed PHE values by the sampler and the actual PHE values by the control shows that it is feasible to use the PHE-PRS for monitoring PAHs (or semi-volatile organic compounds) in BMPs.

Chapter 7 Summary, Conclusions and Recommendations

7.1 Summary and Conclusions

Increasing regulations pertaining to the environment and the quality of our nation's waters & waterways have resulted in a renewed interest in stormwater discharges. Currently, NPDES only requires permitting for highway runoff that discharges into urban receiving waters which are regulated by the MS4 programs. MS4 permits include Stormwater Management Plans which include structural BMPs for providing physical treatment of polluted discharges.

It is in the interest of transportation agencies, like NDOR, to assess current and future highway runoff BMPs as it is anticipated that future regulations will require BMP effectiveness or even effluent discharge concentrations. Current stormwater monitoring procedures including spot, grab and automatic samplers are costly, dangerous as many storms are accompanied by violent weather, and unreliable due to storms' sporadic nature. For an entity such as NDOR that may have hundreds of roadside BMPs to monitor for multiple storms each year, the current methods of stormwater sampling are not practical.

Passive samplers have been effectively applied to groundwater and marine pollutant monitoring. These samplers rely on contaminant uptake in a predictable manner based on diffusion, sorption or other transport mechanisms. They are simple, robust and economical.

The second chapter of this document identifies passive sampling technologies applied in other environmental monitoring scenarios and assesses their feasibility within highway runoff BMP scenarios. More than twenty existing passive samplers and several sorbents were evaluated for their ability to effectively monitor highway runoff BMPs, and three were selected for further testing and analysis. A regenerated cellulose (dialysis) membrane sampler and a chelating ion exchange

sorbent (Amberlite IRC748) were chosen for heavy metal monitoring, and a foam (PUF) was selected for PAHs monitoring.

The third chapter of this document presents the results of testing the regenerated cellulose (dialysis) membrane samplers and the ion exchange resin passive samplers in a series of increasingly complex conditions within the laboratory. Batch tests mimicking stormwater scenarios were employed to assess the feasibility of these two types of passive samplers. Results indicate that the dialysis sampler consisting of a regenerated cellulose membrane filled with DI water performed inconsistently. Metal sorption onto the membrane was noted as well as a release of metals following uptake over time. Another issue was the small amount and slow rate of uptake within the static systems. Due to these inconsistencies the dialysis sampler was deemed infeasible for stormwater applications and not assessed within subsequent experiments. The ion exchange resin sampler consists of Amberlite IRC748 chelating resin encased in a polyester mesh. This sampler performed desirably in various stormwater scenarios, including consistent and rapid metal uptake. This sampler was considered feasible as a stormwater sampler for further feasibility assessment.

The fourth chapter of this document presents the details of sampler placement within lab- and field-scale BMPs for assessment. Lab-scale BMPs were designed and constructed to expose ion exchange resin passive samplers to various flow scenarios. These controlled scenarios included the application of synthetic stormwater at rates expected for storm durations of 0.5, 3, and 12 hours. A field test was also conducted by placing the samplers in deployment units upstream and downstream of pilot BMPs and utilizing velocity sensor data for the site to characterize the storm event. Results indicate that the influent and effluent passive samplers must be placed in two different flow paths in order to obtain representative data for calculation of claimed removal efficiency. Results of supplemental tests indicate that the samplers can be used for monitoring BMPs under the given conditions.

The fifth chapter of this document describes several batch tests conducted on a PUF passive sampler to evaluate its performance for monitoring PAHs in stormwater. The tests included evaluation of kinetic uptake of PHE (used as a representative of PAHs) by the PUF sampler, isotherm studies, total mass uptake by the sampler, and the feasibility of recovering the PHE from the sampler for analysis. The results showed that the PUF sampler was feasible for monitoring PHE in stormwater, the uptake was rapid and showed predictable uptake through time and the PHE accumulated in the sampler could reliably be removed and analyzed.

The sixth chapter of this document evaluated the performance of the PUF sampler as it was installed in lab-scale BMPs to monitor BMP effectiveness for PAH removal. The results of these tests showed that the PUF sampler provided reliable and accurate values of removal efficiency of PHE in the BMP.

7.2 Recommendations

Important factors affecting contaminant uptake in passive samplers were identified in addition to those laid out in the second chapter (e.g., fast uptake, stormwater chemical properties, and ability to handle dry and wet periods). These factors are likely to distort the predictable uptake of contaminants within the sampler. They include i) the interaction of fine particles with the sampler, ii) the assessment of flow interaction with the sampler, iii) the durability of the sampler to handle stormwater flows and iv) a consistent means to deploy the samplers.

A closer look into the details of the lab-scale reactors in an effort to adjust the data according to known exposure times has been initiated. If the lab-scale reactors are able to be more fully understood and a method for interpreting sampler uptake under flow conditions is developed, ion exchange resin samplers might be feasible.

A noticeable amount of fine particles accumulated within the samplers during both the lab-scale and field tests. Adjustments to the reactors were made to overcome this issue within the lab,

but this may not be an option for most field applications. These fine sediment particles are eluted in the acid elution along with the ion exchange resin and could be improperly adding non-dissolved metals to the sampler accumulated mass. Due to the many species of metals within the environment, this issue should be circumvented (Tessier et al. 1979). It can either be incorporated within the sampler itself via a physical means of preventing the fines from entering the sorbent phase or a method incorporated with the analysis of the samplers to remove the sediments prior to the elution. Because the resin may continue to attain metals from the sediments following sampler collection, the physical prevention route is preferred.

Passive samplers are only able to measure the concentrations of water that they come in contact with. If flows shift away from the sampler, the reported concentration is going to be a low misrepresentation of the stormwater. If a sorbent sampler is able to sit within a pool of water longer than the actual storm event, it will continue to accumulate the pollutants it has access to and give a high misrepresentation of the stormwater. These scenarios are very difficult to monitor via outside means. Thus, two methods are recommended to overcome this problem: 1) incorporation of a performance reference compound (PRC) within the sampler system; and 2) attaching a simple device for flow rate measurement.

PRCs are chemicals that act like tracers; they leave the sampler in a predictable manner and provide insight into the local flow environment surrounding the sampler. This technology has been incorporated with passive samplers with some success. Application of a variety of PRCs within the chemcatcher was successful for monitoring in PAHs (Lobpreis et al. 2008). The application of PRCs within the semipermeable membrane device (SPMD) sampler reduced the inaccuracy of the sampler from tenfold to twofold due to facial velocities (Huckins et al. 2002). Specific application of PRCs to the ion exchange resin samplers used within this study would require further evaluation. PRCs would need to offload from the sampler in the same manner that metals upload, thus only certain chemicals would suffice.

There are two approaches to account for flow interaction during sampler exposure. One approach is to use outside means of flow sensing (e.g. flow velocity monitors and rain gauges as were attempted in this study). This may get fairly accurate flow rates into and out of the BMP, but it can't account for small flow variations within the BMP. This approach is not entirely compatible with the purpose of using passive samplers as it may greatly increase the cost and site preparation needed to work effectively. The second approach, such as attaching a device (e.g., a pipe-shape container with the same cross-section area as the passive sampler) with the passive sampler deploying unit, incorporates the monitoring of the flows with the sampler itself, and thus, may allow the device to record the quantity of stormwater passing the passive sampler as both units have the same flow conditions. The quantity can then be used to find the pollutant mass that has passed the sampler. This could be more economical, as the only expense would be for calibration and use of the two units.

Sampler durability is an issue that may have considerable effect on sampler performance. In this study, sampler deployment units were developed to protect the samplers from debris and turbulent flows. These units may not be available in every BMP design. It would be beneficial to construct passive samplers to be able to handle the aforementioned items without the need for deployment units specific for each site.

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Appendix A: Analytical Methods

A.1 Batch Test Standard Operating Procedures (SOPs)

A.1.1 Material Preparation and Sampling SOP

Material Preparation

1. Wash beakers (1L, 50ml and 200ml), volumetric flasks (50ml and 1 liter), glass pipettes (5ml), magnetic stirrer, and sample bottles (Polypropylene tubes) with detergent and rinse with tap water three (3) times.
2. Rinse with de-ionized water three times (3).

Solution Preparation

1. Determine required volume of standard solution
    a. Use the following conservation of mass equation:

$$C_0V_0 = C_1V_1$$

Where: C_0: Concentration of metal to be used in experiment (mg/l)

C_1: Concentration of metal in standard solution (mg/l)

V_0: Volume of aqueous solution to be used in experiment (liters)

V_1: Volume of standard solution to add (liters)

b. <u>Example</u>: Concentration of Lead (Pb) standard is 100mg/L. The volume of the experiment will be 250ml (0.25 liters). The concentration within the experiment is 0.16mg/l. How much standard solution is needed for the experiment?

i. Solution:

1. Known: C_0: 0.16mg/l; V_0: 0.25L; C_1: 100mg/L
2. Rearrange to find V1:

$$V_1 = \frac{C_0V_0}{C_1} = \frac{(0.16mg/L)(0.25L)}{(100mg/L)} = 0.0004L$$

3. Convert to appropriate volume (0.4 ml or 400µL)
2. Pour small amount of solution into beaker (25 ml or less) and retrieve needed amount from small beaker. Waste excess standard solution in "Heavy Metals" waste bottle located within waste tub.

Do not retrieve volume directly from standard or pour left over standard back into bottle – this will contaminate the standard

3. Partly fill 1,000 ml volumetric flask with de-ionized water, add standard solution (from steps 1 and 2), then fill with de-ionized water to mark.
4. Mix standard metal solution with de-ionized water by covering opening with Parafilm and inverting seven (7) times with thumb holding Parafilm over opening.
5. Zero scale with 1,000 ml beaker and stir bar.
6. Pour the prepared standard metal solution into 1,000 ml beaker.
7. Record weight on Batch 1 Data Sheet.
8. Set mixer to pre-determined turbulence, 400 rpm.

Refer to respective Sampler SOP for instructions on how to prepare sampler

Experimental Set-up

1. Secure sampler within beaker, making sure sampler is entirely submerged.
2. Cover top of beaker with Parafilm to reduce losses due to evaporation.
3. Cover both the top and sides with Aluminum foil, preventing light from entering the reactor.
4. Collect first sample following procedure laid out below, record time.
5. Plan and record remaining sampling times in 'Collection Schedule' column within Batch 1 Data Sheet.

Sample Collection

1. Collect samples at predetermined times (i.e. 0min, 15 min, 30 min, 1hour, 5 hours, 1 day, 3 days, 7 days and 14 days for Regenerated Cellulose experiments).

2. Retrieve 5 ml samples with 5,000µL pipette and place in clean sample bottles (Polypropylene tubes).
3. Add 135µL of trace metal grade HNO_3 solution (2.7 ml trace metal grade concentrated HNO_3/100 ml sample).
4. Label sample according to Sample Labeling Procedure with tape and marker.
5. Record 'Date Collected', 'Time Collected' and 'Sample Label' onto Batch 1 Data Sheet.
6. Refrigerate samples until transport to Chemistry lab.

Refer to respective Sampler SOP for instructions on how and when to analyze the sampler itself

A.1.2 Regenerated Cellulose (Dialysis) SOP

Note: the sampler may need to stay wet, thus the solution should be prepared prior to the sampler. Refer to Material Preparation and Sampling SOP for instructions on the preparation of materials and solution.

Regenerated Cellulose Membrane Preparation

1. Determine amount required, approximately four inches for 50 ml.
2. Cut tubing with scissors, use tweezers for assistance.
3. Rinse required piece with De-ionized water three (3) times.
    a. Glycerol within H1 CeluSep membrane has been removed by the manufacturer

Cellulose Tubing Clamp Preparation

1. Wash clamps with detergent and rinse with tap water.
2. Rinse clamps with De-ionized water three (3) times.

Regenerated Cellulose Sampler Assembly

1. Seal clamp on one end of tubing.
2. Pour desired volume of sorbent within tubing, approximately 50 ml.
    a. Volume and type of sorbent to be determined

3. Seal second clamp over open end, making sure no air remains within sampler.

4. Mount loaded sampler into experimental Procedure.

5. Label mixing plate w/ date, experiment, and start time.

*Follow appendix**A.1.1 Material Preparation and Sampling SOP** for instructions during deployment and sampling procedure.*

Regenerated Cellulose Sampler Analysis

1. Retrieve sample from sampler immediately following retrieval of last solution sample.

2. Remove sampler from Beaker and open one end of sampler by removing clamp.

3. Retrieve 5 ml samples with 5,000µL pipette and place in clean Polypropylene tubes sample bottles.

4. Add 135µL of trace metal grade HNO3 solution, located under fume hood. (2.7 ml trace metal grade concentrated HNO3/100 ml sample).

5. Label sample according to Sample Labeling Procedure with tape and marker.

6. Record 'Date Collected' and 'Sample Label' onto Batch 1 Data Sheet.

7. Refrigerate sample until transport to Chemistry lab.

8. Measure volume of water remaining in beaker (Weigh beaker 1st, zero scale, add water, and obtain measurement).

Regenerated Cellulose Sampler Clean-up

1. Dispose of membrane in trash can.

2. Save Clamps for future use.

3. Clean all other materials by washing with soap and placing on drying rack.

A.1.3 Regenerated Cellulose (Dialysis) Elution Procedure SOP

*This procedure is conducted following the collection of the last sample and internal sample of a RC kinetics test detailed in appendix **A.1.2 Regenerated Cellulose SOP** or appendix **A.1.4 Regenerated Cellulose Sorption Desorption Follow-up SOP**.

Regenerated Cellulose Elution Procedure

1. Split bag lengthwise and place into separatory funnel.
2. Swirl each of the following rinses to ensure that the bag has been coated:
   a. Remove excess from the bag using plastic clamps. If desired, collect excess solution for analysis.
   b. Rinse twice (2) with 10 ml of 3M HNO3 (20 ml total)
   c. Rinse twice (2) with 5 ml of De-ionized water (10 ml total)

A.1.4 Regenerated Cellulose (Dialysis) Sorption/Desorption Follow-up SOP

Note: the sampler may need to stay wet, thus the solution should be prepared prior to the sampler. Refer to Material Preparation and Sampling SOP for instructions on the preparation of materials and solution.

Regenerated Cellulose Membrane Preparation

1. Determine amount required, approximately four inches.
2. Cut tubing with scissors, use tweezers for assistance.
   a. Cut tubing lengthwise, and then cut in half lengthwise resulting in two 4x2 in. sheets.
3. Rinse sheets with De-ionized water three (3) times.
   a. Glycerol within H1 CeluSep membrane has been removed by the manufacturer

Cellulose Tubing Clamp Preparation

1. Wash clamps with detergent and rinse with tap water.

2. Rinse clamps with De-ionized water three (3) times.

Membrane Sheet Deployment

1. Seal clamp on one end of membrane.
2. Seal second clamp over bottom, preventing folds during deployment.
3. Mount membranes into beakers (2) of water with predetermined concentrations
    a. Landfill Leachate Concentrations (µg/L): Cu – 5,000; Pb - 2,500; Zn - 500,020
    b. Stormwater Concentrations (µg/L): Cu – 110; Pb – 160; Zn - 910
4. Set turbulence (fastest without excessive folding – 125rpm)
5. Label mixing plate w/ date, experiment, and start time.

Sorption phase of Experiment

1. Deploy membrane within Leachate and Stormwater for 1 day
2. Collect Samples (PS, 0min, & 1 day)

Follow Material Preparation and Sampling SOP for instructions during deployment and sampling procedure.

Transition

1. Let drip dry, proceed to Desorption phase

Desorption phase of Experiment

1. Place membrane sheets in individual beakers filled with 1L De-ionized water.
2. Set turbulence (fastest without excessive folding-125rpm)
3. Collect Samples (PS, 0min, 1hour, 1 day, 5 days, 7 days and 14 days)
4. Conduct elution procedure on each sheet following collection of last sample.

Regenerated Cellulose Elution Procedure

1. Split bag lengthwise prior to placing in separatory funnel.
2. Swirl each of the following rinses to ensure that the bag has been coated:
    a. Remove excess from the bag -> measure solution?

b. Rinse twice (2) with 10 ml of 3M HNO3 (20 ml total)

c. Rinse twice (2) with 5 ml of De-ionized water (10 ml total)

Regenerated Cellulose Sampler Clean-up

1. Dispose of membrane in trash can.
2. Save Clamps for future use.
3. Clean all other materials by washing with soap and placing on drying rack.

A.1.5 Ion Exchange Resin SOP

Refer to appendix **A.1.1 Material Preparation and Sampling SOP** for instructions on the preparation of materials and solution.

Ion Exchange Resin Preparation (Mumford et. al. 2008)

1. Retrieve 30 g (≈ 50 ml) of Amberlite IRC748 chelating ion exchange resin, and place into vacuum apparatus and filter.
2. Wash insoluble residues from resin with 25 ml of de-ionized water three (3) times.
3. Condition resin into hydrogen form by washing with 25 ml of 0.5 M hydrochloric acid (HCl) three (3) times.
4. Rinse with 25 ml of 0.5 M sodium hydroxide (NaOH) three times (3) to replace the resin into Na^+ form.
5. Wash with 25 ml of de-ionized water three (3) times.

Netting Preparation

1. Cut 4” x 6” section of netting from roll.
2. Wash netting with detergent and rinse with tap water.
3. Rinse netting with De-ionized water three (3) times.

Ion Exchange Resin Sampler Assembly

1. Fold netting in half, lengthwise.

2. Seal along the side opposite fold the entire length, setting sealer at power level 7. This should result in a tube-like shape.
3. Seal one end of "tube".
4. Pour 15g of 'prepared' ion exchange resin within netting.
5. Seal open end of sampler, making sure to leave some space for expansion of the resin upon soaking.
6. Mount loaded sampler into beaker.
7. Label mixing plate w/ date, experiment, and start time.

*Follow **A.1.1 Material Preparation and Sampling SOP** for instructions during deployment and sampling procedure.*

Ion Exchange Resin Sampler Analysis

1. Remove sampler from Beaker immediately following retrieval of last solution sample.
2. Allow resin bag to dry overnight then pour from sampler by cutting one end of netting with scissors, into a 50 ml buret. Placing 10 ml of 10% (w/w) H_2SO_4 (1.1M) in the buret prior to pouring the resin, can help avoid tight packing when exposure to the H2SO4 forces it to expand.
3. Using 500mlof 10% (w/w) H_2SO_4 elute the resin at a flow rate of 4 ml/min. Use a peristaltic pump to achieve the flow rate.
4. Retrieve 5 ml sample with 5,000µL pipette from eluted solution and place in clean Polypropylene tubes sample bottles.
5. Add 135µL of trace metal grade HNO_3 solution, located under fume hood. (2.7 ml trace metal grade concentrated HNO_3/100 ml sample)
6. Label sample according to Sample Labeling Procedure with tape and marker.
7. Record 'Date Collected' and 'Sample Label' onto Sample Data Sheet.
8. Refrigerate sample until transport to Chemistry lab.

9. Measure volume of water remaining in beaker (Weigh beaker 1st, zero scale, add water, and obtain measurement).

Ion Exchange Resin Sampler Clean-up

1. Dispose of netting in trash can.
2. Save resin for future use, use netting to prevent from flowing down sink.
3. Clean all other materials by washing with detergent and placing on drying rack.

A.1.6 Ion Exchange Resin Elution Experiment SOP

Ion Exchange Resin Preparation (Mumford et. al. 2008)

1. Retrieve 30 g (≈ 50 ml) of Amberlite IRC748 chelating ion exchange resin, located in overhead cabinets above M. Klein workstation, and place into vacuum apparatus and filter.
2. Wash insoluble residues from resin with 25 ml of de-ionized water three (3) times.
3. Condition resin into hydrogen form by washing with 25 ml of 0.5 M hydrochloric acid (HCl) three (3) times.
4. Rinse with 25 ml of 0.5 M sodium hydroxide (NaOH) three times (3) to replace the resin into Na^+ form.
5. Wash with 25 ml of de-ionized water three (3) times.

Resin Exposure Set-up

1. Place 15g of 'prepared' resin (per iteration) in mesh netting bag.
2. Place in 1 liter beaker of desired solution.
3. Set turbulence for 400rpm.
4. Leave for 3 days.

Sample Collection

1. Collect sample prior to deployment and sample of solution at 3 day completion.

2. Retrieve 5 ml samples with 5,000µL pipette and place in clean sample bottles (Polypropylene tubes).
3. Add 135µL of trace metal grade HNO3 solution (2.7 ml trace metal grade concentrated HNO_3/100 ml sample).
4. Label sample according to Sample Labeling Procedure with tape and marker.
5. Record 'Date Collected', 'Time Collected' and 'Sample Label' onto Batch 1 Data Sheet.
6. Refrigerate samples until transport to Chemistry lab.

Elution Procedure

1. Remove sampler from Beaker immediately following retrieval of last solution sample.
2. Allow resin bag to dry overnight then pour from sampler by cutting one end of netting with scissors, into a 50 ml buret. Placing a small amount of 0.5M HCl in the buret prior to pouring the resin can help avoid tight packing when exposure to the HCl forces it to expand.
3. Use 120 ml of 0.5M HCl elute the resin at a flow rate of 2 ml/min.
4. Retrieve 5 ml sample with 5,000µL pipette from eluted solution and place in clean Polypropylene tubes sample bottles.
5. Add 135µL of trace metal grade HNO_3 solution, located under fume hood. (2.7 ml trace metal grade concentrated HNO_3/100 ml sample)
6. Label sample according to Sample Labeling Procedure with tape and marker.
7. Record 'Date Collected' and 'Sample Label' onto Batch 1 Data Sheet.
8. Refrigerate sample until transport to Chemistry lab.

A.1.7 Phenanthrene-Sorbed PUF Elution Experiment SOP

Batch Test (Single Elution)

1. Remove PUF from glass tube and place it in a clean beaker.

2. Allow the PUF to dry overnight (12 h) in fume hood.
3. Put the dried PUF and 50 ml of methylene chloride or methanol in a beaker, then cover the beaker with parafilm to decrease volatilization.
4. Place the covered beaker into fume hood and stir with a magnetic stirrer.
5. Pour the desorption solvent into a bottle for ^{14}C-PHE analysis.

Batch Test (Multiple Elution in Methanol)

1. Remove the PUF from glass tube, and follow 2-4 of the single elution procedure except use methanol as desorption solvent instead of methylene chloride.
2. After elution in the first beaker containing methanol for 720 min, remove the PUF from the methanol and squeeze the foam dry by tweezers and allow it further dry for one hour in a clean beaker under fume hood
3. Put the PUF into a new beaker (the second) containing 50 ml methanol, after 720 min, repeat step 2.
4. Put the PUF into a new beaker (the third) containing 50 ml methanol, eluting the foam for the third 720 min.
5. After the three elution cycles, sample the elutate, and pour the used desorption solvent (altogether 150 ml) into a bottle for ^{14}C-PHE analysis.

Lab-Scale Tests Elution

1. Removal the PUF-PRS from the lab-scale BMP.
2. Removal the PUF plug from the PRS (PVC tube) by tweezers and allow the foam to dry overnight (12 h), then put it into a beaker containing 50 ml methanol, covering the beaker with parafilm.
3. Stir the beaker with a magnetic stirrer for 1200 min under fume hood.
4. Pour the desorption solvent into a bottle for ^{14}C-PHE analysis.

A.1.8 ^{14}C-Phenanthrene Analytical SOP

^{14}C-PHE Stock Solutions Preparation

1. The source ^{14}C-PHE was purchased from the American Radio Chemicals Inc. Its activity is 100 µCi/ml.

2. Pipet 20 µL source ^{14}C-PHE into a 100-ml volumetric flux, and add DI water to the 100-ml mark to obtain the 100-ml ^{14}C-PHE stock solution that has 0.01 µCi/ml of activity with a concentration of ^{14}C-PHE being 0.03235 µg/ml.

3. Pour the stock solutions into a brown bottle, and then place the bottle in refrigerator.

^{14}C-PHE Analysis

After adsorption or desorption, samples for ^{14}C-PHE detection are all liquid samples.

1. Pipet 200 µL sample into a glass counting vial with 5 mL cocktail (high flash-point LSC-cocktail, purchased from PeakinElmer Inc., 940 Winter St., Waltham, MA, USA).
2. Put the counting vials into a 2500 TR Liquid Scintillation Counter for ^{14}C count. All the result output of the instrument were shown as activity (DPM).

PHE Mass Calculation

The synthetic stormwater contained two kinds of PHE, ^{14}C-labeled and non-labeled PHE. Thus the PHE concentration included both parts. The mass of adsorbed PHE can be calculated by the following equations A.1.8-1 and A.1.8-2:

$$M_{ad} = M_o \times \frac{A_{ad}}{A_o} \qquad \text{(A. 1.8-1)}$$

$$A_{ad} = A_o - A_t \qquad \text{(A. 1.8-2)}$$

The mass of desorbed PHE can be calculated by equation A.1.8-3

$$M_{de} = M_{ad} \times \frac{A_{de}}{A_{ad}} \quad \text{(A. 1.8-3)}$$

where, A_o is the initial solution ^{14}C-PHE activity (DPM) (e.g., influent of a column, or the solution used in batch tests); A_{ad} is the absorbed ^{14}C-PHE activity (DPM) by PUF; A_t is the ^{14}C-PHE activity (DPM) of the test solution sampled at time t; M_o is the total PHE mass in the initial solution; M_{ad} is the absorbed PHE mass by PUF; M_{de} is the desorbed PHE mass from PUF.

A.2 Lab-Scale Test Standard Operating Procedures (SOPs)

A.2.1 Task 2 Pre-Lab Uptake Test Experiment SOP

Ion Exchange Resin Preparation (Mumford et. al. 2008)

1. Retrieve 30 g (≈ 50 ml) of Amberlite IRC748 chelating ion exchange resin, located in overhead cabinets above M. Klein workstation, and place into vacuum apparatus and filter.
2. Wash insoluble residues from resin with 25 ml of de-ionized water three (3) times.
3. Condition resin into hydrogen form by washing with 25 ml of 0.5 M hydrochloric acid (HCl) three (3) times.
4. Rinse with 25 ml of 0.5 M sodium hydroxide (NaOH) three times (3) to replace the resin into Na^+ form.
5. Wash with 25 ml of de-ionized water three (3) times.

Sampler Exposure Set-up

1. Place 15g of ‘prepared’ resin in mesh netting bag.
2. Place in “Ooze” Housing unit
    a. Housing unit consists of ~ 5inches of clear 3inch Diameter acrylic piping capped with 3” inch PVC caps.

b. Each PVC cap contained threaded hose nozzle to attach to Stormwater hose, enabling flow through unit and is sealed via rubber "o"-rings.

c. Passive sampler sits within the housing unit.

3. Align one unit vertically so that pooling does not occur.

4. Align second unit horizontally so some pooling occurs within the sampler.

System Configuration

1. 7 liters of synthetic stormwater is to be mixed (according to concentrations previously detailed) and placed within a large basin. This basin will be agitated to prevent settling of sediment and enable sediment to be pumped throughout the system.

2. Pump will be used to determine flow rate for ½ hour storm (233.3 ml/min).

3. Water will be pumped from basin to housing module and then into effluent basin.

Sample Collection

1. The following samples are to be collected for each housing unit alignment (vertical and horizontal).

a. Influent basin

b. Effluent basin

c. Elution results

A.2.2 Lab Scale BMP Testing with Ion Exchange Sampler – 1 Liter Storm Event

Ion Exchange Resin Preparation (Mumford et. al. 2008)

1. Retrieve 30g (≈ 50 ml) of Amberlite IRC748 chelating ion exchange resin, located in overhead cabinets above M. Klein workstation, and place into vacuum apparatus and filter.

2. Wash insoluble residues from resin with 25 ml of de-ionized water three (3) times.

3. Condition resin into hydrogen form by washing with 25 ml of 0.5 M hydrochloric acid (HCl) three (3) times.
4. Rinse with 25 ml of 0.5 M sodium hydroxide (NaOH) three times (3) to replace the resin into Na^+ form.
5. Wash with 25 ml of de-ionized water three (3) times.

Netting Preparation

1. Cut 4" x 6" section of netting from roll.
2. Wash netting with detergent and rinse with tap water.
3. Rinse netting with De-ionized water three (3) times.

Ion Exchange Resin Sampler Assembly

1. Fold netting in half, widthwise.
2. Seal along the side opposite fold the entire length, setting sealer at power level 7. This should result in a tube-like shape.
3. Seal one end of "tube".
4. Pour 15g of 'prepared' ion exchange resin within netting.
5. Seal open end of sampler, making sure to leave some space for expansion of the resin upon soaking.
6. Place loaded samplers into the influent and effluent reactor housing modules. Completely cover each sample with a 50/50 percent volume mixture of sand and compost.
7. Load the influent and effluent samplers into the desired reactor.

Synthetic Storm Water Preparation and Loading

1. Prepare synthetic storm water according to listed table:

Contaminant	Cu(II)	Pb(II)	Zn(II)	Pond Sediment	Kaolin	Na_2CO_3	NaCl
Conc. (mg/L)	0.11	0.16	0.91	500	60	0.9	200

2. Load 1.0 liter of synthetic storm water into desired reactor at desired rate. A peristaltic pump may need to be used to achieve desired loading rate.
3. Use a 1 liter beaker to collect the effluent from the reactor.
4. Allow a 1 hour time period for the reactor to drain.
5. Remove samplers from reactor immediately following a one hour time period.
6. Measure the final volume of collected effluent at the end of the 1 hour time period.

Ion Exchange Resin Sampler Analysis

1. Allow resin bag to dry for a 24 hour time period.
2. Pour from sampler by cutting one end of netting with scissors, into a 50 ml buret. Placing 10 ml of 10% (w/w) H_2SO_4 (1.1M) in the buret prior to pouring the resin, can help avoid tight packing when exposure to the H2SO4 forces it to expand.
3. Using 500 ml of 10% (w/w) H_2SO_4 elute the resin at a flow rate of 4 ml/min.
4. After all 500 ml has been passed through the buret, mix the collected elute solution with a magnetic stir bar and stir plate.
5. Retrieve 5 ml sample with 5,000µL pipette from eluted solution and place in clean polypropylene tube sample bottles.
6. Add 135µL of trace metal grade HNO_3 solution, located under fume hood. (2.7 ml trace metal grade concentrated HNO_3/100 ml sample)
7. Label sample according to Sample Labeling Procedure with tape and marker.
8. Record 'Date Collected' and 'Sample Label' onto Data Sheet.
9. Refrigerate sample until transport to Chemistry lab.
10. Measure volume of solution in the eluted portion using a volumetric flask.

A.3 Field Test Standard Operating Procedure (SOPs)

Ion Exchange Resin Preparation (Mumford et. al. 2008)

1. Retrieve 30g (≈ 50 ml) of Amberlite IRC748 chelating ion exchange resin, located in overhead cabinets above M. Klein workstation, and place into vacuum apparatus and filter.
2. Wash insoluble residues from resin with 25 ml of de-ionized water three (3) times.
3. Condition resin into hydrogen form by washing with 25 ml of 0.5 M hydrochloric acid (HCl) three (3) times.
4. Rinse with 25 ml of 0.5 M sodium hydroxide (NaOH) three times (3) to replace the resin into Na^+ form.
5. Wash with 25 ml of de-ionized water three (3) times.

Netting Preparation

1. Cut 4" x 6" section of netting from roll.
2. Wash netting with detergent and rinse with tap water.
3. Rinse netting with De-ionized water three (3) times.

Ion Exchange Resin Sampler Assembly

1. Fold netting in half, widthwise.
2. Seal along the side opposite fold the entire length, setting sealer at power level 7. This should result in a tube-like shape.
3. Seal one end of "tube".
4. Pour 15g of 'prepared' ion exchange resin within netting.
5. Seal open end of sampler, making sure to leave some space for expansion of the resin upon soaking.
6. Place loaded samplers into the influent and effluent reactor housing modules. Completely cover each sample with a 50/50 percent volume mixture of sand and compost.
7. Load the influent and effluent samplers into the desired reactor.

Field Sampler Deployment

1. Install Samplers in influent & effluent filter trench deployment units & record time of installation.
2. Install Samplers in each influent & effluent bioretention cell deployment unit, cover with acid-washed sand, & record time of installation. Be sure to place appropriate unit within correct observation well.

Field Sampler Collection

1. Collect Samplers from each deployment unit and record time.
2. Place samplers within bottle, recording time of collection and transport back to lab.

Site Sensor Data Collection

1. Acquire raw data from sensor.
2. Select pertinent data (while samplers were deployed) and develop plots for: cumulative precipitation, velocities, water levels, flow rates, and total flows within excel worksheets.

Site Sensor Data Collection

Ion Exchange Resin Sampler Analysis

1. Allow resin bag to dry for a 24 hour time period.
2. Pour from sampler by cutting one end of netting with scissors, into a 50 ml buret. Placing 10 ml of 10% (w/w) H_2SO_4 (1.1M) in the buret prior to pouring the resin, can help avoid tight packing when exposure to the H2SO4 forces it to expand.
3. Using 500 ml of 10% (w/w) H_2SO_4 elute the resin at a flow rate of 4 ml/min.
4. After all 500 ml has been passed through the buret, mix the collected elute solution with a magnetic stir bar and stir plate.
5. Retrieve 5 ml sample with 5,000µL pipette from eluted solution and place in clean polypropylene tube sample bottles.
6. Add 135µL of trace metal grade HNO_3 solution, located under fume hood. (2.7 ml trace metal grade concentrated HNO_3/100 ml sample)

7. Label sample according to Sample Labeling Procedure with tape and marker.
8. Record ‘Date Collected’ and ‘Sample Label’ onto Data Sheet.
9. Refrigerate sample until transport to Chemistry lab.
10. Measure volume of solution in the eluted portion using a volumetric flask.

Appendix B: Quality Assurance and Quality Control

Quality control (QC) plans include a variety of controls and checks to ensure data quality. This usually includes replicates, precision & accuracy measurements, method detection limits, comparability. Standard operating procedures (SOPs) were compiled and followed for all tests conducted and presented in this report. Some batch tests were run in parallel (results are displayed in Tables B-1, B-2 and B-3). Control and follow-up tests were conducted on the batch systems to identify possible source of mass removal.

Table B-1 Trial 1 ion exchange resin copper individual test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Cu65 (ppb)	Natural Log of Concentration
ie-cu-ps			117.59	4.76
ie-cu-0m	10/9/2012 10:44	0	115.55	4.74
ie-cu-15m	10/9/2012 11:00	16	36.34	3.59
ie-cu-30m	10/9/2012 11:15	31	24.17	3.18
ie-cu-1h	10/9/2012 11:47	63	13.17	2.57
ie-cu-5h	10/9/2012 15:20	276	5.20	1.64
ie-cu-1b	10/10/2012 15:30	1726	2.61	0.95
ie-cu-3d	10/12/2012 14:30	4546	2.10	0.74

Table B-2 Trial 2 ion exchange resin copper individual test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Cu65 (ppb)	Natural Log of Concentration
ie-cu-ps-2			106.15	4.66
ie-cu-0m-2	10/9/2012 10:44	0	106.69	4.67
ie-cu-15m-2	10/9/2012 11:00	16	36.24	3.59
ie-cu-30m-2	10/9/2012 11:15	31	22.90	3.13
ie-cu-1h-2	10/9/2012 11:47	63	12.72	2.54
ie-cu-5h-2	10/9/2012 15:20	276	4.85	1.58
ie-cu-1b-2	10/10/2012 15:30	1726	2.74	1.00
ie-cu-3d-2	10/12/2012 14:30	4546	1.93	0.66

Table B-3 Comparison of parallel ion exchange resin copper individual tests

Exposure Time (min)	Trial 1 (ppb)	Trial 2 (ppb)	% Difference
	117.59	106.15	-10.78%
0	115.55	106.69	-8.30%
16	36.34	36.24	-0.29%
31	24.17	22.90	-5.53%
63	13.17	12.72	-3.54%
276	5.202	4.85	-7.10%
1726	2.61	2.74	4.72%
4546	2.10	1.93	-8.38%

Lab-scale reactor tests were conducted in triplicates, averages and standard deviations are presented within the report body for statistical confidence. Dilutions were avoided, if possible, by either collecting larger samples or using more dilute elution.

Metal were analyzed by a Varian 2004 ICP-MS. This machine provided and internal rhodium calibration to incorporate the effects of sample temperature and viscosity. This machine also combined ten or more measurements to produce a statistically confident concentration. Method detection limits (MDL) were determined in the same way as a sister-project (Jones 2012). Below is an example MDL calculation for nickel, conducted and drafted for a separate project. This describes the calculations shown in Table B-4.

"Four points were used on the standard curve 0, 10, 50, 200 ppb with the related counts per second used by the ICP-MS. The columns from left to right are (1) ppb concentration, (2) counts per second, (3) x values, (4) y values, (5) x values squared, (6) y values squared, (7) x values multiplied by the y values, (8) the calculated y values using the best fit equation, and finally (9) the last column is the residual of each standard point which is the difference in the actual y and the calculated y.

The calculation of the S.D. Residuals, S_y is the standards of deviation of the y residual of each standard point, taking into account the degrees of freedom or n-1. The detection limit is then calculated by 3 times the S.D. Residuals, S_y. The equation of best fit and Correlation Coefficient, R is also reported in this table, which were y = 5299.24x +7437.53with R = 0.99991. The result of the t test for this example is also reported and was 4.30. In addition, the result of the "g" statistic is shown which was 0.0016 and a good value is below 0.005. The method detection limit for nickel for this example is 3.373 µg/L."

Table B-4 Example nickel MDL calculation (Jones 2012)

	Raw Data		Transformed Data						
	(1) x	(2) y	(3) $f(x)$	(4) $f(y)$	(5) $f(x)^2$	(6) $f(y)^2$	(7) $f(x) \cdot f(y)$	(8) $f'(y)$	(9)Residuals
Identity	ppb	Instrument Signal							
Units	ppb	c/s	ppb	c/s					
First 0?	0.000	1358.800049	0	1359	0	1846338	0	7438	-6079
Regio	10.000	59545	10	59545	100	3545607025	595450	60430	-885
	50.000	281625.4063	50	281625	2500	79312869445	14081270	272400	9226
Last	200.000	1065023.25	200	1065023	40000	1134274523041	213004650	1067285	-2262
Totals			260	1407552	42600	1217134845849	227681370		

Count, n =	4		
x bar =	65.000 ppb	Slope, m =	5299.24c/s / c/s
y bar =	351888.11c/s	Intercept, b =	7437.53c/s
S_{xx} =	25700.000	S.D. Residuals, S_y =	7999.024
S_{yy} =	721833866540.40	S.D. Slope, S_m =	49.897
S_{xy} =	136190460.65	S.D. Intercept, S_b =	5149.265
		Correlation Coefficient, R =	0.99991
		t (95%, n - 2 d.f.) =	4.30
		"g" Statistic, g =	0.0016
		Detection Limit = Blank + 3*S_y(resid)=	**3.373**

It should be noted that sulfuric acid should not be used for eluting resin for ICP-MS analysis because sulfuric acid can form different isotopiccombinations (e.g., $^{32}S^{33}S^{+}$, $^{32}S^{16}O^{17}O^{+}$, $^{33}S_{16}O_2^{+}$) that interfere with Cu analysis and Zn ($^{32}S^{16}O_2^{+}$, $^{32}S_2^{+}$, …) that interfere with Zn analysis during the ICP-MS analytical process, which interfere with the ICP results. It is not uncommon for spectroscopic interferences to occur in ICP-MS caused by atomic or molecular ions that have the same mass-to-charge as analytes of interest. For example, for Cu, isotopic combinations of $^{31}P^{16}O_2^{+}$,

$^{40}Ar^{23}Na^{+}$, $^{47}Ti^{16}O^{+}$, $^{23}Na^{40}Ca^{+}$, $^{46}Ca^{16}O^{1}H^{+}$, $^{36}Ar^{12}C^{14}N^{1}H^{+}$, $^{14}N^{12}C^{37}Cl^{+}$, $^{16}O^{12}C^{35}Cl^{+}$ would be reported as ^{63}Cu with 69.1% abundance, and $^{49}Ti^{16}O^{+}$, $^{32}S^{16}O_2{}^{1}H^{+}$, $^{40}Ar^{25}Mg^{+}$, $^{40}Ca^{16}O^{1}H^{+}$, $^{36}Ar^{14}N_2{}^{1}H^{+}$, $^{32}S^{33}S^{+}$, $^{32}S^{16}O^{17}O^{+}$, $^{33}S_{16}O_2{}^{+}$, $^{12}C^{16}O^{37}Cl^{+}$, $^{12}C^{18}O^{35}Cl^{+}$, $^{31}P^{16}O^{18}O^{+}$ reported as ^{65}Cu with 30.9% abundance (May and Wiedmeyer 1998). In this study, trace metal grade HNO_3 was used for tests reported in chapters 3 and section 4.4, but trace metal grade H_2SO_4 was used for column tests reported in chapter 4 except those in section 4.4. Therefore, any column data before section 4.4 are questionable.

Appendix C: Further Data

C.1 Batch Tests

Kinetics curves were derived and presented within Chapter three of the report. The specific concentrations and times used to generate the figures are presented below.

C.1.1 Kinetics Curve Data

C.1.1.1 Regenerated Cellulose

Table C-1 Regenerated cellulose copper individual test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Cu65 (ppb)
Cu-D-RC-DI-0m	6/26/2012 13:50	0	92.51
Cu-D-RC-DI-0m	6/26/2012 13:50	0	87.26
Cu-D-RC-DI-0m	6/26/2012 13:50	0	86.87
Average		0	88.88
Cu-D-RC-DI-15m	6/26/2012 14:05	15	79.74
Cu-D-RC-DI-30m	6/26/2012 14:20	30	70.78
Cu-D-RC-DI-1h	6/26/2012 14:50	60	56.50
Cu-D-RC-DI-5h	6/26/2012 18:50	300	18.81
Cu-D-RC-DI-1d	6/27/2012 12:44	1374	15.16
Cu-D-RC-DI-3d	6/29/2012 14:20	4350	12.38
Cu-D-RC-DI-7d	7/3/2012 14:50	10140	12.12
Cu-D-RC-DI-14d	7/10/2012 15:32	20262	13.03

Table C-2 Regenerated cellulose lead individual test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Zn66 (ppb)
Pb-D-RC-PS(b)	8/9/2012 11:22	0	14.52
Pb-D-RC-15m(b)	8/9/2012 11:37	15	14.37
Pb-D-RC-30m(b)	8/9/2012 11:52	29.9	13.82
Pb-D-RC-1h(b)	8/9/2012 12:22	60	13.65
Pb-RC-1h	41128.63542	60	114.09
Pb-RC-5h	41128.80694	307	255.92
Pb-RC-1d	41129.66319	1540	112.69
Pb-RC-3d	41131.43194	4087	120.55
Pb-RC-7d	41135.58333	10065	125.60
Pb-RC-14d	41142.47917	19995	182.44

Table C-3 Regenerated cellulose zinc individual test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Zn66 (ppb)
Zn-RC-0m dil 1:10	8/7/2012 14:15	0	1298.66
Zn-RC-1h dil 1:10	8/7/2012 15:15	60	726.55
Zn-RC-5h dil 1:10	8/7/2012 19:19	304	701.82
Zn-RC-1d dil 1:10	8/8/2012 15:55	1540	736.32
Zn-RC-3d dil 1:10	8/10/2012 10:22	4087	773.89
Zn-RC-7d dil 1:10	8/14/2012 13:55	10060	2040.30
Zn-RC-14d dil 1:10	8/21/2012 11:30	19995	812.14

Table C-4 Regenerated cellulose copper tri-metal test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Cu65 (ppb)
Cu-Pb-Zn-D-RC-0m	8/14/2012 13:15	0	91.07
Cu-Pb-Zn-D-RC-15m	8/14/2012 13:30	15	90.30
Cu-Pb-Zn-D-RC-30m	8/14/2012 13:45	29.9	89.23
Cu-Pb-Zn-D-RC-1h	8/14/2012 14:15	60	85.89
Cu-Pb-Zn-D-RC-5h	8/14/2012 21:15	480	65.63
Cu-Pb-Zn-D-RC-1d	8/15/2012 14:22	1507	124.36
Cu-Pb-Zn-D-RC-3d	8/17/2012 14:30	4395	79.20
Cu-Pb-Zn-D-RC-7d	8/21/2012 15:30	10215	83.26
Cu-Pb-Zn-D-RC-14d	8/28/2012 15:00	20265	80.03

Table C-5 Regenerated cellulose lead tri-metal test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Pb (ppb)
Cu-Pb-Zn-D-RC-0m	8/14/2012 13:15	0	155.80
Cu-Pb-Zn-D-RC-15m	8/14/2012 13:30	15	148.10
Cu-Pb-Zn-D-RC-30m	8/14/2012 13:45	29.9	146.03
Cu-Pb-Zn-D-RC-1h	8/14/2012 14:15	60	142.79
Cu-Pb-Zn-D-RC-5h	8/14/2012 21:15	480	133.03
Cu-Pb-Zn-D-RC-1d	8/15/2012 14:22	1507	145.79
Cu-Pb-Zn-D-RC-3d	8/17/2012 14:30	4395	141.51
Cu-Pb-Zn-D-RC-7d	8/21/2012 15:30	10215	158.99
Cu-Pb-Zn-D-RC-14d	8/28/2012 15:00	20265	154.81

Table C-6 Regenerated cellulose zinc tri-metal test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Zn66 (ppb)
Cu-Pb-Zn-D-RC-0m	8/14/2012 13:15	0	871.25
Cu-Pb-Zn-D-RC-15m	8/14/2012 13:30	15	867.91
Cu-Pb-Zn-D-RC-30m	8/14/2012 13:45	29.9	860.04
Cu-Pb-Zn-D-RC-1h	8/14/2012 14:15	60	857.06
Cu-Pb-Zn-D-RC-5h	8/14/2012 21:15	480	
Cu-Pb-Zn-D-RC-1d	8/15/2012 14:22	1507	927.52
Cu-Pb-Zn-D-RC-3d	8/17/2012 14:30	4395	917.81
Cu-Pb-Zn-D-RC-7d	8/21/2012 15:30	10215	943.80
Cu-Pb-Zn-D-RC-14d	8/28/2012 15:00	20265	933.36

Table C-7 Regenerated cellulose copper synthetic storm water test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Cu65 (ppb)
sw-rd-rc-ps	10/2/2012 14:00	0	103.51
sw-rd-rc-0m	10/2/2012 14:00	0	100.77
sw-rd-rc-15m	10/2/2012 14:15	15	96.51
sw-rd-rc-30m	10/2/2012 14:40	40	92.99
sw-rd-rc-1h	10/2/2012 15:02	62	93.28
sw-rd-rc-5h	10/2/2012 17:45	225	85.45
sw-rd-rc-1d	10/3/2012 17:15	1635	85.51
sw-rd-rc-3d	10/5/2012 11:25	4165	88.12
sw-rd-rc-7d	10/9/2012 15:25	10165	93.26
sw-rd-rc-14d	10/16/2012 14:45	20205	97.13

Table C-8 Regenerated cellulose lead synthetic storm water test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Pb… ppb
sw-rd-rc-ps	10/2/2012 14:00	0	182.90
sw-rd-rc-0m	10/2/2012 14:00	0	173.78
sw-rd-rc-15m	10/2/2012 14:15	15	162.83
sw-rd-rc-30m	10/2/2012 14:40	40	156.54
sw-rd-rc-1h	10/2/2012 15:02	62	153.26
sw-rd-rc-5h	10/2/2012 17:45	225	143.34
sw-rd-rc-1d	10/3/2012 17:15	1635	139.86
sw-rd-rc-3d	10/5/2012 11:25	4165	137.29
sw-rd-rc-7d	10/9/2012 15:25	10165	138.53
sw-rd-rc-14d	10/16/2012 14:45	20205	138.91

Table C-9 Regenerated cellulose zinc synthetic storm water test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Zn66 ppb
sw-rd-rc-ps	10/2/2012 14:00	0	844.74
sw-rd-rc-0m	10/2/2012 14:00	0	794.32
sw-rd-rc-15m	10/2/2012 14:15	15	799.65
sw-rd-rc-30m	10/2/2012 14:40	40	765.62
sw-rd-rc-1h	10/2/2012 15:02	62	763.20
sw-rd-rc-5h	10/2/2012 17:45	225	744.13
sw-rd-rc-1d	10/3/2012 17:15	1635	728.57
sw-rd-rc-3d	10/5/2012 11:25	4165	714.33
sw-rd-rc-7d	10/9/2012 15:25	10165	776.61
sw-rd-rc-14d	10/16/2012 14:45	20205	772.96

C.1.1.2 Ion Exchange Resin

Table C-10 Trial 1 ion exchange resin copper individual test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Cu65 (ppb)	Natural Log of Concentration
ie-cu-ps			117.59	4.76
ie-cu-0m	10/9/2012 10:44	0	115.55	4.74
ie-cu-15m	10/9/2012 11:00	16	36.34	3.59
ie-cu-30m	10/9/2012 11:15	31	24.17	3.18
ie-cu-1h	10/9/2012 11:47	63	13.17	2.57
ie-cu-5h	10/9/2012 15:20	276	5.20	1.64
ie-cu-1b	10/10/2012 15:30	1726	2.61	0.95
ie-cu-3d	10/12/2012 14:30	4546	2.10	0.74

Table C-11 Trial 2 ion exchange resin copper individual test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Cu65 (ppb)	Natural Log of Concentration
ie-cu-ps-2			106.15	4.66
ie-cu-0m-2	10/9/2012 10:44	0	106.69	4.67
ie-cu-15m-2	10/9/2012 11:00	16	36.24	3.59
ie-cu-30m-2	10/9/2012 11:15	31	22.90	3.13
ie-cu-1h-2	10/9/2012 11:47	63	12.72	2.54
ie-cu-5h-2	10/9/2012 15:20	276	4.85	1.58
ie-cu-1b-2	10/10/2012 15:30	1726	2.74	1.00
ie-cu-3d-2	10/12/2012 14:30	4546	1.93	0.66

Table C-12 Ion exchange resin lead individual test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Pb (ppb)	Natural Log of Concentration
ie-pb-ps			144.42	4.97
ie-pb-0m	11/6/2012 14:40	0	122.00	4.80
ie-pb-15m	11/6/2012 14:55	15	43.42	3.77
ie-pb-1h	11/6/2012 15:40	60	11.80	2.46
ie-pb-3h	11/6/2012 17:40	180	7.12	1.96
ie-pb-4h	11/6/2012 18:40	240	6.65	1.89
ie-pb-1d	11/7/2012 15:05	1465	3.63	1.28
ie-pb-3d	11/9/2012 14:00	4280	1.95	0.66

Table C-13 Ion exchange resin zinc individual test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Zn (ppb)	Natural Log of Concentration
ie-pb-ps			1188.75	7.08
ie-pb-0m	11/6/2012 14:40	0	979.97	6.88
ie-pb-15m	11/6/2012 14:55	15	389.43	5.96
ie-pb-1h	11/6/2012 15:40	60	131.15	4.87
ie-pb-3h	11/6/2012 17:40	180	50.82	3.92
ie-pb-4h	11/6/2012 18:40	240	16.0	2.77
ie-pb-1d	11/7/2012 15:05	1465	9.20	2.21
ie-pb-3d	11/9/2012 14:00	4280	6.12	1.81

Table C-14 Ion exchange resin copper tri-metal test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Cu (ppb)	Natural Log of Concentration
ie-tri-ps			118.95	4.77
ie-tri-0m	11/6/2012 14:40	0	100.53	4.61
ie-tri-15m	11/6/2012 14:55	15	37.90	3.63
ie-tri-30m	11/6/2012 15:10	30	19.94	2.99
ie-tri-1h	11/6/2012 15:40	60	10.76	2.33
ie-tri-4h	11/6/2012 18:40	240	2.97	1.08
ie-tri-1d	11/7/2012 15:05	1465	1.89	0.64
ie-tri-3d	11/9/2012 14:00	4280	1.76	0.57

Table C-15 Ion exchange resin lead tri-metal test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Pb (ppb)	Natural Log of Concentration
ie-tri-ps			148.90	5.00
ie-tri-0m	11/6/2012 14:40	0	122.81	4.81
ie-tri-15m	11/6/2012 14:55	15	31.35	3.44
ie-tri-30m	11/6/2012 15:10	30	13.11	2.57
ie-tri-1h	11/6/2012 15:40	60	4.65	1.53
ie-tri-4h	11/6/2012 18:40	240	0	-
ie-tri-1d	11/7/2012 15:05	1465	0	-
ie-tri-3d	11/9/2012 14:00	4280	0	-

Table C-16 Ion exchange resin zinc tri-metal test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Zn (ppb)	Natural Log of Concentration
ie-tri-ps			1068.75	6.97
ie-tri-0m	11/6/2012 14:40	0	946.99	6.85
ie-tri-15m	11/6/2012 14:55	15	347.66	5.85
ie-tri-30m	11/6/2012 15:10	30	116.01	4.75
ie-tri-1h	11/6/2012 15:40	60	30.25	3.40
ie-tri-4h	11/6/2012 18:40	240	3.96	1.37
ie-tri-1d	11/7/2012 15:05	1465	2.59	0.95
ie-tri-3d	11/9/2012 14:00	4280	2.31	0.84

Table C-17 Ion Exchange resin copper synthetic storm water test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Cu (ppb)	Natural Log of Concentration
ie-tri-ps			136.45	4.91
ie-tri-0m	11/6/2012 14:40	0	111.57	4.71
ie-tri-15m	11/6/2012 14:55	15	82.68	4.41
ie-tri-30m	11/6/2012 15:40	60	71.95	4.27
ie-tri-1h	11/6/2012 17:40	180	65.3	4.17
ie-tri-4h	11/6/2012 18:40	240	36.61	3.60
ie-tri-1d	11/7/2012 15:05	1465	12.30	2.51
ie-tri-3d	11/9/2012 14:00	4280	6.95	1.93

Table C-18 Ion exchange resin lead synthetic storm water test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Pb (ppb)	Natural Log of Concentration
ie-tri-ps			136.24	4.91
ie-tri-0m	11/6/2012 14:40	0	116.30	4.75
ie-tri-15m	11/6/2012 14:55	15	88.97	4.48
ie-tri-30m	11/6/2012 15:40	60	70.59	4.25
ie-tri-1h	11/6/2012 17:40	180	62.60	4.13
ie-tri-4h	11/6/2012 18:40	240	46.33	3.83
ie-tri-1d	11/7/2012 15:05	1465	28.87	3.36
ie-tri-3d	11/9/2012 14:00	4280	17.25	2.84

Table C-19 Ion exchange resin zinc synthetic storm water test data

Sample Label	Time of Collection (min)	Exposure Time (min)	Zn (ppb)	Natural Log of Concentration
ie-tri-ps			1196.12	7.08
ie-tri-0m	11/6/2012 14:40	0	1032.87	6.94
ie-tri-15m	11/6/2012 14:55	15	644.44	6.46
ie-tri-30m	11/6/2012 15:40	60	465.32	6.14
ie-tri-1h	11/6/2012 17:40	180	372.72	5.92
ie-tri-4h	11/6/2012 18:40	240	150.69	5.01
ie-tri-1d	11/7/2012 15:05	1465	44.60	3.79
ie-tri-3d	11/9/2012 14:00	4280	28.53	3.35

C.2 Lab-Scale Tests

Lab-Scale results within the report body include concentrations and calculations, thus no further data is presented within the appendix.

C.3 Field Tests

Sensor data, used to generate storm characteristic plots for cumulative precipitation, water levels, velocities, flow-rates, and total flows within section 4.3.2.1 (Storm Characteristics) of the report are presented below. Sampler deployment and collection times are detailed within Table C-20.

Table C-20 Sampler and grab sample deployment and collection times

	Filter Trench		Bioretention Cells							
			Cell #1		Cell #2		Cell #3		Cell #4	
	Influent	Effluent	Influent	Effluent	In.	Eff.	In.	Eff.	In.	Eff.
Sampler Deployment	6/26/2013 19:00	6/26/2013 19:10	6/26/2013 19:30	6/26/2013 19:30	--	--	--	--	--	--
Sampler Collection	6/27/2013 13:23	6/27/2013 13:27	6/27/2013 13:15	6/27/2013 13:15	--	--	--	--	--	--
Grab Sample Collection	--	6/27/2013 12:00	--	--	--	--	--	--	--	--
	6/27/2013 12:15	6/27/2013 12:15	--	--	--	--	--	--	--	--
	6/27/2013 12:30	6/27/2013 12:30	--	--	--	--	--	--	--	--
	6/27/2013 12:45	6/27/2013 12:45	--	--	--	--	--	--	--	--
	6/27/2013 13:00	6/27/2013 13:00	--	--	--	--	--	--	--	--
	--	--	6/27/2013 13:15	--	--	--	--	--	--	--

C.3.1 Data Logging Rain Gauge

A RG3 Data Logging Rain Gauge manufactured by Onset was utilized to determine site precipitation values. As it rains, the tipping bucket fills and tips once one hundredth of an inch has accumulated. Once the bucket tips it triggers a sensor that records the time and number of tips. Table C-21 displays the data collected by the rain gauge during sampler deployment, which was used to generate the cumulative rainfall plot within the report.

Table C-21 Cumulative precipitation data

#	Date Time, GMT-05:00	Time	Event, units	Tips	Cumulative Precipitation (in.)
34	6/27/2013 7:28	7:28:00 AM	32	1	0.01
35	6/27/2013 7:29	7:29:00 AM	33	2	0.02
36	6/27/2013 7:31	7:31:00 AM	34	3	0.03
37	6/27/2013 7:32	7:32:00 AM	35	4	0.04
38	6/27/2013 7:33	7:33:00 AM	36	5	0.05
39	6/27/2013 7:34	7:34:00 AM	37	6	0.06
40	6/27/2013 7:35	7:35:00 AM	38	7	0.07
41	6/27/2013 7:36	7:36:00 AM	39	8	0.08
42	6/27/2013 7:36	7:36:00 AM	40	9	0.09
43	6/27/2013 7:37	7:37:00 AM	41	10	0.1
44	6/27/2013 7:37	7:37:00 AM	42	11	0.11
45	6/27/2013 7:37	7:37:00 AM	43	12	0.12
46	6/27/2013 7:38	7:38:00 AM	44	13	0.13
47	6/27/2013 7:40	7:40:00 AM	45	14	0.14
48	6/27/2013 7:45	7:45:00 AM	46	15	0.15
49	6/27/2013 7:48	7:48:00 AM	47	16	0.16
50	6/27/2013 8:01	8:01:00 AM	48	17	0.17
51	6/27/2013 8:58	8:58:00 AM	49	18	0.18
52	6/27/2013 8:59	8:59:00 AM	50	19	0.19
53	6/27/2013 9:34	9:34:00 AM	51	20	0.2
54	6/27/2013 12:08	12:08:00 PM	52	21	0.21
55	6/27/2013 12:12	12:12:00 PM	53	22	0.22

C.3.2 Area Velocity Flow Module

A 2150 Area Velocity Flow Module manufactured by ISCO was used to collect the aforementioned data (save precipitation). The sensor attains values by sending and receiving ultrasonic sound waves. Particles or air bubbles within the water flow reflect these waves and enable water level and velocity measurements. Flow rate and total flow values are calculated by using the water height and velocity and incorporating the cross-sectional area of the channel.

C.3.2.1 Water Levels

Table C-22 presents the water level data accumulated during the storm event described in the report during the field test. This data set was used to generate the water level plot used within the report.

Table C-22 Water level data

Time	Level (in)	Time (Cont.)	Level (in)	Time (Cont.)	Level (in)
6/27/2013 7:00	0.424	6/27/2013 9:15	1.797	6/27/2013 11:30	1.072
6/27/2013 7:05	0.448	6/27/2013 9:20	1.892	6/27/2013 11:35	1.152
6/27/2013 7:10	0.472	6/27/2013 9:25	1.951	6/27/2013 11:40	1.14
6/27/2013 7:15	0.453	6/27/2013 9:30	1.884	6/27/2013 11:45	1.079
6/27/2013 7:20	0.467	6/27/2013 9:35	1.97	6/27/2013 11:50	1.022
6/27/2013 7:25	0.456	6/27/2013 9:40	2.1	6/27/2013 11:55	0.973
6/27/2013 7:30	0.608	6/27/2013 9:45	2.103	6/27/2013 12:00	0.941
6/27/2013 7:35	0.414	6/27/2013 9:50	2.064	6/27/2013 12:05	0.936
6/27/2013 7:40	0.45	6/27/2013 9:55	1.964	6/27/2013 12:10	0.897
6/27/2013 7:45	2.576	6/27/2013 10:00	1.843	6/27/2013 12:15	0.868
6/27/2013 7:50	2.874	6/27/2013 10:05	1.743	6/27/2013 12:20	0.876
6/27/2013 7:55	3.122	6/27/2013 10:10	1.652	6/27/2013 12:25	0.856
6/27/2013 8:00	3.294	6/27/2013 10:15	1.567	6/27/2013 12:30	0.857
6/27/2013 8:05	3.25	6/27/2013 10:20	1.483	6/27/2013 12:35	0.971
6/27/2013 8:10	3.11	6/27/2013 10:25	1.421	6/27/2013 12:40	1.113
6/27/2013 8:15	3.001	6/27/2013 10:30	1.439	6/27/2013 12:45	1.148
6/27/2013 8:20	2.876	6/27/2013 10:35	1.394	6/27/2013 12:50	1.114
6/27/2013 8:25	2.738	6/27/2013 10:40	1.36	6/27/2013 12:55	1.093
6/27/2013 8:30	2.622	6/27/2013 10:45	1.327	6/27/2013 13:00	0.809
6/27/2013 8:35	2.509	6/27/2013 10:50	1.317	6/27/2013 13:05	1.348
6/27/2013 8:40	2.356	6/27/2013 10:55	1.296	6/27/2013 13:10	1.39
6/27/2013 8:45	2.189	6/27/2013 11:00	1.25	6/27/2013 13:15	1.335
6/27/2013 8:50	2.06	6/27/2013 11:05	1.25	6/27/2013 13:20	1.309
6/27/2013 8:55	1.927	6/27/2013 11:10	1.222	6/27/2013 13:25	1.341
6/27/2013 9:00	1.776	6/27/2013 11:15	1.166	6/27/2013 13:30	1.163
6/27/2013 9:05	1.7	6/27/2013 11:20	1.119		
6/27/2013 9:10	1.791	6/27/2013 11:25	1.076		

C.3.2.2 Velocities

Table C-23 presents the velocity data accumulated during the storm event described in the report during the field test. This data set was used to generate the velocity plot used within the report.

Table C-23 Velocity data

Date and Time	Velocity (ft/s)	Date and Time (continued)	Velocity (ft/s)	Date and Time (continued)	Velocity (ft/s)
6/27/2013 7:00	0.54	6/27/2013 9:10	0.434	6/27/2013 11:20	0.397
6/27/2013 7:05	0.54	6/27/2013 9:15	0.45	6/27/2013 11:25	0.397
6/27/2013 7:10	0.54	6/27/2013 9:20	0.479	6/27/2013 11:30	0.397
6/27/2013 7:15	0.54	6/27/2013 9:25	0.516	6/27/2013 11:35	0.397
6/27/2013 7:20	0.54	6/27/2013 9:30	0.49	6/27/2013 11:40	0.397
6/27/2013 7:25	0.54	6/27/2013 9:35	0.516	6/27/2013 11:45	0.397
6/27/2013 7:30	0.54	6/27/2013 9:40	0.579	6/27/2013 11:50	0.397
6/27/2013 7:35	0.54	6/27/2013 9:45	0.562	6/27/2013 11:55	0.397
6/27/2013 7:40	0.54	6/27/2013 9:50	0.535	6/27/2013 12:00	0.397
6/27/2013 7:45	0.916	6/27/2013 9:55	0.417	6/27/2013 12:05	0.397
6/27/2013 7:50	1.014	6/27/2013 10:00	0.427	6/27/2013 12:10	0.397
6/27/2013 7:55	1.092	6/27/2013 10:05	0.467	6/27/2013 12:15	0.397
6/27/2013 8:00	1.092	6/27/2013 10:10	0.416	6/27/2013 12:20	0.397
6/27/2013 8:05	1.193	6/27/2013 10:15	0.446	6/27/2013 12:25	0.397
6/27/2013 8:10	1.296	6/27/2013 10:20	0.446	6/27/2013 12:30	0.397
6/27/2013 8:15	1.204	6/27/2013 10:25	0.397	6/27/2013 12:35	0.397
6/27/2013 8:20	1.153	6/27/2013 10:30	0.397	6/27/2013 12:40	0.397
6/27/2013 8:25	0.886	6/27/2013 10:35	0.397	6/27/2013 12:45	0.397
6/27/2013 8:30	0.86	6/27/2013 10:40	0.397	6/27/2013 12:50	0.397
6/27/2013 8:35	0.841	6/27/2013 10:45	0.397	6/27/2013 12:55	0.397
6/27/2013 8:40	0.771	6/27/2013 10:50	0.397	6/27/2013 13:00	0.397
6/27/2013 8:45	0.594	6/27/2013 10:55	0.397	6/27/2013 13:05	0.397
6/27/2013 8:50	0.557	6/27/2013 11:00	0.397	6/27/2013 13:10	0.4
6/27/2013 8:55	0.512	6/27/2013 11:05	0.397	6/27/2013 13:15	0.418
6/27/2013 9:00	0.492	6/27/2013 11:10	0.397	6/27/2013 13:20	0.428
6/27/2013 9:05	0.442	6/27/2013 11:15	0.397	6/27/2013 13:25	0.428
				6/27/2013 13:30	0.421

C.3.2.3 Flow Rates

Table C-24 presents the flow rate data accumulated during the storm event described in the report during the field test. This data set was used to generate the flow rate plot used within the report.

Table C-24 Flow rates data

Date and Time	Flow rate (cfs)	Date and Time (continued)	Flow rate (cfs)	Date and Time (continued)	Flow rate (cfs)
6/27/2013 7:00	0	6/27/2013 9:10	0.17	6/27/2013 11:20	0
6/27/2013 7:05	0	6/27/2013 9:15	0.177	6/27/2013 11:25	0
6/27/2013 7:10	0	6/27/2013 9:20	0.203	6/27/2013 11:30	0
6/27/2013 7:15	0	6/27/2013 9:25	0.229	6/27/2013 11:35	0
6/27/2013 7:20	0	6/27/2013 9:30	0.207	6/27/2013 11:40	0
6/27/2013 7:25	0	6/27/2013 9:35	0.233	6/27/2013 11:45	0
6/27/2013 7:30	0	6/27/2013 9:40	0.287	6/27/2013 11:50	0
6/27/2013 7:35	0	6/27/2013 9:45	0.28	6/27/2013 11:55	0
6/27/2013 7:40	0	6/27/2013 9:50	0.259	6/27/2013 12:00	0
6/27/2013 7:45	0.618	6/27/2013 9:55	0.187	6/27/2013 12:05	0
6/27/2013 7:50	0.806	6/27/2013 10:00	0.174	6/27/2013 12:10	0
6/27/2013 7:55	0.982	6/27/2013 10:05	0.176	6/27/2013 12:15	0
6/27/2013 8:00	1.064	6/27/2013 10:10	0.144	6/27/2013 12:20	0
6/27/2013 8:05	1.139	6/27/2013 10:15	0.143	6/27/2013 12:25	0
6/27/2013 8:10	1.159	6/27/2013 10:20	0	6/27/2013 12:30	0
6/27/2013 8:15	1.021	6/27/2013 10:25	0.11	6/27/2013 12:35	0
6/27/2013 8:20	0.917	6/27/2013 10:30	0	6/27/2013 12:40	0
6/27/2013 8:25	0.655	6/27/2013 10:35	0	6/27/2013 12:45	0
6/27/2013 8:30	0.595	6/27/2013 10:40	0	6/27/2013 12:50	0
6/27/2013 8:35	0.546	6/27/2013 10:45	0	6/27/2013 12:55	0
6/27/2013 8:40	0.455	6/27/2013 10:50	0	6/27/2013 13:00	0
6/27/2013 8:45	0.314	6/27/2013 10:55	0	6/27/2013 13:05	0
6/27/2013 8:50	0.269	6/27/2013 11:00	0	6/27/2013 13:10	0.107
6/27/2013 8:55	0.224	6/27/2013 11:05	0	6/27/2013 13:15	0.105
6/27/2013 9:00	0.19	6/27/2013 11:10	0	6/27/2013 13:20	0.105
6/27/2013 9:05	0.16	6/27/2013 11:15	0	6/27/2013 13:25	0

C.3.2.4 Total Flow

Table C-25 presents the total flow data accumulated during the storm event described in the report during the field test. This data set was used to generate the total flow plot used within the report.

Table C-25 Total flow data

Date and Time	Total Flow (cf)	Date and Time (continued)	Total Flow (cf)	Date and Time (continued)	Total Flow (cf)
6/27/2013 7:00	0	6/27/2013 9:10	50.915	6/27/2013 11:20	0
6/27/2013 7:05	0	6/27/2013 9:15	53.078	6/27/2013 11:25	0
6/27/2013 7:10	0	6/27/2013 9:20	61.044	6/27/2013 11:30	0
6/27/2013 7:15	0	6/27/2013 9:25	68.839	6/27/2013 11:35	0
6/27/2013 7:20	0	6/27/2013 9:30	62.104	6/27/2013 11:40	0
6/27/2013 7:25	0	6/27/2013 9:35	69.897	6/27/2013 11:45	0
6/27/2013 7:30	0	6/27/2013 9:40	86.205	6/27/2013 11:50	0
6/27/2013 7:35	0	6/27/2013 9:45	83.857	6/27/2013 11:55	0
6/27/2013 7:40	0	6/27/2013 9:50	77.736	6/27/2013 12:00	0
6/27/2013 7:45	185.424	6/27/2013 9:55	56.189	6/27/2013 12:05	0
6/27/2013 7:50	241.689	6/27/2013 10:00	52.304	6/27/2013 12:10	0
6/27/2013 7:55	294.53	6/27/2013 10:05	52.685	6/27/2013 12:15	0
6/27/2013 8:00	319.312	6/27/2013 10:10	43.237	6/27/2013 12:20	0
6/27/2013 8:05	341.848	6/27/2013 10:15	42.913	6/27/2013 12:25	0
6/27/2013 8:10	347.703	6/27/2013 10:20	0	6/27/2013 12:30	0
6/27/2013 8:15	306.251	6/27/2013 10:25	32.957	6/27/2013 12:35	0
6/27/2013 8:20	275.027	6/27/2013 10:30	0	6/27/2013 12:40	0
6/27/2013 8:25	196.355	6/27/2013 10:35	0	6/27/2013 12:45	0
6/27/2013 8:30	178.622	6/27/2013 10:40	0	6/27/2013 12:50	0
6/27/2013 8:35	163.668	6/27/2013 10:45	0	6/27/2013 12:55	0
6/27/2013 8:40	136.457	6/27/2013 10:50	0	6/27/2013 13:00	0
6/27/2013 8:45	94.13	6/27/2013 10:55	0	6/27/2013 13:05	0
6/27/2013 8:50	80.693	6/27/2013 11:00	0	6/27/2013 13:10	32.13
6/27/2013 8:55	67.134	6/27/2013 11:05	0	6/27/2013 13:15	31.569
6/27/2013 9:00	57.039	6/27/2013 11:10	0	6/27/2013 13:20	31.44
6/27/2013 9:05	47.952	6/27/2013 11:15	0	6/27/2013 13:25	0
				6/27/2013 13:30	25.902