

PERFORMANCE OF A CATCH BASIN FILTER AND LEACHATE FROM BIOCIDAL MEDIA FOR STORMWATER TREATMENT

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ABSTRACT

Performance of a Catch Basin Filter and Leachate from Biocidal Media for Stormwater Treatment

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The feasibility of installing biocidal beads into a catch basin filter insert for simultaneous stormwater disinfection and contaminant removal was tested. The catch basin filter insert (DrainPac[®]) was tested for its sediment, oil and grease, and coliform bacteria removal efficiency in conjunction with bench-scale testing of biocidal polymer beads. DrainPac[®] catch basin filters are composed of a metal frame, polypropylene filter fabric, and a high-density polymer support basket, and are installed below storm drains. A 12 x 41 in. DrainPac[®] filter (United Stormwater, Inc.) insert was set in a flume that simulated a large-scale catchment basin. Pond water was gravity fed to the flume at flow rates up to 200 gpm. The pond water contained fine sediments at concentrations ranging from 30-50 mg/L. The biocidal beads were tested in a small laboratory column for potential application to stormwater treatment.

The head loss through the clean filter insert varied from 0.5 cm at 20 gpm to 9.1 cm at 200 gpm. Head loss of 21.5 cm occurred after 625 g of solids were added to the filter at 200 gpm at which point water began bypassing the filter fabric and flowing through the mesh screen. The highest flow rate that could be filtered through the loaded filter was 80 gpm.

The DrainPac[®] filter removed total suspended solids with efficiencies ranging from 83% to 91% at flow rates of 20 to 200 gpm, with higher removal efficiencies at lower flow rates. The oil and grease removal efficiency of the DrainPac[®] filter ranged from 40% to 82%. The DrainPac[®] filter exhibited no removal of coliform bacteria under these test conditions.

Biocidal brominated polystyrene beads, developed by Dr. S. D. Worley at Auburn University, were tested in a 1-cm diameter laboratory column apparatus for leaching of bromine compounds, which is important for determining if the filters will meet water quality regulations of the receiving waters. Removal efficiencies of coliform bacteria were tested in a companion study by Cal Poly graduate student Alex Bowerman. Pond water was passed through a 1-cm thick bed of beads in an up-flow direction. Leachate was analyzed for bromine, bromide, and bromoform. Leaching from both 0.3-mm and 0.8-mm biocidal beads was tested in the column apparatus. Samples collected for bromoform analysis were quenched with sodium thiosulfate, and the time before samples were quenched had a drastic effect on bromoform concentrations. Samples quenched after the collection of the total sample were assumed to be the most realistic for stormwater conditions since stormwater entering catch basins isn't immediately discharged into its receiving waters. Effluent from a 1-cm bed of 0.3-mm beads at 0.56 mL/sec contained the following average concentrations: 0.47 mg/L bromine, 2.45 mg/L bromoform, and 0.53 mg/L bromide. The same conditions for 0.8 mm beads resulted in effluent containing the following average concentrations: 0.27 mg/L bromine, 0.06 mg/L bromoform, and 0.50 mg/L bromide. The much lower concentrations of bromine measured in the 0.8-mm bead leachate was likely due to the greater surface area of the

smaller beads. The greater leaching of bromoform from the 0.3 mm beads may be partly attributed to the greater surface area of the smaller beads, but also the manufacturer of the beads reported that different production methods were used for the 0.3 mm beads.

Higher bromine compound concentrations were found at lower flow rates, due to the longer contact times with the beads.

Deionized (DI) water that was used to initially wet the biocidal beads before passing pond water through the column was also analyzed for bromoform. The DI flush water from the 0.3 mm beads contained 1.25 mg/L bromoform at a flow rate of 0.28 mL/sec. Bromoform concentrations in the DI flush water from the 0.8 mm beads at the same flow rate were below detection. Bromoform is expected to be formed as bromine is reduced to bromide by the presence of organics. Since there are no organics present in DI water to form such high concentrations of bromoform as those found from the 0.3-mm bead DI flush water, it appears that bromoform could have leached from the surface of the 0.3 mm beads.

The longevity of the bromine treatment of the biocidal beads was tested on one set of 0.3-mm beads by simulating five use cycles, and also by testing another set of beads after dry storage. Each use cycle was simulated by pumping pond water through a 1-cm bed of 0.3 mm beads at 0.56 mL/sec for one hour and then connecting the column to an air pump to dry for 23 hours. After five simulated uses, leachate from the beads showed only a slight reduction in concentrations of bromine and bromide (21% and 4% less than fresh beads, respectively), while the concentration of bromoform was nearly 100 times less. The drastic decrease in bromoform concentration suggests that after five simulated uses, much of the bromoform was exhausted or conditions for the formation of bromoform were no

longer present. For the dry storage test, 0.3 mm beads were wetted with 1-L DI water and then stored dry for 162 days. Then pond water was pumped through the column at 0.56 mL/sec and the leachate was analyzed. After dry storage for 162 days, the leachate showed no reduction in bromine concentrations compared to fresh beads, a 97% reduction in bromoform, and a 30% increase in bromide concentrations. This significant reduction in bromoform could be due to the volatilization of bromoform off the surface of the 0.3 mm beads during dry storage. The 0.3 mm beads are no longer being manufactured, and leachate from the 0.8 mm beads contained bromoform at concentrations below the potable drinking water maximum contaminant level of 80 µg/L. Under all tested conditions, bromine, bromide, and bromoform are present in the leachate from the biocidal beads, and thus their applicability for stormwater disinfection depends on the longevity of the bromine compounds in receiving waters, and on the regulations governing these compounds.

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CHAPTER 1: INTRODUCTION

As human population and urbanization increase, stormwater pollution is becoming a serious threat to the water quality of receiving rivers, creeks, and the ocean. Nonpoint source pollution resulting from urban stormwater runoff is a major cause of poor water quality in receiving waters (Lehner et al., 2001). Nonpoint source pollution is responsible for 65% of all water pollution in the United States (Chiras, 2006). Urban stormwater often contains high concentrations of fecal indicator bacteria, causing over 5,000 beach closures in California in 2005 (He & He, 2008).

Under the Clean Water Act, the National Pollutant Discharge Elimination System (NPDES) regulates stormwater discharges from industrial, construction, and municipal storm sewer systems. Many methods to comply with NPDES requirements have been developed and continue to be researched. Stormwater contamination can be reduced with the use of structural and nonstructural Best Management Practices (BMPs) (Vassilios & Hamid, 1997). Structural BMPs remove contaminants by intercepting stormwater flows and allowing solids and other contaminants to settle out, be filtered out, or adsorb to organic material (Horner and May, 1999). Common structural BMPs are: catch basin inlet filters, infiltration trenches, infiltration basins, porous pavement, detention basins, sand filters, and oil/grit separators (Vassilios & Hamid, 1997). Nonstructural BMPs reduce the amount of stormwater contamination through street sweeping, education, and limiting the amount of impervious surfaces with land use planning (Vassilios & Hamid, 1997). Low impact development (LID) is a technique to use stormwater BMPs to develop land without significantly altering the historical hydrology of the site (Dietz and

Claussen, 2008). Onsite treatment is often implemented for larger industrial or construction sites, and it often involves proprietary systems that settle out solids, separate oils and grease, and adsorb heavy metals. Unfortunately, even with BMPs in place, stormwater pollution is still a problem.

The use of catch basin inlet filters is a simple, relatively inexpensive method to reduce stormwater contamination (Walch et al., 2004). United Stormwater Inc. produces DrainPac[®] stormwater filters, which are custom manufactured for each inlet and consist of a metal frame, a high-density polymer support basket, and a polypropylene filter cloth. United Stormwater Inc. provided a grant to Cal Poly to test the filter's sediment, oil and grease, and coliform bacteria removal efficiencies. The efficacy of the DrainPac[®] stormwater filter for removing sediment, oil and grease, and coliform bacteria was tested in a full-scale mock catch basin, constructed of wood, at the Cal Poly Irrigation and Training Research Center (ITRC). Water was gravity fed to the test apparatus from a pond at Cal Poly, San Luis Obispo.

In a past study conducted by Dr. Stenstrom of UCLA (Stenstrom, 1998), DrainPac[®] stormwater filters were tested for the removal of oil and grease, suspended solids, and polycyclic aromatic hydrocarbons (PAHs). Using the solids provided by United Pumping Service Inc., Dr. Stenstrom reported an average total suspended solids removal efficiency of 96% and an average oil and grease removal efficiency of 67% (Stenstrom, 1998).

Other studies on the performance of stormwater inlet filters have been conducted in the field; however, many of these studies have produced highly variable data, likely because of the high maintenance requirements of the filters, such as the removal of accumulated debris, and their design of bypassing flow once clogged (Walch et al., 2004).

In addition to testing the DrainPac[®] stormwater filter, biocidal brominated polystyrene beads were tested for their application to stormwater treatment. These beads were originally developed in the laboratories of Dr. S.D. Worley (Sun et al., 1996). Similar beads (with chlorine treatment instead of bromine treatment) were tested by Sun et al. (1996) by passing deionized (DI) water at 0.7 mL/min through 0.91 g of chlorinated biocidal polystyrene beads held in a Pasteur pipette. Concentrations of viable bacteria were reduced by six orders of magnitude, and the leachate contained less than 0.5 mg/L free chlorine and chloroform at concentrations ranging from 9- 16 µg/L (Sun et al., 1996). In a study using brominated polystyrene beads in a column, less than 2.0 mg/L free bromine was detected in the effluent water (Chen et al., 2003). Concentrations of bromoform in the effluent water were not reported. Worley et al. (1996) found chloroform concentrations from chlorinated beads to be below the potable water maximum contaminant level (MCL) of 100 ppb, and by analogy it was hoped that bromoform concentrations in leachate from this study would be below the potable water MCL of 80 ppb (US EPA, 2008c). Thus it is important that leachate of bromoform be determined before these beads are deployed for stormwater applications.

United Stormwater Inc. requested the investigation of the use of biocidal beads in DrainPac[®] stormwater filters to provide a stormwater inlet filter that inactivates bacteria as well as removing solids and oils. In the companion study mentioned above, the coliform removal efficiencies of the biocidal beads were tested by Alex Bowerman under various conditions. In the present research, the biocidal beads were evaluated for their leaching of bromine, bromide, and bromoform. This leaching is of particular interest if the beads are to be used for stormwater disinfection applications because their feasibility

could depend on the regulatory limits on discharge of bromine compounds to receiving waters. The longevity of the beads is also of interest, and this research investigates the concentration of bromine compounds leaching from the beads after five simulated use cycles and after over five months of dry storage. The longevity of the beads is important for their application to stormwater disinfection because they must be able to withstand periods of wet and dry conditions in the stormwater filter.

To test the brominated beads, a glass laboratory column was constructed with a 1-cm inside diameter. To model a 1-cm thick layer of biocidal beads at the bottom of a DrainPac[®] filter, the column was packed with a 1-cm bed depth of beads. Pond water was pumped in an up-flow direction through the beads. Influent and effluent coliform counts were measured in the companion study. For this study, effluent water was analyzed for bromine using a colorimetric Hach[®] kit, bromide was measured with ion chromatography, and bromoform was measured with gas chromatography using a mass spectrometer detector. The leachate from both 0.3 mm and 0.8 mm biocidal beads were tested for the aforementioned bromine compounds.

This project was designed as a joint research project between Ryan MacLure and Alex Bowerman. Construction of the full-scale mock catch basin and all DrainPac[®] filter testing was conducted together. The biocidal beads were tested in a bench-top column apparatus for their inactivation of bacteria by Alex Bowerman and the leaching of bromine compounds was tested by Ryan MacLure. In addition, the long-term biocidal effectiveness of the beads was tested by Alex Bowerman, and the leaching characteristics after multiple, simulated use cycles was tested by Ryan MacLure.

CHAPTER 2: BACKGROUND

2.1 STORMWATER

Stormwater is water that flows through or over landscape during or after a rain or snow-storm event. For the purpose of this study, stormwater will be referred to as water that flows over or through man-made structures such as pipes, gutters, concrete canals, pavement, etc. In natural watersheds, not impacted by humans, stormwater infiltrates into the groundwater and excess water flows with its destination subject to the natural gradient of the land. Stormwater in natural environments is generally clean, and what nutrients and contaminants are present, are often treated by microbes in the soil during groundwater infiltration (Horner, 1993). It is in urban environments where stormwater contamination becomes an issue.

2.1.1 Issues with Stormwater

In urban environments, impervious surfaces inhibit stormwater from infiltrating into the groundwater and being treated by microbes in the soil. Stormwater soil infiltration can remove many contaminants such as organics, metals, and PAHs (Murakami et al., 2008). The increase of impervious surfaces in urban environments increases the volume of stormwater run off, increases the peak flow rate, reduces stormwater infiltration, and reduces the time that runoff occurs (Brezonik and Stadelmann, 2002). In urban environments, stormwater flows with increased velocities over streets, pavement, and through pipes, picking up pollutants along the way. Man-made water conveyance

structures often have smooth surfaces that allow the stormwater to pick up high velocities where they are eventually discharged directly into streams and creeks, often causing erosion and sedimentation, and eventually into the ocean or other receiving waters. A study by Hascic and Wu (2006) found a strong association of water quality degradation with urban and agricultural land use.

If a rainfall event has not occurred for an extended amount of time, pollutants can build up on impervious surfaces and be dislodged by the “first flush” rainfall event. The stormwater runoff contained in the beginning of the runoff volume often has much higher pollutant concentrations than later in the rainfall event because of the release of accumulated contaminants on impervious surfaces (Metcalf & Eddy 2003). Lee et al. (2004) found water contaminant concentrations to be 1.2 to 20 times greater during the beginning of the rainy season compared to the end of the wet season with monitoring sites located throughout Los Angeles County.

2.1.2 Stormwater Characteristics

Stormwater characteristics vary depending on the surrounding environment, the degree of urbanization present, and the type of urban land use (Brinkmann, 1983 and Brezonik and Stadelmann, 2002). The majority of pollutants found in urban stormwater are generated by automobiles; other sources include: construction, animal waste, trash, agriculture, etc. (Brinkmann, 1985). Brinkmann (1985) described sources of atmospheric pollutants as either dry or wet deposition. Dry deposition can be the emissions of pollutants from cars, power plants, industry, etc., and wet deposition can be atmospheric pollutants transferred

to the liquid phase by precipitation (Brinkmann, 1985). Pollutants commonly found in stormwater include: sediment, metals, hydrocarbons, pesticides, bacteria, organics, nitrogen, and phosphorus (US EPA, 1999). Booth and Jackson (1997) reported that when a watershed has at least 10% effective impervious area, there is a noticeable loss of physical and biological aquatic habitat function.

Kayhanian et al. (2002) characterized stormwater runoff at several Caltrans facilities including highways, park and rides, maintenance areas, etc. The average total suspended solids (TSS) of the stormwater runoff from various Caltrans facilities ranged from approximately 45-123 mg/L (Kayhanian et al. 2002). Table 1 shows that typical contaminant concentrations in stormwater are consistently higher than pollutant concentrations in rainfall water (Metcalf & Eddy, 2003). Bacterial contamination has also been known to be present in stormwater and has contributed to the degradation of aquatic habitats. Typical stormwater runoff contains 10^3 - 10^4 MPN/100 mL fecal coliform bacteria (Table 1, Metcalf& Eddy, 2003). Urban stormwater runoff contributes a large amount of bacterial contamination to receiving waters, however, marine animals and waterfowl also contribute to the contamination especially around lagoons and estuaries (Noble et al., 2000). Ocean water quality sampled in close proximity to a stormwater outfall consistently had poor bacteriological water quality (Noble et al., 2000). With such high contaminant concentrations possible in urban stormwater, stormwater controls are necessary for protecting the water quality of receiving waters, the health of aquatic habitats, and the safety of the public.

Table 1. Stormwater characteristics compared to rainfall and wastewater (Metcalf & Eddy 2003)

Parameter	Unit	Range of parameter concentrations			
		Rainfall ^a	Stormwater Runoff ^b	Combined wastewater ^c	Municipal wastewater
Total suspended solids, TSS	mg/L	< 1	67-101	270-550	120-370
Biological Oxygen Demand, BOD	mg/L	1-13	8-10	60-220	120-380
Chemical Oxygen Demand, COD	mg/L	9-16	40-73	260-480	260-900
Fecal coliform bacteria	MPN/100 mL		10^3 - 10^4	10^5 - 10^6	10^5 - 10^7
Total Kjeldahl Nitrogen	mg/L		0.43-1.00	4-17	20-705
Nitrate	mg/L	0.05-1	0.48-0.91		0
Phosphorus	mg/L	0.02-0.15	0.67-1.66	1.2-2.8	4-12
Copper	µg/L		27-33		
Lead	µg/L	30-70	30-144	140-600	
Zinc	µg/L		135-226		
^a Adapted from Huber (1984)					
^b Adapted from US EPA (1983)					
^c Adapted from Metcalf & Eddy (1977)					

2.2 STORMWATER TREATMENT

Today, stormwater is treated in a variety of ways, often depending on the volume of water to be treated, site characteristics, and desired treatment level. Many stormwater treatment devices are used as part of construction Best Management Practices or BMP's that may be necessary to comply with National Pollutant Discharge Elimination System

(NPDES) requirements. Under the Clean Water Act, the NPDES program was created in 1972 to control point-source discharges from municipal separate storm sewer systems (MS4s), construction activities, and industrial activities (US EPA, 2008b). Phase 1 of the NPDES system was created in 1990, and it regulates municipalities over 100,000 people and Phase 2 was created in 1999 to regulate small municipalities and construction sites disturbing one to five acres of land (US EPA, 2008b).

Since construction sites are now being regulated for their on-site stormwater, many on-site treatment technologies have been developed. One example of a proprietary on-site treatment technology is the Stormceptor[®] (Figure 1), which is marketed for industrial and commercial construction sites. The Stormceptor[®] by Imbrium Systems Corp. (Rockville, M.D.) is a hydrodynamic separator device that dissipates the energy of the stormwater and allows solids to settle to the bottom, oils and grease to rise and separate to the top, while treated stormwater is released (Imbrium Systems Corp., 2008). Some proprietary devices contain adsorbents to eliminate trace metals and hydrocarbons, but these require replacement after exhaustion (Devinny et al, 2005). The disadvantages of many proprietary on-site stormwater treatment devices are that many are designed to bypass treatment during high flows, maintenance is necessary, and installation costs are high (Devinny et al., 2005). While proprietary on-site treatment devices may prove adequate for large industrial or commercial sites, many municipalities are turning to BMPs to meet water quality standards and goals.



Figure 1. Stormceptor® on-site stormwater treatment device

Booth et al. (2002) reported that effective stormwater management cannot solely rely on structural stormwater BMPs such as stormwater detention, but the control of impervious surfaces must be incorporated into development to minimize impacts on aquatic habitats. Low impact development (LID) is a relatively new approach that incorporates stormwater management into the development of sites to treat stormwater on-site and minimize impervious surfaces (US EPA, 2008a). The goal of LID is to develop land without significantly altering the pre-development hydrology of the land by increasing imperviousness and increasing runoff volumes (Dietz and Claussen, 2008). Green spaces in parking lots, green roofs on commercial buildings, rain gardens, permeable pavement, and vegetated swales are all techniques used to reduce the amount of run-off by increasing stormwater infiltration into the groundwater (Lehner et al., 2001).

LID reduces the amount of stormwater that enters municipal storm sewers, and some techniques can remove sediments, metals, and nutrients as water infiltrates through plants and soil (Lehner et al., 2001). Hatt et al. (2007) and Henderson et al. (2007) found that non-vegetated biofilters consisting of just soil, not including sand, are actually sources for nitrogen, and thus vegetation is required if nutrient removal is a goal. In a similar study, Bratieres et al. (2008) reported that any soil-based biofilter can remove total suspended solids (TSS), however, if nutrient removal is desired, a sandy-loam biofilter media planted with *C. appressa* or *M. ericifolia* or other species with strong nutrient removal capacities is effective. Constructed wetlands for the treatment of urban and agricultural stormwater are of recent interest due to their natural tendencies to filter and absorb nutrients and other contaminants from water. One study found decreased contaminant concentrations in the effluent from a constructed wetland, created by the simple installation of an outlet weir to an existing dry detention pond and the growth of natural volunteer wetland species (Carleton et al., 2000).

2.2.1 Stormwater Filters

Stormwater filters or catch basin inserts are common approaches to reducing contaminants from stormwater that flows through catch basins (Morgan et al., 2005). Stormwater filters are typically installed at street level or below grade to control urban runoff (Hipp et al., 2006). Morgan et al. (2005) tested several catch basin inserts in a stormwater simulator, including the DrainPac[®] filter (the type used in the present study), for removal of total suspended solids (TSS) and total petroleum hydrocarbons (TPH). This study found decreasing TSS removal efficiency as the amount of water filtered

increased (Morgan et al., 2005). This study used sediment from street sweepings and fed a 225 mg/L influent TSS concentration into the catch basin inserts (Morgan et al., 2005). Each insert was tested for 30 minutes at flow rates of 207 to 213 gpm, and Morgan et al. (2005) found that the DrainPac[®] filter had an average TSS removal efficiency of approximately 25%.

The Civil and Environmental Engineering Department of the University of California, Los Angeles, conducted a test for United Pumping Service, Inc. testing the DrainPac[®] filters for head loss, and removal of suspended solids, oil and grease, and polycyclic aromatic hydrocarbon (PAH) removal (Stenstrom, 1998). Their experimental setup included a mock catch basin where they could insert the filters, a stilling chamber, and a 10 x 2 ft. flume constructed of plywood. The sediment removal test used trash and debris extracted from catch basins in southern California provided by United Pumping Service, Inc. that included sediment, cigarette butts, leaves, etc. (Stenstrom, 1998). The UCLA study found that the DrainPac[®] filter removed 95% to 98% of TSS at a flow rate of 75 gpm (Stenstrom, 1998). The UCLA study reported that the DrainPac[®] filter had a 49% to 86% removal efficiency of oil and grease, and that removal efficiency was lower at higher oil and grease concentrations, decreasing after the accumulation of oil and grease (Stenstrom, 1998).

In a study by Walch et al. (2004), the DrainPac[®] filter and various other catch basin inserts were installed in different locations in Delaware, and tested for their sediment and hydrocarbon removal capabilities. Nearby catch basins without insert filters were used as the control, to compare data to the catch basins containing inlet filters (Walch et al., 2004). The DrainPac[®] filter produced variable results, with some pollutant

concentrations higher in the “protected” inlets than in the controls; however, this trend was not statistically significant (Walch et al., 2004). Further research of the DrainPac[®] filter’s ability to remove solids, oils and greases, and coliforms was necessary to better understand the conflicting results of Stenstrom (1998) and Walch et al. (2004). The performance of many inlet filters often depends on the amount of maintenance provided to keep the filter unclogged and clean.

2.2.2 Stormwater Disinfection

High coliform bacteria concentrations are common in urban stormwater (Table 1), making onsite stormwater disinfection a possible method to reduce bacterial contamination of receiving waters. To date, there is little published research for the on-site disinfection of stormwater. However, several studies have investigated disinfection for combined sewer systems, which treat sanitary sewage as well as urban stormwater. When these combined systems exceed their treatable water capacity during storm events, combined sewer overflow (CSO) occurs, releasing untreated water into the receiving waters (US EPA, 2004). In a study by Thomas et al. (1990), combined stormwater and sanitary sewage was disinfected in a hydrodynamic separator with peracetic acid, but the required doses were very high. More research is required to determine the feasibility of using peracetic acid for water disinfection (Casson et al., 2006). One advantage of peracetic acid is that it biodegrades into hydrogen peroxide, acetic acid, and oxygen, which are relatively benign substances (Casson et al., 2006). The disadvantage is that it is a hazardous material, and is slightly unstable, requiring onsite generation (Casson et al., 2006).

Although stormwater alone has not been disinfected onsite, CSO water has been disinfected by UV radiation treatment, ozone, chlorine, chlorine dioxide, etc. (Field et al., 1993). One issue with chlorine disinfection and other halogens is the formation of disinfection byproducts, necessitating dechlorination (Field et al., 1993).

2.3 BIOCIDAL POLYMER BEADS

Dr. S. D. Worley of Auburn University developed novel heterocyclic N-halamine biocidal disinfectants that have some advantages over current biocides in use today. Most biocidal materials currently in use consist of quaternary ammonium salt derivatives (“quats”) and polymeric derivatives (“polyquats”) (Chen et al., 2004a). These materials deactivate bacteria by penetrating the bacterial cell wall and releasing alkyl cations (Chen et al., 2004a). Quats and polyquats are stable in aqueous solution and have adequate disinfecting longevity, however, they cannot be reactivated once exhausted and require long contact times (Chen et al., 2004a).

Biocidal polymer beads composed of poly[1,3-dichloro-5-methyl-5-(4'-vinylphenyl)hydantoin] and poly[1,3-dibromo-5-methyl-5-(4'-vinylphenyl)hydantoin] were developed and tested by Dr. Worley for their water disinfection properties (Chen et al., 2003). These N-halamine biocidal polymer beads can be activated with chlorine or bromine. Bacterial cells are reported to be deactivated upon contact with the halogen atom, and the release of free halogen into aqueous solution is less common than with quats or polyquats (Chen et al., 2004a). The stability of these compounds is due to their chemical structures (Figure 2), with electron-donating alkyl components adjacent to the N-Br and N-Cl functional groups, which control the release of free halogen (Chen et al.,

2003). Benefits of the N-halamine biocides are that the halogen atom can be regenerated simply by exposure to free halogen and the required retention time for bacterial cell deactivation is less than for quats and polyquats (Chen et al., 2004a).

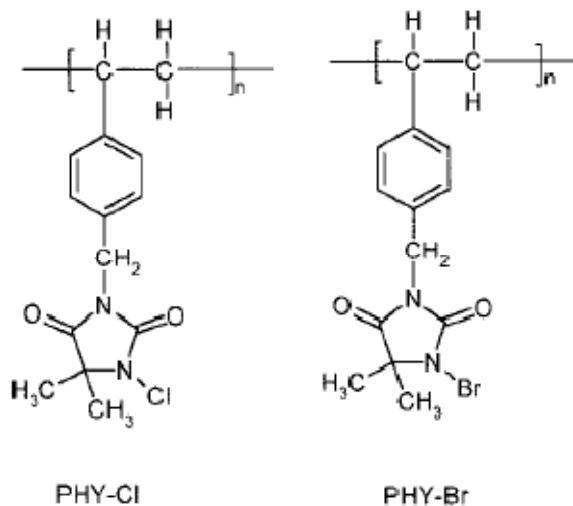


Figure 2. Structures of chlorinated and brominated polymeric beads (Chen et al., 2004b)

These halogenated polymeric beads were tested for bacterial disinfection of water by passing water through a 1.3-cm inside diameter, 7.6-cm length column packed with brominated beads such that it contained an empty bed volume of 3.1 mL (Chen et al., 2003). Dr. Worley found that a 6.8-log reduction of the bacteria *S. Aureus* was possible with a 1 second or less contact time. Samples were plated to enumerate active bacteria after the effluent was quenched with 0.02 N sodium thiosulfate (Chen et al., 2003). The time elapsed before quenching was not reported. It was also found that free bromine concentrations in the effluent water were less than 2.0 mg/L (Chen et al., 2003).

The longevity of the beads was also tested in a similar column experiment by Dr. Worley, in which 3-L solution of *E. coli* (10^6 CFU/mL) in buffered demand-free water at pH 7.0

was passed through a column of brominated beads for a five-day period. A six-log inactivation was observed for the entire length of the experiment (Sun et al., 1995). The amount of bromine in the effluent water in this experiment was not reported. Chen et al. (2004b) found that brominated polymer beads can deactivate bacteria with less contact time than the chlorinated polymer beads; however, the brominated beads can release free halogen more readily than the chlorinated beads.

CHAPTER 3: MATERIALS AND METHODS

3.1 DRAINPAC[®] STORMWATER FILTER TESTING

3.1.1 Flume Apparatus

The full-scale DrainPac[®] filter insert was tested using a flume constructed of wood and sealed with polyurethane (Figures 3 and 4). The bed slope was 2%, the bed length was eight feet, and the bed width matched the width of the filter insert (41 inches). Water was gravity fed to the system from a pond located on the campus at Cal Poly, San Luis Obispo. The pond water was supplied by a six-inch diameter PVC pipe, which was then reduced to a diameter of four inches. Flow rate was monitored using a magnetic flow meter (Seametrics[®]). Water entered the flume via a mixing chamber, which could be used to mix in additional contaminants (e.g. solids and oil). The mixing chamber was constructed by cutting twelve 1-inch diameter holes around the bottom sides of a 5-gallon HDPE bucket. At the higher flow rates of 150 GPM and 200 GPM, a perforated metal weir was added to the flume to slow the water velocity and prevent the water from overshooting the cloth portion of the DrainPac[®] filter.

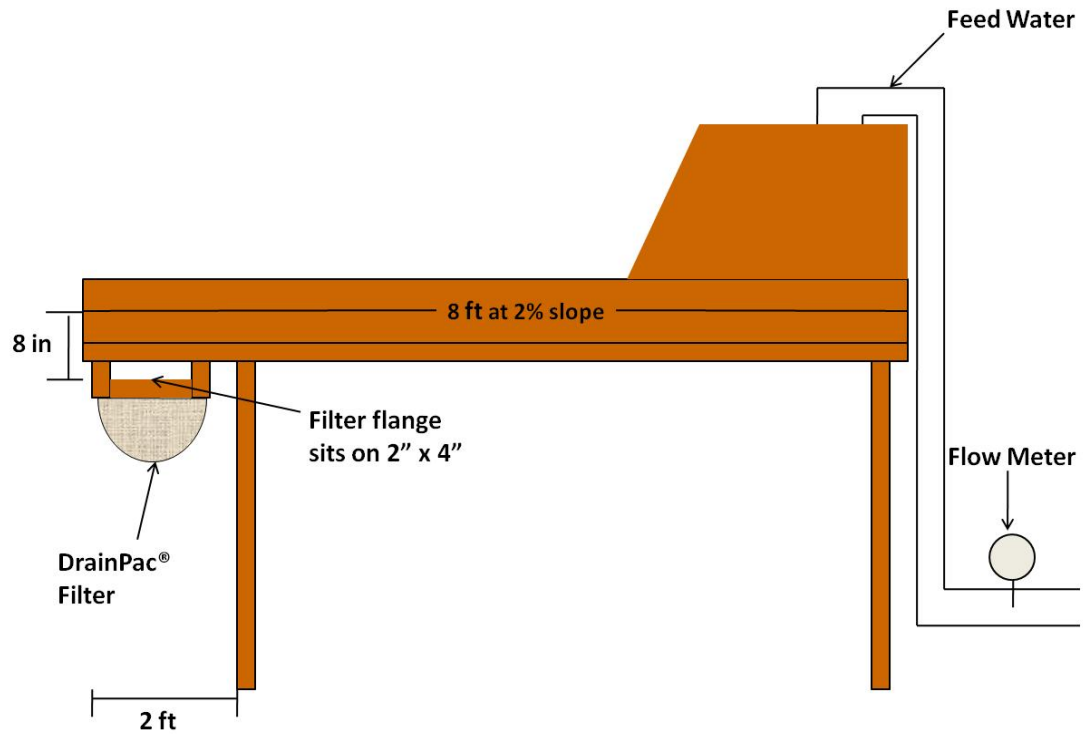


Figure 3. Side view of test flume schematic



Figure 4. Photograph of test flume

The DrainPac[®] filter used in our testing was provided by United Storm Water Inc. (Figure 5). This type of filter was designed for inlet type storm drains. The dimensions for the stainless steel frame assembly were 12 x 41 in. The DrainPac[®] contained a nonwoven geotextile (polypropylene) filter liner that covered a 9-inch depth of the filter and a 3.5-inch PVC mesh for overflow by-pass (Figure 5).



Figure 5. Photograph of DrainPac[®] filter

3.1.2 DrainPac[®] Filter Head Loss

Head Loss of Clean DrainPac[®] Filter

The filter head loss was tested with a clean DrainPac[®] filter using pond water as the only source of solids (30-50 mg/L total suspended solids). The head loss was measured at flow rates of 20, 50, 115, 150, 175, and 200 gpm. Once the desired flow rate was reached, head loss measurements were taken by measuring the water level from the same position in the bottom of the filter fabric. The head loss measurements were taken as swiftly as possible, with approximately two minutes passing between each measurement, to avoid developing a filter cake that could affect the head loss through the filter.

DrainPac[®] Filter Loading Test at 200 gpm

The filter was loaded at 200 gpm (superficial water velocity of 3.98 cm/sec) with a solids concentration of approximately 80-100 mg/L to determine the amount of solids that would cause the filter to overflow (overflowing the filter fabric and passing through the mesh screen). Since the pond water only contained 30-50 mg/L solids, an additional 40 g/min solids was added to the mixing chamber as poorly graded sand (see Table 2 and Figure 6) to provide the target concentration of 80-100 mg/L solids (sieve analysis below). The volume of water that passed through the filter and the amount of solids added to the mixing chamber were recorded for each head loss measurement until the head loss became high enough that water began by-passing the filter. The total amount of solids loaded into the filter was calculated using the volume of water passed through the

filter, the approximate solids concentration of the pond water, and the amount of solids added to the mixing chamber.

Loaded DrainPac[®] Filter Head Loss

The filter was considered fully loaded after the addition of solids from the previous test caused the filter to overflow at 200 gpm. With the solids left in the filter, the head loss of water through the loaded filter was measured at various flow rates, starting at 20 gpm until water began to overflow the filter and pass through the mesh. Head loss measurements were taken at each flow rate by measuring the water level from the same position in the bottom of the filter fabric and increasing the flow rate after each measurement until water began to overflow the filter.

3.1.3 Suspended Solids Removal

The suspended solids removal efficiency of the DrainPac[®] filter was tested at 20, 60, 150, and 200 gpm. The filter was thoroughly cleaned with tap water before testing at each flow rate. After cleaning, the filter was installed into the flume and the flow of sediment-laden water was started. Poorly graded sand with less than 5% fines along with solids naturally present in pond water was used for all tests. The results of a sieve analysis on the sand are displayed in Table 2 and Figure 6. From the sieve analysis, the coefficient of uniformity (Cu) was 2.88 and the coefficient of curvature (Cc) was 1.09, corresponding to a poorly-graded sand classification (USCS ASTM D 2487).

Table 2. Sieve analysis of sediment used for all DrainPac® solids tests

Sieve No.	Sieve Size (mm)	Weight Retained (g)	% Cumulative Retained	% Passing
4	4.75	0	0.00	100.00
10	2	0	0.00	100.00
20	0.85	839.06	32.37	67.63
40	0.425	1075.77	73.88	26.12
60	0.25	431.66	90.53	9.47
100	0.15	180.97	97.51	2.49
200	0.075	48.24	99.38	0.62
	<0.075	16.19	100	
	Total=	2591.89		

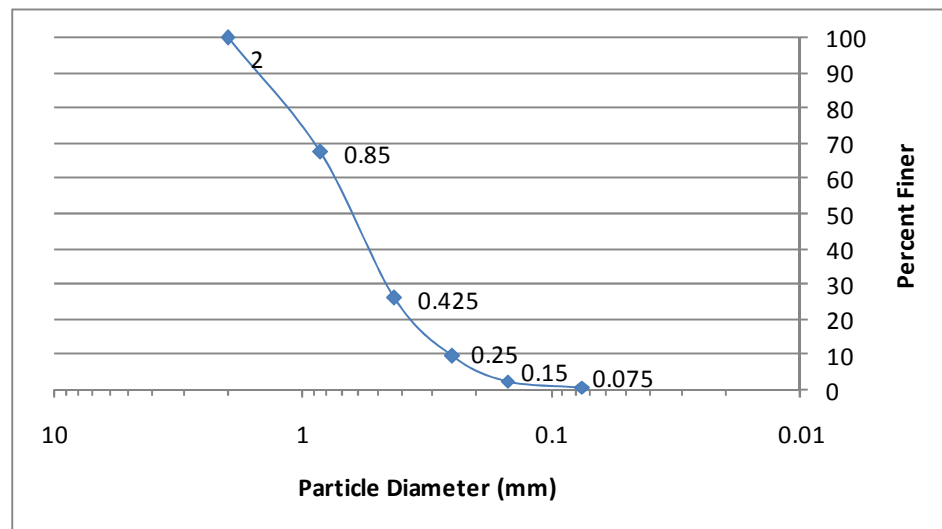


Figure 6. Particle size analysis of sediment

For each test, approximately 200 gallons of water was allowed to pass through the filter before samples were taken. Since the solids which build up in the bottom of the filter may affect removal efficiency, this uniform pre-loading was used for all tests at each flow rate. Three influent and three effluent samples were collected using clean 0.5-L plastic sample bottles for each test. Each set of influent and effluent samples were

collected simultaneously with one person collecting influent at the spillway before the water entered the DrainPac[®] filter and the other person collecting effluent samples where the catchment flume spilled into the concrete channel.

Samples were analyzed for total suspended solids (TSS) following Standard Method #2540 D (APHA, 1999c). Each 500-mL sample bottle was split into two 250-mL replicates and filtered with Type G4 glass fiber filters (Fisher Scientific) with a pore size of 1.2 µm and a diameter of 42.5 mm. The entire volume of each 500-mL sample bottle was filtered along with DI water used to rinse the sample bottle. A separate glass fiber filter and aluminum weigh tray was used for each replicate sample. All glass fiber filters were pre-rinsed with DI water using a Millipore[®] filter apparatus then dried at 105°C and weighed. Each replicate sample was vacuum filtered through the Millipore[®] filter apparatus, and the filter paper was removed with tweezers and transferred to its designated weigh tray. The weigh trays containing the filters were then transferred to an oven at 105°C and dried for one hour. Weigh trays and filters were then transferred to a desiccator to cool for 15 minutes. Filters and weigh trays were weighed a second time. Total suspended solids measurements were determined using the difference between the filter weights and the volume filtered. The TSS of each sample was calculated by the following equation:

$$TSS = \frac{Final\ Weight - Initial\ Weight}{Volume\ Filtered}$$

The sediment removal efficiency was calculated using the following equation:

$$Removal\ Efficiency\ (\%) = \frac{Influent\ TSS - Effluent\ TSS}{Influent\ TSS} * 100$$

3.1.4 DrainPac[®] Oil and Grease Removal

Oil and grease removal efficiency was tested at flow rates of 20, 60, 150, and 200 gpm. Biodegradable vegetable oil was used to simulate oil and grease deposits found on streets and parking lots. Oil was added to the influent stream using a Cole Palmer[®] Masterflex[®] L/S[™] peristaltic pump. Before each test, the filter was thoroughly cleaned with tap water. For each flow rate, 200 gallons of oil-laden water was allowed to pass through the filter in order to maintain a uniform initial buildup of oil and pond sediment for each test. For the flow rates of 20, 60, 150, and 200 gpm, oil was pumped into the mixing chamber at 2.5, 7.6, 19.0, and 25.4 mL/sec, respectively, to simulate an approximate oil concentration of 30 mg/L in the water. Influent samples were collected where the water spills into the DrainPac[®] filter and effluent samples were collected where the catchment flume spills into the concrete channel. Triplicate influent and effluent samples were collected with one person collecting an influent sample and another person collecting the effluent sample at the same time.

Influent and effluent samples were analyzed using a modified Standard Method 5520 B Partition-Gravimetric Method (APHA, 1999a). In this method the oil is extracted into hexane and quantified gravimetrically after all the hexane has been evaporated. Oil extractions were performed in 2-L separatory funnels using a set-up similar to the apparatus described below for bromoform extraction in Figure 9. Hexane extracts were collected in 200-mL TurboVap[®] vials (Zymark). The Turbovap[®] vials were thoroughly cleaned with DI water and soap, thoroughly dried, and initially weighed. All water samples were acidified within one hour of collection with 1:1 HCl to pH 2, which

generally took 5 mL of HCl per liter of water. For oil extraction, a 100-mL water sample was added to a separatory funnel along with 30 mL of hexane. The separatory funnel was capped and shaken vigorously for approximately one minute, while making sure to release pressure intermittently by opening the stopcock. The separatory funnel was then set back in the ring stand and allowed to settle for 10 minutes. Hexane, being less dense than water settled on top of the aqueous layer. The aqueous layer and a small portion of the organic layer was drained into the original sample container and the rest of the organic layer was drained through approximately 10 g of anhydrous sodium sulfate in a funnel and collected in a clean Zymark 200-mL TurboVap[®] vial. The aqueous layer collected in the original sample container was shaken to collect any residual oils in the sample container and added back into the separatory funnel along with an additional 30 mL of hexane. This procedure was repeated twice more, and after the last extraction step, the final aqueous layer was discarded and 20 mL of hexane was used to rinse the funnel of anhydrous sodium sulfate to collect any residual oils, and all of the hexane rinsings were collected in the Turbovap[®] vial. Once extracts for all samples and final rinsings were collected, the Turbovap[®] vials were transferred to an automated Zymark TurboVap[®] concentrator (Caliper Lifesciences, Hopkinton, MA), which concentrated the extracts by evaporation with nitrogen, in a 35°C water bath. Once the extract finished evaporating, the Turbovap[®] vials were removed from the water bath, thoroughly dried, and weighed. The difference of the initial and final weights was used to determine the oil concentration in each water sample.

3.15 Testing Coliform Removal by a Full-Scale DrainPac[®] Filter

Coliform bacteria removal efficiency was tested in the full-scale DrainPac[®] at flow rates of 20, 60, 150, and 200 gpm. Before each test, the filter was thoroughly cleaned with tap water. Samples were collected after 200 gallons of water had passed through the filter in order to maintain a uniform buildup of pond sediment for each test. Preliminary analysis indicated that the pond water contained greater than 2420 CFU/100 mL coliform bacteria which seemed sufficient for coliform removal testing, so no additional bacteria were added. For each flow rate, three influent and three effluent samples were collected in 0.5 L plastic sample bottles. Paired influent and effluent samples were collected simultaneously with one person collecting the influent sample as the water spilled into the DrainPac[®] Filter and the other person collecting the effluent sample at the bottom of the catchment flume where the water spills into the concrete channel. The samples were diluted 10:1 and analyzed using Idexx[®] Colilert[®] reagents in Idexx[®] Quanti-Tray[®]/2000 trays. The trays were prepared, sealed and incubated using Idexx[®] equipment, and analyzed in the Cal Poly Microbiology Department. This method tests for viable coliform bacteria using fluorescent indicators.

3.2 BIOCIDAL BEAD TESTING

3.2.1 Column Apparatus

A laboratory-scale column apparatus was constructed for testing head loss, bacterial deactivation, and leaching of bromine compounds from the biocidal beads. Two different bead sizes were tested: 0.3 and 0.8 mm diameter, each with slightly different bromine treatments. The test apparatus consisted of a 17.5-cm long, 1-cm inside diameter glass column. The column was packed with a 1-cm bed depth of beads, corresponding to 0.62 g of the 0.3 mm beads or 0.55 g of the 0.8 mm beads. The beads were held in place with 0.2 g of silane-treated glass wool above and below the beads (Figure 7). Pond water was pumped in an up-flow direction with a Masterflex[®] L/S[™] Model 7554-90 peristaltic pump (Cole Parmer[®]). Cole Parmer[®] 3-stop purple-purple PVC Solva[®] tubing with a 2.06-mm inside diameter was used in the peristaltic pump. The pump tubing was connected to the column using 0.5-cm inside-diameter Cole Parmer[®] Tygon[®] tubing connected with rubber connectors and short glass tubing connectors. Situating the beads at the top of the column and pumping water through the column in an up-flow direction, allowed us to see the direct bacterial-killing and leaching action of the beads, without the complication of additional retention time in the lower empty part of the column. Passing water through the column in an upward direction also alleviated any possible channeling effects. Fresh biocidal beads and glass wool were loaded in the column before each analysis, including for similar analyses at different flow rates. Before each test, 1 L DI water was passed through the column at 0.56 mL/sec so that the beads were in the identical wetted condition for each run prior to analysis.

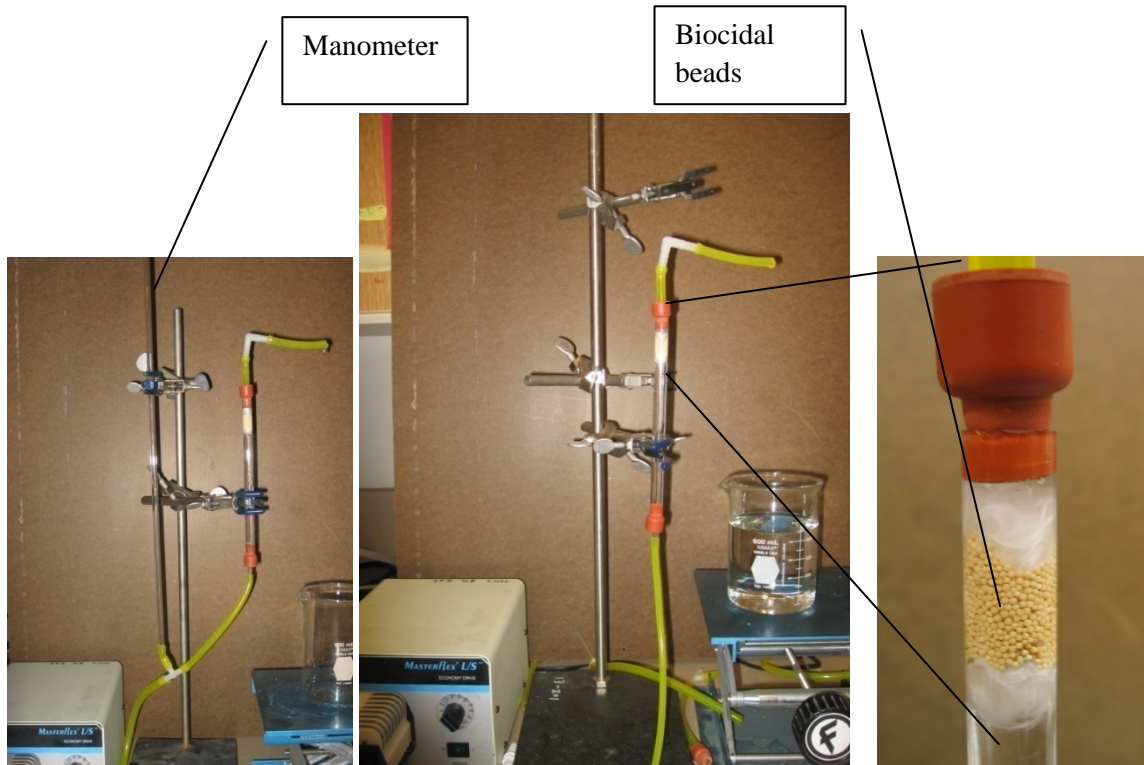


Figure 7. Photograph of column apparatus with manometer in-line for head loss testing (left) and biocidal beads packed in column apparatus (right)

3.2.2 Column Head Loss Testing

Head loss was measured through the biocidal beads in the glass laboratory column to estimate the expected head loss in the DrainPac[®] filter under natural stormwater conditions. This procedure was performed for both the 0.3 mm beads and the 0.8 mm beads to determine the head loss differences and feasibility of using the different sized beads in the DrainPac[®] filter. To determine the head loss of water through the beads alone, head loss was measured while water was pumped through the column under three conditions: empty, with glass wool alone, and with biocidal beads and glass wool. The head loss was measured by connecting a 0.5-cm inside-diameter glass column between

the peristaltic pump and biocidal bead column to act as a manometer (Figure 7). Head loss measurements were taken under the three conditions at various flow rates by measuring the height of the water in the manometer from the level of the column outlet. For all conditions, DI water was pumped through the column apparatus using a peristaltic pump at 0.28, 0.56, 0.84, 1.12, and 1.4 ml/sec. These flow rates correspond to superficial velocities of 0.36, 0.71, 1.07, 1.43, and 1.78 cm/sec which correspond to equivalent flow rates of 18, 36, 54, 72, 90 gpm, respectively, through a DrainPac[®] filter with dimensions of 12 x 41 in. (Table 3).

Table 3. Laboratory column and 12 x 41 in. DrainPac[®] filter equivalent flow rates

Flow Rate in Column (mL/sec)	Superficial Velocity (cm/sec)	Equivalent Flow Rate in DrainPac Filter (gpm)
0.28	0.36	18
0.56	0.71	36
0.84	1.07	54
1.12	1.43	72
1.4	1.78	90

DI water was pumped through the empty column to measure the head loss due to the column apparatus alone at various flow rates. 0.2 g glass wool was then packed into the column, DI water was pumped through the column at the flow rates of 0.28, 0.56, 0.84, 1.12, and 1.4 ml/sec, and head-loss measurements were taken. Then, the glass wool was removed and 0.62 g of 0.3 mm beads were placed in the column and held in place with 0.2 g glass wool. DI water was pumped through the column at the same flow rates and head loss measurements were taken. For testing the 0.8 mm biocidal beads, the same procedure was followed using approximately 0.55 g of the 0.8 mm beads, equivalent to a 1-cm height of beads in the column.

3.2.3 Measurement of Leaching

Bromine, bromoform, and bromide leaching was tested by sampling pond water that had been passed through the laboratory column containing a 1-cm deep bed of biocidal beads at three different flow rates. The biocidal beads were suspended at the top of the column in between approximately 0.2 g of glass wool. Both 0.3 mm (Lot # 06-HPBR-0507) and 0.8 mm beads (Lot # 08-HPBR-0519) were used for all leaching tests. Pond water was passed through the column in an up-flow direction at 0.28, 0.56, and 0.84 mL/sec, equivalent to 18, 36, and 54 gpm flow rates in a Drainpac[®] filter measuring 12 x 41 in. (Table 3). At each of the three flow rates, 1 L of DI water was passed through the column of fresh beads at 0.56 mL/sec prior to introducing pond water to the column so the beads would be at the same condition for tests at all three flow rates.

3.2.4 Bromine Sample Collection and Analysis

For bromine analysis, samples were collected directly in 25-mL volumetric flasks and analyzed after collection. Approximately 200-mL of pond water passed through the column in between the collection of each sample.

Bromine was analyzed using a Hach[®] bromine test kit utilizing a colorimetric N, N-diethyl-p-phenylenediamine (DPD) Total Chlorine Reagent. The DPD Total Chlorine Reagent acts the same way with bromine as with chlorine, only with a different colorimetric scale. Leachate samples from 0.3 mm and 0.8 mm biocidal beads and 0.8 mm unactivated control beads were analyzed by immediately adding DPD reagent to

each 25-mL sample. The flask was capped and gently shaken for three minutes and transferred to the Hach[®] bromine test kit for a color comparison of the sample to the scale on the side of the test cube. Samples were read by fellow graduate students, unaware of the experiment, so that the color interpolation would not be biased.

To test the bromine method for these analyses, a dilution experiment was conducted to determine how the DPD reagent reacts to diluted bromine samples. A 25-mL DI flush water effluent sample collected from a 1-cm depth of 0.3 mm beads at a flow rate of 0.56 mL/sec was analyzed for bromine after the addition of the DPD reagent. The observed bromine concentration of the undiluted 25-mL sample was 1.4 mg/L. Then, separate 10, 5, and 3-mL DI flush water effluent samples were collected, diluted with 15, 20, and 22 mL fresh DI water, respectively, and analyzed for bromine. The solution containing only 3 mL of effluent sample produced a very subtle pink color in the volumetric flask, but no color was observed once it was transferred to the Hach[®] kit containing the colorimetric scale. The DPD reagent produced a linear reaction to diluted bromine samples (Figure 8). The lower detection limit of the DPD reagent for bromine was estimated from this analysis to be 0.05 mg/L.

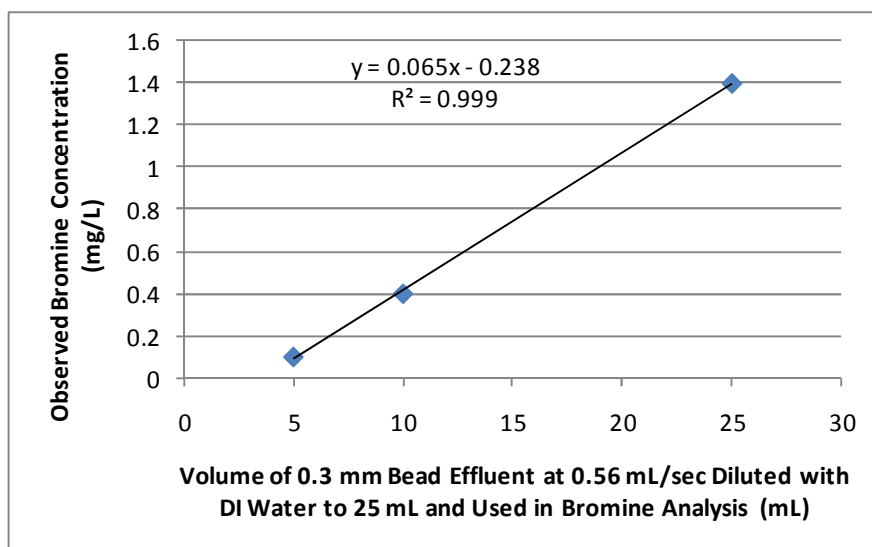


Figure 8. Reaction of DPD reagent to diluted bromine samples

3.2.5 Bromoform Sample Collection and Analysis

Effluent water samples for bromoform analysis were collected in a graduated cylinder. Approximately 100 mL of pond water was allowed to pass through the column between the collection of each pond water effluent sample. Bromoform samples were quenched with 0.04 N sodium thiosulfate reducing bromine into bromide, thus deactivating the disinfecting properties of the bromine. This quenching is also expected to stop additional bromoform from being formed. Four different sample quenching scenarios were used: one sample was taken without quenching with sodium thiosulfate, and other samples were quenched immediately after passing through the column (samples collected in graduated cylinder containing sodium thiosulfate), once the entire 147 mL sample had been taken, and after 10 minutes of an entire sample being taken. Duplicate samples for each of the four quenching scenarios were taken at all three flow rates. In addition, DI

flush water samples from 0.3 and 0.8 mm beads were quenched after sample collection and analyzed for bromoform.

A modified Standard Method 6232 B (APHA, 1999b) was used to extract bromoform contained in the water samples into methylene chloride (MeCl). Water samples were placed in the refrigerator and extracted the same day that they were collected. All glassware was washed prior to extraction with Alconox soap and DI water and then rinsed twice with MeCl. All extractions were performed in a fume hood using ring stands to hold up 1-L separatory funnels and Pyrex[®] funnels as shown in Figure 12. The Pyrex[®] funnels were filled with anhydrous sodium sulfate and held with ring stands below the separatory funnels. The anhydrous sodium sulfate was used to remove any water that may be in the MeCl phase. Glass wool was used to plug the bottom of the funnel so that anhydrous sodium sulfate wouldn't come out as the extract was trickled through it. Zymark 200-mL TurboVap[®] vials were clamped below the funnels to collect the extract.

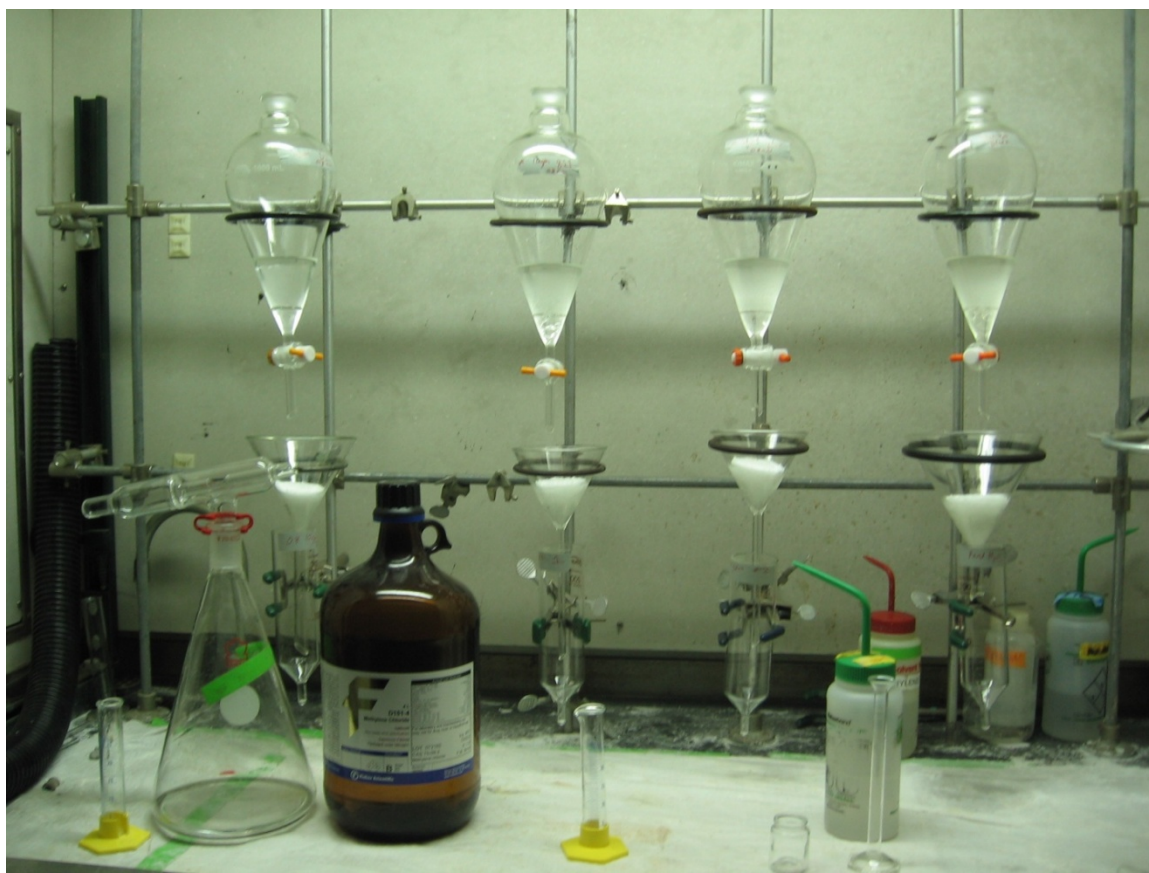


Figure 9. Photograph of bromoform extraction set-up

Bromoform water samples in 100-mL aliquots were pipetted into the 1-L separatory funnels using a 100-mL pipette. 15 mL of MeCl was measured out using a 25-mL graduated cylinder and poured into each separatory funnel. Each separatory funnel was then capped and vigorously shaken for approximately one minute, while being careful to release built up pressure by tilting the separatory funnel back and opening the stopcock. The separatory funnel was then set back in the ring stand, uncapped, and let to sit for 10 minutes. Since the MeCl with dissolved bromoform phase is denser than water, it settled to the bottom below the aqueous layer. The MeCl extract layer was then slowly drained through the funnel filled with anhydrous sodium sulfate and into the TurboVap[®] vial. An

additional 15 mL of MeCl was then added to the separatory funnel, and the extraction was repeated twice more. After the third cycle, the funnel filled with anhydrous sodium sulfate was thoroughly rinsed with approximately 30 mL of MeCl to collect any residual bromoform that may be present in the anhydrous sodium sulfate or glass wool.

Once the extract and MeCl final rinse were collected, the TurboVap[®] vials were placed in an automated Zymark TurboVap[®] concentrator (Caliper Lifesciences, Hopkinton, MA). This unit concentrated the extract by evaporation with nitrogen gas while the TurboVap[®] beakers were set in a 35°C water bath. The Zymark TurboVap[®] unit was set at an end point sensor which concentrated the extract to a final volume of 0.75 mL. After evaporation, the TurboVap[®] vials were transferred back to the fume hood and set in a metal holder. The 0.75 mL of concentrated extract was transferred to a 10-mL graduated cylinder with a 2-mL glass Pasteur pipette. The vial was then rinsed with approximately 1 mL of MeCl and the rinsed MeCl was then transferred to the 10-mL graduated cylinder. This was repeated until the final volume in the graduated cylinder reached approximately 5 mL. The exact final volume in the graduated cylinder was recorded and later used to calculate the actual concentration of bromoform in the water samples. The extract was then transferred into two 2-mL crimp-top vials which were then capped and stored in a freezer for future analysis by gas chromatography.

All extracted samples were analyzed in an Agilent Technologies 6890N Gas Chromatograph (GC) and an Agilent Technologies 5975 B inert mass spectrometer (MS) with an Agilent Technologies 7683 B Series injector. An Agilent Technologies HP-5ms capillary column (part number 19091S-433) containing a 5% phenyl and 95% dimethylpolysiloxane wall coating with nominal diameter of 0.25 mm, nominal length of

30 m, and nominal film thickness of 0.25 μm was used in the GC (Table 4). Operating conditions used in the GC are displayed in Table 4. The GC temperature program used in the bromoform analysis is displayed in Table 5.

Table 4. GC operating conditions

Front Inlet			
Mode:	Splitless	Purge Flow:	50 mL/min
Initial Temp:	200°C	Total Flow:	54.4 mL/min
Pressure:	11.55 psi	Gas Type:	Helium
Column			
Model:	Agilent 19091S-433	Nominal Film Thickness:	0.25 μm
Max Temp:	325°C	Initial Flow:	1.5 mL/min
Nominal Length:	30.0 m	Average Velocity:	44 cm/sec
Nominal Diameter:	250 μm	Nominal Init. Pressure:	11.56 psi
Mode:	Constant Flow		

Table 5. GC oven temperature program

Initial Temperature: 35°C		
Final Temperature: 200°C		
Rate (°C/min)	Final Temperature (°C)	Final Time (min)
0	35	5
10	70	8.5
20	200	15

Bromoform standards were prepared gravimetrically at concentrations of 10, 50, 100, 250, and 350 mg/L in MeCl. These standards were run in the GC and the resulting peak curves were used to make a standard curve (Figure 10). Additional bromoform standards were prepared for analysis of the dry storage longevity beads and the standard curve is displayed in the Appendix (Figure A-4).

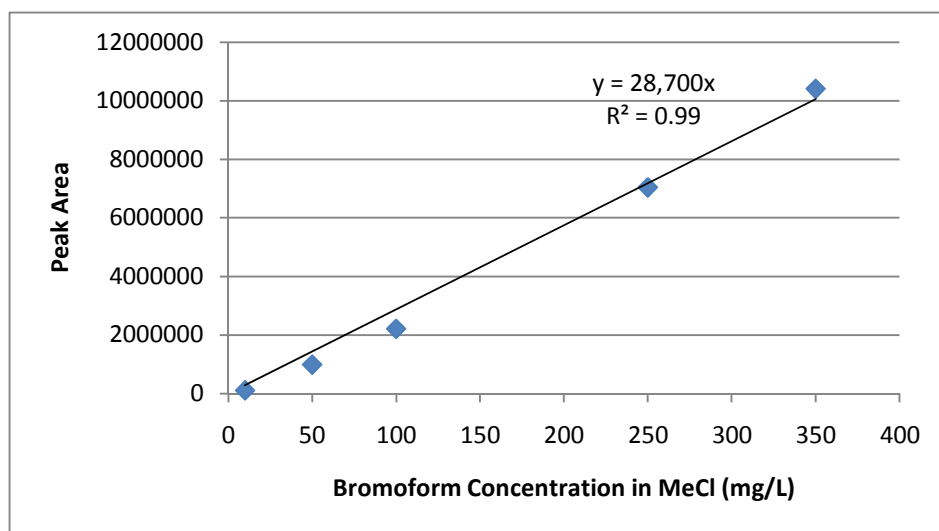


Figure 10. Bromoform standard curve

A MeCl blank and at least one bromoform standard were run with all sets of samples to detect any potential operating problems with the GC. The average peak area produced by 10 MeCl blanks was 4940. The highest MeCl blank out of the 10 blanks produced a peak area of 9523, which corresponds to 0.33 mg/L in MeCl (using the bromoform standard curve in Figure A-4) or about 0.025 mg/L bromoform concentration in water. The MeCl blank that produced the highest peak area was taken as a conservative lower detection limit for bromoform. For quality control, a blind duplicate sample of the pond water effluent from the 0.8 mm beads at a 0.28 mL/sec flow rate was analyzed for bromoform by Creek Environmental Laboratories, Inc. in San Luis Obispo.

3.2.6 Bromide Sample Collection and Analysis

Bromide was measured in DI flush water and pond water passed through 0.3 mm beads at a flow rate of 0.56 mL/sec and through 0.8 mm beads at flow rates of 0.56 mL/sec and 0.28 mL/sec. Effluent samples were collected in 40-mL volatile organic analysis (VOA) vials. Approximately 100 mL of pond water was allowed to pass through the column between the collection of each bromide sample.

Bromide effluent concentrations were analyzed using a Dionex[®] DX-120 ion chromatogram (IC) with an IonPac[®] AS22 4x250-mm column (Figure 14). Bromide effluent samples were filtered within one hour of sample collection with 0.22- μ m Millipore Express PLUS[®] membrane filters using a HDPE plunger syringe, placed in 5-mL Dionex[®] PolyVials, and capped with Dionex[®] 20- μ m filter caps before analysis. Samples were placed in the freezer for no more than one week before analysis.



Figure 11. Dionex[®] DX-120 ion chromatograph

Bromide standards were prepared by diluting Dionex[®] 7-Anion Standard with DI water to bromide concentrations of 0.25, 0.5, 0.75, 1, and 2 mg/L. New standards were prepared for each set of samples run through the IC. Data for preparing the standard curve for the 0.3 mm bead run are displayed in Table 6 and the resulting calibration curve is in Figure 12. Other bromide standard curves can be found in Appendix A. The standard curves were created by comparing the peak areas of the bromide peaks to the known concentrations of each standard. Duplicate standards were made and the average area was used for each point on the standard curve. Sample concentrations were then calculated using the peak area of each samples' bromide peak in the bromide standard curve formula created for that specific sample run.

Table 6. Bromide standard data for 0.3 mm bead run

Standard Concentration (mg/L)	Peak Area	Retention Time	Average Area
0.25	0.023	7.30	0.022
	0.021	7.20	
0.5	0.045	7.20	0.048
	0.051	7.18	
0.75	0.067	7.18	0.070
	0.073	7.20	
1	0.084	7.17	0.091
	0.097	7.20	

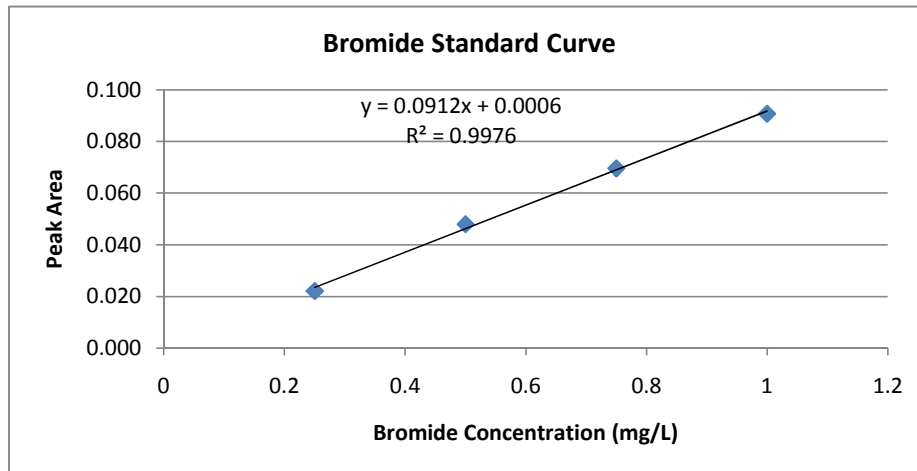


Figure 12. Bromide standard curve for 0.3 mm bead test

3.2.7 Measurement of Bromine Leaching During Longevity Testing

Simulated Use Cycles

The longevity of the 0.3 mm biocidal beads was tested by inducing five simulated use cycles in the laboratory column consisting of five consecutive wet and dry cycles to simulate realistic stormwater conditions in actual storm drains. Only the 0.3 mm biocidal beads were tested for their longevity because the 0.8 mm beads were not available at the time the experiment began. Each wet cycle consisted of pumping pond water through the column packed with a 1-cm bed depth of 0.3-mm biocidal beads for one hour at a flow rate of 0.56 mL/sec, corresponding to a superficial water velocity of 0.71 cm/sec. Each wet cycle involved approximately 2 L of pond water passing through the beads. To avoid accumulation of organic material from the pond water clogging the column, a separate 1.5-inch long glass column was packed with glass wool and attached before the

bead column to filter the water prior to entering the bead column (Figure 13). The glass wool in the filter column was replaced before each wet cycle to avoid clogging.

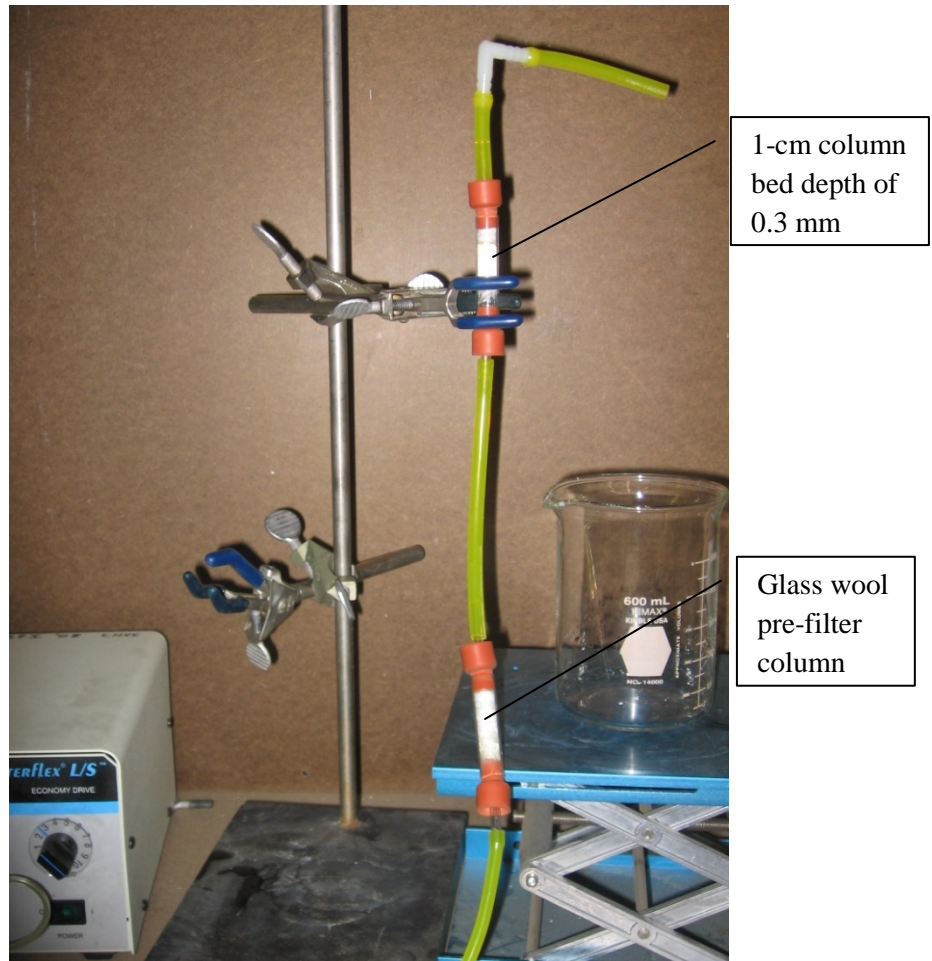


Figure 13. Simulated use cycle test apparatus with separate glass wool filter column

After each wet cycle, the bead column was attached to a Profile[®] 2900 aquarium air pump and air was pumped through the column of beads overnight. At the end of each dry cycle, the biocidal beads were often floating around, suspended by the air being pumped through the column, suggesting that the beads were dry. The biocidal beads were initially flushed by pumping 1 liter of DI water through the column at 0.56 mL/sec prior to the

first wet cycle. On the fifth day, directly after the fifth wet cycle, the pond water effluent was sampled for bromine, bromide, and bromoform. Coliform bacteria removal was determined separately in a companion study.

Bromine was tested first since it requires immediate analysis. Three separate bromine samples were tested immediately after collecting each sample in a 25-mL volumetric flask. Bromine was analyzed using a Hach[®] Bromine Test Cube and DPD Total Chlorine Reagent as previously described. Approximately 250 mL of pond water passed through the beads between the collection of each bromine sample.

Bromoform samples were collected and quenched immediately after collection with sodium thiosulfate after and placed in the refrigerator. An approximately 147-mL effluent sample was collected in a 200-mL graduated cylinder and added to 73 mL sodium thiosulfate in a 250-mL beaker. Two 100-mL aliquots of the 220-mL total sample were extracted into MeCl and analyzed with a GC/MS as described above.

Approximately 50 ml of pond water passed through the beads after the first 147-mL sample was taken and 300 mL pond water passed through the beads after the collection of the last bromoform sample. Bromoform samples were then extracted into MeCl and the extracts were placed in two 2-mL crimp-top vials, capped, and placed in the freezer for future analysis with a GC/MS.

Three bromide effluent samples were then collected in 40-mL VOA vials.

Approximately 50 ml of pond water was allowed to pass through the beads between the collection of each sample. Bromide samples were filtered with 25-mm diameter, 0.22- μ m Millipore Express PLUS[®] membrane filters and placed in 5-mL Dionex[®] PolyVials

and capped with Dionex[®] PolyVial 20- μ m filter caps and placed in the freezer until IC analysis as described above.

Dry Storage

Leachate from 0.3 mm biocidal beads was analyzed for bromine, bromoform, and bromide after fresh beads were initially wet and then stored in a laboratory fume hood, open to ambient air for over five months (162 days). Prior to dry storage, fresh beads were wetted by passing one liter of DI water through the beads at 0.56 mL/sec. The beads were then removed from the column and set in a beaker in the fume hood for 162 days. After dry storage, 0.62 g of the beads were set in the laboratory column and one liter of DI water was pumped through the beads at 0.56 ml/sec, followed by pond water at the same flow rate. The pond water leachate was sampled and tested for bromine, bromoform, and bromide as described above.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 DRAINPAC[®] FILTER RESULTS

4.1.1 DrainPac[®] Filter Head Loss Results

Head Loss of Clean DrainPac[®] Filter

The head loss in the clean DrainPac[®] filter varied from 0.5 cm at 20 gpm to 9.1 cm at 200 gpm (Table 7). Head loss in the full-scale DrainPac[®] filter increased linearly with increasing flow rate (Figure 14, $r^2 = 0.955$). At all of these flow rates, the water did not overflow the filter (bypass the filter fabric and pass through the mesh screen). At the end of the 200 gpm head loss measurement there was a very thin film of solids that accumulated on the bottom of the filter from solids in the pond water.

Table 7. Clean filter head loss at various flow rates

Flow (GPM)	Head Loss (cm)
20	0.5
50	2.8
80	3.8
115	4.9
150	5.5
175	8.5
200	9.1

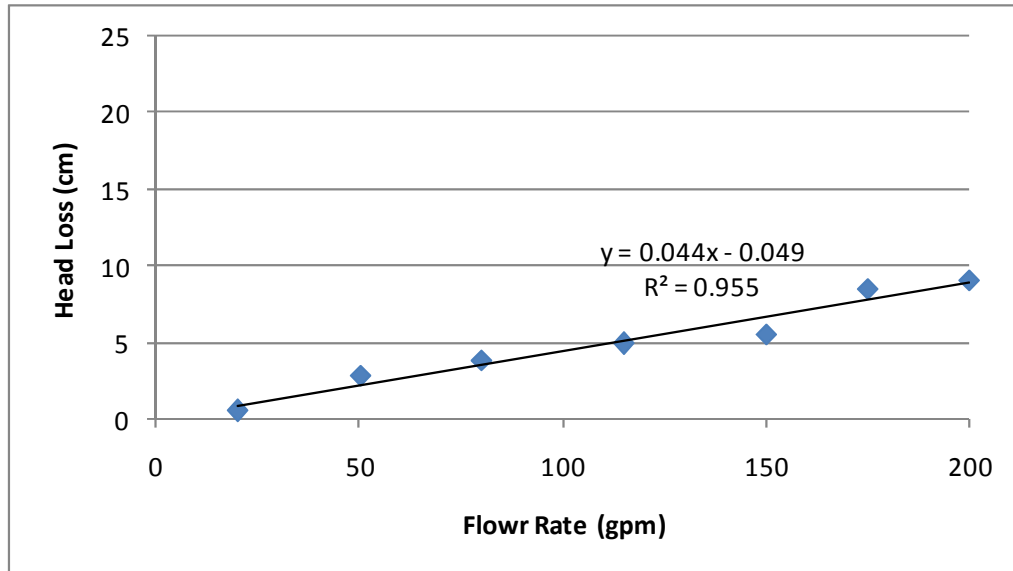


Figure 14. Clean filter head loss at various flow rates

DrainPac® Filter Loading Test at 200 GPM

The DrainPac® filter was loaded at 200 gpm at a solids concentration of 80-100 mg/L. The total amount of solids, including the solids present in the pond water, that caused the filter to overflow (21.5 cm head loss) at 200 gpm was 625 grams (Table 8). The approximate loading rate was thus 40 g/min. Head loss increased linearly as solids were added to the filter, until water began to flow over the top of the filter fabric at full loading (Figure 15).

Table 8. Head loss of DrainPac® filter at 200 gpm during solids loading (40 g/min)

Head Loss (cm) at 200 gpm	Total Filter Loading (g)
8	147
11.5	269
13.8	378
16.7	511
21.5	625

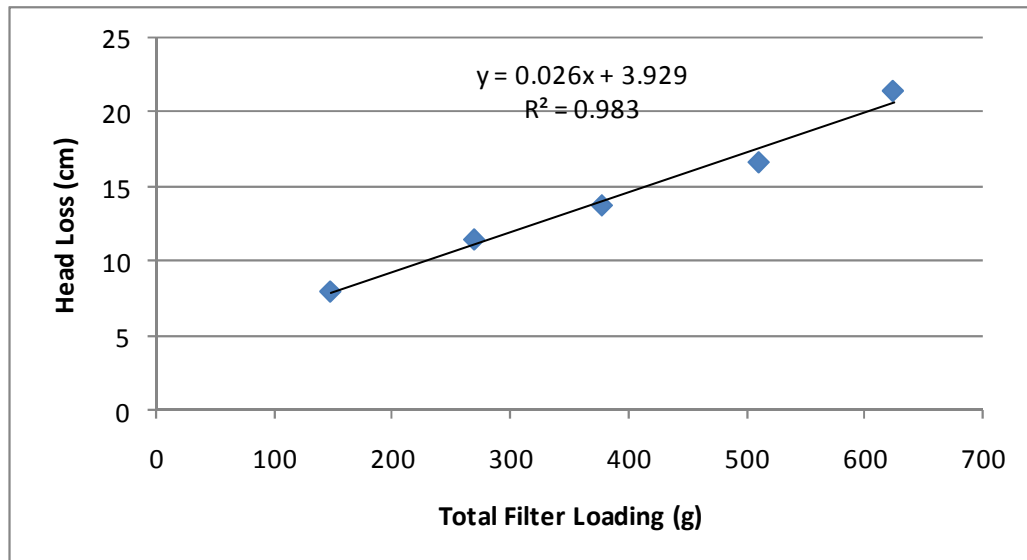


Figure 15. Head loss of DrainPac® filter at 200 gpm during solids loading (40 g/min)

Loaded DrainPac® Filter Head Loss

This test evaluated the head loss in the DrainPac® filter at various flow rates after the filter was completely loaded by the previous test above. The filter was considered fully loaded once the addition of solids into flowing water at 200 gpm caused water to overflow through the mesh screen. The filter was completely loaded at 200 gpm once a total of 625 g of solids (including solids present in the pond water) was added to the filter

as described above. The head loss in the loaded filter was measured at flow rates of 20 and 80 gpm. At higher flow rates the filter began to overflow. At 80 gpm, the loaded filter had a head loss of 17.5 cm (Figure 16). The DrainPac[®] filter was first loaded at 200 gpm, similar to high sediment loading in a catch basin filter during a large storm event, and then later failed to filter pond water at flow rates higher than 80 gpm. This proves how vital routine maintenance of the DrainPac[®] filter is to its performance after large storm events.

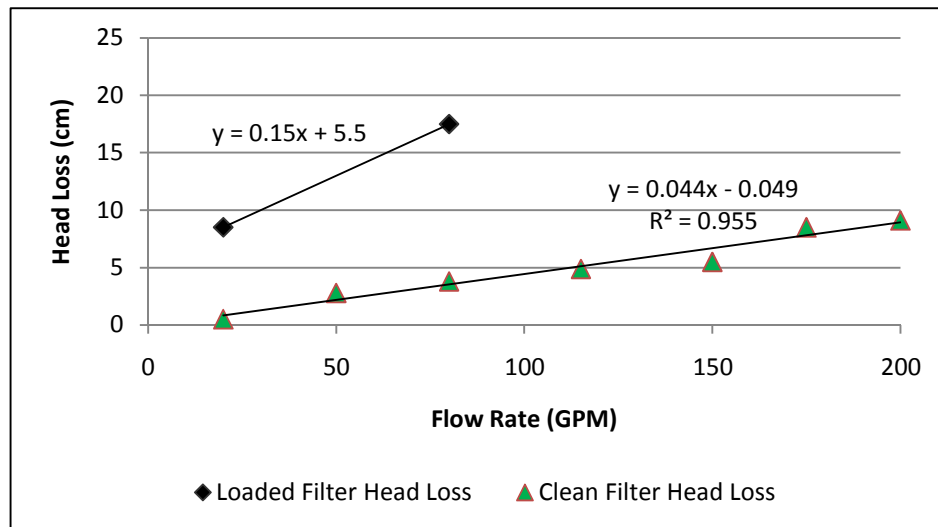


Figure 16. Head loss through DrainPac[®] filter loaded with 625 g solids compared to clean filter head loss

4.1.2 Sediment Removal by the Full-Scale DrainPac[®] Filter

Average influent and effluent TSS concentrations are displayed in Table 9 for each flow rate. Average sediment removal efficiencies ranged from 83% to 91% (Table 10). The sediment removal efficiency decreased slightly with increasing flow rate, however this trend is not statistically significant based on the error bars in Figure 17. Variation in TSS

concentrations among influent samples in Table 9 could be partly due to sand settling along the sides of the test flume. Although sediment removal efficiencies were variable, the DrainPac[®] filter performed relatively well at higher flow rates, with sediment removal efficiencies ranging from 72-93% at 200 gpm (Table 10).

Table 9. Influent and effluent TSS measurements for DrainPac[®] filter testing at various flow rates

Sample	Replicate	TSS (mg/L)			
		20 gpm	60 gpm	150 gpm	200 gpm
Influent	1	62.6	23.0	62.8	35.6
	2	54.6	37.6	130.5	39.8
	3	63.3	51.8	110.3	26.2
Effluent	1	5.7	4.7	18.6	2.6
	2	4.2	1.3	12.8	5.9
	3	6.5	4.3	13.1	7.3

Table 10. DrainPac[®] filter sediment removal efficiency

Sample	Sediment Removal Efficiency (%)			
	20 gpm	60 gpm	150 gpm	200 gpm
1	90.8	79.4	70.4	92.7
2	92.2	96.5	90.2	85.3
3	89.7	91.6	88.1	72.0
Average	90.9	89.2	82.9	83.3
Std. Dev.	1.3	8.9	10.9	10.5

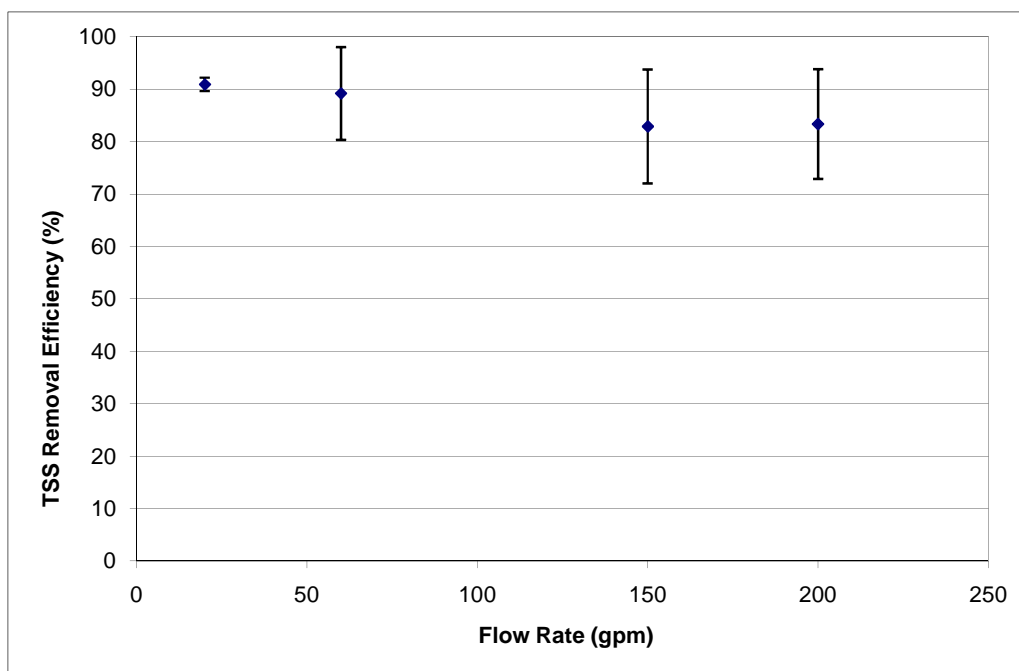


Figure 17. DrainPac[®] filter sediment removal efficiency (error bars indicate standard deviations)

4.1.3 Oil and Grease Removal by the Full-Scale DrainPac[®] Filter

Oil concentrations of three consecutive influent and effluent sample pairs at four different flow rates were determined gravimetrically by extracting oil/water samples into hexane and evaporating off the hexane. Influent concentrations were as high as 45.4 mg/L while effluent concentrations ranged from 2.6 to 9.7 mg/L (Table 11). Average oil removal efficiencies ranged from 40% to 82% as shown in Table 12 and Figure 18. Based on the high standard deviations (Table 12) and error bars in Figure 18, there was no discernible trend of oil removal efficiency with flow rate. High standard deviations in oil removal efficiencies could be due to the low concentrations of oil that were present in influent and effluent samples, making gravimetric measurement errors more significant. Metering in

oil at a higher loading rate would result in higher influent oil concentrations and could lead to more consistent results.

Table 11. Oil concentration in water before and after DrainPac[®] filter at various flow rates

Sample	Replicate	Oil Concentration in Water (mg/L)			
		20 gpm	60 gpm	150 gpm	200 gpm
Influent	1	16.9	14.3	11.5	45.4
	2	21.9	3.6	15.5	17.3
	3	14.6	14.9	12.2	27.0
Effluent	1	9.7	2.6	6.8	7.2
	2	8.8	4.9	6.6	4.6
	3	8.4	6.7	9.6	3.2

Table 12. DrainPac[®] filter oil removal efficiency

Flow Rate (gpm)	Average Removal Efficiency (%)	Standard Deviation
20	48.5	9.7
60	68.4	18.7
150	40.0	18.1
200	81.8	7.7

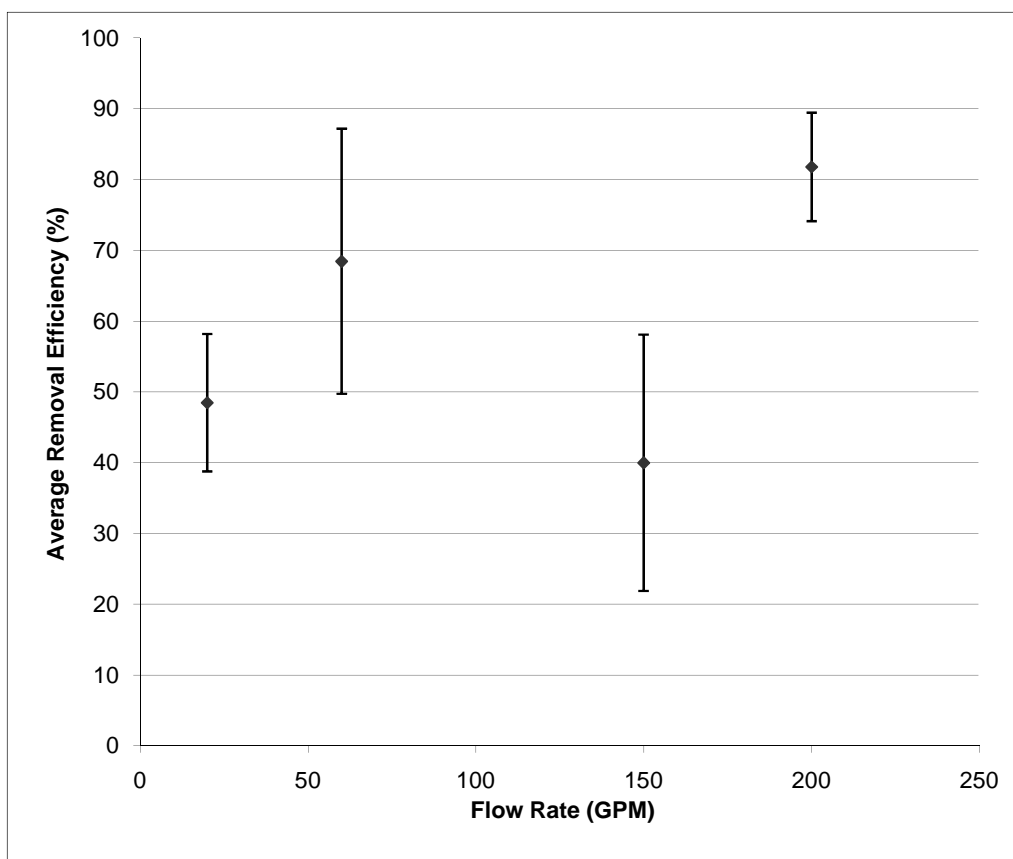


Figure 18. DrainPac[®] filter oil removal efficiency at various flow rates

4.1.4 Coliform Removal by the Full-Scale DrainPac[®] Filter

The DrainPac[®] filter showed no evidence of coliform bacteria removal, in fact higher coliform counts were observed in the effluent water than the influent water at all tested flow rates (Table 13). Higher coliform counts in the effluent water were likely due to the high variability of microbiological analyses, so it was concluded that the DrainPac[®] filter does not remove coliform bacteria. At flow rates of 60, 150, and 200 gpm, the average effluent coliform concentrations were 4 to 19% higher than the average influent concentrations. However, at a flow rate of 20 gpm, the average effluent coliform

concentration was 44% higher than the average influent coliform concentration. It is likely that given the small colloidal size of bacteria, they were flowing through the fabric filter. This test was only conducted with a small accumulation of solids from the pond water. Better coliform removal might be achieved if a layer of solids develops on the filter, like a schmutzdecker in a slow sand filter. Possible future research could test whether the addition of solids and the development of a filter cake could increase the bacterial removal efficiency of the filter.

Table 13. DrainPac[®] filter coliform removal results at various flow rates

Flow Rate (gpm)	Average Coliform Bacteria Concentration (CFU/100 mL)*	
	Influent	Effluent
20	1931 (430)	3423 (616)
60	2561 (450)	2668 (219)
150	2495 (702)	2676 (865)
200	2267 (408)	2783 (414)

*Average of triplicate samples, standard deviations in parentheses

4.2 BIOCIDAL BEAD RESULTS

4.2.1 Laboratory Column and Biocidal Bead Head Loss Results

Head losses through a 1-cm bed of 0.3-mm beads in the laboratory column increased with increasing flow rates (Table 14). The head loss due to the empty column apparatus alone was very low (0.8-1.5 cm) and considered negligible (Figure 19). The head loss due to the glass wool was significant, but much less than when the beads were present. Head loss through the glass wool increased linearly with flow rate (Figure 19). The head losses due to the beads alone were determined by subtracting the head loss of the glass wool and column apparatus from the total head loss (Table 14).

Table 14. 0.3 mm Biocidal bead head loss results

Flow Rate (mL/sec)	Superficial Velocity in Column (cm/sec)	Equivalent Flow Rate in DrainPac Filter (gpm)	Head Loss (cm)			
			Glass Column	Glass Column with Glass Wool	Glass Column, Glass Wool, and 1 cm of Beads	Beads Alone
0.28	0.36	18	0.8	11	30	19
0.56	0.71	36	0.9	17.2	48	30.8
0.84	1.07	54	1.1	28	64	36
1.12	1.43	72	1.3	35	80.5	45.5
1.4	1.78	90	1.5	42.5	94.2	51.7

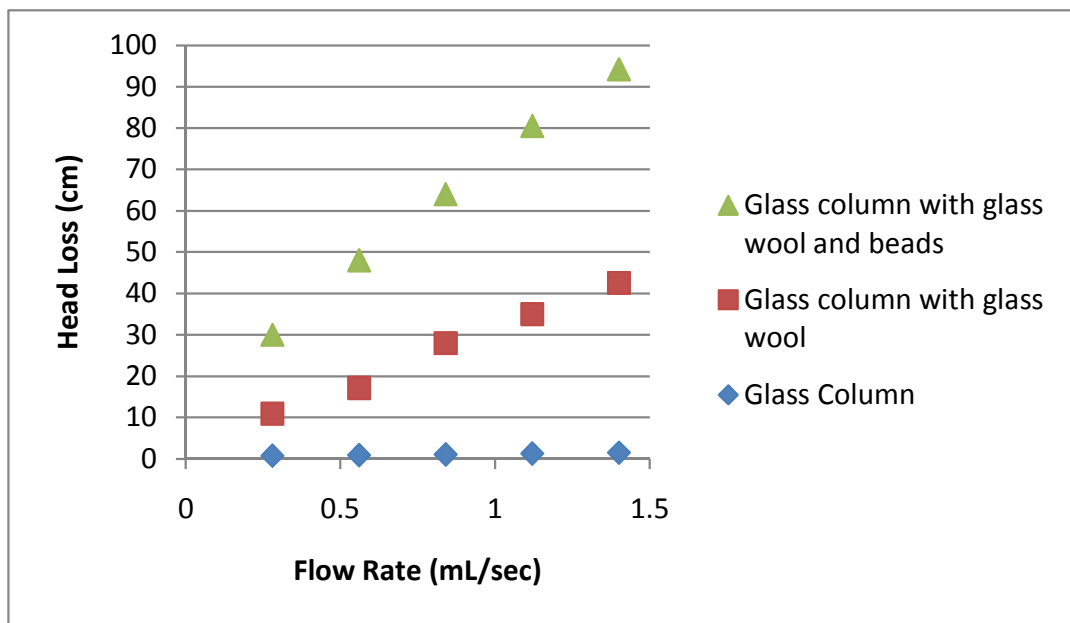


Figure 19. 0.3 mm Biocidal bead head loss results

Head loss for the 0.8-mm biocidal beads followed a similar trend as the 0.3 mm beads, with head loss increasing linearly with flow rate (Figure 20). The head losses of the beads alone at various flow rates are displayed in Table 15. Figure 20 displays the trend of increasing head loss with an increase in flow rate.

Table 15. 0.8 mm Biocidal bead head loss results

Flow Rate (mL/sec)	Superficial Velocity in Column (cm/sec)	Equivalent Flow Rate in Drain Pac Filter (gpm)	Head Loss (cm)			
			Glass Column	Glass Column with Glass Wool	Glass Column, Glass Wool, and 1 cm of Beads	Beads Alone
0.28	0.36	10	0.4	9.4	21.3	11.9
0.56	0.71	20	0.5	16.7	40.5	23.8
0.84	1.07	30	0.6	23.1	56	32.9
1.12	1.43	40	0.8	28.9	69.9	41
1.4	1.78	50	1.1	37.3	85	47.7

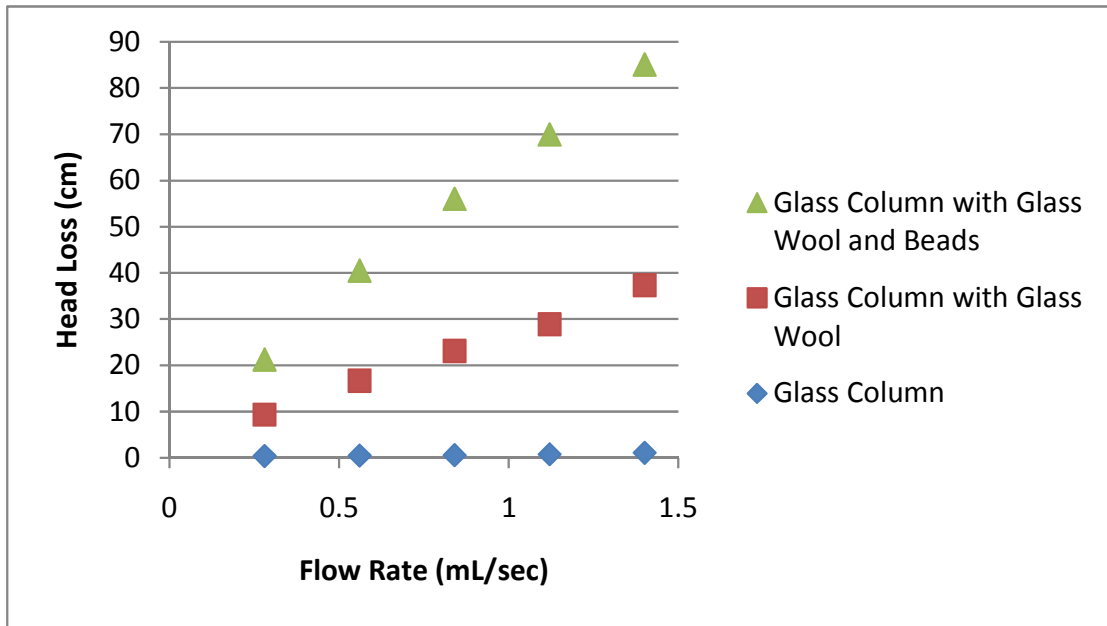


Figure 20. 0.8 mm Biocidal bead head loss results

Head losses of the 0.3 mm and 0.8 mm biocidal beads alone followed a linear relationship with flow rate (Figure 21). The head losses of the 0.8 mm beads were consistently lower than the head losses of the 0.3 mm beads at all flow rates, however, the difference in head losses were slightly greater at lower flow rates than at higher flow rates (Figure 21). For instance, the head loss of the 0.3 mm beads alone at the lowest flow rate was 37% higher than the head loss of the 0.8 mm beads. At the highest two flow rates (1.12 and 1.4 mL/sec) the head losses of the 0.3 mm beads alone were only 10% and 8% higher, respectively than the head losses of the 0.8 mm beads (Tables 14 and 15).

At the higher flow rates of 1.12 and 1.4 mL/sec, the head loss of the beads alone exceeded 38 cm. Since this exceeds the 30.5-38 cm manufactured depth of the DrainPac[®] filter, subsequent column tests were only conducted at the lowest three flow

rates of 0.28, 0.56, and 0.84 mL/sec, equivalent to 18, 36, and 54 gpm through the DrainPac[®] filter.

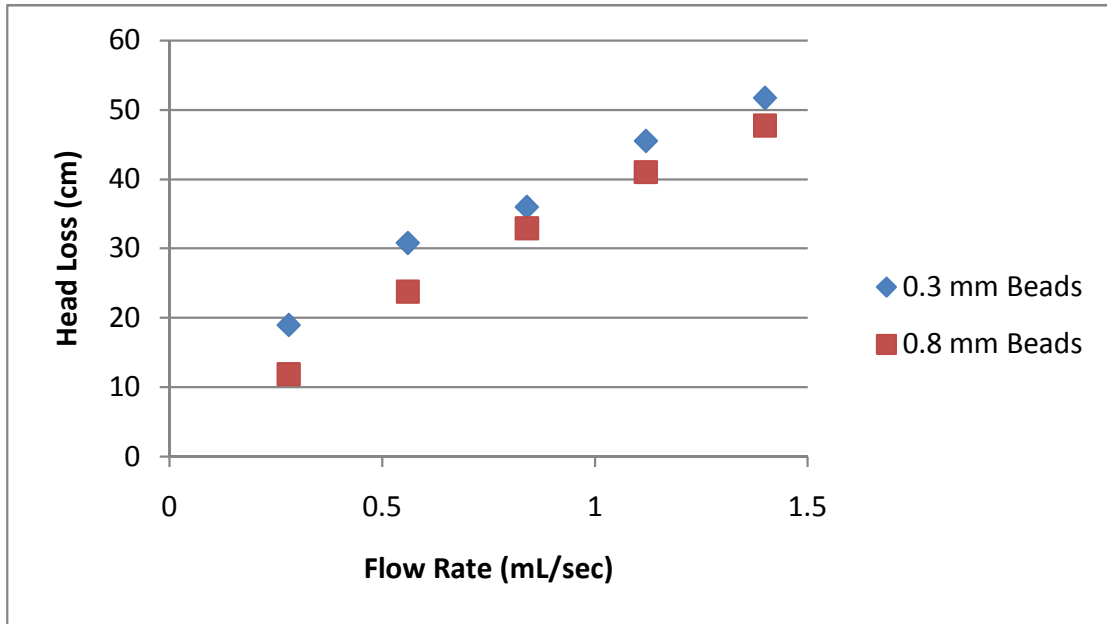


Figure 21. Biocidal bead size and head loss comparison

4.2.2 Bromine Leaching Results

Bromine concentrations of water passed through a 1-cm deep bed of 0.3 mm beads, 0.8 mm beads, and 0.8 mm unactivated control beads at a flow rate of 0.56 mL/sec are shown in Table 16. The pond water effluent that passed through the 0.3 mm beads had an average bromine concentration of 0.47 mg/L, which was nearly double the average concentration leached from the activated 0.8 mm beads (0.27 mg/L). The bromine concentration in the initial DI flush water from the 0.3 mm beads was also nearly double the concentration in the DI flush water of the 0.8 mm beads (Table 16). The higher bromine concentrations in the 0.3 mm bead effluent is likely partly due to the larger surface area of the 0.3 mm beads, allowing for greater mass transfer capabilities than the

0.8 mm beads. However, the formulation used by the manufacturer for charging the beads was different for the two bead sizes.

As expected, the 0.8 mm inactivated (unbrominated) control beads showed no leaching of bromine at all (Table 16). The color from the Hach[®] test kit was completely clear, suggesting a 0 mg/L bromine concentration.

Table 16. Effluent bromine concentrations from the laboratory column with 0.3 mm and 0.8 mm biocidal beads at 0.56 mL/sec

Testing Scenario	Sample	Bromine Concentration (mg/L)
0.3 mm beads	DI Flush Water	0.9
	Pond 1	0.5
	Pond 2	0.5
	Pond 3	0.4
	Pond average	0.47
0.8 mm beads	DI Flush Water	0.5
	Pond 1	0.3
	Pond 2	0.3
	Pond 3	0.2
	Pond average	0.27
0.8 mm Inactivated beads	DI Flush Water	0
	Pond 1	0
	Pond 2	0
	Pond 3	0

To compare expected mass transfer rates of bromine from the two bead sizes, the surface area in a given bed volume for both size beads was calculated by measuring the void fraction (volume of voids divided by the total bed volume). The void fraction (ϵ) and

bead diameter (D_p) were then used to calculate a , the surface area of the beads per bed volume (cm^2/cm^3) using the following equation (Geankoplis, 2003):

$$a_{0.3 \text{ mm beads}} = \frac{6(1 - \varepsilon)}{D_p} = \frac{6(1 - 0.546)}{0.03 \text{ cm}} = 90.8 \text{ cm}^2/\text{cm}^3$$

$$a_{0.8 \text{ mm beads}} = \frac{6(1 - \varepsilon)}{D_p} = \frac{6(1 - 0.692)}{0.08 \text{ cm}} = 23.0 \text{ cm}^2/\text{cm}^3$$

The surface area in a column packed with a 1-cm depth of beads is as follows:

$$A_{0.3 \text{ mm beads}} = 90.8 \frac{\text{cm}^2}{\text{cm}^3} * \frac{\pi}{4} * (1\text{cm})^2 * 1\text{cm} = 71.3 \text{ cm}^2$$

$$A_{0.8 \text{ mm beads}} = 23.0 \frac{\text{cm}^2}{\text{cm}^3} * \frac{\pi}{4} * (1\text{cm})^2 * 1\text{cm} = 18.1 \text{ cm}^2$$

Thus the available surface area in a column packed with a 1-cm depth of 0.3 mm beads is nearly 4 times greater than the total surface area in a column packed with a 1-cm depth of 0.8 mm beads. This allows for much greater mass transfer of bromine from the 0.3 mm beads, which explains the higher leaching rate of bromine from the 0.3 mm beads.

4.2.3 Bromoform Results

Average bromoform concentrations in the pond water that passed through the 1 cm x 1 cm column of 0.3 mm beads ranged from 0.14 mg/L to over 13 mg/L, as shown in Table 17. The quenching scenario had a dramatic effect on bromoform measured. Unquenched sample bromoform concentrations were consistently higher, most likely due to the longer contact times allowing for more formation of bromoform by the reaction of bromine with organic matter in the pond water. To compare the bromoform concentrations in water from different flow rates, data with the identical quenching scenario must be used. At a flow rate of 0.56 mL/sec with the sample quenched after collection, the 0.3 mm beads leached approximately 2.45 mg/L bromoform, which is much higher than the 0.14 mg/L average bromoform concentration in the water that passed through the beads at a 0.84 mL/sec flow rate under the same quenching condition. The bromoform concentration is likely higher from the 0.56 mL/sec flow rate sample because at that flow rate, the water contact time with the beads is nearly 1.5 times greater than at a flow rate of 0.84 mL/sec. DI flush water at 0.28 mL/sec contained 1.25 mg/L bromoform (Table 17), which seems high since there are no organics present in DI water, which are expected to react with bromine by reducing it to bromide, forming bromoform (Westerhoff, et al., 2004). It is possible that bromoform could have leached from the surface of the 0.3 mm beads since bromoform was formed without the presence of organics in the DI flush water.

Table 17. Effluent bromoform concentrations from 0.3 mm biocidal beads

Flow Rate	Quenching Scenario	Sample	GC Peak Area	Concentration Factor*	Bromoform Concentration in Water (mg/L)	Average Bromoform Concentration (mg/L)	Coefficient of Variance
0.28 mL/sec	Quenched after sample collected	DI Flush	721007	20	1.25	1.25	-----
0.56 mL/sec	Quenched immediately	1	455343	16.13	0.98	1.17	22.3%
		2	744394	19.23	1.35		
	Quenched after sample collected	1	1608096	20.83	2.69	2.45	13.9%
		2	1321779	20.83	2.21		
	Quenched after 10 min.	1	150283	19.61	0.27	0.38	42.1%
		2	262203	18.52	0.49		
	Unquenched	1	5579696	19.23	10.10	13.4	34.7%
		2	9978720	20.83	16.67		
0.84 mL/sec	Quenched immediately	1	1340391	20	2.33	2.43	5.8%
		2	1192262	16.4	2.53		
	Quenched after sample collected	1	84793	20.83	0.14	0.14	20.9%
		2	80112	19.23	0.15		
	Quenched after 10 min.	1	240502	20.83	0.40	0.55	36.7%
		2	412148	20.83	0.69		
	Unquenched	1	3803805	20.41	6.49	6.98	10.0%
		2	4380874	20.41	7.47		

* Based on the final concentrated MeCl volume of the 100-mL aliquots (roughly 5 mL)

The 0.8 mm beads were tested at 0.56 and 0.28 mL/sec flow rates, equivalent to 18 and 36 gpm, respectively, through a 12 x 41 in. DrainPac[®] filter. Bromoform concentrations leached from the 0.8 mm beads proved to be much lower than from the 0.3 mm beads, with all samples less than 0.1 mg/L (Table 18). A blind duplicate of the 0.28 mL/sec flow rate sample that was quenched after sample collection was sent to Creek Environmental Laboratories, Inc. (San Luis Obispo) and analyzed for bromoform for quality control. Creek Environmental Laboratories, Inc. reported a bromoform concentration of 0.044 mg/L in water. This compares favorably with my internal GC/MS analysis which gave a value of 0.05 mg/L (Table 18). Pond water that had not passed through the beads was also analyzed for bromoform by GC/MS, and this pond water

blank produced a peak area corresponding to a concentration of 0.02 mg/L bromoform, which is below the lower detection limit (0.025 mg/L). Unlike DI flush water effluent from the 0.3 mm beads, the bromoform concentration of DI flush water from 0.8 mm beads was below detection (Table 18). This is likely due to the different manufacturing process of the 0.8 mm beads.

Table 18. Effluent bromoform concentrations from 0.8 mm biocidal beads

Flow Rate	Quenching Scenario	Sample	Area	Concentration Factor	Bromoform Concentration in Water (mg/L)	Average Bromoform Concentration (mg/L)	Coefficient of Variance
0.56 mL/sec	Quenched immediately	1	5649	16.13	0.01	0.05	104.9%
		2	45434	19.23	0.08		
	Quenched after sample collected	1	23762	20.83	0.04	0.06	43.2%
		2	44657	20.83	0.07		
	Quenched after 10 min.	1	32949	19.61	0.06	0.04	78.9%
		2	8823	18.52	0.02		
0.28 mL/sec	Quenched after sample collected*	1	31667	20.80	0.05	0.05	1.1%
		2	30279	19.60	0.05		
	Quenched after Sample	DI Flush	6656	20	0.01	0.01	-----
	Pond Water Blank	1	13974	20.00	0.02	0.02	-----

*Blind duplicate sample analyzed for bromoform by Creek Environmental Inc. (San Luis Obispo) with a reported bromoform concentration of 0.044 mg/L

4.2.4 Bromide Results

For the 0.3 mm beads, the average bromide concentration in the DI flush water effluent was 0.64 mg/L (Table 19.) The average pond water effluent bromide concentration for the 0.3 mm beads at a flow rate of 0.56 mL/sec was 0.53 mg/L.

Table 19. Effluent bromide concentrations from 0.3 mm biocidal beads at 0.56 mL/sec

Sample*	Area	Retention Time	Bromide Concentration (mg/L)	Average Concentration (mg/L)
DI Water 1 a	0.055	7.17	0.60	0.64
DI Water 1 b	0.063	7.25	0.69	
Pond 1 a	0.046	7.18	0.50	0.54
Pond 1 b	0.053	7.20	0.58	
Pond 2 a	0.050	7.22	0.54	0.52
Pond 2 b	0.046	7.22	0.50	
Pond 3 a	0.050	7.20	0.54	0.54
Pond 3 b	0.050	7.22	0.54	
		Pond Water Average=		0.53

*Replicate samples labeled “a” or “b” and “DI Water” refers to DI flush water

The 0.8 mm beads were tested for bromide at two flow rates: 0.56 and 0.28 mL/sec, equivalent to 36 and 18 gpm through a 12 x 41 in. DrainPac® filter, respectively. The average bromide concentration from pond water effluent from the 0.8 mm beads at 0.56 mL/sec was 0.50 mg/L (Table 20). For this analysis, pond water blanks were also tested for bromide. Bromide in pond water was small with duplicate pond water blanks averaging 0.17 mg/L for the 0.56 mL/sec flow rate test (Table 20) and 0.09 mg/L for the 0.28 mL/sec flow rate test (Table 21). The average pond water effluent bromide concentration from 0.8 mm beads at 0.28 mL/sec was 1.38 mg/L (Table 21), which is 64% higher than the 0.50 mg/L effluent bromide concentration from 0.8 mm beads at 0.56 mL/sec (Table 20). This difference in bromide concentration is likely due to the longer retention time in the column at the lower flow rate.

In this analysis, the DI flush water contained significantly lower bromide concentrations than the pond water that was flushed through the beads. This is expected because

bromide is formed when bromine is reduced as it oxidizes organic material such as that in the pond water. In both the 0.8 mm bead effluents at 0.28 and 0.56 mL/sec flow rates, the average bromide concentration in the DI flush water was lower than the average pond water effluent (Tables 20 and 21).

Table 20. Effluent bromide concentrations from 0.8 mm biocidal beads at a 0.56 mL/sec flow rate

Sample	Area	Retention Time	Bromide Concentration (mg/L)	Average Concentration (mg/L)
Pond Blank 1	0.015	7.07	0.19	0.17
Pond Blank 2	0.012	6.97	0.15	
DI Water 1 a	0.03	6.82	0.37	0.38
DI Water 1 b	0.032	6.82	0.39	
Pond 1	0.036	6.85	0.44	0.50
Pond 2	0.057	6.92	0.68	
Pond 3	0.031	6.87	0.38	

Table 21. Effluent bromide concentrations from 0.8 mm biocidal beads at a 0.28 mL/sec flow rate

Sample	Area	Retention Time	Bromide Concentration (mg/L)	Average Concentration (mg/L)
Pond Blank 1	0	-----	0.00	0.09
Pond Blank 2	0.014	7.30	0.17	
DI Water 1 a	0.026	7.12	0.30	0.30
DI Water 1 b	0.027	7.12	0.31	
Pond 1	0.164	7.30	1.77	1.38
Pond 2	0.112	7.22	1.21	
Pond 3	0.108	7.18	1.17	

4.2.5 Bromine Compound Leaching During Longevity Testing

Simulated Use Cycles

The laboratory column with 1-cm bed depth of 0.3 mm biocidal beads, was subjected to five daily one-hour wet cycles at a flow rate of 0.56 mL/sec and four daily drying cycles to test the longevity of the beads. Following the wet/dry cycles, leachate from the beads was tested as described above at a flow rate of 0.56 mL/sec and analyzed for bromine, bromoform, and bromide.

The average bromine concentration leached from the 0.3 mm beads after five use cycles at 0.56 mL/sec was 0.37 mg/L (Table 22). This was approximately 20% less than the average bromine concentration in the leachate from a bed of fresh 0.3 mm beads at the same flow rate. To put this in perspective, each wet cycle consisted of passing approximately 2 liters of pond water through the beads, equivalent to 2,135 gallons of stormwater passing through a 1-cm thick layer of biocidal beads set in a 12 x 41 in. DrainPac[®] filter.

Table 22. Effluent bromine concentrations from 0.3 mm biocidal beads at 0.56 mL/sec flow rate under simulated use longevity conditions

Sample	Bromine Concentration (mg/L)
Pond 1	0.30
Pond 2	0.40
Pond 3	0.40
Average	0.37

Effluent from the 0.3 mm longevity bead run was also analyzed for bromide. After five simulated use cycles, the average bromide concentration leached from the beads was 0.51

mg/L (Table 23). This is about the same as the average bromide concentration from fresh 0.3 mm beads tested at the same flow rate (Table 19). The average bromide concentration in the leachate from the longevity bead run is also about the same as that in the effluent from fresh 0.8 mm beads at the same flow rate (Table 20).

Table 23. Effluent bromide concentrations from 0.3 mm biocidal beads at 0.56 mL/sec flow rate under longevity conditions

Sample	Area	Retention Time	Bromide Concentration (mg/L)	Average Concentration (mg/L)
1	0.041	6.9	0.50	0.51
2	0.042	6.9	0.51	
3	0.045	6.92	0.54	

After the bromine was analyzed and the bromide was sampled, bromoform samples were collected and quenched with sodium thiosulfate immediately after each 147-mL sample was collected. After the five use cycles, the average observed bromoform concentration in the leachate was 0.03 mg/L (Table 24). In comparison, the average bromoform concentration in the effluent from fresh 0.3 mm beads at the same flow rate and quenching scenario was 2.45 mg/L.

Table 24. Effluent bromoform concentrations from 0.3 mm biocidal beads at 0.56 mL/sec flow rate under longevity conditions

Longevity Conditions	Quenching Scenario	Sample	Area	Concentration Factor	Bromoform Concentration in Water (mg/L)	Average Concentration (mg/L)	Coefficient of Variance
	Quenched After Sample	1	21156	20.41	0.036	0.03	0.53
		2	9646	20.41	0.016		

In summary, bromine and bromide concentrations in the leachate were similar before and after the five simulated use cycles (Figure 22). However, the leachate from the 0.3 mm

beads that underwent five wet cycles and four dry cycles contained nearly 100 times less bromoform than pond water passed through fresh 0.3 mm beads. This suggests that much of the bromoform was exhausted sometime during the five simulated use cycles, possibly leaching off the surface of the beads. It is also possible that less bromoform was formed because less organic material was present in the pond water after the column of glass wool filtered the water prior to the column of beads. However, this may not be true since organic material also aids in the reduction of bromine into bromide, and bromide concentrations in the leachate were not significantly less than leachate from fresh 0.3 mm beads.

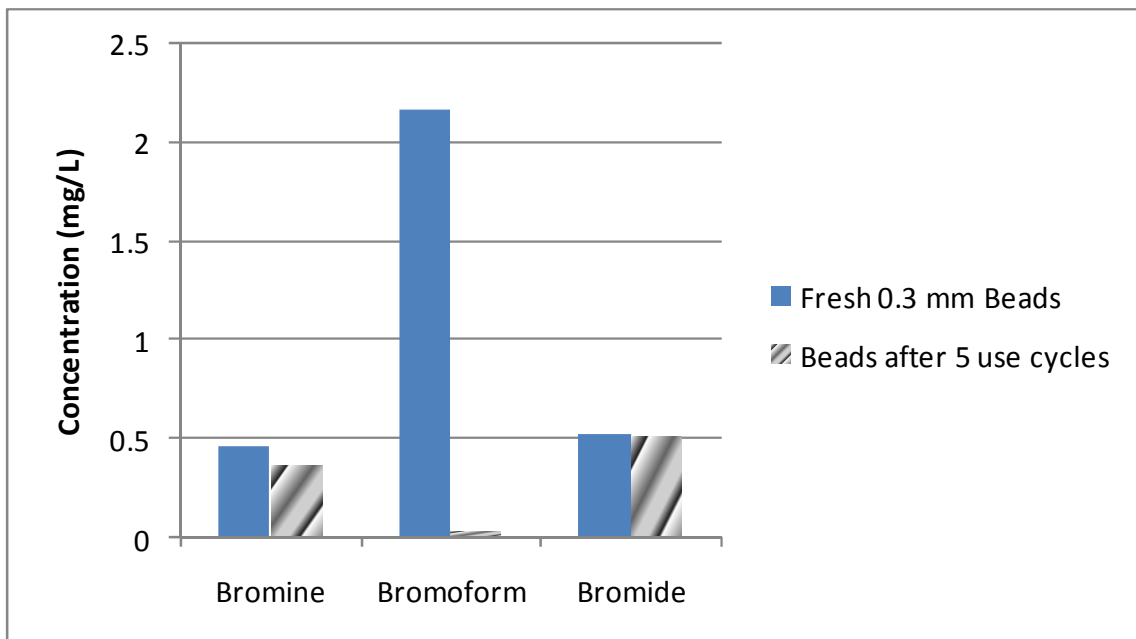


Figure 22. Bromine compound concentrations of fresh 0.3 mm biocidal bead effluent vs. 0.3 mm biocidal beads after five simulated use cycles at 0.56 mL/sec flow rate

Dry Storage

After 162 days of dry storage, the 0.3 mm biocidal beads were set in a column and pond water was passed through the beads at 0.56 mL/sec. The bromine concentration in leachate from these beads was 0.47 mg/L (Table 25). The concentration of bromine in pond water passed through fresh 0.3 mm beads was exactly the same (Table 16). Thus the 0.3 mm biocidal beads exhibited no loss of bromine after 162 days of dry storage.

Table 25. Effluent bromine concentrations from 0.3 mm beads at a flow rate of 0.56 mL/sec after 162 days of dry storage

Sample	Bromine Concentration (mg/L)
Pond 1	0.5
Pond 2	0.5
Pond 3	0.4
Average	0.47

Bromide was analyzed from the same pond water leachate of the 0.3 mm beads that were placed in dry storage for over five months, and the effluent actually contained 43% more bromide than effluent passed through fresh 0.3 mm beads at the same flow rate. The effluent from fresh 0.3 mm beads at 0.56 mL/sec contained an average bromide concentration of 0.53 mg/L (Table 19), while effluent from the stored beads contained an average bromide concentration of 0.76 mg/L (Table 26).

Table 26. Effluent bromide concentrations from 0.3 mm beads after 162 days of dry storage

Sample	Area	Retention Time	Bromide Concentration (mg/L)	Average Concentration (mg/L)
Pond 1a	0.048	7.1	0.66	0.76
Pond 1b	0.063	7.13	0.86	
Pond 2a	0.057	7.1	0.78	0.75
Pond 2b	0.052	7.1	0.71	

Leachate from the 0.3 mm beads that sat in dry storage for 162 days contained approximately 0.06 mg/L bromoform (Table 27). In comparison, the bromoform concentration was 2.45 mg/L in leachate from fresh 0.3 mm beads (Table 17).

Table 27. Bromoform concentrations from 0.3 mm bead effluent at 0.56 mL/sec after 162 days of dry storage

Dry Storage Longevity Conditions	Quenching Scenario	Sample	Area	Concentration Factor	Bromoform Concentration in Water (mg/L)	Average Concentration (mg/L)	Coefficient of Variance
	Quenched After Sample	1	25361	19.61	0.07	0.06	0.10
		2	22600	20.00	0.06		

In summary, after 162 days of dry storage, pond water effluent from a column of the 0.3 mm beads contained the same concentration of bromine, nearly 98% less bromoform, and approximately 30% more bromide than effluent from fresh 0.3 mm biocidal beads (Figure 23). Similar to the set of 0.3 mm beads that underwent five simulated use cycles, the beads that were stored for 162 days also exhibited a drastic reduction in bromoform. The majority of the bromoform appears to have volatilized off the surface of the 0.3 mm beads.

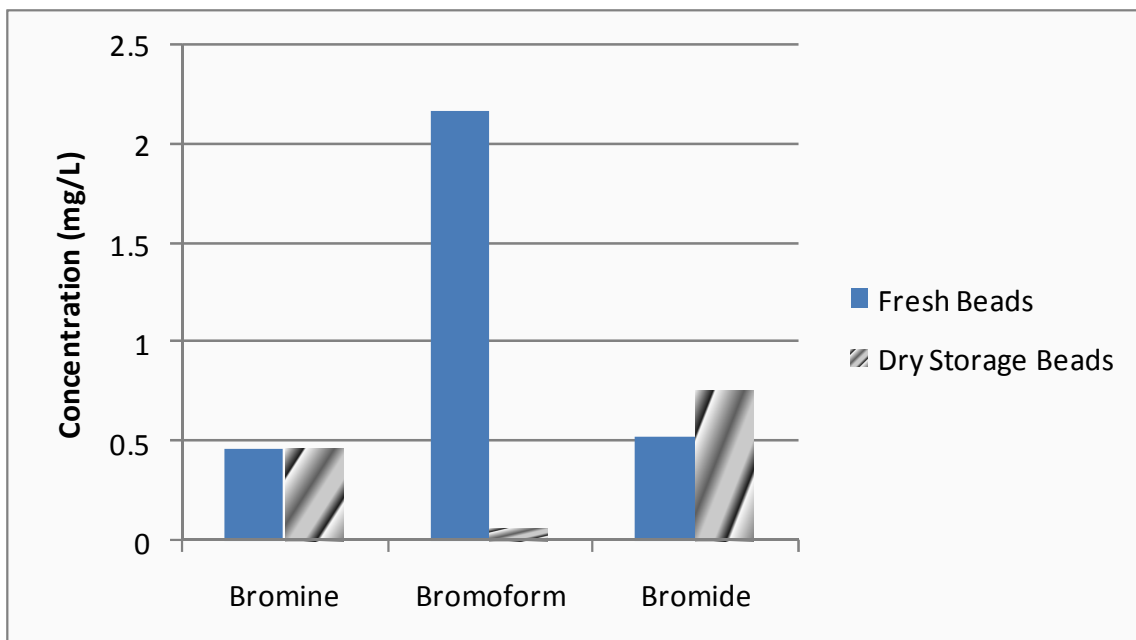


Figure 23. Bromine compound concentrations of fresh 0.3 mm bead effluent vs. 0.3 mm bead effluent after 162 days of dry storage at 0.56 mL/sec flow rate

CHAPTER 5: CONCLUSIONS AND RECCOMENDATIONS

DrainPac[®] Filter Conclusions

Maintenance is vital to the efficacy of the DrainPac[®] filter because solids loading reduces the flow rate at which the filter will be by-passed. The highest filterable flow rate of a DrainPac[®] filter with dimensions of 12 x 41 in. that was loaded with 625 g of solids was 80 gpm. Head loss data, along with the precipitation characteristics of the specific site for the stormwater filter could be key factors in determining how often routine maintenance of the DrainPac[®] filters is required.

Compared to past research of the DrainPac[®] filter (Table 28), the results of this study were most similar to that of Stenstrom (1998). In the present study the average suspended solids removal efficiency of the DrainPac[®] filter ranged from 83% to 91% at various flow rates, compared to 95 to 98% reported by Stenstrom (Table 28). The higher total suspended solids removal efficiencies reported by Stenstrom, could be due to differences in the solids used for testing. Stenstrom used solids which were removed from catch basins and included sediment and larger items such as cigarette butts, small leaves, and pebbles. In comparison, the solids removed by the DrainPac[®] were fine sediments in the pond water and sand added to the feed water. In this study, sediment removal efficiency of the filter once it was loaded was not tested. It is possible that higher removal efficiencies could be obtained with a loaded filter if the solids act like a schmutzdecker in a slow-sand filter. Future research could explore the performance of the DrainPac[®] filter at removing sediments when it is loaded.

The DrainPac[®] filter insert removed oil from oil-laden pond water at average efficiencies of 40%-82%, which is similar to the 49-86% oil removal efficiency that Stenstrom (1998) reported (Table 28). There was no apparent trend in oil removal efficiency with flow rate. Solids other than those already present in the pond water were never added during oil removal tests. Future tests could add solids at the same time as the oil to determine the effect of oil adsorption to the solids on the oil removal efficiency of the filter.

Table 28. Studies of the DrainPac[®] filter

Study	Flow Rate	Test	Removal Efficiency
Morgan et al., 2005	207-213 gpm	TSS	25
Stenstrom, 1998	75 gpm	TSS	95-98%
		Oil and grease	49-86%
Walch et al., 2004	Natural stormwater conditions	Compared protected inlets against controls	Variable Results
This Study	20-200 gpm	TSS	83-91%
		Oil and grease	40-82%

The DrainPac[®] filter showed no evidence of coliform bacteria removal. This is likely due to the small colloidal size of the bacteria allowing them to pass through the filter fabric. To date, there are no other studies of the coliform bacteria removal efficiency of the DrainPac[®] filter. Solids were never added during the coliform removal tests, except the solids naturally present in the pond water. Future research could test the coliform removal efficiency of a loaded filter and also test coliform removals while adding

sediment-laden water to an unloaded filter to determine if the accumulation of solids in the filter has any effect on the coliform removal efficiency of the filter.

Conclusions for Leachate from Biocidal Beads

The time at which leachate samples were quenched with sodium thiosulfate was found to have drastic effects on bromoform concentrations in leachate from the biocidal beads. Past studies such as Chen et al. (2003) quenched samples with 0.02 N sodium thiosulfate, however, the time elapsed before quenching was not reported. Quenching samples after the collection of the total sample was probably the most realistic in terms of typical scenarios for real stormwater because there is usually some contact time in catch basins before discharge to receiving waters. Thus, it is most appropriate to use the leachate concentrations in samples quenched accordingly for predicting bromoform concentrations in the leachate from biocidal beads in a stormwater filter. Higher bromoform concentrations were generally found in samples quenched after the collection of the total sample, followed by samples quenched immediately. Samples quenched after ten minutes usually contained the lowest bromoform concentrations. More research is needed to determine the full effects of time elapsed before quenching samples on bromoform concentrations in the leachate.

The 0.3 mm biocidal beads leached more bromine compounds than the 0.8 mm beads, particularly bromoform. The greater leaching from the smaller beads can be partly explained by the greater surface area of a 1-cm bed of the 0.3 mm beads. The surface area in a 1-cm diameter column packed with a 1-cm depth of 0.3 mm beads is nearly 4

times greater than the same column packed with a 1-cm depth of 0.8 mm beads, allowing for more mass transfer of bromine. This could explain the higher bromine concentrations in leachate from the 0.3 mm beads, which was 43% higher than for the 0.8 mm beads at a test flow rate of 0.56 mL/sec. However, 98% higher bromoform concentrations were observed for the 0.3 mm beads compared to the 0.8 mm beads, and this cannot be explained by greater surface area alone. This large amount of bromoform leaching was most likely due to the different manufacturing process used for the 0.3 mm beads.

According to the manufacturer, the new 0.8 mm beads are made using different conditions which dramatically reduced the bromoform leaching from the beads. The manufacturer has discontinued production of the 0.3 mm brominated beads.

The source of the bromoform can be better understood by considering the chemistry of bromoform formation. As bromine leaches into the water, it is expected to react with organics present in the water and be reduced to bromide, forming bromoform (Westerhoff, et al., 2004). However, DI flush water that passed through a 1-cm bed of 0.3 mm beads at 0.28 mL/sec contained 1.25 mg/L bromoform, even though no organics are present in DI water. This suggests that bromoform was already on the surface of the 0.3 mm beads. In contrast, the concentration of bromoform in DI flush water passed through 0.8 mm beads at the same flow rate was below detection. Therefore the new manufacturing process used for the 0.8 mm beads appears to have greatly reduced or eliminated the bromoform on the beads. Further, it was found that there was a 97% reduction of bromoform in the leachate of 0.3 mm beads after the beads were stored dry for 162 days. Thus bromoform on the surface of the 0.3 mm beads, appears to have volatilized during dry storage.

Although the 0.8 mm beads do not appear to have free bromoform on their surfaces, there is some bromoform formed by reaction of free bromine with organic material in the leachate. Pond water leachate from a 1-cm bed of 0.8 mm beads contained an average bromine concentration of 0.27 mg/L, an average bromoform concentration of 0.06 mg/L, and an average bromide concentration of 0.5 mg/L. Similar to Chen et al. (2003), the leachate contained less than 2.0 mg/L bromine. The bromoform concentrations in the leachate from the 0.8 mm beads were lower than the bromoform drinking water maximum contaminant level of 80 µg/L (U.S. EPA, 2008c).

Higher bromine compound concentrations were found at lower flow rates, likely because of the longer retention time in contact with the beads. Longer retention times allow for more mass transfer of bromine compounds. Leachate from 0.8 mm beads contained 64% higher bromide concentrations at a flow rate of 0.28 mL/sec compared to a flow rate of 0.56 mL/sec.

Slight reductions in bromine and bromide concentrations were found in leachate from the 0.3 mm beads that underwent five simulated use cycles compared to leachate from fresh beads. A 99% reduction in bromoform was found after five simulated use cycles. This drastic reduction in bromoform formation suggests that much of the bromoform is exhausted early on. The longevity of bromine in the leachate from the biocidal beads was only tested for the 0.3 mm beads. Future research could test the 0.8 mm biocidal beads after each simulated use cycle to determine the rate of bromoform exhaustion so that, if needed, the beads could be pre-rinsed to decrease the amount of bromoform leaching from the beads before use in actual catchment basins. The biocidal beads tested in this study seem promising for stormwater treatment in catchment basins, however, more

research is needed to determine if the bromine compound concentrations in the leachate would have any negative effects on aquatic habitats.

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APPENDIX A

Table A-1. Bromide standard data for 0.8 mm bead run

Standard Concentration (mg/L)	Area	Retention Time	Average Area
0.25	0.021	7.07	0.021
	0.020	7.10	
0.5	0.047	7.08	0.045
	0.042	7.10	
0.75	0.071	7.12	0.072
	0.073	7.10	
1	0.091	7.12	0.093
	0.094	7.10	
2	0.181	7.15	0.187
	0.193	7.12	

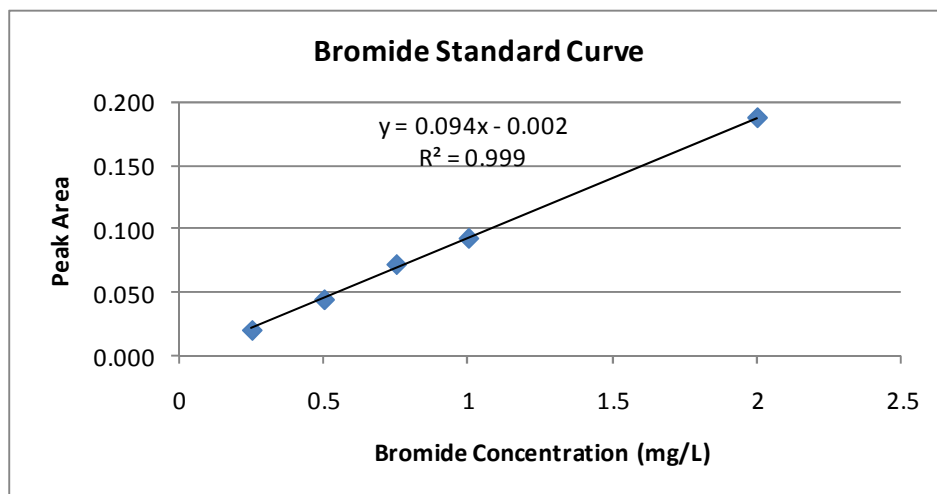


Figure A-1. Bromide standard curve for 0.8 mm bead run

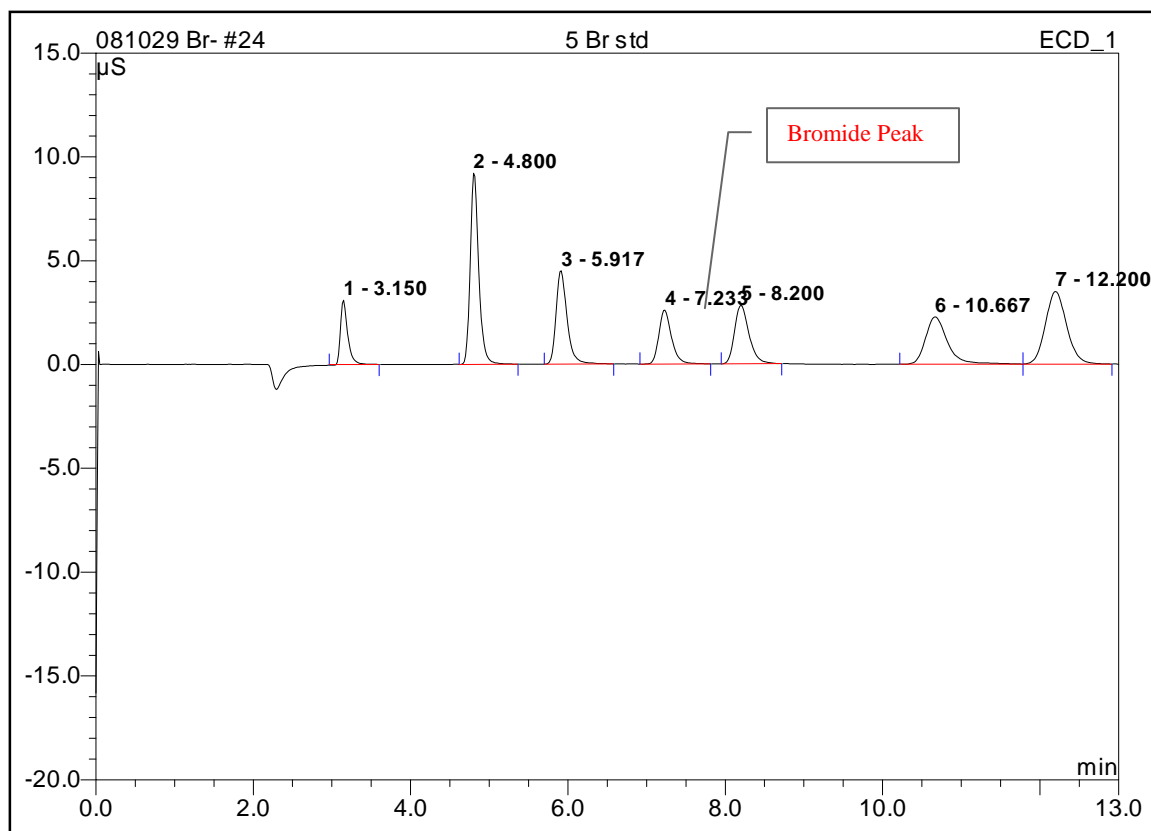


Figure A-2. 5 mg/L bromide standard ion chromatogram

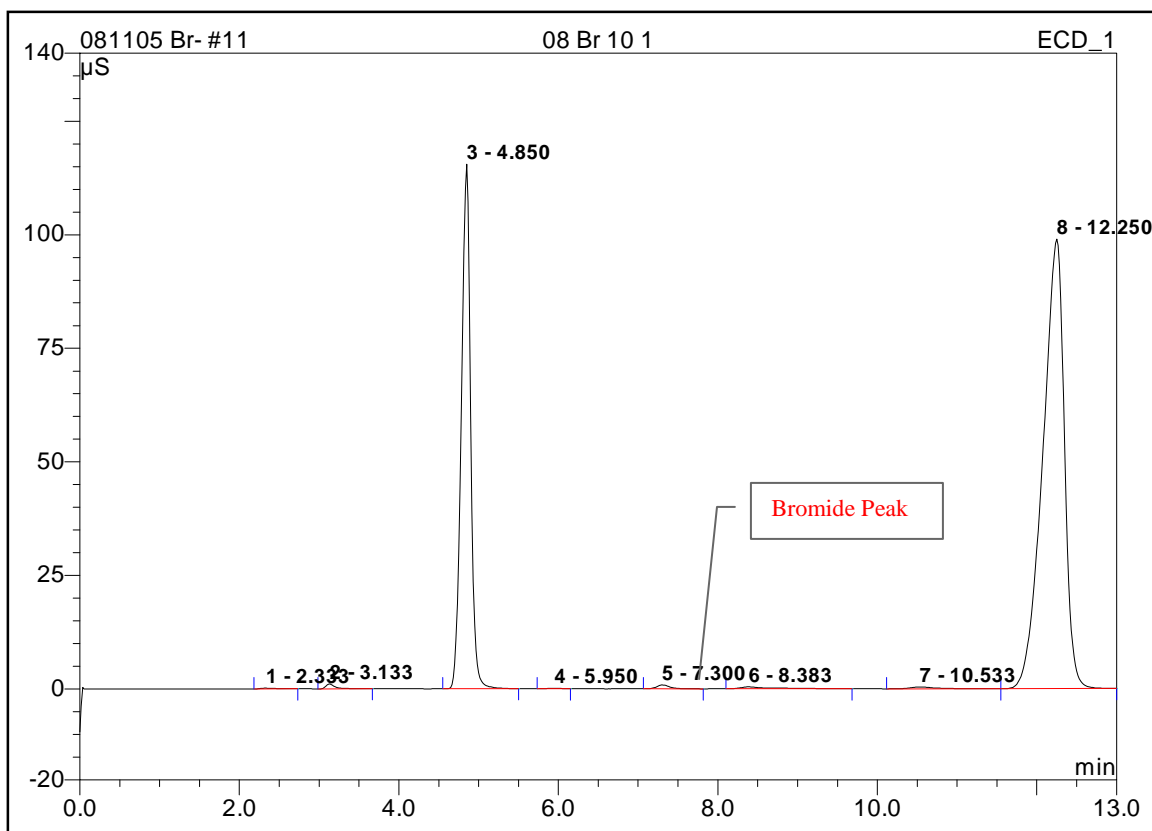


Figure A-3. Ion chromatogram of leachate from 0.8 mm beads at 0.28 mL/sec- pond water sample contained 1.8 mg/L bromide

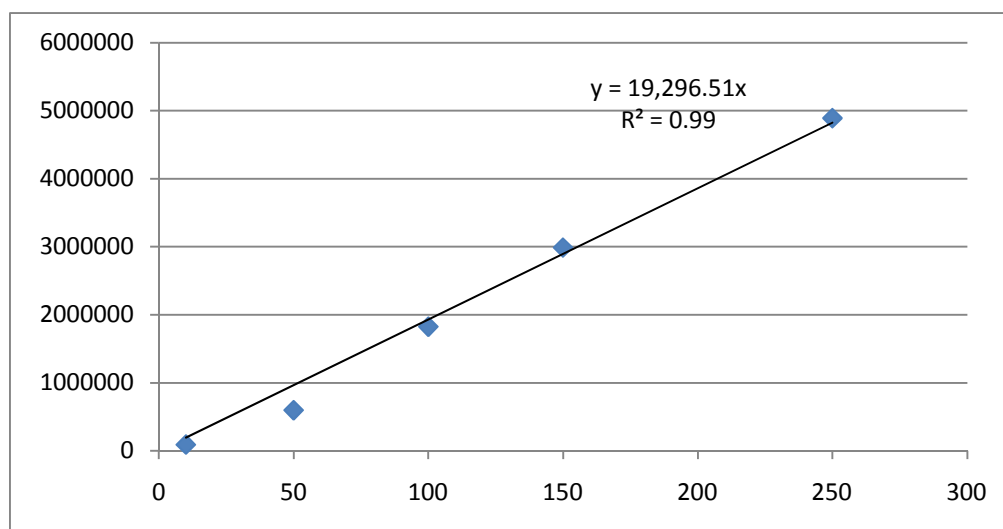


Figure A-4. Bromoform standard curve for dry storage beads