

# Treatability of Stormwater Toxicants Using Biofiltration Media

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## ABSTRACT

Bioretention has been promoted as a stormwater management technique that can reduce the loads of solids, heavy metals, and nutrients to surface waters. Many researchers have reported the treatment effectiveness of bioretention both in terms of percent removal and periodically in terms of effluent concentration. No studies, however, have evaluated the ability of carefully-selected bioretention media to treat pollutants to meet specific permit limits. This project focused on the selection of a bioretention media mixture from pre-selected components – a granular activated carbon (GAC), two zeolites, two sands, and a peat moss – with the goal of treating numerous constituents, including dioxins, mercury, perchlorate, oil and grease, and radioactive components to numeric permit limits. Two series of column tests, one focusing on long-term pollutant removal behavior and the other on the effect of depth/contact time on removal and using stormwater as the base test fluid, showed that a bioretention media containing a specific granular activated carbon (GAC) was able to treat these constituents to the permit limits under a wide range of likely site conditions. Supplemental batch tests, not reported here, also examined treatment capacity, kinetics, and holding ability under interevent aerobic and anaerobic conditions.

## INTRODUCTION

Bioretention is becoming more widely adopted in stormwater management plans because of its well documented potential, if designed and maintained properly, to reduce the water volume and the loads of nutrients, metals, and solids reaching receiving waters. Many researchers have published extensive results on the performance of bioretention for these pollutants, and the results of a representative number of these studies are summarized in the International Stormwater BMP Database ([www.bmpdatabase.org](http://www.bmpdatabase.org)). For example, biofilters/bioretention devices are shown to be capable of reducing suspended solids from an average influent concentration of 50 mg/L to approximately 24 mg/L effluent concentration, on average. Concentration removals, on average, for nitrogen and phosphorus were poor to negligible. Where

bioretention provides the benefit for the nutrients was through the reduction in water volume, and therefore the loading, of these nutrients discharged to the surface water.

What has not been investigated thoroughly has been the performance of bioretention systems for organic toxicants and radionuclides. The studies that exist for organic toxicants and bioretention media typically focus on the petroleum hydrocarbons, either individually or as a total, since these devices may be installed to treat runoff from gas stations, parking lots, etc. For example, DiBlasi et al. (2009) documented, in a soil-sand-organic matter bioretention cell, polycyclic aromatic hydrocarbon (PAH) event mean concentration (EMC) reductions of 31 to 99%, with a mean effluent EMC of 0.22  $\mu\text{g/L}$ . When combined with the water volume reduction, the PAH loads were reduced by 87%. Other researchers who have looked at organics removal as a function of media characteristics in (bio)filtration/bioretention have found that PAH removal can be correlated directly with the hydrophobicity of the compound and the organic content of the media (Gasperi et al. 2010; DiBlasi et al. 2009; Jaradat et al. 2009; Clark and Pitt 1999). No published studies were located that focused on field-scale bioretention removal of radionuclides. This paper presents the results of a study that evaluated several candidate bioretention media for their ability, either singly or in mixtures, to treat selected organic toxicants and radionuclides to specified effluent concentrations. The site for which these units are being designed is subject to a NPDES stormwater permit having very low numeric benchmark concentrations.

### **Site and Bioretention Information**

The drainage areas for these bioretention units consist primarily of steep catchments with significant open space, primarily chaparral habitat and exposed bedrock (generally sandstone). Significant sediment loads occur during intense storms. An addition feature of the project is that existing runoff concentrations for the pollutants of interest are generally below levels typically seen in urban and industrial stormwater runoff, making it difficult to apply traditional industrial and commercial stormwater treatment results to order to predict whether bioretention effluent could meet permit limits.

Stormwater treatment systems investigated for the site generally consist of advanced engineered natural treatment systems (ENTS), which are treatment trains containing a combination of detention basins followed by bioretention filter basins (i.e., large, vegetated, vertical-flow, outlet-controlled media filters). The preliminary design goal was to treat 90% of the long-term runoff volume from drainage areas ranging from 5 to 60 acres at the site. The pollutants of most interest are those that have periodically exceeded the numeric discharge benchmarks and include cadmium, copper, lead, and dioxins. This paper will focus on a subset of the pollutants contained in the discharge permit: oil and grease, perchlorate, dioxin (TCDD), gross alpha and gross beta radioactivity, strontium-90, uranium, and tritium.

### Candidate Bioretention Media

The media examined included six materials: a rhyolite sand, a granular activated carbon (GAC), a surface-modified zeolite, a zeolite currently used on the site, a filter sand used on the site (all supplied by the client or client's representative), and a sphagnum peat moss. The column tests examined each of these six materials separately, along with four mixtures of these components. Figure 1 shows five of the six candidate media, with the sixth media being the site filter sand. Past research by Clark (2000) had shown that while sand was not inert, comparatively it was a much poorer treatment medium compared to modified sands, zeolites, carbons, and organic-based media such as peat and compost. Sand, though, often had to be added to the other media in order to control flow rates through the media, similar to what was done in this study in the columns that evaluated the candidate media individually. The granular media without added sand had flow rates too high to achieve acceptable contact time between the media and the water without creating very deep filters, or restrictive outlets. The organic-based media typically compressed or were very well-graded and had very slow flow rates, which were unacceptable because they required a very large surface area to achieve the required drain down times. Therefore, the site filter sand was mixed with the treatment media 50/50 v/v in those column tests, in addition to being evaluated by itself.



**Figure 1. Media (from left to right): GAC, Rhyolite Sand, Site Zeolite, Surface Modified Zeolite, Sphagnum Peat Moss**

Tables 1 through 3 provide the physical properties of the media individually and in the mixtures that were examined as part of this project. As can be seen from Table 1, with the exception of the peat moss, the candidate media were uniformly graded with uniformity coefficients ranging between 1.5 and 2.5. The peat moss was classified as well-graded, with a uniformity coefficient greater than 7. Table 2 provides additional information on several of the media, including the composition of the rhyolite sand and the fact that site filter sand and site zeolite were selected because they were approved already for treatment operations on the site. Table 3 shows the porosities and bulk densities for the candidate media and mixtures. In general, the porosities ranged between 30 and 50%, as would be expected for uncompacted filter media. The highest bulk density was for the sand itself. The other mixtures had smaller bulk densities since the proportion of sand was reduced, compared to the 100% sand column.

**Table 1. Description of Media Tested**

Media	Manufacture's description	Bulk density	Approx. cost	median particle size (D <sub>50</sub> ) (mm)*	uniformity coefficient (D <sub>60</sub> /D <sub>10</sub> )**
Granular Activated Carbon (GAC)	VCC 8X30 Virgin Coconut Shell Activated Carbon (Baker Corp.)	29 lbs/ft <sup>3</sup> (1.8 to 2.1 g/cm <sup>3</sup> )	\$0.98/lb	1.45	2.13
Rhyolite Sand (R)	D1 biofilter media sand (Rhyolite Topdressing Sand) from Golf Sand, Inc., North Las Vegas, NV	1.28 g/cm <sup>3</sup>	\$0.10/lb delivered	0.39	1.79
Site Zeolite (Z)	Z-200 Modified Zeolite (Baker Corp.)		\$1.36/lb	2.9	1.55
Surface Modified Zeolite (SMZ)	14-40 Saint Cloud Zeolite with 325 µm Modified Zeolite at 3% Vol:Vol		\$0.15/lb delivered	0.73	2.35
Sphagnum Peat Moss (PM)	Purchased from nursery in Elizabethtown, PA			0.60	7.31
Site Filter Sand (S)	Fine textured silica sand from source local to project site			0.95	2.3

\* measured in UA soils lab using standard 8 inch sieves and shaker

\*\* calculated based on the measured particle size distribution; uniformity coefficient <5 indicates a very uniform medium; 5 is moderate uniformity; >5 indicates a well-graded and non-uniform medium

**Table 2. Additional Media Information**

Medium	Additional Information
Rhyolite Sand	75 in/hr infiltration rate; 98.6% sand, 1.1% silt, 0.3% clay; 45.4% greater than 0.25 mm; 44.6% between 0.18 and 0.25 mm.
Site Zeolite	material currently used on site for stormwater treatment
Site Filter Sand	material currently used on site for stormwater treatment

**Table 3. Porosity for Test Mixtures Measured in Lab**

Full-Depth Column Tests – Candidate Individual Media	Porosity	Bulk Density (g/cc)
SMZ (with 50% Filter Sand)	0.40	1.35
R (w/ 50% Filter Sand)	0.36	1.48
PM (w/ 50% Filter Sand)	0.50	0.93
GAC (sub) (w/ 50% Filter Sand)	0.32	1.21
Z (w/ 50% Filter Sand)	0.35	1.24
Sand	0.32	1.66
Full-Depth Column Tests – Candidate Mixtures		
R-SMZ-GAC (1/3 each)	0.41	0.94
R-SMZ-GAC-PM (30% R, SMZ, GAC; 10% PM)	0.43	0.87
R-SMZ (75% R, 25% S)	0.43	1.23
Layered (S-Z-GAC)	N/A	1.00
Additional Mixture used in Varying Column Depth Tests		
GAC (2/3 Sand, 1/3 GAC)	0.36	1.25

## **MATERIALS AND METHODS**

### **Description of Media Testing**

Prior research has shown that a targeted suite of controlled laboratory tests can evaluate the potential effectiveness of filtration/biofiltration media for stormwater runoff treatment. These tests include standard column tests to determine flow rates, breakthrough capacity, clogging problems, and general contaminant removal; contact time and media depth tests to optimize depth as a design parameter; traditional isotherm and kinetics tests to determine the contaminant retention in the media as a function of contact time; and aerobic and anaerobic retention tests to determine whether pollutant retention is permanent under changing pore water chemistry conditions. Because of the analytical expense of measuring these pollutants in the influent stormwater and in the treated effluent, long-term full-depth column breakthrough tests were only conducted using the four mixed-media columns. Only mercury, perchlorate, and oil and grease were investigated during the vary-depth column tests that investigated contact time/media depth removal relationships. Of the pollutants of interest for this paper, only mercury, oil and grease, and perchlorates were spiked into previously-collected stormwater runoff from the campus of Penn State Harrisburg. The dioxins and radioactive constituents were not added to the naturally occurring campus runoff due to safety issues.

**Removal to Chemical Breakthrough Tests.** In these traditional long-term column tests, the media were subjected to intermittent stormwater flows over several months. The primary information from these tests included: treatment flow rates, pollutant removal, and clogging/maintenance requirements. The results of the clogging and maintenance tests can be found in Pitt et al. (2010), and the full technical report will be posted at: [http://www.boeing.com/aboutus/environment/santa\\_susana/tech\\_reports.html](http://www.boeing.com/aboutus/environment/santa_susana/tech_reports.html). The test water used during these investigations was a modified stormwater. Based on experience, stormwater should be used to test media, even in a laboratory situation. The inherent chemistry (particle size distributions of the suspended solids, major ions, pH and alkalinity, etc.) of stormwater is substantially different from most artificial mixes reported in the literature and can affect the pollutant removal and retention mechanisms in treatment systems. The collected runoff water was modified for each day's experiments for some of the constituents of interest to increase their concentration to a target at about the 90<sup>th</sup> percentile concentration levels seen in the runoff water from the site. Most of these targeted concentrations are substantially lower than the industrial wastewater and artificial stormwater concentrations used in many of the past tests of treatment media. These test results reported here have been used to confirm the ability of these media to treat runoff at relatively low influent concentrations over time. The challenge stormwater also contains a mixture of constituents/pollutants that may affect the treatment performance of the media, again in contrast to traditional media tests that only examine individual contaminants at a time.

Ten media columns were constructed on a wooden test frame in the PSH pilot-scale laboratory. Prior to column construction, the Kimax™ glass columns and glass drainage funnels were washed with hydrochloric acid and rinsed with deionized water. Squares of pre-washed fiberglass window screen were placed across the bottom of the glass column as a support for the column media. The columns were inserted into the wooden supports on top of the funnel. Gravel purchased at a local home improvement store was washed, air dried and placed to a depth of approximately 0.05 m (2 inches) in the bottom of each column. The media was then added to a depth of approximately 0.97 m (38 inches) in three batches. After each batch was added (approximately 1 foot in depth), the media was rinsed with deionized water. Figure 2 shows the column set-up. One column contained only Site Sand to evaluate the effectiveness of unmodified sand. Unmodified sand was expected to provide only removal of the particulates and particulate-associated pollutants. The other media listed were placed into five individual columns after being mixed 50-50 (v/v) with the Site Sand. The last four columns were used to evaluate several mixes of the media, as described and designated in Table 3.



**Figure 2. Long-Term Column Breakthrough Testing Setup. Left: Glass column under construction. Right: Complete column testing setup.**

At the start of each testing day, approximately 200 L of stored stormwater were transferred to the day tank after the storage tank was mixed for at least 20 minutes. Spike chemicals were added to the day tank to create the targeted concentrations as described above. The day tank was then stirred to aid equilibrium and dissolution of the spiked constituents. While the spike salts were selected based on solubility, based on the analytical results, several spikes did not dissolve or emulsify to a large extent in the water. Examples include oil and grease and lead spikes, where the concentrations were recovered in the unfiltered water analysis, but very little was recovered

in the filtered fraction. For oil and grease, little was recovered in the initial analyses, although a sheen was seen on the top of the tank water and the water pumped to the columns appeared to have oil drops mixed in the water.

A Teflon<sup>TM</sup> cone splitter (USGS/Dekaport) was used to distribute water evenly among the 10 columns. Because of the nature of the test water, a bilge pump was used to transfer test water from the day tank to the cone splitter (see Figure 2 Right). Water was pumped to the column until the water level on top of the column reached a level of 15 cm (6 inches) above the media. This corresponded to the maximum ponding depth expected in the field. After the media was saturated each day and a steady flow was achieved, the treatment flow rate was measured by collecting a volume of water in a small clean bucket and measuring the time it took to collect the volume with a stopwatch. Columns were refilled once the water level dropped to the level of the top of the media. The time that the pump was on was recorded using a stopwatch. When the flow rate dropped below 5 m/day, the top of the media was disturbed. When disturbing the media no longer benefited the flow rates, the top 0.025 – 0.5 m (1 – 2 inches) of media were removed from the affected column.

Separate effluent water samples were collected after treatment in each column for the analysis of the constituents listed in Table 4. Samples were collected on the first day, and then periodically throughout the testing. Influent water was collected from one of the tubes distributing water to the columns.

**Short-Term Contact Time Depth Breakthrough Tests.** The purpose of this series of tests was to investigate the impact of media contact time on pollutant removal. Contact time was controlled by adjusting the media depth in the columns. These tests involved intermittent loading of the filter columns for five sampling days (to approximately 20 m of volumetric loading, depending on the flow rate through the media). These tests were performed in two separate filtering setups. For each test setup, twelve columns were constructed as described in the prior section. Two columns of each media or mix were 0.97 m (38 inches) in depth, one was 0.66 m (26 inches) and one was 0.36 m (14 inches). The first test setup investigated the effects of media depth on pollutant removal for the mixes R-SMZ, R-SMZ-GAC, and R-SMZ-GAC-PM (see Table 3 for percentages of each component in the mixture). The second test setup investigated the same effects, but for three media components separately (each were mixed with 50% by volume with the site sand for hydraulic purposes, as described earlier): GAC, PM, and SMZ. These media components were selected based on the testing results from the long-term tests.

#### **Analytical Methods**

Table 4 lists the analytical methods used during this project for the pollutants of interest for this paper. The limits of detection routinely obtained are all well below the site benchmark limits, except for mercury which was somewhat higher than the associated limit.

**Table 4. Analyses Supporting Media Tests**

Test Constituent	Method Number	Limit of Detection (LOD)	Site Benchmark Permit Limit
Oil & grease <sup>1, 2</sup>	EPA 1664	2.1 mg/L	15 mg/L
Mercury <sup>1</sup>	Standard Methods 3500-Hg.B cold vapor fluorescence	0.2 µg/L	0.13 µg/L
TCDD <sup>1</sup>	EPA 1613	$6.3 \times 10^{-7}$ µg/L	$2.8 \times 10^{-8}$ µg/L
Perchlorate <sup>3</sup>	EPA 314.0	4 µg/L	6 µg/L
Gross alpha radioactivity <sup>1</sup>	EPA 900	1.2 pCi/L	15 pCi/L
Gross beta radioactivity <sup>3</sup>	EPA 900	2.0 pCi/L	50 pCi/L
Tritium <sup>3</sup>	EPA 906	180 pCi/L	20,000 µg/L
Uranium <sup>3</sup>	ASTM 5174	0.29 µg/L	20 pCi/L
Strontium-90 <sup>3</sup>	EPA 905	1.2 pCi/L	300 pCi/L
Radium 226+228 <sup>3</sup>	EPA 903 (Radium 226) and EPA 904 (Radium 228)	0.6 pCi/L	5 pCi/L

Footnotes:

- 1: constituents in untreated stormwater that may periodically exceed permit limit >1% of the time over long monitoring periods
- 2: constituents that likely affect performance of media in removing contaminants
- 3: other constituents listed on permit, but are expected to rarely, if ever, exceed limits over a long period

## RESULTS AND DISCUSSION

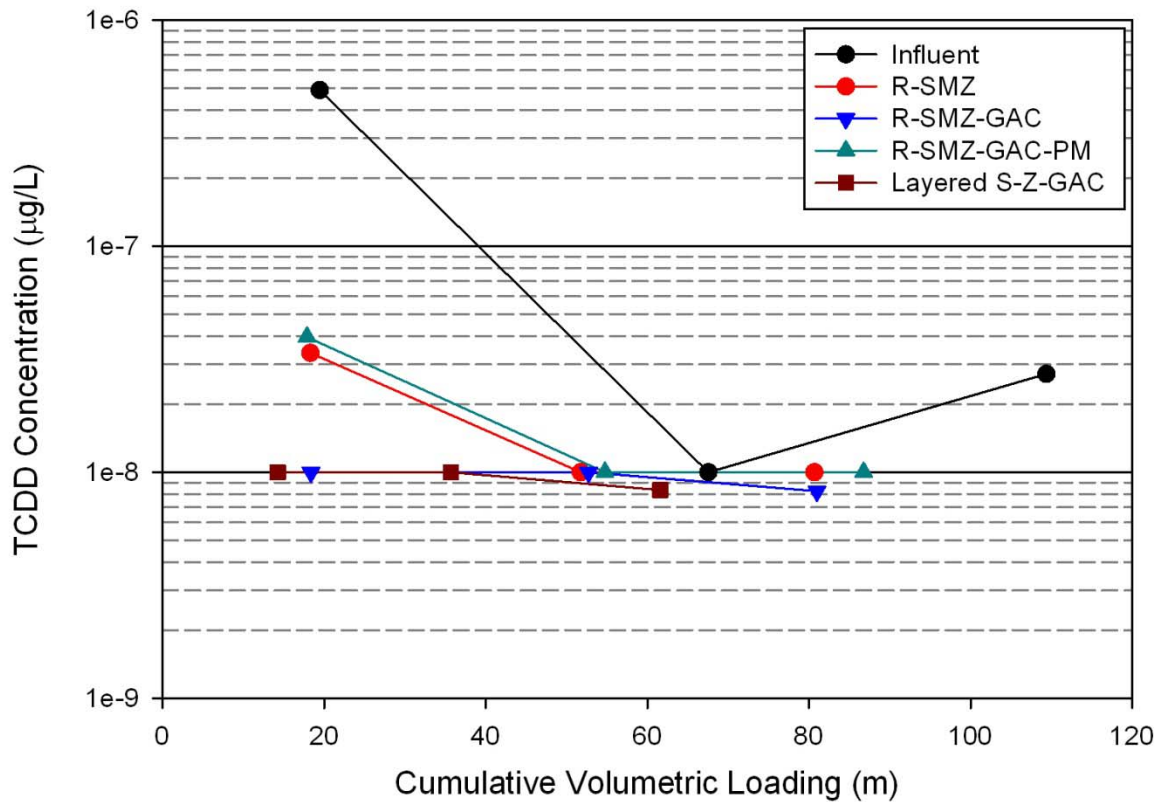
For the long-term chemical breakthrough testing, the tests were performed using a 0.97-m media depth for the mixtures described in Table 3. Because of the analytical expense, these parameters were only analyzed three times during the test period. Because of initial problems in spiking suitable concentrations of oil and grease, mercury and perchlorates into the water during the long-term column tests, these three constituents were also examined during the contact time column tests where different depths of media (0.97, 0.66, 0.36 m) were examined for their effectiveness. The first constituents discussed in this section will be those that were analyzed only during the long-term column breakthrough testing, followed by the other constituents.

**Dioxin.** When the influent had a comparatively high concentration of TCDD, the removals by all media were excellent and, after the first sampling event, were below the permit limit of  $2.8 \times 10^{-8}$  µg/L for all media. The media that tended to have the best performance were those with the higher concentration of GAC (R-SMZ-GAC and Layered S-Z-GAC). Literature-reported Kow values for dioxins typically exceed 10,000, indicating that dioxin are hydrophobic and should have a strong affinity for carbon media. The comparatively-high initial result for the effluent of



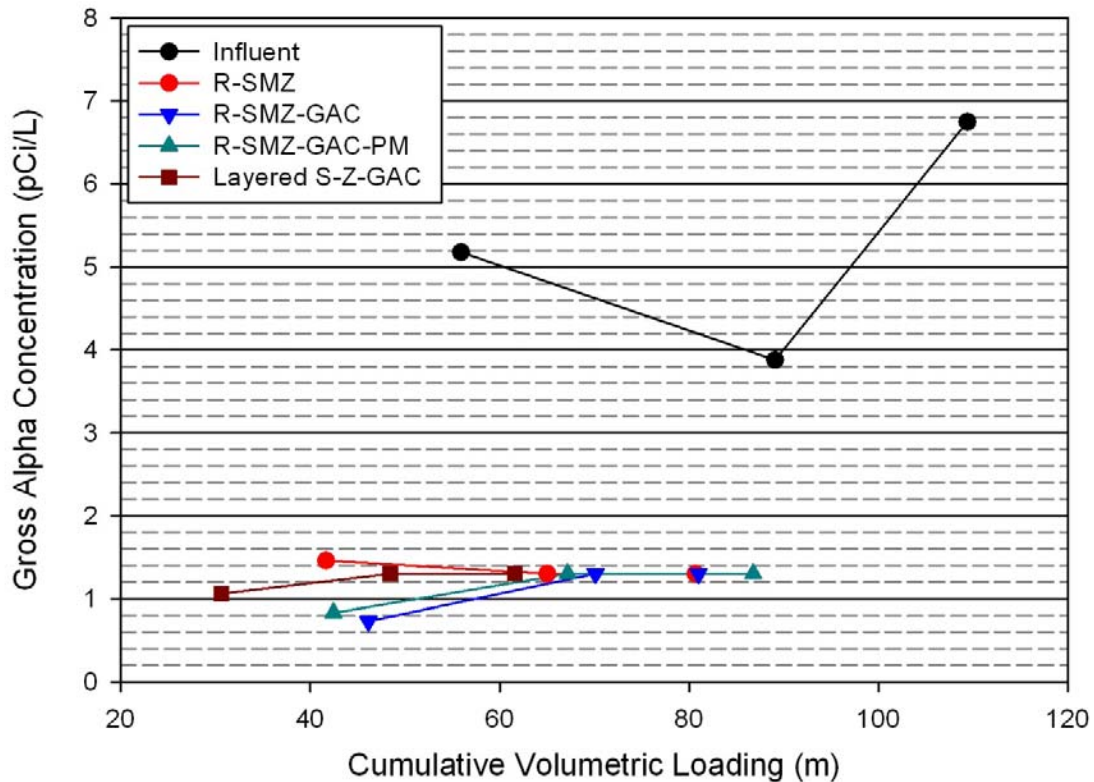
the R-SMZ-GAC-PM column was unexpected since it was anticipated that the peat moss would add an additional source of carbon for dioxin uptake. Studies on PAHs have indicated that peat moss can provide excellent removals for hydrophobic compounds. It is possible that, since peat moss is a natural media and dioxin contamination has been documented throughout the world, the peat moss had been contaminated with dioxin and this result reflected a flushing out of small media particles that contained dioxin.

As shown in Figure 3, it does not appear that any of the media show breakthrough. Effluent concentrations remain constant and low throughout the testing period. Therefore, these can be treated as independent observations of filter performance (see full justification for this approach in Clark, 2000) and statistical comparisons of influent versus effluent can be performed. A paired sign-test (nonparametric since the underlying data distribution is unknown) showed that only the R-SMZ-GAC and Layered S-Z-GAC columns had statistically-significant differences between the influent and effluent at a significance level of 0.05. These results indicate that, especially given the very small sample size, this GAC added to bioretention media can remove dioxin down to below the permit limits and detection limits through 60 to 80 m of volumetric loading.

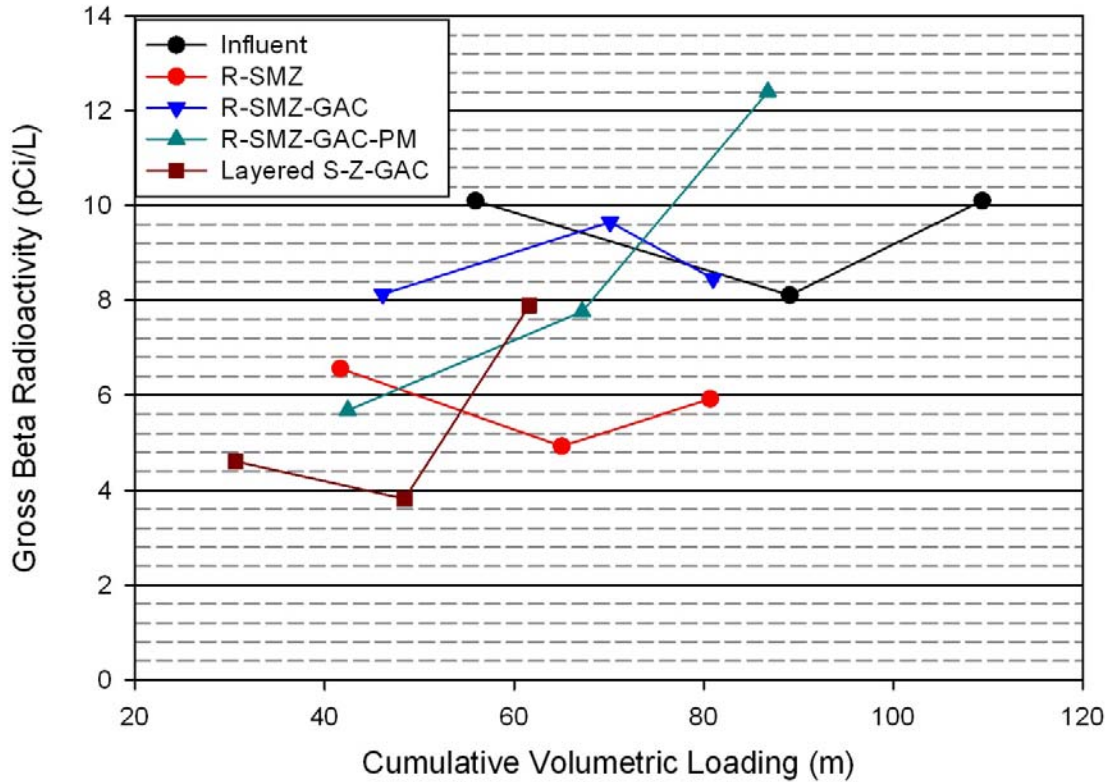


**Figure 3. Dioxin (Total TCDD) Breakthrough Curve for Bioretention Media Mixtures.**

**Gross Alpha and Gross Beta Radioactivity.** Figures 4 and 5 show the breakthrough curves for gross alpha and gross beta radioactivity. All of the media mixtures were able to reduce gross alpha radioactivity to the analytical detection limits. Since breakthrough was not observed during this test, the three measurements for each medium can be considered independent observations, i.e., the effluent concentration does not appear to be influenced by the amount previously removed by the media. A paired sign-test showed that statistically significant removals occurred in each mixture. However, these removals were not seen for gross beta radioactivity (Figure 5). These results show that the mixture with 10% peat moss appeared to break through between 60 and 80 m of cumulative stormwater load on the media. The mixtures with GAC had poorer performance than the R-SMZ mixture, which contained no GAC. These results illustrate the trade-offs that may have to be made when selecting a bioretention media to address multiple constituents, and illustrate why testing of only the pollutants and not understanding the exchanging ions' effect can result in the release of undocumented problems, potentially at levels of concern.

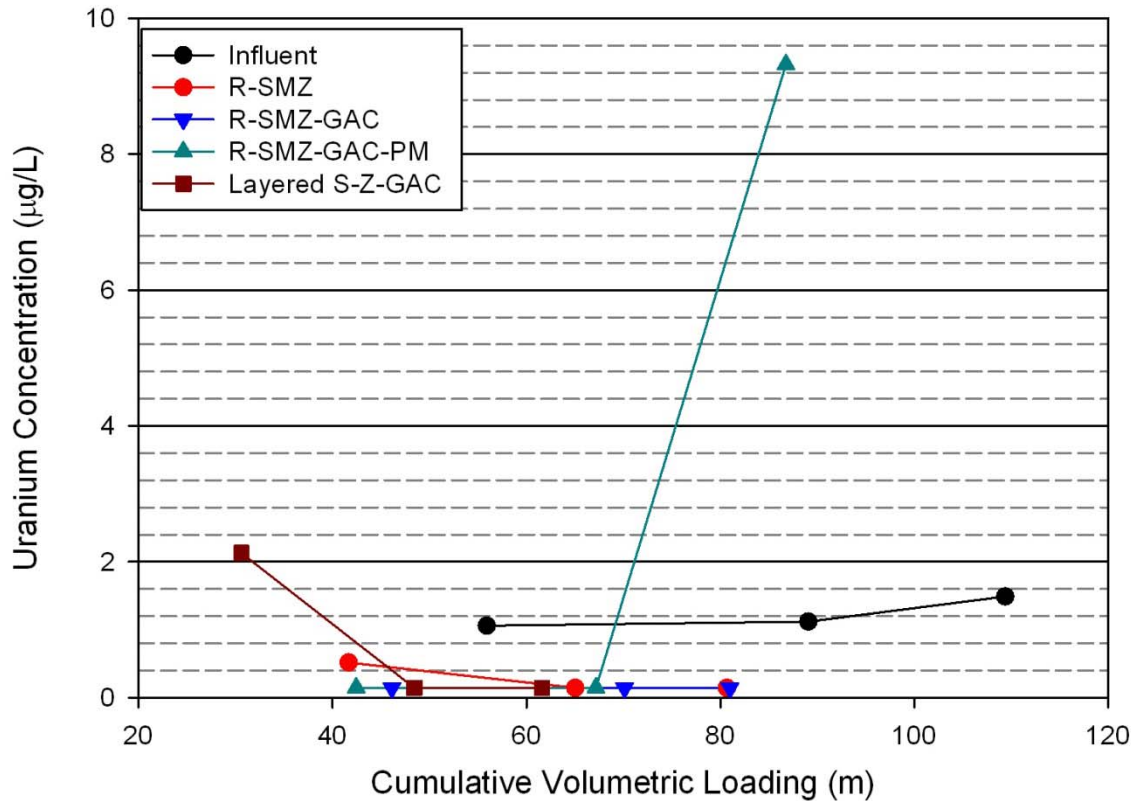


**Figure 4. Gross Alpha Radioactivity Breakthrough.**



**Figure 5. Gross Beta Radioactivity Breakthrough.**

**Uranium, Tritium, Strontium, Radium 226+228.** In the case of tritium and strontium, removal abilities could not be determined because both the influent and effluent concentrations were below the detection limits. All media mixtures were able to remove uranium, as shown in Figure 6, although it appears that the mixture with peat moss reached breakthrough at between 60 and 80 m of cumulative stormwater loading and the layered S-Z-GAC had an initial sample whose effluent was greater than the influent. Because replicate columns were not tested, it is unknown whether the higher layered effluent reading was a valid result. For radium 226+228, with the exception of the mixture containing peat moss, the variabilities of the influent and effluent sample concentrations were large enough to overshadow any removals occurring in the media mixtures. For the R-SMZ-GAC-PM mixture, the effluent radium 226+228 averaged about 0.18 pCi/L, compared to average influent concentrations of about 0.92 pCi/L.

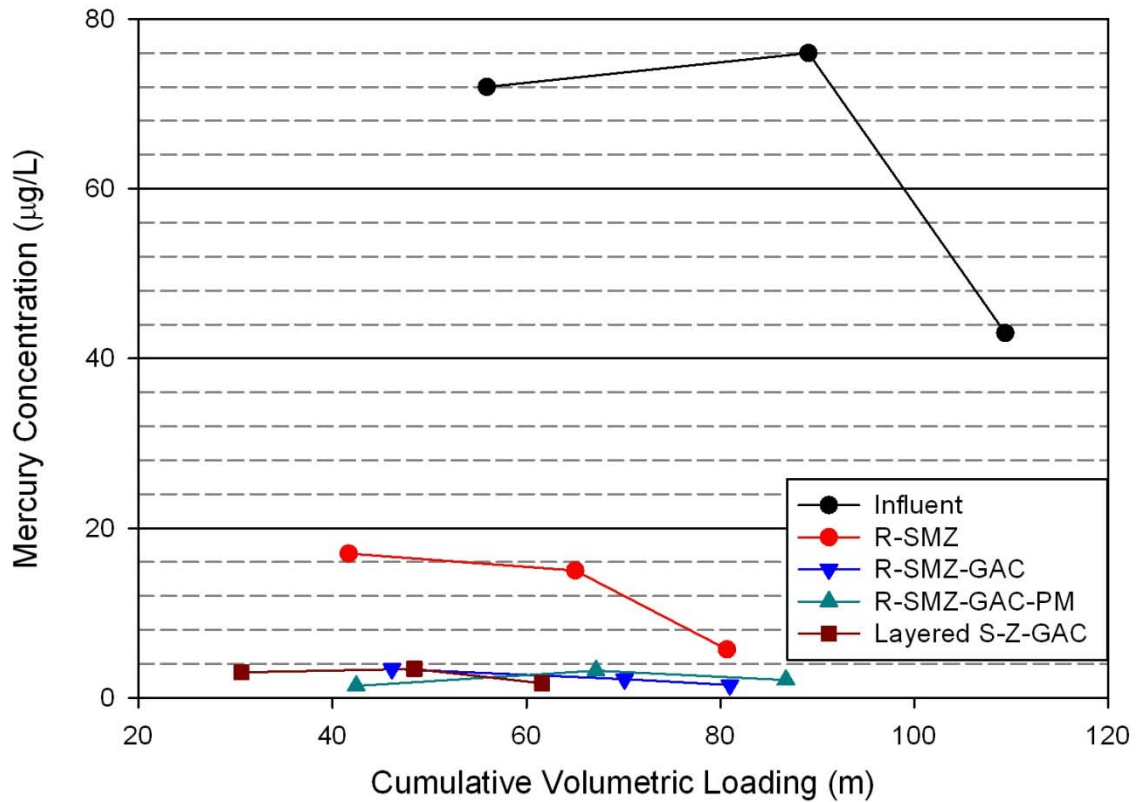


**Figure 6. Uranium Breakthrough.**

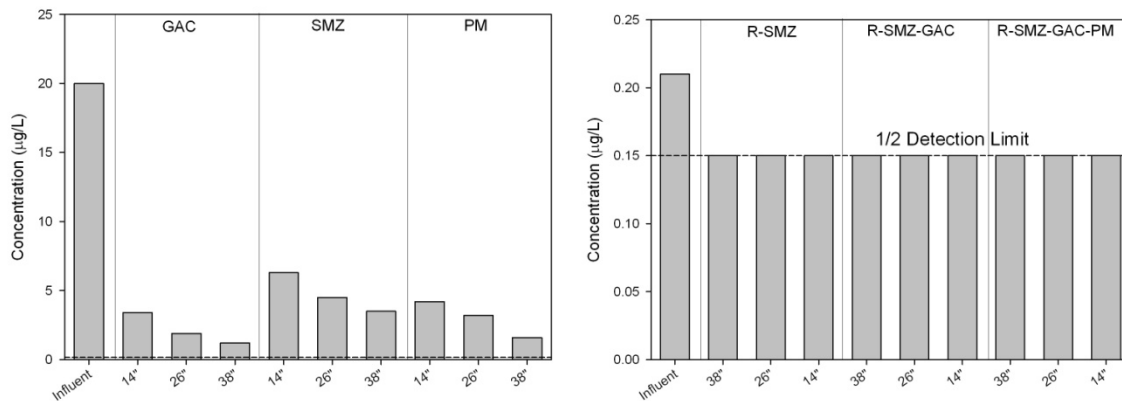
Mercury, oil and grease, and perchlorate were analyzed both during the long-term column breakthrough testing and during the investigation of contact time, as controlled by media depth. In the breakthrough testing, these pollutants were analyzed three times, similar to the pollutants described above. In the column contact time testing, they were analyzed only once per column at the end of the experiment. The end of the column contact time experiment correlated with approximately 20 m of stormwater loading. The contact column experiments were performed on both a subset of component media and on the mixtures described above, except for the layered S-Z-GAC media.

**Mercury.** Figure 7 shows the breakthrough curves for mercury for the mixed media columns during the long-term breakthrough tests. As the results show, all media mixtures were able to provide excellent removal of mercury. A paired sign-test showed that the removals were statistically significant. Figure 8 shows the contribution to the removals for each of the potentially chemically-active media components, along with the effect of depth on the removal ability. For the potential mixture components, GAC may have slightly better removal ability, but it is not substantially different from the surface modified zeolite or the peat moss. For all three potential mixture components, an increase in column depth resulted in a decrease in effluent concentration. However, for the mixtures themselves, the depth of the column had little effect on

the removal ability, as all effluent samples had non-detectable mercury concentrations. This was likely due to the fact that the measured influent concentration of mercury was much smaller during these mixed media tests than in the component tests or the long-term breakthrough tests. These results, though, do agree with the results of the column breakthrough testing, where the mixture composition did not impact the significant removal of the mercury.



**Figure 7. Mercury Breakthrough.**

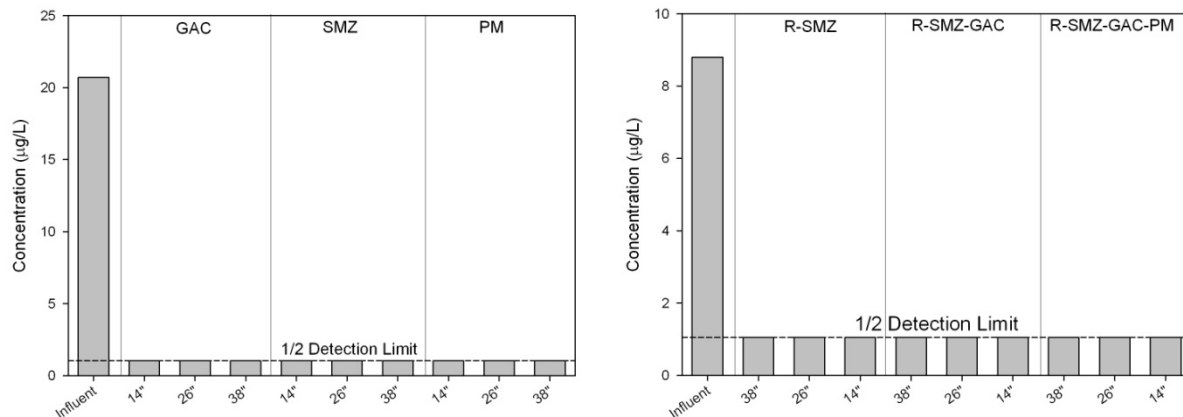


**Figure 8. Mercury Influent and Effluent Concentrations for Media Mixture Components (left) and Mixtures.**

As indicated by the results for the long-term breakthrough and mixture component testing, if the influent mercury concentrations are high, then the media may not be able to meet the low discharge benchmark value. However, the peak mercury concentration observed at the site has only been slightly greater than 0.2 µg/L, so the media tested are likely to reduce this low influent value to concentrations less than the benchmark value.

**Oil and Grease.** All of the media containing GAC during the long-term breakthrough column tests, except for the layered S-Z-GAC, were able to treat the influent oil and grease down to the analytical detection limits. However, two out of the three influent samples also had concentrations at the detection limits due to problems associated with spiking oil and grease to the influent water.

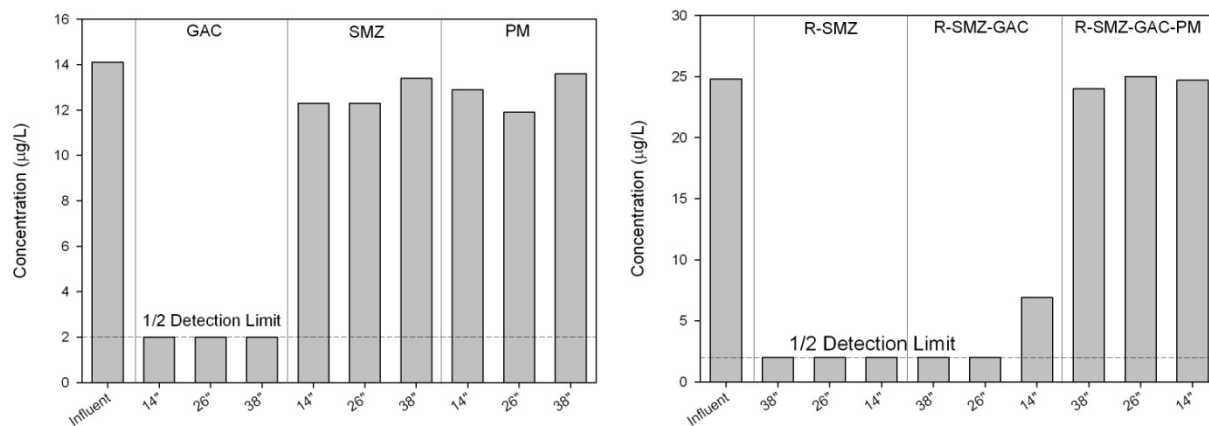
Figure 9 shows the treatability of oil and grease by the components and media mixtures as a function of column depth. For oil and grease, the depth of the column was not a factor in removals, as all of the effluents were below the detection limits, with all of the component media and mixtures able to provide excellent removals of oil and grease. Based on the literature, it would be expected that oil and grease may be preferentially removed by the GAC and peat moss because of their organic content. However, the R-SMZ mixture performed equally as well.



**Figure 9. Oil and Grease Component and Mixture Contact Time Evaluations.**

**Perchlorate.** In the long-term column breakthrough testing, the added perchlorate was not recovered in the influent and the concentrations were therefore too low to measure or evaluate. However, perchlorate removals were measureable and evaluated using the varying depth column tests. Figure 10 shows the ability of the media components and mixtures to remove perchlorate from the water. Unlike dioxin, perchlorate is highly water soluble and has a low Kow. It would

be anticipated that its primary removal mechanism would be through ion exchange and not through uncharged-ion reactions with the media surface. Perchlorate is a negatively charged ion (valence charge of -1) and it would be expected to be removed by media with anion exchange capacities. Anion exchange capacity was not measured during this study and it is not measured typically in any study of pollutant treatability using media filters, but the results indicate that GAC may have a measurable anion exchange capacity.



**Figure 10. Perchlorate Contact Time Evaluation for Component Media (left) and Media Mixtures (right).**

For the GAC alone (with the site sand), the effluent concentrations were all below the detection limit. For the media mixtures, both the R-SMZ and R-SMZ-GAC columns were also able to treat perchlorate to the detection limit. Since SMZ showed minimal removal ability in the components' testing, this result was unexpected. Rhyolite was not tested for perchlorate as an individual component, so it is not known if the rhyolite was the source of the removal. However, given the poor removals in the mixtures containing rhyolite and peat moss, it is not anticipated that the rhyolite was a substantial contributor to treatability.

The advantage to analyzing for a suite of pollutants, rather than just the targeted ones, is that other issues that affect design may become apparent. For example, the selected GAC provided excellent removals of the dioxins and perchlorate, but comparatively added little to the removal for many of the other pollutants. In addition to the pollutants described in this paper, the influent and effluent were also analyzed for more conventional parameters, with the results reported in Pitt et al. (2010). This GAC, which was effective for the removal of dioxins and perchlorate, also was effective at removing nitrate, but flushed out phosphorus and potassium. For this project, where phosphorus and potassium were not constituents of concern, the GAC would be an excellent medium to include in a final mixture. However, in a phosphorus-limited watershed, the magnitude of the phosphorus release and the uptake by the plants would need to be considered before the GAC was selected for the bioretention media. Clark and Pitt (2010) and Pitt et al.

(2010) review the trade-offs in potential pollutant removal when selecting bioretention media and highlight the limitations of studies that do not investigate these trade-offs. In addition, while this GAC performed well in these studies, not all GAC is equal in performance. The GAC used in Clark (2000) did not provide the same treatability for nitrate as this GAC did and therefore, it would be anticipated that, at least for the perchlorate ion, treatability would also be reduced.

## CONCLUSIONS

Bioretention has been promoted in many studies as an effective way to reduce the loading of solids, nutrients, and heavy metals to surface waters from urban runoff. Bioretention, however, has not been widely studied as a potential treatment device for organic and radioactive toxicants. This study showed that the testing of potential component media in a series of column tests can provide rapid information about the media's effectiveness. In addition, it showed that bioretention media, when carefully selected based on chemical properties of the pollutants and media, has the potential to remove organic toxicants, potentially down to very low permit limits. The following are the major findings from these tests:

- When the influent had a comparatively high concentration of TCDD, the removals by all media were excellent and generally were below the very low permit benchmark limit of  $2.8 \times 10^{-8}$   $\mu\text{g/L}$  for all media tested. However, the media that tended to have the best removal performance of TCDD were those with the higher amounts of GAC in the mixture.
- All of the media mixtures were also able to reduce gross alpha radioactivity to the analytical detection limits, but gross beta removals were only found to be significant for the layered S-SMZ-GAC and for the R-SMZ mixtures.
- All media mixtures were able to remove uranium, although the mixture with peat moss reached breakthrough at a high loading rate.
- All media mixtures were able to provide excellent removal of mercury. Increases in column depth resulted in a decrease in effluent mercury concentrations.
- All of the media containing GAC during the long-term breakthrough column tests, except for the layered S-Z-GAC, were able to treat the influent oil and grease down to the analytical detection limits.
- For the GAC alone (with the site sand), the effluent concentrations of perchlorate were all below the detection limit. For the media mixtures, both the R-SMZ and R-SMZ-GAC columns were also able to treat perchlorate to the detection limit.



The results for mercury, oil and grease, and some of the radioactive constituents, though, reinforced the result seen by many other researchers, that there a lower limit to the removal ability when using stormwater treatment practices.

The most robust biofiltration media for the treatment of a broad range of stormwater constituents to low concentrations would be a mixture of several components that offer complimentary treatment mechanisms.

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