Laboratory Evaluations to Support the Design of Bioretention Systems in the Southwestern U.S.

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Abstract
This paper describes the detailed laboratory tests of biofiltration media that are being considered for use in engineered stormwater treatment systems proposed for a large field site in the southwestern United States. These stormwater treatment systems were designed to treat 90% of the long-term runoff volume from drainage areas ranging from 5 to 60 acres at the site. The main pollutants of interest for the project include cadmium, copper, lead, and dioxins, and the effluent concentrations had to meet design criteria that are based on numeric effluent limits that are applied to stormwater discharges through the site’s NPDES permit. An additional 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, therefore the tests needed to simulate site-specific conditions by adjusting raw influent samples to representative levels, where possible. The purpose of this study is to determine optimal biofiltration media combinations and contact times (based on achievement of permit limits in treated effluent), hydraulic properties, and clogging/breakthrough frequency for design purposes and maintenance planning.

Information Needs to Support Bioretention/Biofiltration Designs
The final design, including sizing, of a biofiltration or bioretention treatment system at a specific location requires various types of information. The media information that is needed to size a bioretention or biofiltration device can be separated into several categories, including:

1) flow rates. The treatment flow rate that can be handled by the media is of critical importance. This rate must be adequate to treat most of the annual flows in the smallest area possible. However, too rapid of a flow rate through the media may result in poor treatment. Changes in flow rate with use are also needed to be known.

2) clogging potential. The service life of the media is usually limited by the amount of sediment that can be accumulated both on the surface and in the pore space before the treatment flow rate becomes so low it requires maintenance or replacement. The efficacy of the maintenance also needs to be known.
3) contaminant treatment. The main purpose of a stormwater treatment device is to reduce discharge mass or concentrations to levels below critical values, which are usually set by a regulatory agency.

4) chemical treatment capacity. Contaminant removal is usually finite, based on the removal capacity of the media. The media would have to be replaced when it becomes exhausted. The capacity usually varies for different contaminants of interest, and this maintenance interval needs to be compared to the clogging maintenance interval.

5) other operational and performance issues. Residence time in the media may affect pollutant removal, media may be a source of some contaminants due to leaching, captured contaminants may be released during varying chemical conditions in the media, controlled drainage of the treated water can be difficult, etc.

This paper summarizes our experimental efforts and some of our results pertaining to these issues.

**Laboratory Media Evaluation Tests**

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). They were designed 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 for the project include cadmium, copper, lead, and dioxins, with effluent concentration design criteria that are based on stringent water quality criteria expressed as numeric effluent limits. These are applied to site stormwater discharges through a NPDES permit for the site. The drainage areas consist primarily of steep catchments with significant open space comprised primarily of chaparral habitat and exposed bedrock (generally sandstone). Significant sediment loads are expected during intense storms.

Prior research has shown that a targeted suite of controlled laboratory tests can effectively evaluate filtration/biofiltration media for stormwater runoff treatment. The tests conducted included 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 uptake capacity of the media for the different constituents; and aerobic and anaerobic retention tests to determine whether pollutant retention is permanent under changing pore water chemistry conditions. These tests were conducted using stormwater collected from the Pennsylvania State – Harrisburg campus with adjustments to bring some of the contaminant concentrations (including sediment loading) into the desired testing range, as determined by site-specific stormwater quality monitoring data.
The media examined included six different materials: rhyolite sand, granular activated carbon (GAC), surface-modified zeolite (SMZ), 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 combinations of these components:

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

<table>
<thead>
<tr>
<th>Media Description</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granular Activated Carbon (GAC)</td>
<td>VCC 8X30 Virgin Coconut Shell Activated Carbon (Baker Corp.); 29 lbs/ft³ (1.8 to 2.1 g/cm³); $0.98/lb</td>
</tr>
<tr>
<td>Rhyolite Sand</td>
<td>D1 biofilter media sand (Rhyolite Topdressing Sand) from Golf Sand, Inc., North Las Vegas, NV; 75 in/hr infiltration rate; particle density 2.38 g/cm³; bulk density 1.28 g/cm³; 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.</td>
</tr>
<tr>
<td>Site Zeolite</td>
<td>Z-200 Modified Zeolite (Baker Corp.); $1.36/lb</td>
</tr>
<tr>
<td>Surface Modified Zeolite (SMZ)</td>
<td>14-40 Saint Cloud Zeolite with 325 µm Modified Zeolite at 3% Vol:Vol</td>
</tr>
<tr>
<td>Sphagnum Peat Moss (PM)</td>
<td>Purchased from nursery in Elizabethtown, PA</td>
</tr>
<tr>
<td>Site Sand</td>
<td>Fine textured silica sand</td>
</tr>
</tbody>
</table>

Major Testing Phases

1) **Clogging, breakthrough, and removal tests.** In these traditional 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 test water was a modified stormwater.

2) **Contact time and media depth tests.** These tests determined the effect of contact time (controlled by the media depth for a given loading rate) on pollutant removal. For many of the filterable pollutants, longer contact times should enhance pollutant removals. Increased contact time corresponds in the design to either larger surface areas (to distribute the flow and reduce the loading rate) or increased media depths. These data enable more detailed calculations of expected performance to be made for the treatment systems for the candidate media.
3) **Media batch tests.** These traditional kinetics batch tests have been adapted to meet the range of conditions seen in stormwater filtration. The purpose of these tests is to determine the amount of contaminant that can be retained by the media, given a specific contact time. These tests, unlike some of the tests reported in the literature, are multicomponent tests with stormwater as the base test water.

4) **Aerobic and anaerobic effects on contaminant retention in media.** These tests examined long-term retention of captured pollutants by the media under varying porewater chemical conditions.

**Study Findings**

**Flow Rates and Particulate Loadings before Maintenance**

The following chart shows the typical flow rates observed for each of the ten media combinations tested, along with the accumulative sediment load to initial maintenance.

It is desired to use media having a moderate flow rate (to provide suitable contact time for treatment) and a long run time before maintenance (and certainly clogging) occurs. The above chart shows that the site sand has too low of a flow rate and a low loading before clogging occurs limiting its use for filtration purposes. The GAC, in contrast, has too rapid of a flow rate for adequate contact time and removal effectiveness. The media combinations, which include layered and blended combinations, provide better balances of flow rates and loading before clogging.

![Figure 2. Flow rates and clogging of media and mixtures.](image)
Infiltration rates typically decrease over a device’s life due to solids capture on the surface of and in the media, as shown on the following plot for the peat moss column tests. We examined potential maintenance options once the flow rate decreased to 5 m/d. The options examined included disturbing the surface of the media vs. removing several inches of the media from the top of the filter. The removal of the media from the surface of the column was generally more effective than simple disturbing the media surface, but removal of at least 4 – 6” was needed because clogging solids are captured deep in the media (deeper than visible solids buildup). However, these maintenance options had relatively minor benefits. As shown on the plot above, the run times after maintenance were only about ½ to 1/4th as long as the run time before the initial maintenance.

![Flow Rate vs. Cumulative Solids Loading: Peat Moss](image)

**Figure 3. Flow rate and clogging example for peat moss.**

**Statistically Significant Removals for the Tested Media Mixes**

The following table lists the media combinations that had the most significant removals of selected constituents. The significance levels were determined using the paired sign test comparing the influent vs. the effluent water quality. It should be noted that these tests were not conducted in random order, but in a time series. They therefore are likely strongly serially correlated. The sign test was not corrected for these serial correlations for these evaluations. Because of the small number of replicate observations during these tests, the confidence level used for this table is generally at p=0.1, and lower. The yellow high-lighted columns are the constituents of greatest concern at the site monitoring locations.

In terms of statistically significant removals, both R-SMZ-GAC and S-Z-GAC (layered) media combinations performed similarly, although the current site layered media combination didn’t demonstrate statistically significant removals for lead. As shown in the detailed test results in the full report, the bioretention media combinations met all current site permit limits, except for copper and mercury during
peak conditions, and had significant removals for all constituents measured, except for phosphorus and gross beta radioactivity. The current site layered media combination resulted in all effluent samples meeting the current site permit limits, except for a slightly elevated pH, when maximum site runoff conditions were considered. In addition, most of the media combinations were effective for Cu and Pb reductions (the site does not need to reduce the filtered metal fractions to meet permit limits). Also, any media combination that included GAC was effective for TCDD removal.

Table 2. Significant Removals for Media Mixture Tests

<table>
<thead>
<tr>
<th>Media Type</th>
<th>SSC</th>
<th>As, B</th>
<th>Cr, Cu, Sb, Al</th>
<th>Pb, Zn</th>
<th>Mn</th>
<th>Cd, Ni, Ti, Fe</th>
<th>Hg</th>
<th>NO3</th>
<th>TN</th>
<th>TP</th>
<th>TCDD</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-SMZ T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T, F</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-SMZ-GAC T</td>
<td></td>
<td>T, F</td>
<td>T, F</td>
<td>T</td>
<td>T</td>
<td>T, F</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>R-SMZ-GAC-PM T</td>
<td></td>
<td>T, F</td>
<td>T, F</td>
<td>T</td>
<td>T</td>
<td>T, F</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>S-Z-GAC (layered) T</td>
<td></td>
<td>T, F</td>
<td>T, F</td>
<td>T</td>
<td>T</td>
<td>T, F</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

R = rhyolite; SMZ = surface modified zeolite; GAC = granular activated carbon; PM = peat moss; S = site sand; Z = site zeolite

T = significant removal for total forms; F = removal for filtered form only (passed through 0.45 µm membrane filter)

Long-Term Removal as a Function of Pollutant Form

All of the individual media and mixture tests demonstrated excellent removals of solids and particulate-associated pollutants. However, the removal of dissolved, colloidal, or complexed components varied greatly by media type. For example, the following plots show the removal of total and filtered forms of copper for the different media.
The primary removal mechanism in the media is physical straining/removal of particulate-associated copper. The best removal of copper was by GAC, followed by peat, which may be related to organic complexation of copper in the influent water or complexation with the organic content of the media. Poorer removal of filtered copper was observed by zeolites (typically associated with CEC removal mechanisms) and sands (only physical straining mechanisms).

Of the individual media types studied, peat and the GAC demonstrated the best removals for total and dissolved copper, even with the relatively high influent concentrations.

It may be asked if the zeolite and sand contact times were too low to allow for substantial removals of filtered copper by CEC. This is not thought to be an issue for these tests. Copper complexes likely formed which are not readily removed by cation exchange, but sorption by the GAC was effective. However, peat moss was also reasonably effective, which offers high CEC capacity, but possibly also destabilized the complexes with the pH drop in the media, or the copper formed complexes with the organics in the peat. The filtered copper includes colloids and organometallic complexes also, plus copper readily forms amalgams with zinc; it is possible that only small fractions of the filtered copper were in ionic forms and therefore amenable for cation exchange (Clark and Pitt 2010).

**Long-Term Removal: Effects of Media Mixtures on Pollutant Removals and Breakthrough**

The following examples show that nitrate removal is excellent in mixtures containing GAC. However, breakthrough occurs more rapidly as the fraction of GAC in the media mix decreases. Similar trends were noted for the removal of zinc in mixtures containing SMZ, although it is not as pronounced.
Figure 5. Breakthrough of nitrate and zinc.

Figure 6 is an example line plot for filtered arsenic showing how most of the removal by the different media types decreased in performance with time: initially, the Ce/Co values (ratio of effluent to influent concentrations) were quite low indicating high removal rates, however, the ratios increased with increasing treatment volumes, with several of the media indicating eventual breakthrough.

Figure 6. Breakthrough plots for filtered arsenic full-depth column tests showing both flushing for peat moss and breakthrough for several of the media types.

As the loadings increase, even for constituents that did not show any breakthrough, the potential for media clogging by particulate matter also increases. Therefore, there is a practical upper limit to the chemical capacity estimates based on likely premature failure due to clogging. In fact, unless supported by extensive pre-treatment to
remove the particulates most likely to cause clogging, it is very likely that most stormwater treatment media will have chemical removal capacity remaining when the system fails due to clogging. This may not necessarily be such a bad condition, as extra treatment capacity offers a margin of error during periods of unusually high contaminant concentrations. Also, completely “saturated” media may potentially present disposal problems. During TCLP leaching tests of saturated treatment media as part of prior stormwater research, Johnson, et al. (2003) only identified potential TCLP leaching problems associated with cadmium during tests of stormwater treatment of heavy metals. However, they found that clogging would most likely occur well before the cadmium could reach problematic levels in the different treatment media, for example.

The amount of the different media types in each test column obviously affects these unit area treatment capacity calculations. Table 3 lists the amount of each media type used in the full-depth columns. The mixtures were created on a volume basis, while the treatment capacities depend on the mass of the different materials. In the single medium tests, the test medium was mixed with an approximate equal volume of the site filter sand. This was done to moderate the flows. As found during prior filter media research (Clark 2000 and Clark and Pitt 1999), coarse material resulted in too high of a treatment flow rate that caused very low residence time in the filters, and reduced performance. For fine or organic material (such as the peat moss), the mixtures had too low of a flow, causing immature clogging. The organic material would compress and dramatically restrict flows. By mixing these with a filter sand (or the rhyolite sand), the organic material was supported by the sand grains reducing compaction problems, and the filter sand provided a reasonable flow path for finer grained media. This fundamental mixture resulted in a much more balanced flow rate for the different media types, along with reasonable contact times for treatment.

Table 3. Capacity of Filter Columns for Retention of Selected Contaminants
(mg/m² of filter surface)

<table>
<thead>
<tr>
<th></th>
<th>GAC</th>
<th>Peat Moss</th>
<th>Rhyolite Sand</th>
<th>Site Sand</th>
<th>Site Zeolite</th>
<th>SMZ</th>
<th>R-SMZ-GAC</th>
<th>R-SMZ-GAC-PM</th>
<th>Site Sand-GAC-Site Zeolite Layered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium, Total</td>
<td>&gt;4,380</td>
<td>&gt;4,250</td>
<td>&gt;4,890</td>
<td>&gt;1,660</td>
<td>&gt;5,590</td>
<td>&gt;5,110</td>
<td>&gt;5,120</td>
<td>&gt;5,160</td>
<td>&gt;5,420</td>
</tr>
<tr>
<td>Copper, Total</td>
<td>&gt;8,280</td>
<td>&gt;7,440</td>
<td>&gt;6,390</td>
<td>&gt;2,450</td>
<td>&gt;7,400</td>
<td>&gt;6,880</td>
<td>&gt;6,180</td>
<td>&gt;9,490</td>
<td>&gt;9,140</td>
</tr>
<tr>
<td>Lead, Total</td>
<td>&gt;729</td>
<td>&gt;707</td>
<td>&gt;803</td>
<td>&gt;275</td>
<td>&gt;938</td>
<td>&gt;824</td>
<td>&gt;857</td>
<td>&gt;860</td>
<td>&gt;911</td>
</tr>
<tr>
<td>Mercury</td>
<td>not tested</td>
<td>not tested</td>
<td>not tested</td>
<td>not tested</td>
<td>not tested</td>
<td>not tested</td>
<td>not tested</td>
<td>&gt;4,120</td>
<td>&gt;4,960</td>
</tr>
<tr>
<td>Oil and Grease</td>
<td>not tested</td>
<td>not tested</td>
<td>not tested</td>
<td>not tested</td>
<td>not tested</td>
<td>not tested</td>
<td>not tested</td>
<td>16,700</td>
<td>&gt;32,400</td>
</tr>
<tr>
<td>TCDD</td>
<td>not tested</td>
<td>not tested</td>
<td>not tested</td>
<td>not tested</td>
<td>not tested</td>
<td>not tested</td>
<td>not tested</td>
<td>&gt;1.2E-5</td>
<td>&gt;1.3E-5</td>
</tr>
</tbody>
</table>

Ion-Exchanging Media: Trade-Offs between Pollutant Removals and Releases
With ion-exchange, ions must be released as other ions are retained. For example for retention of nitrates on the GAC, phosphates are released early, while chlorides are released later (Clark and Pitt 2010).

**Media Depth Tests: Contact Time vs. Pollutant Removal**

In Figures 7 and 8, cadmium was effectively removed for all media depths in all media types. Low cadmium effluent concentrations were observed for all tests, irrespective of influent concentrations. However, as shown in Figure 9, there was more of a pronounced effect of residence time (media depth) for nitrates for some media types. Also, as expected, low effluent concentrations for ineffective media only occurred concurrently with low influent concentrations.

![Granular Activated Carbon: Anion Capture](image)

**Figure 7.** Ion exchange releases of phosphate and chloride during nitrate removal.
Batch Testing to Optimize Contact Time

Figure 10 shows the effects of contact time on the removal of nickel for the different media. Metal uptake was most significant and rapid for peat moss and GAC. The optimal contact times for metals removal ranged from 10 to 1,000 minutes, depending on the metal and the media type. There were minimal metal removals observed for all media, except for peat, when the contact time was less than 10 minutes. Metal uptake was most significant and rapid for peat and the GAC.
Figure 10. Nickel capacity and contact time tests.

Removal of Particulates

All of the media tested were very effective for the removal of a wide range of particle sizes. Figure 11 shows the removals for very small 0.45 to 3 µm particles and for larger 12 to 30 µm particles in the GAC media, the media with the fastest flow rate.
Figure 11. Removals for different particle sizes.

**Contaminant Losses during Anaerobic and Aerobic Storage Conditions between Events**

Figures 12 and 13 are examples showing the behavior of retained COD and lead on the media during long-term storage tests under both anaerobic and aerobic storage conditions. The stripping of COD was more severe during anaerobic conditions for the media having poor retention mechanisms (the sands).

The lead retention was almost perfect under all conditions for both anaerobic and aerobic storage conditions.

**Chemical Oxygen Demand**

Figure 12. Anaerobic and aerobic storage effects on COD.
Conclusions
These extensive media evaluation tests were unique in that they used a coordinated set of tests with actual stormwater runoff that was spiked to site concentrations (typically lower than urban runoff). A suite of parameters was also analyzed so that interactions and exchanges of pollutants could be evaluated. In addition, many of the constituents on the extensive analytical list have never been tested in stormwater filter/biofilter media evaluations before. Combinations of media in addition to individual materials were also evaluated. In most cases, there were very extensive removals of particulates larger than just a few micrometers in size. The removal of filterable constituents varies, with some materials being more effective than others for different constituents. Therefore, combinations of media are expected to provide the most effective control of stormwater.

The following are the most important conclusions found during these studies:

- During these studies, the media mixtures that had the longest run times before clogging and moderate flow rates were:
  - Sand and zeolite currently in use at the site, with GAC (layered mixture)
  - Rhyolite sand, SMZ, and GAC mixture (much better flow rates and cumulative loading until maintenance and until eventual clogging run times compared to the above layered mixture)
• The Rhyolite sand, SMZ, and GAC mixture met all current site permit limits, except for copper and mercury during peak conditions, and had significant removals for all constituents measured, except for phosphorus and gross beta radioactivity. This mixture, plus the layered sand, site zeolite, and GAC mixture, also met the very low permit limits for dioxins.

• The layered sand, site zeolite, and GAC mixture resulted in all effluents meeting the current site permit limits, except for a slightly elevated pH, which was slightly exceeded for 25% of the samples. The pH was highest in the first sample following column construction. Aging generally reduced the pH.

• The addition of peat to the mixtures improved the removal of certain constituents having relatively low influent concentrations and short residence times, such as during periods of high flows.

• Longer retention times (deeper media beds or slower flow rates and larger surface areas) improved effluent quality for some constituents, but not all. These tests all had relatively slow flow rates and long residence times (5 to 20 meters/day).

• Both anion and cation exchange occurred in media filters, with different releases for different media types. Phosphorus, chlorides, potassium, and sodium were found to be commonly released constituents, along with pH shifts.

• Some constituents and some media required a certain contact time before retention began, while others were more capable of pollutant retention immediately and at lower influent concentrations.

• The development of anaerobic conditions, which may occur in filters that do not experience much water exchange such as between storm events, resulted in the release of some constituents (generally more of a problem for organics and nutrients than for metals).

• Media mixtures performed better than individual components separately.

• Fine grained sands clogged quickly and had poor flow rates, while large-grained media flow too quickly with very short residence times, and likely poorer effluent quality.

• Some constituents had breakthrough before others, but clogging by sediments likely occurred before chemical retention capacity was exceeded for most bioretention devices and media mixtures. Highly effective (sedimentation) pretreatment is therefore critical to reduce the sediment load.
- Maintenance by scraping the surface layers was only partially effective and for only short durations. It is expected that plants in a biofilter, with the underlying media mixtures, will provide the longest run times before clogging.

- Nitrate removals were excellent with the specific GAC that was tested; results for other GACs will likely be different. Breakthrough occurred more rapidly as the fraction of GAC in the media mixture decreased. However, significant phosphorus releases occurred with the GAC.

- Phosphorus and phosphate had significant (but relatively small) removals in the Rhyolite sand, the site sand, the site zeolite and the surface modified zeolite.

- The filtered forms of cadmium, thallium, and nickel had significant removals by most media and met permit limits consistently, while filtered lead and filtered zinc were poorly removed by all of the tested media and mixtures. Filtered copper removals were significant, but small, and were best in the GAC mixtures.

- All of the media tests had very good removals of particulates, even down to very small particle sizes, and concurrent good removals of pollutants strongly associated with the particulates.

- Radionuclide, mercury and dioxins also had significant removals by most of the media mixtures tested (particularly those including GAC for dioxins).

- The media performance studies demonstrated significant advances in optimizing the design and effectiveness of stormwater controls. Although in some cases such design elements (e.g., specially-selected and relatively expensive media) may only be cost-effective for advanced treatment systems at critical source areas.

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References