

## **FILTRATION FOR METALS REMOVAL FROM STORMWATER**

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### **ABSTRACT**

Filtration as a method of stormwater treatment was investigated in a 3-year study. Equilibrium and kinetic studies of metals' capture were performed initially on twelve media. The three best performing media: peat-sand mix, compost, and zeolite were then selected for in-depth study. Upflow filters did not clog as easily as downflow, and longer-term performance was better in the upflow column. Metals were retained on the filters during anaerobiosis. Metal retention by the filters was not different from what was observed in oxygenated environments. Tests also indicated that the heavy metals of concern remain strongly bound to the particulates during long exposures at the extreme pH conditions likely to occur in receiving water sediments. Several media were tested in a pilot-scale device using water from a detention pond that drains a medium-density residential area. In this series of tests, the metals concentrations in the influent were extremely low (near the detection limit of the analysis). When the influent metals concentration was higher, such as shortly after a rain storm, the filters proved effective at removing influent concentrations down to a level of approximately 10 – 15 µg/L. Removals to concentrations lower than that were not possible on a consistent basis.

### **INTRODUCTION**

Heavy metals in urban stormwater primarily originate from automobile-related activities and the exposure of building materials to rain. Heavy metals may occur as dissolved, colloidal or particulate bound species; however most metals are predominantly associated with particulates. Particle associations and speciation critically affect the toxicity and bioavailability of metals and are greatly dependent upon chemical and physical parameters. A successful control strategy for the reduction of heavy metals from stormwater must therefore be effective in capturing a variety of metals that are in the particle-bound, colloidal and dissolved states.

Opportunities for the control of metal-bearing urban runoff can be grouped into three basic strategies: source avoidance/reduction; passive systems; and installed treatment technologies. While the concept of pollution avoidance and minimization at critical sources is the most preferred option, it is unlikely that any one method will provide either a realistic or effective solution to the problem. The scope of this project, funded by the Water Environment Research Foundation (Johnson, *et al.* 2003) was to address emerging stormwater control technologies for the capture of heavy metals from urban runoff, with a focus on media filtration systems and grass swales.

### **METHODOLOGY**

Actual stormwater runoff was used for many of the lab scale tests conducted in this study. The runoff source was a UA campus parking lot in Tuscaloosa. A series of runoff samples

was collected from this parking lot in order to characterize the runoff's quality. Iron, zinc and copper were the most prevalent metals detected in the collected runoff along with small amounts of particulate bound lead.

#### *Lab Studies of Equilibrium and Kinetics*

Twelve media were initially evaluated through batch equilibrium and kinetic tests to compare the rate and extent of metals capture. The three best performing media: peat-sand mix, compost, and zeolite were then selected for an in-depth study column study using parallel upflow columns in packed media beds. Metal removal efficiency was examined for different rates of flow and influent conditions. TCLP tests were performed on the spent media to investigate disposal options. A summary of methods employed follows.

The batch equilibrium and kinetics tests were performed using baffled batch adsorbers constructed according to standardized tank design for Continuously Stirred Tank Reactors (CSTRs), using tanks that were constructed from materials that minimized metal-ion sorption. A known mass of media was added to a stirred tank with a known metals concentration. For the equilibrium tests, the media were exposed to increasing metals concentration with aliquots withdrawn at the end of a pre-specified time period. The purpose was to analyze the metals' uptake based on initial concentration and to assist in understanding uptake based on concentration gradients. For the kinetics test, at increasing time intervals over a four-hour period, aliquots of sample were withdrawn. The results of these experiments indicated the time required to remove a sufficient quantity of metal and should be related to the contact time that will be required in an installed filter. All metals analysis was performed using a Perkin Elmer Inductively Coupled Plasma – Optical Emission Spectrophotometer (ICP-OES) DV3000.

Laboratory-scale filter columns (30-cm media depth) were then constructed for fixed-bed column studies so as to evaluate the dynamic characteristics of the metal capture process. Stormwater runoff was treated using parallel lab-scale upflow filter columns to investigate parameters affecting the breakthrough curve and performance of the column. Stormwater was used in a parametric study to investigate the effect of variables such as media, single and multicomponent metals concentrations, and flowrate on the breakthrough curve (column design details in Johnson, *et al.* 2003). The runoff was collected from a local parking lot prior to testing. Samples of the effluent were collected at regular intervals. Samples of the influent were also collected periodically from the holding tanks throughout the column run to check for changes in the influent concentrations.

#### *The Role of Biomass in Metals Uptake*

Engineered filter systems that have been developed to treat metal-contaminated waters in field situations most frequently develop microbial populations (Pitt, personal communication). The effect of microbial growth within filter systems in stormwater metal retention was studied in laboratory column experiments using sterile and non-sterile column systems. The 'sterile' column was constructed with sterilized sorbent matrix, isolated from light (to prevent growth of phototrophic microorganisms) and fed with pasteurized (at 80°C) stormwater. The non-sterile column containing the non-sterile sorbent matrix, was exposed to light and fed with untreated stormwater. Microbial biomass (as protein) was quantified using the BCA protein determination procedure (Urrutia and Roden, submitted). Metal retention, head loss and pH in both columns were compared to determine the influence of biomass on the capture of metals.

### *Testing of the Pilot-Scale Device*

Testing on the pilot-scale filters was performed in a manner expected to simulate the intermittent use that they would receive in a full-scale application. Eight filtering events were performed, using settled stormwater runoff from two medium-density residential areas in Hoover, AL. Grab samples of approximately 1 L were collected every hour from the effluent of each filter and composited into a sample of that testing day's effluent. A similar composite sample of the influent water was collected. Periodically during a sampling event, the effluent flow rate and depth of water on top of the filter were noted for each media. The collected samples were analyzed for pH, conductivity, turbidity, color, hardness, toxicity, heavy metals and major cations (Pb, Cd, Zn, Cu, Cr, Fe, Ca and Mg), and solids (total, dissolved, suspended and volatile).

This task lasted for approximately 4 weeks. Prior to performing the pilot-scale testing, several potential endpoints for the filtering were noted: (1) physical clogging, (2) chemical breakthrough for several pollutants, or (3) end of the project. By testing these filters intermittently for several weeks, the effects of intermittent drying (by comparing the results with the laboratory experiments where the filters were run continuously until chemical breakthrough occurred) on filter performance could be determined.

The filtration columns used during the pilot-scale tests were constructed in 0.21-m<sup>3</sup> (55 gallon) polyethylene tanks purchased from Aquatic Eco-Systems, Inc. in Apopka, Florida. The inner diameters of the tanks were 0.53 m and the surface area of the tank at any cross-section was 0.217 m<sup>2</sup>. The media selected for study in the pilot-scale filters included sand, activated carbon, peat moss, compost, cotton textile waste, agrofiber, loamy topsoil and a lightweight "sand." The two additional filter containers included a Jacuzzi filter set (sold by Aquatic Eco-Systems, Inc., Apopka, Florida) and the StormFilter cartridge test tank (for use with the compost) supplied by Stormwater Management, Inc., of Portland, Oregon. The filtration columns were constructed using the same guidelines as was used in the bench-scale tests (see Johnson, *et al.* [2003] for additional information). The active media depth was 0.3 m. The flow rates through the media were measured prior to the start of testing. The ratio of column diameter to median filter grain particle size for the sand filter (the media used to determine filter height and column diameter) was significantly greater than 100, which, according to other researchers should be sufficient to avoid significant wall effects.

Nonwoven, synthetic fabrics were also placed on the surface of the filters to improve run times and make cleaning of the filters easier. The porosity of the fabric was such that significant interception of particles in the pre-settled runoff by the filter was not anticipated. The primary reason for using the filter fabric was that, during the design of the filter chamber of the MCTT (Pitt, *et al.* 1999), bypassing of large amounts of filter area was noted. Test water to the pilot-scale filters was supplied through two submersible pumps and then through a distribution manifold.

## **RESULTS AND DISCUSSION**

### *Laboratory-Scale Filter Studies*

Results of filter studies emphasized the importance of characterizing the stormwater before selecting a treatment media since the type and quantity of metals, pH, and other runoff characteristics can vary a great deal between sites. For example, determining the range of metal concentrations to be treated is crucial to selecting the best media, since the removal

efficiencies of the media relative to each other changed with varying metal concentration. Media that were effective at high metals concentrations were outperformed by some media at the low metals concentrations typically found in stormwater. In addition, some media that offer potential as sorbents of metals may create water quality problems of their own. In equilibrium tests for all media, correlations were evident between the metals sorbed and the Ca, Mg, K, and Na ions desorbed. The ions desorbing and their quantity varied depending on the media and exchange metals present. The three best performing media (peat-sand mix, compost, and zeolite) were then selected for in-depth study.

Based on the unsteady-state tests representing unsaturated media, the order of preference for removal on a mass basis was  $Pb > Cr=Cu > Cd > Zn=Fe$  for the peat-sand,  $Pb=Cr > Cu=Fe > Zn=Cd$  for the St. Cloud zeolite, and  $Cd > Zn > Pb > Cu > Fe > Cr$  for the compost. The order of preference for removal based equilibrium conditions on the low concentration metal uptake tests, was  $Cd=Pb > Zn=Cu > Cr > Fe$  for peat-sand,  $Zn=Cd > Pb > Cu > Cr > Fe$  for St. Cloud zeolite, and  $Cd > Zn > Pb > Cu > Cr > Fe$  for compost. In extensive comparisons of the three media, the peat-sand mix performed best at removing dissolved metals.

All three media removed total suspended solids well over all laboratory column runs, but only peat showed any removal of total dissolved solids. Compost increased the total dissolved solids concentrations. As expected, the behavior of the total suspended solids and particulate-bound metals paralleled each other. Copper and chromium typically had lower removal efficiencies than the other metals; one possible explanation is that these metals had a larger fraction of their particulate-bound metal concentrations associated with smaller particulates which passed more easily through the columns. Peat had the best removal efficiencies for particulate-bound metals. Removal efficiencies of compost and zeolite were approximately the same.

Peat-sand had the greatest headloss and the greatest change in headloss over the course of each run. Zeolite and compost beds offered considerably less headloss. The degree of change in headloss increased as the total suspended solids concentration of the influent increased for all media. The advantages and disadvantages of the three media summarized in Table 1 below.

**Table 1.** Overview of Metals Removal in Laboratory-Column Studies

Media	Main advantages	Main drawbacks
Peat-Sand mix	Best metal capture capability	Most detrimental impact on pH, the greatest headloss, and showed the most potential for clogging
Compost	Second best metal capture capability	Added color to the effluent. less impact on the pH of the effluent, less headloss, and exhibited less potential for clogging
Zeolite	Lowest metal capture capability	Less impact on the pH of the effluent, less headloss, and exhibited less potential for clogging

Upflow columns proved more effective than downflow columns in the control of detention time and a reduction in clogging of the media by solids and associated head loss in the columns. At residence times of 3 to 10 min, most of the suspended solids settled out in the sump area of the columns. Compost and zeolite columns showed little sign of increased

headloss during these runs, even when influent suspended solids concentrations were around 400 mg/L.

Samples of spent media from column studies underwent TCLP analysis for those metals regulated by RCRA. Chromium and lead did not present a problem, however, the cadmium concentration in the leachate was above the acceptable limit for peat-sand, and was close to the limit for zeolite and compost. Compost performed best in retaining all three RCRA metals.

#### *Results of the Pilot-Scale Testing*

Heavy metals removal. Figure 1 depicts the ability of the filters to remove copper. Copper, lead, and zinc removals were not found to be statistically significant for any of the filter media, even though the media loading was small. It has been assumed in the modeling equations that adsorption is irreversible, assuming that the influent water characteristics, especially pH and conductivity, do not change significantly. However, at a certain low concentration, it would be expected that an equilibrium would be established where removal below that equilibrium concentration would not occur. Concentrations below the equilibrium concentration, whether due to low removal efficiencies or to low influent concentrations, would encourage the reversal of the driving force for the sorption reaction, resulting in desorption. The locations of this equilibrium for many of the media are indicated on the figures for these three metals. For copper and lead, the minimum effluent water concentration attainable appears to be approximately 5 to 10  $\mu\text{g/L}$ , and approximately 10 to 20  $\mu\text{g/L}$  for zinc, for all media.

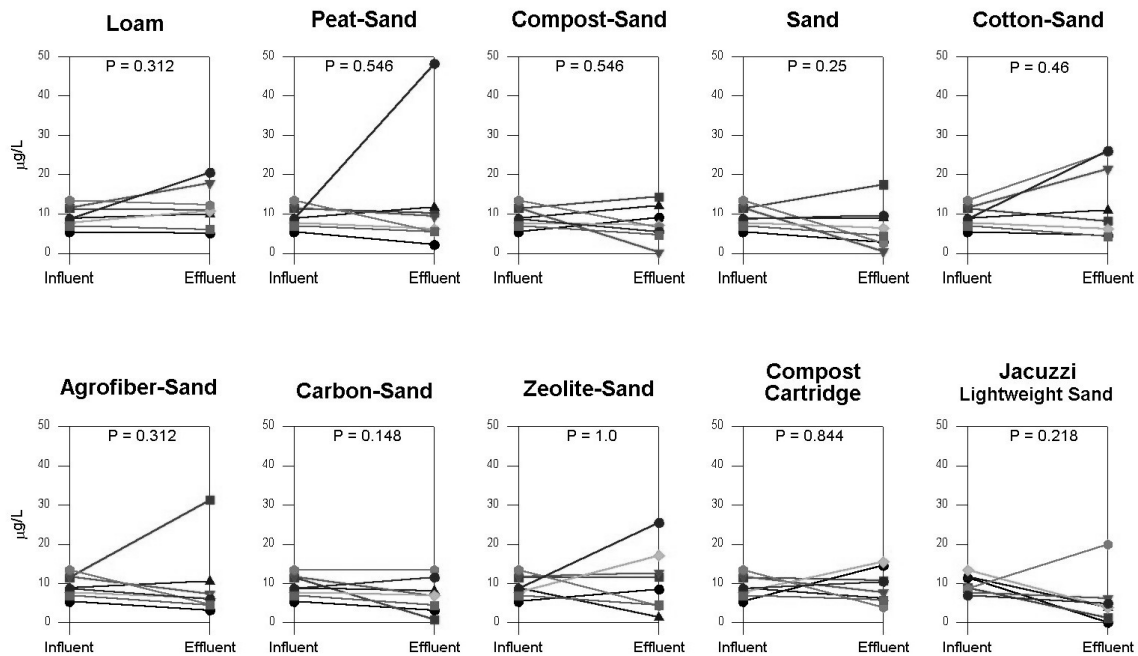
The influent iron concentrations are significantly greater than the influent copper, lead and zinc concentrations. Therefore, adsorption is the primary removal mechanism occurring. It is overwhelming the desorption and makes it appear that the adsorption is irreversible. Statistically significant removals ( $\alpha \leq 0.05$ ) were seen for the sand, cotton-sand, agrofiber-sand and carbon-sand filters. The peat-sand and compost-sand filters had a probability of 0.054 that the effluent was less than the influent concentrations – not statistically significant at  $\alpha \leq 0.05$  but with more testing, the results would likely show statistically significant removals.

Major ion removal (calcium, magnesium, hardness). The removal ability for these ions is not shown. The loam, peat-sand, and cotton-sand filters were able to consistently remove calcium from the influent water. The behavior of the peat-sand filter was not unexpected based upon the literature review and the behavior of the laboratory filter column. The potential of the cotton to remove a small amount of calcium was also seen in the laboratory columns. Only the peat had the ability to almost completely remove the calcium from the influent water. The compost-sand filter consistently added calcium to the runoff water. This also is in agreement with the laboratory column results and with the ability of compost-sand filters to neutralize its influent when the influent pH is significantly different from 7.0 to 7.5.

No filter had the ability to remove magnesium consistently. Hardness removal was only statistically significant with the peat-sand and loam filters, with only the peat-sand filter able to remove large percentages of hardness. This is not unexpected given the ability of the peat filter to remove calcium. Mimicking its behavior with calcium, the compost-sand filter contributed hardness to the runoff water.

*pH*. The peat-sand filter is the only filter that had a measurable effect on pH. Hydrogen as the hydronium ion,  $H_3O^+$ , is one of peat's easily exchangeable ions, and in general, as peat adsorbs other cations, it releases the hydronium ion. pH has been proposed as a method of monitoring remaining life in a peat-filter. The other filter media, when treating an influent at a neutral or near-neutral pH, tend not to affect the pH measurably. This is in contrast to the previous research in Clark (1996) where when the influent water to a compost-sand column was not near a neutral pH, compost-sand attempted to neutralize it.

In real-world applications for stormwater treatment, filters that contain adsorption media typically clog before the media can experience chemical break-through. It is not yet clear if depth filtering media will be a cost-effective stormwater control, considering the pre-treatment needed to prevent this clogging. The necessary pretreatment alone may provide adequate control, without the additional filtration cost. Large-scale filtration installations (especially sand) have been shown to perform well for extended periods of time with minimal problems. The use of supplemental materials (such as organic compounds) should increase their performance for soluble compounds. The use of upflow filtration is also expected to increase the life of filters before clogging, for some media types (not for peat/sand combinations).



**Figure 1.** Copper removal during pilot-scale filtration experiments.

The confirmation of the modeling equations for a few pollutants for some media indicate that this modeling approach has the potential to provide an estimate of the life of the filter, i.e., the time until media replacement is needed, for applications where the influent concentration is not quite as low as it was in the two detention ponds used in this pilot-scale study. The best application for these filters may then be to further treat the effluent from a detention pond in critical source areas, such as scrap metal recyclers, rather than as a polisher for effluent from a detention pond in a residential area. During these field pilot-scale tests and related full-scale

tests, the minimum attainable concentration for these metals using media filtration appears to be approximately 5 to 10 µg/L for copper and lead, and approximately 10 to 20 µg/L for zinc, irrespective of media. These tests do confirm the utility of different filtration arrangements, especially concerning the problems associated with clogging and reduced filtration performance.

#### *Treatability Testing*

Treatability tests were performed to assess the effectiveness of different treatment trains and processes quantifying improvements in stormwater toxicity and metals capture. The treatability tests included intensive analyses of samples from twelve sampling locations in the Birmingham, AL, area that all had elevated toxicant concentrations, compared to the other urban source areas initially examined. The treatability tests conducted were: settling column, floatation, screening and filtering, photo-degradation, aeration, combined photo-degradation and aeration and an undisturbed control sample. More than 900 toxicity tests were performed using the Microtox™ procedure. Turbidity was also analyzed on all samples. Results indicated a reduction in toxicity as the level of treatment increased. All samples, with one exception, showed dramatic reductions in toxicity with increasing settling times.

#### *Metals Associations*

Metal-particulate association tests on the parking lot runoff revealed that more than 90% of the filterable forms of Ca, Mg, K, Fe, and Zn were in ionic forms, with very little colloidal, or other bound forms. Also, more than 80% of the filterable Cr and Pb were also ionic, while only about 50% of the filterable Cu and 30% of the filterable Cd were ionic. This data can be used to estimate the level of control that may be associated with different designs of particle trapping devices. Some pollutants can be significantly reduced by a reduction in particulates, such as suspended solids, total phosphorus and most heavy metals. Other pollutants, such as nitrates, are reduced much less, even after filtration down to 0.45 µm.

Experiments were also conducted to examine the likelihood of the metals disassociating from the particulates under pH conditions ranging from about 4 to 11 with both weak and strong acids. These tests indicated that the heavy metals of concern remain strongly bound to the particulates during long exposures at the extreme pH conditions likely to occur in receiving water sediments and in control device sumps and stormwater pond sediments.

Related tests were conducted as part of the filter media evaluation task of this research to measure the disassociation potential of heavy metals and nutrients under aerobic and anaerobic conditions having extreme Eh values. Studies on the effect of anaerobiosis on metal retention by filter systems indicated that heavy metals were not mobilized from filter systems under anaerobic conditions. It was found that metal retention within the filters was not different from what was observed in oxygenated environments. However, it is plausible that under certain specific environmental conditions, co-precipitation of metals by iron- and sulfate- reducing bacteria may take place in stormwater treatment systems.

## **CONCLUSIONS**

The results of this investigation emphasize the importance of characterizing the stormwater before selecting a treatment media since the type and quantity of metals, pH, and other runoff characteristics can vary a great deal between sites. For example, determining the range of metal concentrations to be treated is crucial to selecting the best media, since the removal

efficiencies of the media relative to each other changed with varying metal concentration. Media that were effective at high metals concentrations were outperformed by some media at the low metals concentrations typically found in stormwater. Upflow columns proved more effective than downflow columns in the control of detention time and a reduction in clogging of the media by solids and associated head loss in the column. Studies on the effect of anaerobiosis on metal retention by filter systems indicated that heavy metals were not mobilized from filter systems under anaerobic conditions. It was found that metal retention within the filters was not different from what was observed in oxygenated environments. However, it is plausible that under certain specific environmental conditions, co-precipitation of metals by iron- and sulfate- reducing bacteria may take place in stormwater treatment systems. Tests also indicate that the heavy metals of concern remain strongly bound to the particulates during long exposures at the extreme pH conditions likely to occur in receiving water sediments. They will also likely remain strongly bound to the particulates in stormwater control device sumps or detention pond sediments where particulate-bound metals are captured. The pilot-scale testing showed that there is a lower limit, however, to the effluent quality. Removals to concentrations below 10 – 20 µg/L for most metals is not feasible.

### **ACKNOWLEDGEMENTS**

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