High Level Treatment of Stormwater Heavy Metals

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Abstract
This presentation reviews the results of several recent and related stormwater research projects that focused on the treatability of stormwater heavy metals.

Pollutant Associations with Various Stormwater Particle Sizes and Filter Components
Figure 1 illustrates typical stormwater outfall particle size distributions, indicating that median particle sizes in the range of about 2 to 20 µm. The data was obtained from about 50 storms monitored over a 2 year period using both automatic samplers for the suspended solids, in addition to bed load samplers that captured the larger particulates.
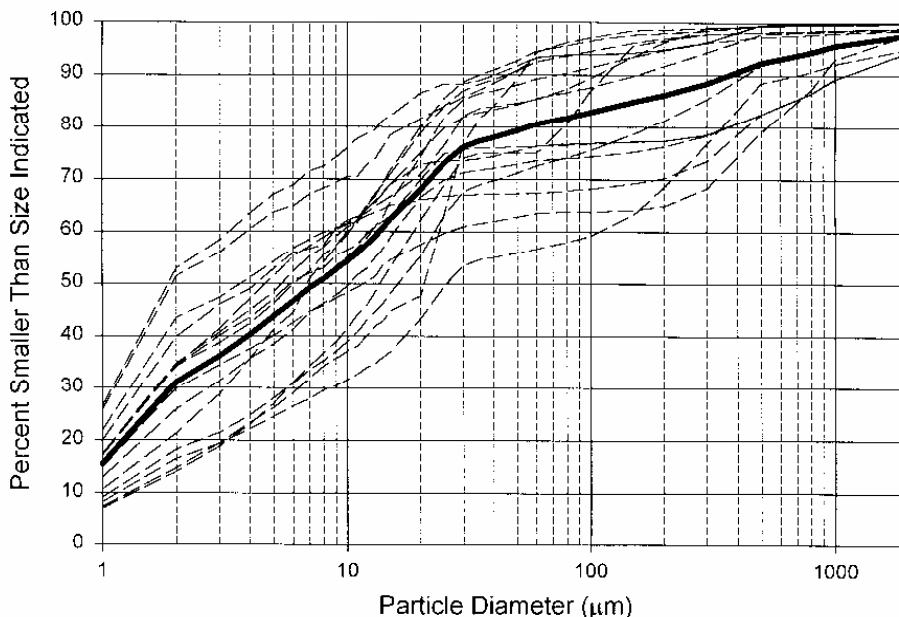

Figure 1. Inlet particle size distributions observed at the Monroe St. (Madison, WI) wet detention pond (WI DNR and USGS).

Table 1 (Johnson, *et al.* 2003) summarizes the calculated "potency" factors (mg constituent per kg of suspended solids) for several size ranges for stormwater heavy metals collected in Tuscaloosa, AL. Table 2 shows the results from detailed analyses that were conducted on 10 outfall samples, using manual sampling to ensure that the complete range of stormwater particulates were represented. This table indicated the percentage of the various pollutants that would be removed if stormwater control devices were effective in removing all particulate-

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associated pollutants greater than the specified particle sizes. Table 3 shows the pollutant associations with colloidal material and those in ionic forms for filtered stormwater collected at Tuscaloosa, AL, outfalls.

Table 1. Summary Table Showing Heavy Metal Associations for Different Particle Sizes

particle size (μm)	Copper		Iron		Lead		Zinc	
	mg Cu/kg SS	COV	mg Fe/kg SS	COV	mg Pb/kg SS	COV	mg Zn/kg SS	COV
>250	50	na	28604	1.50	117	0.58	266	0.88
106 to 250	2137	1.45	21730	0.85	375	1.03	3486	0.79
45 to 106	1312	1.16	14615	0.72	226	0.85	2076	0.88
10 to 45	735	0.97	26221	0.54	229	0.50	1559	0.74
2 to 10	4668	1.60	18508	1.16	868	0.78	13641	1.88
0.45 to 2	2894	1.21	29267	1.31	199	1.40	13540	1.56

Table 2. Average Percentage Reduction in Pollutants after Controlling for Different Particle Sizes

Percent Pollutant Reduction after Removing all Particulates Greater

	20 μm	5 μm	1 μm	0.45 μm
Total Solids	40%	43%	52%	53%
Suspended Solids	76	81	98	100
Turbidity	43	55	92	96
Total-P	68	82	89	92
Total-N	30	41	35	23
Nitrate	0	0	12	17
Phosphate	71	78	81	88
COD	48	52	52	47
Ammonia	35	46	54	58
Cadmium	20	22	22	22
Chromium	69	81	82	84
Copper	26	34	34	37
Iron	52	63	95	97
Lead	41	62	76	82
Zinc	64	70	70	72

Table 3. Ionic and Colloidal Associations with Filtered (<0.45 μm) Pollutants

Constituent	% of filtered constituent in ionic forms	% of filtered constituent in colloidal forms
Magnesium	100	0
Calcium	99.1	0.9
Zinc	98.7	1.3
Iron	97	3
Chromium	94.5	5.5
Potassium	86.7	13.3
Lead	78.4	21.6
Copper	77.4	22.6
Cadmium	10	90

Figure 2 is an example plot showing the reduction in toxicity associated with the removal of different stormwater fractions for runoff collected at industrial loading docks and parking areas in Birmingham, AL (Pitt, *et al.* 1995).
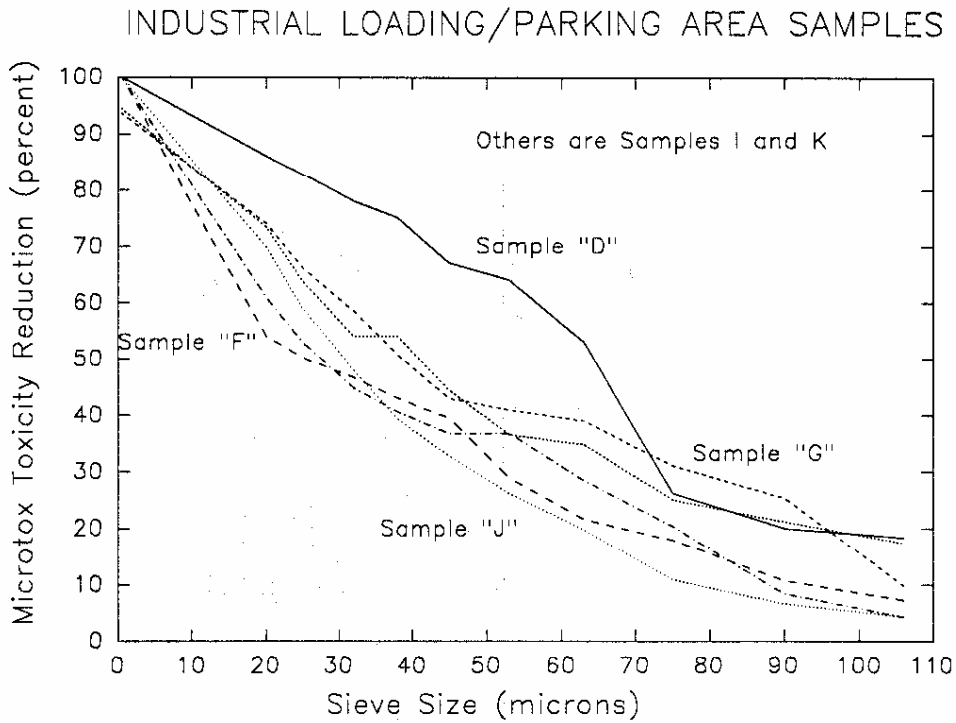

Figure 2. Toxicity reduction from sieve treatment - industrial loading and parking areas (Pitt, *et al.* 1995).

These data indicate the fraction of the various pollutants that are associated with the different particle sizes, and the filtered fractions (including colloidal and ionic forms) of stormwater. If a stormwater control objective includes high levels of heavy metal removals, then fine particles must be removed, along with portions of the "dissolved" fraction. This will most likely require a treatment train approach incorporating multiple unit processes.

Chemical Treatment of Stormwater
Numerous chemical treatability tests were conducted by Pitt, *et al.* (1998) to identify the most effective coagulant, mixing time, and dosage for heavy metal control for stormwater. These tests also examined floc settling and capture and stability. These tests involved bench-scale jar tests using several categories of coagulants, with and without supplements.

Coagulation is a two-step process, the first step is destabilization of particles (by chemical addition), followed by amalgamation (by mixing) to form faster sinking particles. Added chemicals affect the surface charges on the particles so they will join into flocs. The flocs are larger than the initial primary particles, but have a much lower specific gravity (because of

entrapped water). However, the increased size usually overcomes the decreased density and the flocs settle much more rapidly than the primary particles. In some cases and for some chemicals, the flocs will rise to the water surface where they are removed by skimming. In most water and wastewater treatment processes, initial flash mixing is followed by 20 to 60 minutes of slow mixing to help the particles collide to form the flocs. The floc is then allowed to settle for 2 to 8 hours in a sedimentation basin. These tests were conducted with much less time in an attempt to simulate field conditions where rapid treatment is desired. Chemicals that form heavy flocs quickly are needed, and filtration was investigated to replace slow sedimentation.

Hydrolyzing metal ions are a common family of coagulants used to destabilize the surface charges of the particles. These include alum (aluminum sulfate), the most commonly used coagulant used in the U.S., ferrous sulfate, ferric chloride, and mixtures of ferrous sulfate and ferric chloride (chlorinated copperas). Another common group of coagulants are organic polymers (polyelectrolytes) and synthetic polymers. Polymers are long chain molecules having many available active sites for adsorption. Besides coagulants and polymers, many coagulant aids are available to enhance coagulation and flocculation. In addition, many blends of chemicals are used. Because these chemicals react differently with different waters, bench-scale jar tests are needed to determine the most efficient dosages and pH conditions of the water being treated. The objective was to identify chemicals having relatively robust behavior for the range of water conditions likely found in stormwater.

Water can be grouped into four types according to turbidity and alkalinity conditions. Low turbidity is defined as <10 NTU and high turbidity is defined as >100 NTU. Turbidity is important because it has associated small particulates that form nuclei for the flocs. In most cases, stormwater is of intermediate turbidity, although locations affected by eroding areas can have extremely high turbidity values. Low alkalinity water has alkalinity levels < 50 mg/L, as $CaCO_3$, while high alkalinity water has alkalinity levels >250 mg/L. Alkalinity is important because the bicarbonates are important intermediate products in most coagulation processes. Most stormwaters likely have high alkalinity. Each water type has a preferred coagulant type:

• Type one water (high turbidity and high alkalinity): The easiest water to coagulate. Either alum (effective in pH range of 5 - 7), or ferric chloride (pH range of 6 - 7), or high molecular weight polymers work well. Cationic polymers are very effective, while anionic and non-ionic polymers may also be effective.

• Type two water (high turbidity, low alkalinity): The polymer recommendations are the same as for type one water, while alkalinity may need to be added for alum or ferric chloride, if the pH drops during water treatment.

• Type three water (low turbidity, high alkalinity): This is the likely category for many stormwaters. Polymers cannot work alone due to the low turbidity. Coagulant aids that increase the turbidity (such as clays) should be added before the polymer. Alum is needed in relatively large dosages, which forms a precipitate. Weighing agents may be needed to promote settling. Ferric chloride is also needed in relatively high dosages which also promotes hydroxide precipitates. Again, coagulant aids to weigh the floc is needed to improve settling.

• Type four water (low turbidity and low alkalinity): The most difficult water to coagulate. Must add alkalinity or turbidity to form type 2 or 3 water for either alum or ferric chloride. Polymers cannot work alone without added aids, such as clay, to increase the turbidity.

The addition of coagulant aids to increase turbidity may be mandatory in some cases, and may improve the treatment in other cases. Microsand (silica sand with a nominal size range of about 75 to 150 µm in diameter) has recently been used to improve treatment of wastewaters. In most cases, the sand is separated from the floc after settling for recycling. This material is larger than clay material and may improve the weighting of the flocs for more rapid settling, while increasing turbidity.

Alum is commonly used in the U.S. for water treatment. However, during our preliminary tests on chemical treatment of stormwater, it was found to contribute toxicity to the finished waters (possibly due to dissolved aluminum at pH conditions encountered, or due to zinc contamination of the alum). The flocs formed with alum were also found to be more fragile and settle slower than with ferric chloride. Experience using full-scale ferric-chloride treatment of stormwater at European installations for phosphate control has been very successful, especially in low alkalinity waters where alum toxicity may be an issue. Ferric chloride also forms a floc that settles much more rapidly than alum flocs and does not add toxicity to the finished water. However, ferric chloride stock solutions are corrosive and must be handled carefully. The dilute solutions used for coagulation are not corrosive. Ferric chloride is also about twice as expensive as alum, on a weight basis.

The recommended pH range of the water for ferric chloride coagulation is 6 to 9 pH. Before the tests, the pH of the water samples were 7.5. After the coagulation addition, the pH dropped to the range of 6.4 to 7.2. The tests were divided into three subsets, each having the same ferric chloride concentration (25, 50, or 75 mg/L). Each set included 4 beakers, covering all combinations of high and low turbidity (3 and 24 NTU), plus high and low conductivity (500 and 1600 µS/cm), in a full 2^2 factorial experimental design. There was good floc formation and fast setting for all concentrations of ferric chloride coagulant tested (25 to 75 mg/L). The percentage turbidity removals were very sensitive to the initial turbidities of the test waters. The high turbidity water (22 NTU) had the greatest turbidity reductions (87 to 95%), while the low turbidity test water (1.6 NTU) had minimal turbidity changes. The final turbidities (after the coagulation tests) were all less than 2 NTU. Initial turbidity conditions (affected by the presence of microsand) did not affect the removal of any of the other pollutants examined. Salinity did not affect the removals of any of the pollutants examined during the ferric chloride tests. The optimal dosage of ferric chloride was not clear during these tests, as all concentrations in the test range (25 to 75 mg/L) produced excellent metal control.

Buffered alum was tested over a wide range of coagulant concentrations (3.5 to 105 mg/L). As for ferric chloride, the percentage turbidity removal was very sensitive to the initial turbidities of the test waters for these alum tests. The high turbidity water (22 NTU) had the greatest turbidity reductions (37 to 83%), while the low turbidity test water (1.5 NTU) had increases in turbidity (to about 3 to 9 NTU). Initial turbidity conditions (affected by the presence of microsand) did not affect the removal of any of the other pollutants examined. Salinity also did not affect the removals of any of the pollutants examined during these buffered alum tests. Because of the lack

of noticeable effects of turbidity and salinity on the removal of the pollutants, the further coagulant tests only examined single turbidity (about 22 NTU) and salinity (about 1600 µS/cm) conditions with more coagulant concentrations. The optimal dosage for the buffered alum coagulant was about 70 mg/L.

Ferric chloride, with a microsand additive, was the most successful coagulant and aid for rapid treatment over a wide range of water conditions. A wide range of ferric chloride levels produced excellent reductions of heavy metals (lead >99%, copper >90%) and phosphate (about 50%) within about 10 minutes. In addition, the toxicity (measured using the Microtox™ screening method) also indicated >80% reductions. No adverse changes were observed with ferric chloride. Other major chemicals tested included alum (with and without organic polymers), ferric sulfate, organic polymers, plus several priority mixtures (most likely mixtures of alum and polymers). None of these other chemicals produced results as good as the ferric chloride, and some added large amounts of phosphates and COD to the test water.

Multi-Chambered Treatment Train

The Multi-Chambered Treatment Train (MCTT) was developed to control toxicants in stormwater from critical source areas (Pitt, *et al.* 1999). The MCTT is most suitable for use at relatively small areas, about 0.1 to 1 ha in size, such as vehicle service facilities, convenience store parking areas, equipment storage and maintenance areas, and salvage yards. The MCTT is an underground device and is typically sized between 0.5 to 1.5 percent of the paved drainage area. It is comprised of three main sections, an inlet having a conventional catchbasin with litter traps, a main settling chamber having lamella plate separators and oil sorbent pillows, and a final chamber having a mixed sorbent media (usually peat moss and sand). During monitoring, the pilot-scale MCTT provided median reductions of >90% for toxicity, lead, zinc, and most organic toxicants. Suspended solids was reduced by 83% and COD was reduced by 60%. The full-scale tests substantiated these excellent reductions.

Figure 3 shows a cross section of the MCTT. The catchbasin functions primarily as a protector for the other two units by removing large, grit-sized material. The setting chamber is the primary treatment chamber for removing settleable solids and associated constituents. The sand-peat filter is for final polishing of the effluent, using a combination of sorption and ion exchange for the removal of soluble pollutants, for example.

Catchbasins have been found to be effective in removing coarser runoff solids. Moderate reductions in total and suspended solids (SS) (up to 45%, depending on the inflowing water rate). While relatively few pollutants are associated with these coarser solids, their removal decreases maintenance problems of the other MCTT chambers. This design uses a circular catchbasin with the diameter 4 times the diameter of the circular outlet. The outlet is then placed 1.5 times its diameter from the top and 4 times its diameter from the bottom of the catchbasin, thus providing a total depth of 6.5 times the outlet diameter. The size of the MCTT catchbasin is controlled by three factors: the runoff flow rate, the SS concentration in the runoff, and the desired frequency at which the catchbasin will be cleaned so as not to sacrifice efficiency.

In addition to housing plate or tube settlers, the main settling chamber also contains floating sorbent "pillows" to trap floating oils and a fine bubble aerator that operates during the filling time of the MCTT. Plate settlers (or inclined tubes) increase solids removal by reducing the distance particles travel to the chamber floor and by reducing scour potential. Bench-scale tests found that depth/time ratios of at least 3×10^{-5} m/s (1×10^{-4} ft/s) are needed to obtain a median toxicity reduction of at least 70 percent in the main settling chamber.

If the rains are infrequent, long detention periods are easily obtained without having "left-over" water in the tank at the beginning of the next event. However, if the rains are frequent, the available holding times are shortened, requiring shallower main settling chamber tanks for the same level of treatment. A continuous hydrology model was used to develop design curves for many locations of the U.S. based on long-term rain records, desired levels of control, and tank geometry.

The final MCTT chamber is a mixed media filter (sorption/ion exchange) device. It receives water previously treated by the grit and the main settling chambers. The initial designs used a 50/50 mix of sand and peat moss, while the Ruby Garage full-scale MCTT in Milwaukee used a 33/33/33 mixture of sand, peat moss, and granulated activated carbon. The MCTT can be easily modified to contain any mixture of media in the last chamber. However, care must be taken to ensure an adequate hydraulic capacity. As an example, peat moss alone was not effective because it compressed quickly, preventing water from flowing through the media. However, when mixed with sand, the hydraulic capacity was much greater and didn't change rapidly with time.

The sand-peat filter possesses ion exchange, adsorption, and filtration reduction mechanisms. As the media ages, the performance of these processes will change. Ion exchange capacity and adsorption sites, primarily associated with the peat moss, will be depleted. Filtration, primarily associated with the sand, however, is expected to increase, especially for the trapping of smaller particles. Eventually though, the sand-peat filter will become clogged by solids and the exchange capacity of the peat will be exceeded, requiring replacement of the media. Replacement of the media in the MCTT is expected to be necessary about every 3 to 5 years.
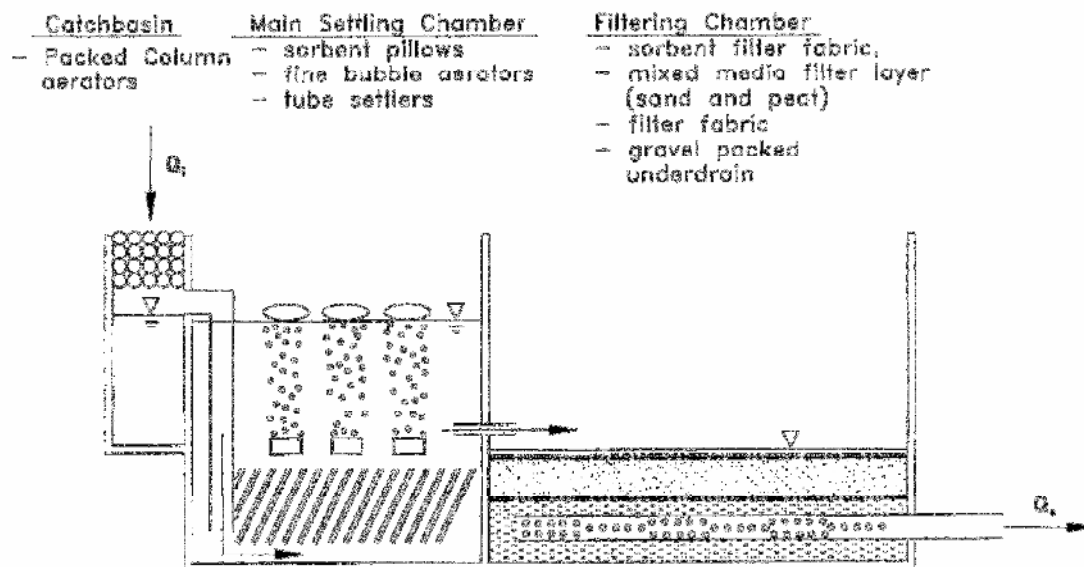
Figure 3. MCTT cross section.

Table 4 summarizes the heavy metal removal performance of two full-scale MCTT units installed in Wisconsin and tested by the USGS and the WI Dept of Natural Resources.

Table 4. Performance for Full-Scale MCTT Tests (median % reductions and median effluent quality)

	Milwaukee MCTT (15 events)	Minocqua MCTT (7 events)
suspended solids	98 (<5 mg/L)	85 (10 mg/L)
Cadmium (total)	91 (0.1 µg/L)	na
Cadmium (filtered)	66 (0.05 µg/L)	na
Copper (total)	90 (3 µg/L)	65 (15 µg/L)
Copper (filtered)	73 (1.4 µg/L)	na
Lead (total)	96 (1.8 µg/L)	nd (<3 µg/L)
Lead (filtered)	78 (<0.4 µg/L)	na
Zinc (total)	91 (<20 µg/L)	90 (15 µg/L)
Zinc (filtered)	68 (<8 µg/L)	na

Upflow Filtration
More recent tests associated with a research project sponsored by WERF (Johnson, *et al*. 2003) examined a number of issues related to stormwater heavy metal treatment, including the associations of heavy metals with different-sized particulates in stormwater, their binding strengths, and the characteristics of the filterable (<0.45 µm) portion. Most of the heavy metals in stormwater are associated with particulates larger than 0.45 µm in size, although some exceptions exist (usually zinc, and sometimes copper, can predominantly be associated with the filterable fraction of stormwater). Experiments were also conducted to examine the likelihood of

the metals disassociating from the particulates under pH conditions ranging from about 4 to 11. 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. 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. 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 associated tests examining metal binding to filtration media under aerobic and anaerobic conditions also found that the heavy metals will likely remain strongly associated with a variety of organic and inorganic media under varying Eh conditions.

Special upflow filter tests were also conducted to examine the potential of this filter design for longer, sustained, high flow rates, without clogging, while maintaining high levels of removal. Figure 4 show high removals of dissolved zinc in a mixed sand/peat upflow filter, even with very short residence times:
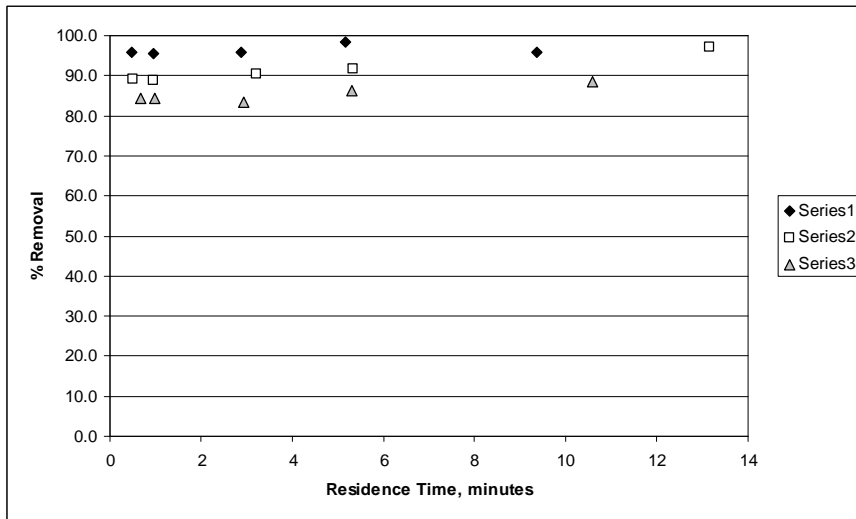

Figure 4. Dissolved zinc removal in sand/peat upflow filter (Johnson, *et al.* 2003)

A recently completed first-phase SBIR project sponsored by the EPA included pilot-scale and prototype upflow filter tests (USInfrastructure 2003). Figure 5 shows the high rate of flow possible with this new design for a stormwater treatment unit. The current second-phase SBIR project is further developing this unit which includes several different removal mechanisms for a broad range of critical source area applications.
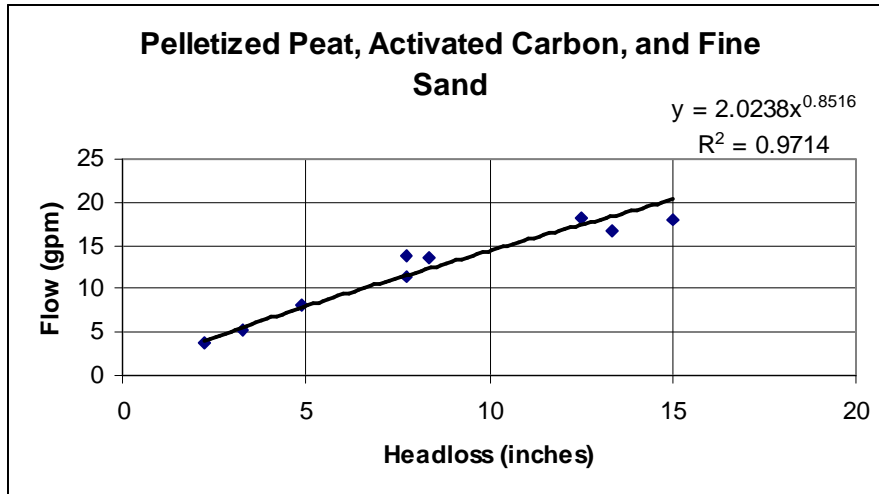
Pelletized Peat, Activated Carbon, and Fine Sand

$y = 2.0238x^{0.8516}$

$R^2 = 0.9714$

Figure 5. Upflow filter flow capacity tests.

References

Johnson, P.D., R. Pitt, S.R. Durrans, M. Urrutia, and S. Clark. *Innovative Metals Removal Technologies for Urban Stormwater*. Water Environment Research Foundation. WERF 97-IRM-2. Alexandria, VA. 2003.

Pitt, R., R. Field, M. Lalor, and M. Brown. "Urban Stormwater Toxic Pollutants: Assessment, Sources and Treatability." *Water Environment Research*. Vol. 67, No. 3, pp. 260-275. May/June 1995.

Pitt. R. S. Clark, J. Lantrip, and J. Day. *Telecommunication Manhole Water and Sediment Study;* Bellcore, Inc., Special Report SR-3841. Morriston, NJ. December 1998.

Pitt, R., B. Robertson, P. Barron, A. Ayyoubi, and S. Clark. *Stormwater Treatment at Critical Areas: The Multi-Chambered Treatment Train (MCTT)*. U.S. Environmental Protection Agency, Wet Weather Flow Management Program, National Risk Management Research Laboratory. EPA/600/R-99/017. Cincinnati, Ohio. 505 pgs. March 1999.

USInfrastructure. *Upflow Filters for the Rapid and Effective Treatment of Stormwater at Critical Source Areas*. SBIR phase-1 final report. US. Environmental Protection Agency, Washington, D.C. 2003.