

# Treatability of Filtered Heavy Metals by (Bio)(In)filtration Media: Water and Soil Chemistry Effects

Shirley E. Clark<sup>1</sup>, Ph.D., P.E., D.WRE, and Robert Pitt<sup>2</sup>, Ph.D., P.E, BCEE, D.WRE

<sup>1</sup>Associate Professor of Environmental Engineering, Environmental Engineering Program, Penn State Harrisburg, Middletown, PA USA, email: [seclark@psu.edu](mailto:seclark@psu.edu)

<sup>2</sup>Cudworth Professor of Urban Water Systems, Department of Civil, Construction and Environmental Engineering, University of Alabama, Tuscaloosa, AL, USA, email: [rpitt@eng.ua.edu](mailto:rpitt@eng.ua.edu)

## ABSTRACT

To address water quality concerns and numeric effluent limits, the designers of (bio)(in)filtration systems will need to integrate water and soil chemistry into the selection of filtration media mixtures. For the “dissolved” metals, designers will need to consider the ratio of valence states of the metals as they consider the proportion of ion exchange resins versus organic-based media in the final media mixture. As the correlations between pollutant capacity and soil/media chemistry showed, metals’ capacity is directly related to organic matter content and the effective cation exchange capacity of the soil. Available stormwater treatment organic media provides a wide range of treatment sites, but possibly smaller numbers of each site type, compared to ion exchange resins such as zeolites. An activated organic media, such as granular activated carbon (GAC), will have an increased number of surface active sites potentially available for treatment, but this media may not sustain plant growth and may not be desired as a component of (bio)retention media. Other trade-offs also have to be considered in a complete analysis of (bio)(in)filtration media, such as the trade-off between organic content for plant growth versus nutrient leaching. Finally, there is a lower limit to treatment, after which no further pollutant removal occurs, especially given the contact time requirements based on draindown times required for many bioretention devices. Slightly improved removals for many metals may be achieved with much longer contact times, but the substantial increase in surface area devoted to (bio)(in)filtration may not be cost-effective (given the draindown time requirements). This paper uses “dissolved” copper as an example of how to use both soil and water chemistry to design an optimal bioretention media from a subset of potential mixture components.

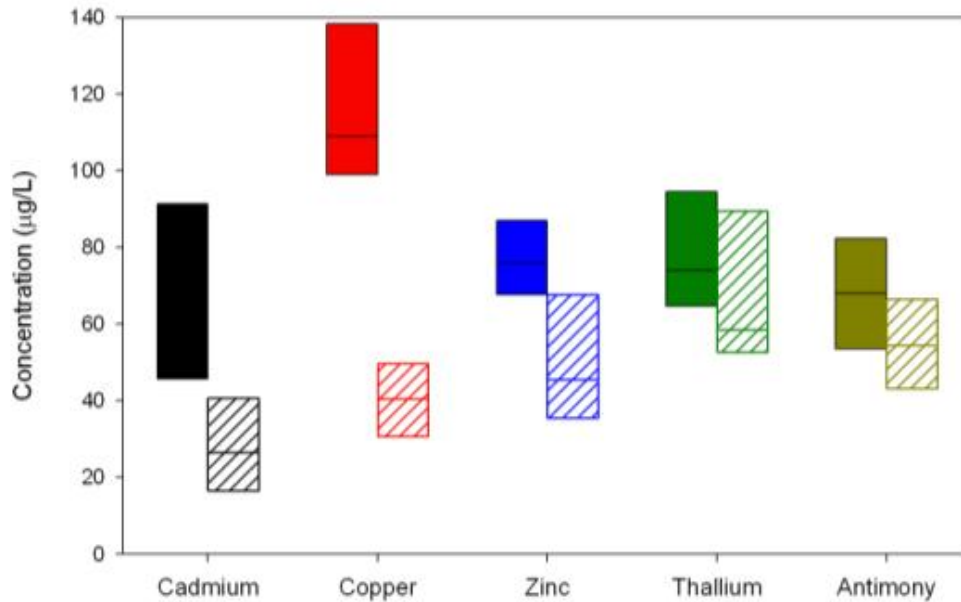
## INTRODUCTION

Many guidance documents, published studies, and online performance databases list percent removal rates for stormwater treatment practices. For filtration, infiltration, and biofiltration/bioretention treatment devices, these efficiencies (often extracted from the literature)

may range from <30% to almost 100% for pollutants such as metals and phosphorus and the percent removals for these devices appear to vary in the different guidance documents for each state, but are rarely based on regional studies. With the development of Total Maximum Daily Load (TMDL) and other Clean Water Act program requirements to protect stream reaches and lakes around the U.S., it is imperative that reasonably accurate and defensible predictions of treatment device pollutant removals and effluent quality be made. This is not possible with the current guidance, which, in addition to being problematic, is often misapplied. TMDLs, at least in the Chesapeake Bay watershed, appear to be pushing the stormwater industry toward a quantitative description of the treated runoff, especially for nutrients and sediments. In some watersheds or on sites where metals are a known problem, it is anticipated that TMDLs will be written that put numeric effluent limits on metals. At one site (Pitt *et al.* 2010), numeric effluent limits on metals, toxic organics, sediments, and other pollutants have been applied through the site's NPDES permit. While the numeric effluent limits for metals may be presented as total recoverable (total) metal concentrations in the effluent water (often based on wastewater total-to-dissolved fractions and not reflecting the greater fraction of particulate-bound metals in untreated stormwater), such as on the permit described in Pitt *et al.* (2010), achieving those concentrations may require removal of both particulate-associated and filtered ("dissolved") pollutants.

"Dissolved" pollutants are defined traditionally as the total pollutant quantity that is measured after the water has passed through a 0.45- $\mu\text{m}$  membrane filter. These are the pollutants that are considered to be the most bioavailable to the aquatic biota and therefore the greatest toxicity/bioaccumulation concern when they are discharged to receiving waters. For metals, the fraction of a certain metal that passes through the 0.45- $\mu\text{m}$  filter is dependent on the metal and other constituents in the source water, so a consistent ratio of filtered to total metals is generally not observed (Figure 1). For metals such as copper and cadmium values shown in Figure 1, much of the total metals concentration can be particulate-associated (not filtered through a 0.45- $\mu\text{m}$  membrane filter), while for others, such as thallium and antimony, most of the total concentration was associated with the filtered fraction, although the range of the filtered fraction can be highly variable, even for the same sampling location.

Compared to the removal of "dissolved" pollutants, particulate-associated pollutant removal is relatively easy in (bio)(in)filtration systems. As the water passes through the pores of the media, the larger particulates are strained out and trapped in the pore spaces of the media. Assuming that pore-water chemistry does not affect this trapping mechanism such as through repulsive charges, this removal does not depend on the chemistry of the water and media, but on the pore size and the particle diameters. The removal of filtered pollutants, though, is dependent on the chemistry of the influent water and of the media. Laboratory testing and ranking of media has often been based on "synthetic" stormwater where the pollutants, particularly the metals, are in ionic form. However, researchers such as Morquecho *et al.* (2005) have shown that metals that pass through these filters are not just ionic, but also can be associated with colloidal particles (both organic and inorganic) (Table 1). These complexes have different charge states than the original metal ions and therefore will react differently than the metal ion by itself. A media's ability to remove "dissolved" pollutants thus should be expressed not in generic terms but instead as a function of both the soil and water chemistry.



**Figure 1.** Total (solid fill) versus filtered (striped fill) metals concentration in example stormwater runoff.

**Table 1.** Fraction Ionic vs. Bound Metals in Filtered Fraction from Source Area Stormwater (data from Morquecho *et al.* 2005).

	% Ionic	% Bound
Zinc	15	85
Copper	70	30
Cadmium	10	90
Lead	12	88

This paper describes the preliminary investigation of the impact of both water and soil chemistry on pollutant removal. This paper is based on several studies (referenced in the following discussions) of (bio)(in)filtration media. It focuses on generic measures of pollutant removal as a function of the water and soil chemistry. The preliminary conclusions in this paper will be further refined as data from ongoing research projects are produced.

## INFLUENT WATER CHEMISTRY

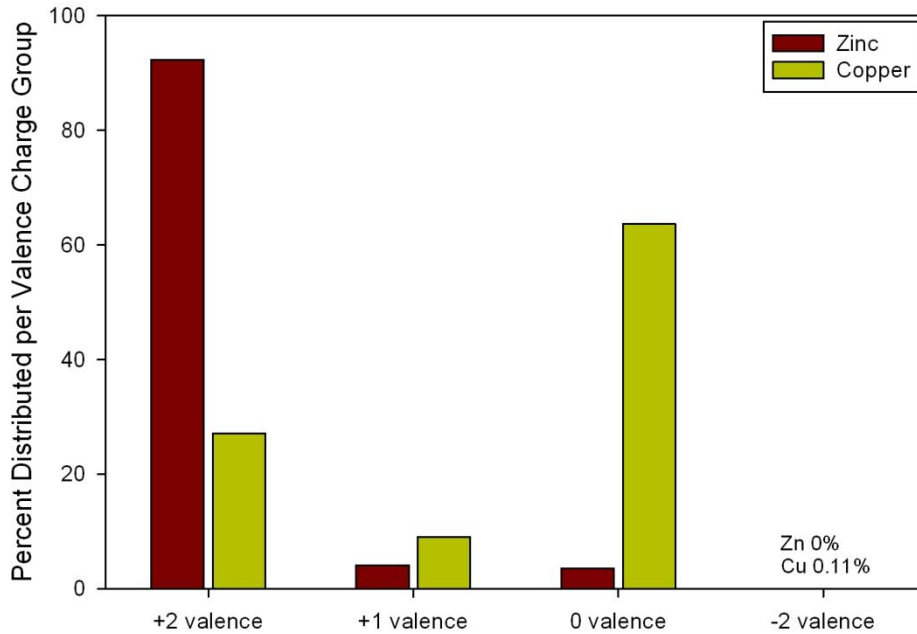
Figure 1 and Table 1 emphasize the challenge of treating metals in stormwater runoff to low effluent concentrations. The fraction of the metals that are associated with particulate matter varies by metal, and as Pitt *et al.* (1999) also noted, by location on the site.

**Table 2.** “Dissolved” vs. Particulate-Associated Metals by Sample Location

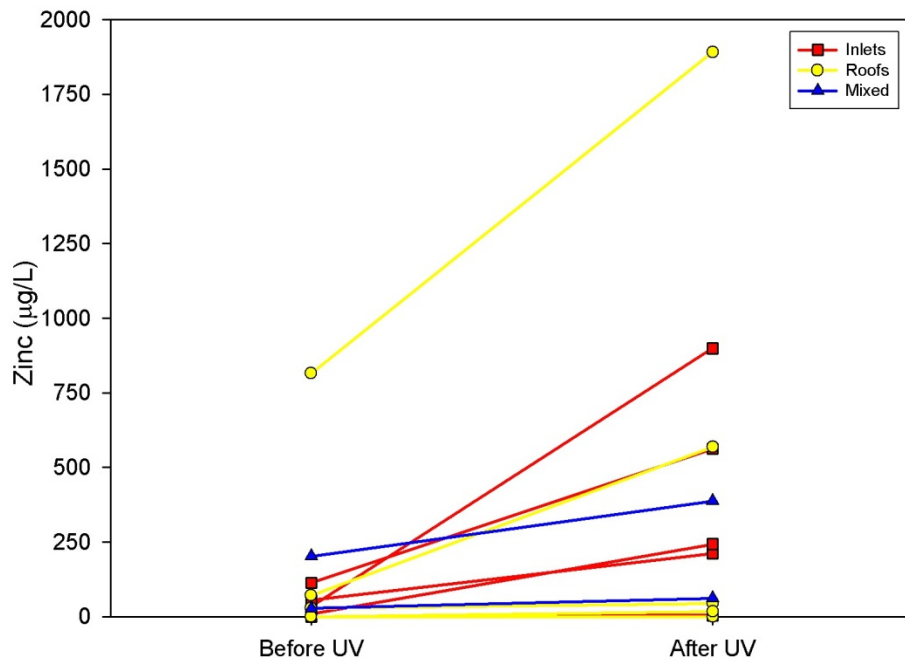
Constituent	Sample Location					
	Roofs		Vehicle Service Areas		Storage Areas	
	Ave % Particulate	Ave % Filterable	Ave % Particulate	Ave % Filterable	Ave % Particulate	Ave % Filterable
Zinc	12	88	40	60	99	1
Copper	97	3	94	6	14	86
Cadmium	88	12	97	3	64	36
Lead	97	3	96	4	97	3

In addition, for that fraction of the metal that passes through a 0.45- $\mu\text{m}$  filter, much of that is not ionic, but instead is bound in forms that may be more difficult to treat. The first step in developing treatment trains for metals involves understanding the forms of the metals entering the treatment system. Modeling using Visual Minteq 3.0 and assuming no dissolved organic matter (DOM) in the system (Figure 2) shows that, for copper and zinc, the “dissolved” fraction can have a variety of valence states, ranging from +2 to 0 (for zinc) and through -2 for copper. This run was performed at pH = 7, based on the average pH of urban runoff reported in the literature; had the pH been different, the distribution of valence charges would change. It is anticipated that lowering the pH of the runoff will increase the percentage of the +2 valence charges, since metals tend to be more soluble at lower pHs.

The addition of DOM increases the likelihood that the metals are bound into organic complexes. Figure 3 shows the results of UV digestion of stormwater and subsequent anodic stripping voltammetry (ASV) analyses (Morquecho 2005). The UV digestion degrades the organometallic bond, making the ionic form of the metal available for the ASV analyses. Therefore, the increase in concentration after the UV exposure indicates the fraction of these complexes that are present. This creation of organometallic complexes increases the difficulty of treating these compounds since the charge state of these complexes is not known, but many of them may be at a neutral valence. Neutral charge states, whether through organic or inorganic complexation, indicate that the metal will not be removed through traditional ion-exchange reactions. Weak charge states (+1 or -1) typically indicate that the metal complex may be displaced by a “stronger” ion/complex if the media site favors the stronger valence compounds.



**Figure 2.** Zinc and Copper Species Distribution by Valence State.



**Figure 3.** Ionic zinc concentration before and after organometallic zinc complex degradation by UV light (data from Morquecho 2005).

## SOIL/MEDIA CHEMISTRY EFFECTS

In terms of metals removal, soil is composed of many different types of reaction sites, resulting from the natural processes that generate the soil – decomposition of organic matter at the surface and leaching into the lower soil horizons and degradation of the underlying rock through weathering processes. Many generalizations have been made in the literature about chemical behavior of soils based on textural designations; however, soil texture does not define the soil's pollutant removal ability. The soil's two physical properties of interest – porosity and intrinsic permeability – dictate the rate of water transport, and thus dictate the minimum contact time the pollutants have with the medium. If the pollutant can react with the soil in that time, it is reasonable to assume that pollutant removals will be good.

In general, the chemical makeup of soils is the following, with the different horizons having different percentages of each of these components. It is the percentage of these components that affects the number and types of pollutant removal sites available in the soil.

- ◆ Inorganic mineral matter (50 – 60% in total). This is soil material consisting mostly of oxygen, silicon, and aluminum, plus many other metals in small quantities.
- ◆ Organic mineral matter (< 10%). This is soil material derived from plant residues and consisting mostly of carbon, oxygen and hydrogen.
- ◆ Solutes. This component is the portion of the soil that includes water and mostly dissolved salts (plant nutrients).
- ◆ Air. Soil air is mostly composed of the same gases as the atmosphere, but in different ratios, plus byproducts of decomposing organic matter or from chemical reactions.

Treese *et al.* (2009) highlighted the impacts of soil horizons on stormwater pollutant removal in two natural soils – a silt loam and a loamy sand.

The six primary chemical properties of soil that impact pollutant transport include the following (Evangelou 1998):

1. Permanent charge (permanent Cation Exchange Capacity [CEC]) – not pH dependent, but are ions that will exchange at all pHs.
2. Variable charge (pH-dependent CEC)
3. Point of zero charge, ZPC (pH at which the net surface charge is zero or the pH where the CEC minus the Anion Exchange Capacity [AEC] is zero)
4. Inner-sphere/outer-sphere complexes (defined as strong surface complexes or inner-sphere complexes, as opposed to weak surface complexes or outer-sphere complexes)
5. Hydrophobic-hydrophilic potential (defined as the potential of soil to adsorb water)
6. pH buffering (ability of the soil to resist pH change).

**Cation Exchange Capacity.** Much of the groundwater protection offered by soils is associated with its ability to remove cationic (positively-charged) pollutants, measured as cation-exchange capacity (CEC) (Pitt, *et al.* 1999; Johnson *et al.* 2003). The CEC of a material is defined as the sum of the exchangeable cations that can be adsorbed at a given pH and is used to evaluate the ability of a soil to attract and retain phosphorus, heavy metals, and other targeted cations of concern. The CEC is pH-specific. Sands have low CEC values, typically ranging from about 1 to 3 cmolc/kg (centimol positive charge per kg of soil; also equal to meq/100 g) of material, while rich organic soils may have greater than 30 cmolc/kg CEC. As the organic content of the soil increases, so does its CEC content. Natural soils therefore vary widely in their CEC content. Organic soil amendments, such as compost, increase the CEC of a soil that is naturally low in organic material or clays. There are a variety of methods to estimate CEC. All are based on measuring the amount of a small-sized inorganic compound removed from a water solution by a treatment medium. Many state soils labs report CEC as effective CEC. Rather than measuring the uptake of a small molecule, they report CECe as the sum of the magnesium, calcium and potassium contents of the soil since these ions are typically the ones exchanged during an ion-exchange reaction. It has been proposed that CEC should generally diminish over time in a soil used to treat stormwater runoff because the quantity of exchangeable cations decreases as cations, such as metals, are removed from the infiltrating water. However, as shown in Figure 4, this does not necessary happen for CECe, even when a soil layer has reached capacity (note the capacity of copper for the uppermost layer appears to be reached after 32 storm events [left], yet the CECe is not depleted in this layer [right], but has only undergone a slight decrease).

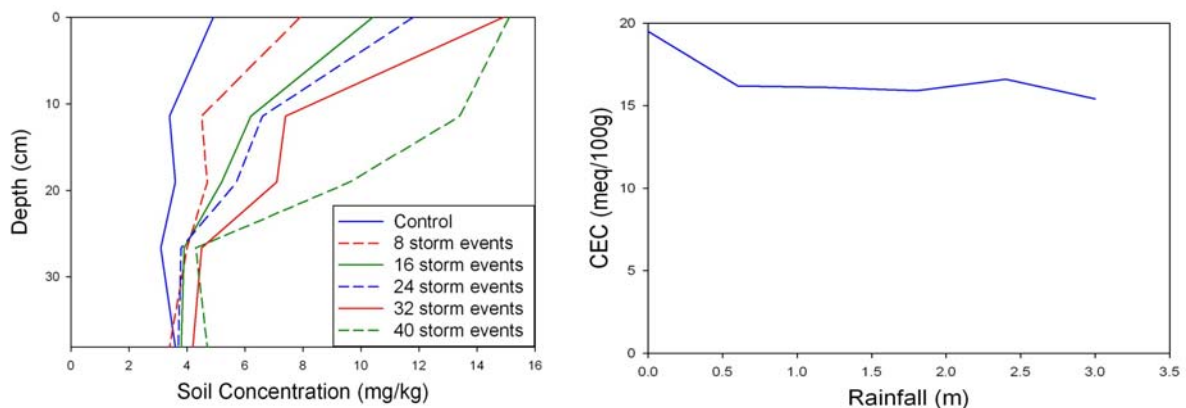


Figure 4. Breakthrough of copper (left) in a natural soil column and corresponding CECe measurements in the 0 – 3” (0 – 7.5 cm layer)

**Anion Exchange Capacity.** Similar to the cation exchange capacity, the anion exchange capacity (AEC) is the sum of the exchangeable anions that can be adsorbed at a given pH. It is a measure of the positive charges on the surface of the soil particles that can participate in pollutant removal. The AEC also is pH-specific. AEC values rarely are measured for stormwater filter/biofilter media.

In general, soils where the predominant colloids are oxides of Fe and Al may have a net positive charge and may contribute to ion exchange. For example, a clay-size particle of hydrous aluminum oxide has a positive charge under acid conditions. However, this charge may be pH-dependent. At sufficiently high pH, this soil may contribute to cation exchange capacity. These soils, though, are naturally acidic and are more likely to contribute to AEC (UBC Soil Web, accessed 2008). According to Troeh and Thompson (2005), anion-exchange sites in soils result from: 1) amine groups in humus, 2) structures terminating in a cation at the edge of a silicate-clay material, 3) OH<sup>-</sup> ionizing from materials such as Al(OH)<sub>3</sub> or Fe(OH)<sub>3</sub>, and 4) isomorphic exchange of Ti<sup>4+</sup> for Fe<sup>3+</sup> in iron oxides. Anion exchange capacity can increase in a soil as the soil ages and weathering occurs. Younger soils, such as illite, vermiculite and smectite, have higher cation exchange abilities compared to anion exchange. As the soil weathers, the fraction of kaolinite and oxide clays increases and the anion exchange ability increases as the cation exchange capacity decreases. AECs are typically low in natural soils.

**Mineral Matter.** Aluminosilicates, also often known as the clay minerals, make up a large fraction of soil particles < 0.2 mm (<200µm). The silica or aluminum ion is surrounded by four or six oxygen atoms. Substituting aluminum for silica and substituting divalent cations for the aluminum is common. If the substitution replaces the given coordinating cation with a cation of lower valence, a permanent negative charge or CEC increase occurs (Evangelou, 1998). These substitutions do not occur in the molecular structure itself so further substitutions with preferred cations may occur. In addition, although this is likely impractical in stormwater infiltration devices, this material may be regenerable through washing of the media with high concentrations of the readily exchangeable cation. The concern with road salt entering infiltration devices is that sodium may act as an exchangeable cation and wash out previously-captured heavy metals.

Metal oxides, such as those of iron and manganese, have oxygen atoms at the edges of the mineral. These oxygen atoms release and capture cations in reactions that are pH dependent. This cation exchange capacity, which captures heavy metals and releases protons, can range from 1 – 30 meq/100 g. The release of the proton (or hydronium ion) may result in a more acidic water (Evangelou, 1998). Green roof researchers, such as Long *et al.* (2008), have demonstrated the pollutant removal ability of certain expanded shales, slates and clays, indicating that these materials may be candidates for underdrains in constructed infiltration devices.

**Organic Matter Content.** Soil organic matter results from two major groups of compounds – the non-nitrogenous compounds (primarily carbohydrates) and the nitrogenous compounds (compounds derived from proteins). Seventy to eighty percent of the organic matter by weight in soils are humic substances (condensed polymers of organic compounds). They have a wide range of molecular weights and a large number of functional groups which participate in reactions in the soil that remove large quantities of pollutants. Heavy metal and soil colloid (including soil clays, humic substances or a combination) interactions result from ion exchange, surface adsorption, or chelation reactions. Humic substances may form complexes with heavy metals because of their oxygen-containing functional groups on their surface. The retention of heavy metals in native soils by the clays and humics varies with ionic strength, pH, clay mineral type, functional group type, and types of competing cations (Evangelou 1998). Commonly, the amount of metal ions adsorbed increases with increasing pH for humics and clays. The reactions that may occur in humic substances include the following:



- ◆ Protons ( $H^+$ ) compete with cations for organic binding sites
- ◆ Hydroxyl ions ( $OH^-$ ) competes with humic substances for the cationic-metal ion
- ◆ Soft metals ( $Ca^{2+}$ ,  $Mg^{2+}$ , etc.) compete with the hard/heavy metals for organic functional groups.

Complexation of metals also is a viable reaction in humic substances. These complexation reactions may be weak (outer-sphere of the particle) and reversible, or relatively strong (inner-sphere). Inner-sphere cations can be displaced only by other cations that can form inner sphere complexes (Evangelou 1998).

**Soil pH.** As noted above, soil pH plays a strong role in the resultant reactions. As Evangelou (1998) describes, low soil pH and acidity often results from hydrolysis reactions occurring in the soil. Aluminum ions on a mineral surface hydrolyze to produce  $H^+$ , which attacks the clay surface to produce more acidity. Soil pH is a controlling factor for CEC and AEC, which in terms describes the ability of a soil to remove charged pollutants. Soil and water pH also affect precipitation reactions. Many metals form sparingly soluble hydroxide precipitates at certain pHs. These precipitates would be expected to remain in the soil profiles once created, unless the soil and water pH change sufficiently to cause the precipitate to dissolve and the metal to be transported further.

**Oxidation-Reduction Potential.** Many metals in soil-water systems, such as iron and manganese, have the potential to change oxidation states. In oxidized soil-water systems, the system is electron deficient, and the higher oxidation states are more stable. The reverse is true for reduced environments. The implication for pollutant removal and retention is that the lower valence states of these metals generally are more soluble. This solubility may be mitigated by the presence of ions that will react with these lower valence ions to form insoluble compounds (Evangelou, 1998).

The impact of redox chemistry on pollutant retention is especially important when infiltration devices go quiescent between storms. Water remains in the pores and microbial activity may consume the oxygen, converting the water from aerobic to anaerobic. This may result in the release of previously-captured pollutants. Adsorption under anaerobic conditions has been shown to lead to weaker bonding between phenolic compounds and activated carbon (Abuzald and Nakhla, 1994). As shown in Johnson *et al.* (2003), Clark (2000), and Clark and Pitt (2009), heavy metal retention, except for iron, was good under anaerobic conditions, but previously-trapped nutrients were released from the organic media.

**Sodium Adsorption Ratio (SAR).** The sodium adsorption ratio is defined as the ratio of the sodium concentration to the square root of the average of the calcium and magnesium concentrations. The ratio of these ions in the soil can affect radically the performance of an infiltration device that contains even relatively small amounts of clay in the soil-media mixture. Clays in soils with an excess of sodium ions, compared to calcium and magnesium ions, remain in a dispersed condition, and are almost impermeable to rain or applied water. An SAR value of 15, or greater, indicates that an excess of sodium will be adsorbed by the soil clay particles. SAR values near 5 also can cause problems, depending on the type of clay present. Suarez, *et al.*

(2006) reported that SAR values above 4 caused decreased infiltration rates in a clay soil; SAR levels starting above 2 degraded infiltration in a loam soil.

**Impact of Soil Chemistry on Pollutant Capacity as Measured in Batch Tests.** As noted above, many factors affect the potential pollutant removal ability of a soil-based media. Table 3 summarizes a Pearson correlation analysis used to investigate potential relationships between soil chemistry parameters, as reported by the Pennsylvania State Agricultural Services Lab, of sixteen treatment media, including four Pennsylvania soils, and their batch-tested filtered-metal capacity. The analytical methods for this work are described in Pitt *et al.* (2010). The significance level for this correlation matrix was set at 0.05.

**Table 3.** Correlations between Soil Chemistry Parameters and Pollutant Removal Capacity.

	<b>Water-Phase Metals Removal Capacity</b>									
	<b>Al</b>	<b>Cd</b>	<b>Cu</b>	<b>Fe</b>	<b>Ni</b>	<b>Mn</b>	<b>Zn</b>	<b>Cr</b>	<b>Tl</b>	<b>Sb</b>
<b>Soil CEC</b>		+	+	-	+		+		+	
<b>Soil OM</b>		+	+		+			-	+	
<b>Soil pH</b>	+					+		+		+
<b>Soil C</b>		+	+		+			-	+	+
<b>Soil N</b>		+	+	-	+		+		+	
<b>Soil P</b>		+		-	+		+			
<b>Soil K</b>							+			
<b>Soil Ca</b>		+		-	+		+			
<b>Soil Mg</b>		+	+	-	+		+		+	
<b>Soil S</b>										
<b>Soil Cu</b>						-				
<b>Soil Zn</b>		+		-	+		+			

As expected, soil CECe (sum of exchangeable K, Mg, Ca) was directly correlated with the removal capacity for many of the heavy metals (Cd, Cu, Ni, Zn, Tl), but not for others (Al, Mn, Cr, Sb, Pb). CEC was negatively correlated with Fe capacity. Organic matter (OM) followed a similar trend to CECe for all the metals listed above, except for zinc. Zinc capacity was positively correlated with CEC but not OM. Soil carbon content's correlations with capacity tracked with OM content, as would be expected since carbon is a significant fraction of the organic matter. Soil nitrogen tracked with CEC but not identical to OM, which was not expected. It was anticipated that it would match the correlations of the organic matter since much of the nitrogen likely resulted from organic matter.

Soil pH was positively correlated with pollutant removal capacities for Al, Mn, Cr, and Sb – the metals that were not positively correlated with CEC. This may imply that there is another mechanism causing their removal, instead of ion exchange. Many of these metals are not soluble at neutral to high pHs. They also tend to participate relatively easily in redox reactions. It is possible that the soil pH affected the valence/redox state of these metals and encouraged removal at the higher pHs. For example, aluminum solubility in natural waters where reactions with phosphates and hydroxides are likely increases as the pH drops below 5 or is above 7 (Snoeyink and Jenkins 1980).

In terms of the CECe components, many of the heavy metals' capacities are positively correlated with soil Mg content and to a lesser extent to soil Ca content. This may indicate that soil Mg participates in an exchange reaction with these metals on the media. Mg is considered the readily-exchangeable +2 cation, with more of its salts considered soluble in water. Soil K is positively correlated with Zn and soil Ca is positively correlated with Cd, Ni, and Zn. Comparing the Mg correlations to the CEC correlations, it appears that Mg is the component of CEC that provides much of the exchange, likely because it is abundant in many of the media examined during this project.

Soil sulfur content was not correlated with the capacity for any of the metals.

**Impact of Soil Chemistry on Pollutant Capacity as Measured in Column Tests.** Table 4 summarizes the results of a Pearson correlation used to investigate potential relationships between soil chemistry parameters, as reported by the Pennsylvania State Agricultural Services Lab, and the batch-tested filtered-metal capacities of six stormwater treatment media. The analytical methods for this work are described in Pitt and Clark (2010). The significance level for this correlation matrix was set at 0.10, since the number of columns, and thus data points, is much smaller than for the soil results reported above.

**Table 4.** Correlations between Chemistry Parameters of Stormwater Treatment Media and Pollutant Removal Capacity.

	Water-Phase Metals Removal Capacity									
	Cd	Cu	Fe	Pb	Ni	Mn	Zn	Cr	Tl	Sb
Soil CEC <sub>e</sub>										
Soil OM										+
Soil C	+	+			+					
Soil N	+				+					
Soil P										
Soil pH										
Soil K										
Soil Mg										+
Soil Cu							-			
Soil Zn										+
Soil Ca				-						

When capacity is investigated through column testing (as described in Pitt *et al.* 2010), it is apparent that fewer soil chemistry parameters are correlated with capacity, even though the level of significance was relaxed, from 0.05 to 0.10. One potential reason for this was that capacity was calculated from mixed media columns, typically consisting of a treatment medium and a relatively-inert sand that was incorporated into the mixture to provide structure and control the hydraulics in the column. A second reason for the difference would be the fact that not all metals reached capacity in the column tests. For those metals where capacity was not reached during the testing, capacity was estimated based on the last measurement from the columns, and the actual capacity would be greater than the reported values. A third reason for the difference may be the need to define a functional capacity, as described below.

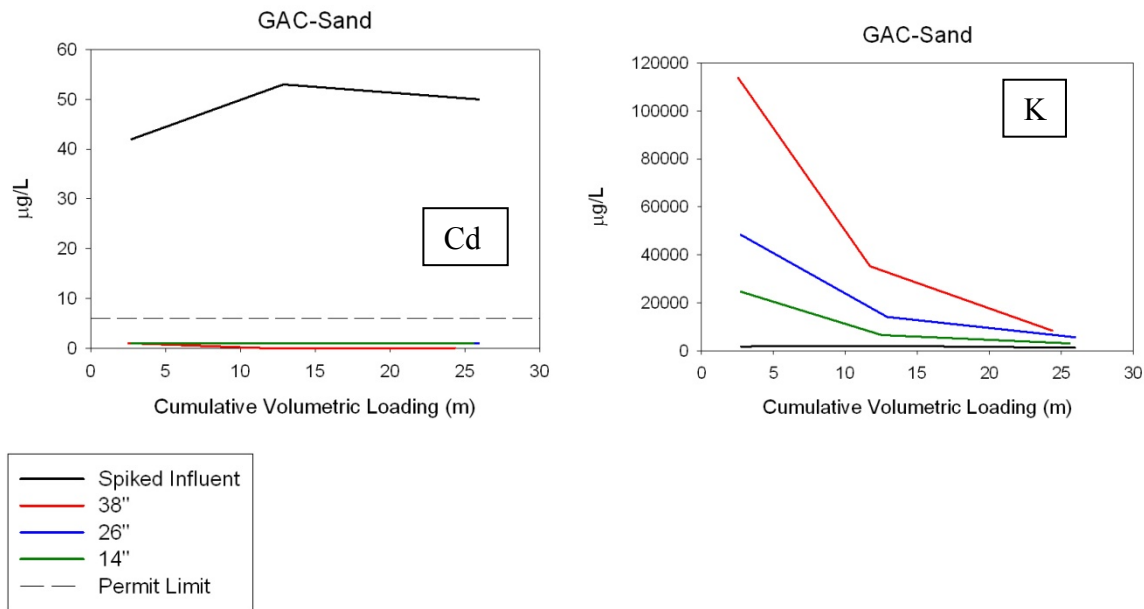
Compared to the batch testing, the CEC<sub>e</sub> is not correlated with the estimated media capacities for the listed metals. Organic matter is correlated only with Sb. Soil C, though, is correlated with the capacities for Cd, Cu and Ni. In the batch testing, C and OM almost tracked each other in terms of their relationships with a specific metal's capacity. In the column study, though, this was not the case. One possible reason for this is the subset of media chosen for this experiment. This subset contains two sands, two zeolites, a coconut based granular activated carbon (GAC), and peat moss. The batch testing added several other organic media to the testing, although the percentage of organic media did not change between the column testing and batch testing. GAC

typically is heat and/or acid activated and much of the organic matter is removed, leaving inorganic carbon. In the smaller data set, the use of only one organic media may have affected whether OM was critical in predicting capacity. In this series of column tests, soil Cu content was negatively correlated with zinc capacity. In the batch testing, soil Cu content had no impact on zinc removal. Soil Mg also demonstrated less of an influence on capacity.

Treese *et al.* (2009, 2010) (Figure 4) shows that for the upper organic layer of the soil, breakthrough occurred when the soil Cu content was 15 mg/kg. However, using the batch tests described in Table 3, the calculated capacity was approximately 40 mg/kg for the same soil. The functional capacity, or the capacity at which substantial downward migration of the saturation front could be expected, should be taken as 15 mg/kg, and not the 40 mg/kg. This also highlights the challenges of translating simple batch laboratory tests to field applications. If the lifespan of a bioretention device was estimated based on the laboratory tests, the media would reach capacity in approximately 1/3 of the estimated lifespan and after that, no copper removal would occur. One question that remains is how to translate batch testing results, even those performed with stormwater as the base fluid, to field applications, especially since  $CEC_e$  also cannot be used to predict lifespan. Batch testing typically encourages equilibrium conditions and provides time for the pollutants to migrate into the media, plus attach to the surface sites. Column tests in stormwater field operations, where the media are free-draining, rarely provide sufficient contact time for pollutants to migrate to the interior pores of the media. Only the surface sites are readily used for pollutant removal.

**Trade-Offs.** Pollutant removals in (bio)(in)filtration media generally occur through ion-exchange reactions. Therefore, it is important to know what ions are being exchanged during pollutant removal and to determine whether these exchanged ions are problematic in the effluent water and discharge location. An example of the trade-offs in pollutant capture versus ion export is shown in Figure 5 for a GAC-sand column of varying depths. In this case, the capture of cadmium was excellent and was not a function of column depth. However, deeper columns results in greater export of potassium from the media, likely as a result of increased ion-exchange reactions occurring in the media due to increasing media contact as the residence time increases. These ion exchange reactions likely involve the capture of the metals as well as the capture of the hydrogen (hydronium) ion, since the pH of the effluent water was at least 1 pH unit higher than the influent water for these columns.

Based on the results in Figure 5, it appears that a treatment media depth of 14 inches would be ideal since cadmium capture is not a function of depth in the ranges investigated during the supporting study, and it would minimize export of potassium from the media. However, this is not true for all pollutants. This GAC provided excellent capture of nitrate until its removal capacity was saturated. Increasing the depth increased the nitrate capture substantially, but it also increased the phosphate leaching.

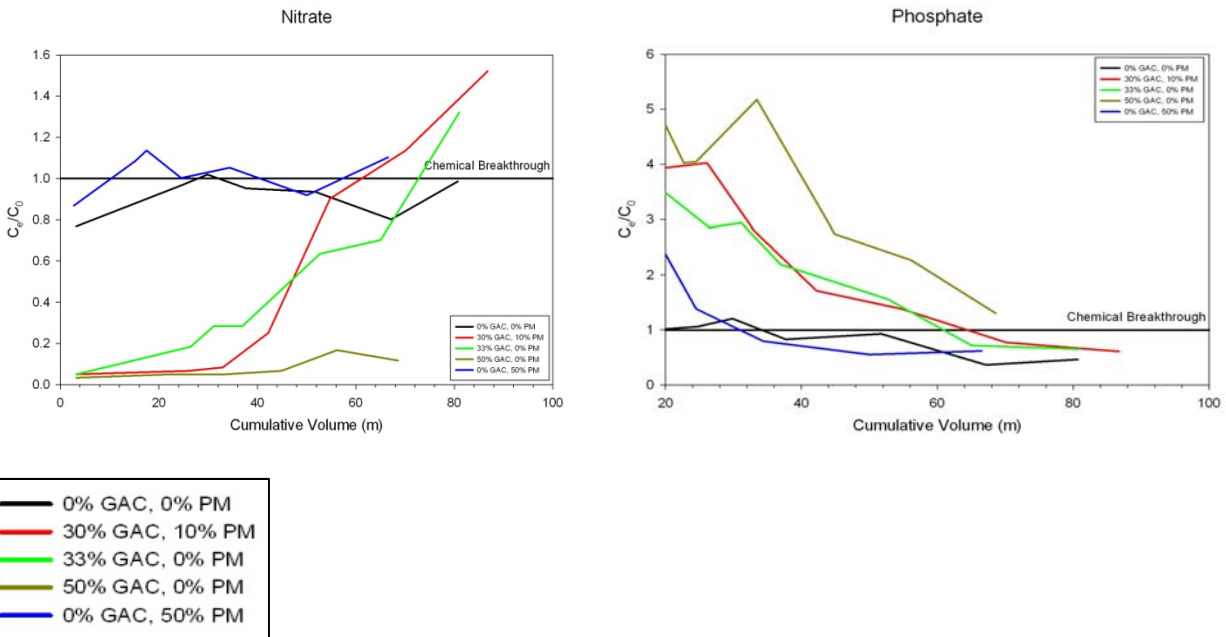


**Figure 5.** Ion exchanges for a coconut-hull GAC-sand mixture as a function of column depth for cadmium (left) and potassium (right).

These trade-offs greatly affect the design of (bio)(in)filtration devices. While metals may be captured well, as noted above, these trade-offs affect the capture or release of other pollutants. Figure 6 highlights these trade-offs for nitrate and phosphate with various percentages of the coconut-based GAC and peat moss in the column. Another trade-off that has been addressed in the literature has been the fraction of organic matter that is incorporated into the design. Treese *et al.* (2010) describe how the disturbance of native soil profiles results in initial high releases of nutrients. Hunt *et al.* (2006) state that the use of compost in bioretention should be limited to low-phosphorus compost. Compost whose phosphorus content exceeds the needs of the plants grown in it will leach phosphorus in the passing stormwater runoff and will export both nitrogen and phosphorus.

## DESIGNING A (BIO)(IN)FILTRATION SYSTEM TO TREAT “DISSOLVED” HEAVY METALS

Filtered or “dissolved” copper is used as an example of how to integrate the water chemistry and soil media information to design a (bio)(in)filtration system. Assuming a runoff water pH of approximately 7, filtered copper can exist in multiple forms. If no DOM is in the runoff, it can be assumed that approximately 25% will have a +2 valence charge, 10% will have a +1 valence charge, 65% will have a 0 valence charge and less than 1% will have a -2 valence charge. With DOM in the system, it could be assumed that approximately one third of the copper will be associated with organic complexes (and the percentages described above would be that portion that was not associated with organic complexes).



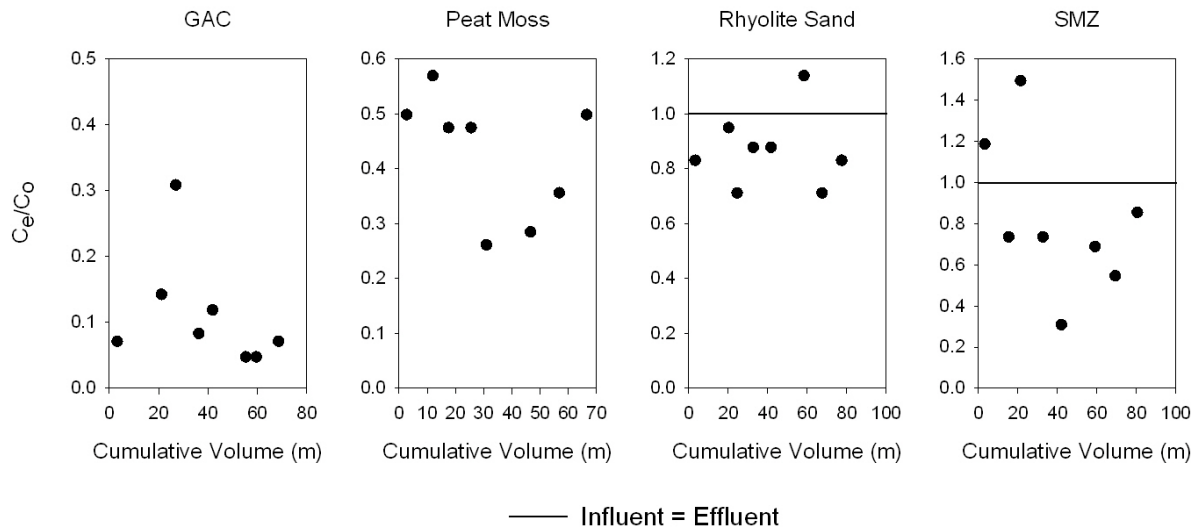
**Figure 6.** Trade-offs during design of (bio)(in)filtration systems – nitrate capture versus phosphate release.

A valence charge of +2 indicates that ion exchange may be viable for that portion of the copper. Therefore, an ion exchange resin such as a zeolite could be considered. However, a valence charge of +1, particularly for a copper hydroxide complex, may not be readily removed by ion exchange. The complex is likely to be larger than most of the lattice openings on traditional ion exchange resins such as zeolites. If the percentage of -2 copper was greater, then anion exchange may need to be considered. The valence charge of 0 certainly will not be removable by ion exchange and therefore, other removal mechanisms need to be considered. The valence charge of 0 and +1 may need to be removed through the use of a media that participates in what appear to be non-charge reactions. The molecules themselves may not have a valence charge but may have a dipole and participate in weak ionic bonding to the media or they may be bound by other mechanisms that are not well characterized.

Applying this to the selection of media, Table 3 from the batch capacity testing indicates that copper capacity is related to  $CEC_e$ , OM content, soil C content, soil N content, and soil Mg content. Table 4 from the column capacity testing indicates that capacity is related to soil C.  $CEC_e$  and soil Mg content relate to the ability of the media to participate in ion exchange reactions. Therefore, at least one component in a media mixture should provide excellent ion exchange, such as would be found with a good zeolite. This media should be able to participate in reactions with the +2 copper and a portion of the +1 copper, although the +1 copper may not be as strongly bound and may be displaced if a more preferable exchangeable ion approaches the media's removal site. Soil OM, soil C, and soil N all relate to the organic matter content and indicate that these are sites that may participate in a variety of reactions and may be able to remove pollutants that do not carry a valence charge. Therefore, an organic component should be

incorporated. Sand may be needed for structure and controlling flow rate to a level that allows for sufficient contact time.

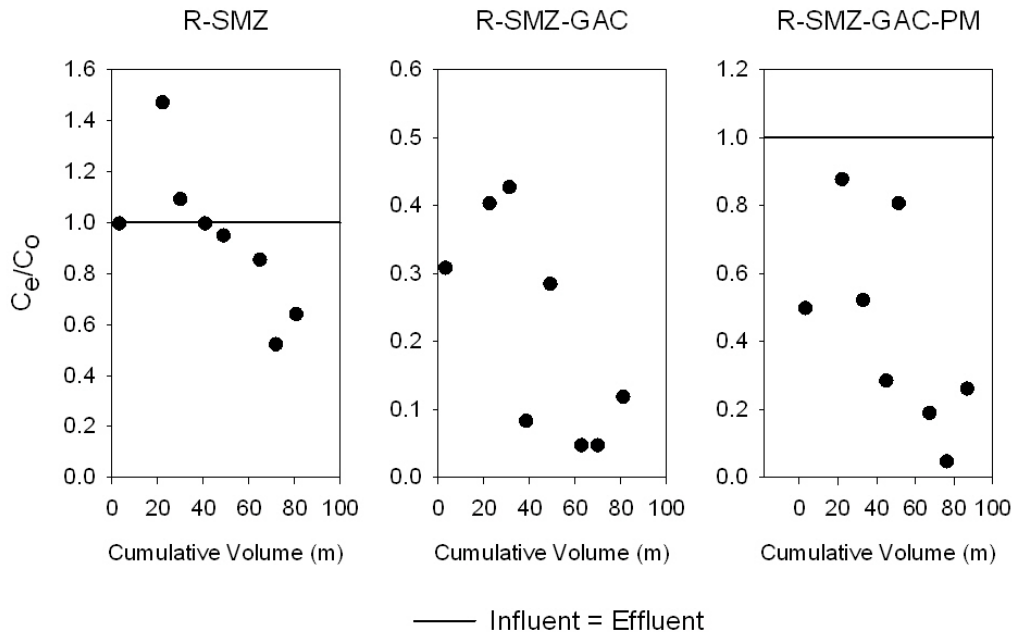
For the project described in Pitt *et al.* (2010), this can be applied to optimizing a bioretention design to remove filtered copper. Four candidate media are being evaluated: a rhyolite sand, peat moss, a coconut-based GAC, and a surface-modified zeolite (SMZ). Figure 7 shows the removal ability of these four media for filtered copper expressed as the ratio of effluent concentration to influent concentration. The four media in Figure 7 were mixed with sand (50/50 v/v) to improve hydraulics.



**Figure 7.** Ratio of filtered copper effluent concentration to influent concentration for four candidate bioretention media.

Based on Figure 7, filtered copper removal can be ranked from best to worst as  $GAC \ll Peat Moss < SMZ \leq rhyolite\ sand$ . Therefore, if copper is the only pollutant of interest after the trade-offs have been evaluated, then the final bioretention design should be a mixture of GAC and sand. However, this may not provide enough organic content in a bioretention design to support plant life. Also, GAC can be very expensive and its use may need to be curtailed based on economics. To provide that organic matter for plant growth and acceptable pollutant removal, peat moss could be incorporated with GAC in the mixture. While this should provide good removal, the addition of the zeolite will encourage the +2 ion exchange reactions described above. Since rhyolite sand provided some removal (slightly greater than the site's process sand), rhyolite sand could be substituted for the site sand if the price differential is not substantial. Figure 8 shows how this translates to the creation of media mixtures for copper treatment.





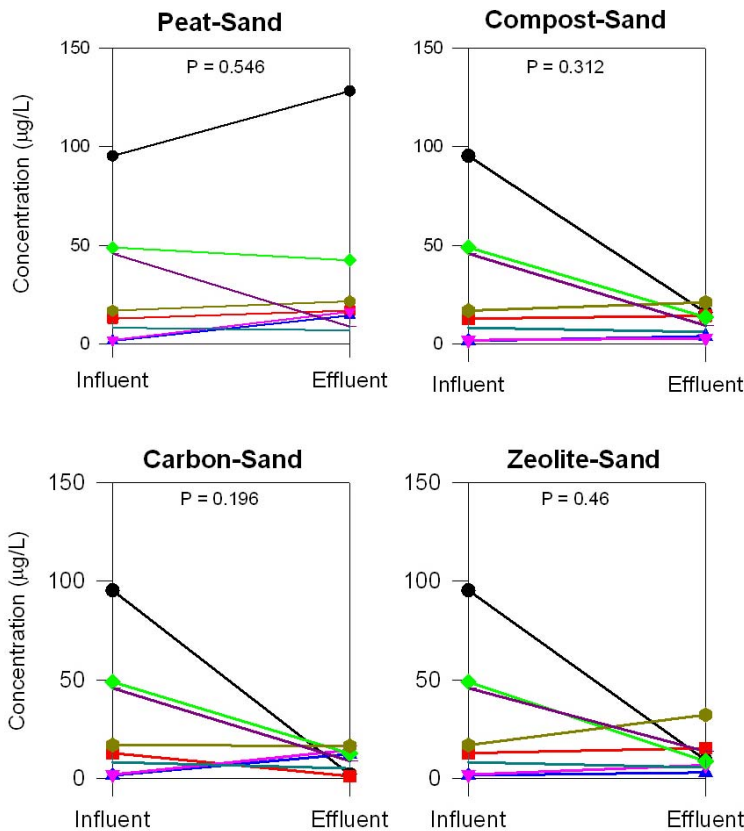
**Figure 8.** Filtered copper removal by media mixtures.

The R-SMZ (75% rhyolite sand and 25% surface modified zeolite) mixture contains no GAC and no organic matter. Its ability to treat copper would be limited primarily to ion exchange reactions with the +2 and some +1 valence copper (30 – 35% of the influent copper if no DOM is in the system; less if organic complexation is a substantial fraction of the influent copper association).

As can be seen in the left figure, removal efficiencies range from 0 to 70%, but with most ranging from 0 to 40%. This is in line with the prediction based on the fraction of the influent water that is associated with ion exchange reactions. Reducing the fraction of rhyolite (from 75% to 1/3), increasing the SMZ from 25% to 1/3, and adding 1/3 GAC (center) improve the removal of filtered copper from the runoff water. Removal efficiencies range from 60 to 95%. The addition of GAC has provided sites that will capture and retain the +1 and 0 valence charge copper compounds. Because this mixture has no organic matter to support plant growth, the fractions of rhyolite sand, SMZ, and GAC were reduced to 30% and 10% by volume peat moss was added (right). The removal efficiencies range from 10% to 95%, with the median removal being approximately 50% (compared to 20 – 25% for the mixture with no peat moss). The addition of peat moss did not improve the copper removal.

For the specific project described in Pitt *et al.* (2010), only peat moss was evaluated as the organic matter source. Clark (2000) evaluated other potential filtration media for their ability to remove filtered copper (Figure 9 shows the influent and effluent concentrations after treatment by a GAC, a zeolite, a municipal leaf compost, and peat moss – all mixed 50/50 v/v with sand). None of the media in the Clark (2000) study were obtained from the same suppliers as in the Pitt *et al.* (2010) study. However, the results appear to be similar in terms of trends of removal ability. None of the removals are statistically significant and conclusions about removal ability

and efficiency cannot be drawn. At the higher influent concentrations, the compost, carbon, and zeolite were able to treat filtered copper to approximately 10 – 25  $\mu\text{g/L}$ . In this case, in terms of removal ability, the ranking would be GAC < compost < zeolite < peat moss. Based on these results, the compost would be the better choice, compared to the peat moss, to provide organic content for the plant growth. The Pitt *et al.* (2010) study, however, did not evaluate compost as an organic component for the final media mixtures and therefore, its performance can only be speculated as part of a final bioretention mixture.



**Figure 9.** Removal of filtered copper by four potential (bio)(in)filtration media.

These results also highlight another challenge of all natural filtration systems that do not use chemical or UV pretreatment. There is a lower limit to the removal. In general, effluent concentrations ranged from approximately 2 to 20 – 25  $\mu\text{g/L}$ . Increasing contact time through media depth or outlet control likely will not substantially increase removal since these filters were operated in the flow range of slow filters.

These results do not address the effects of the biological component of (bio)filtration systems. They focus on the media results only. It is anticipated that the addition of plants to these systems may improve their ability to capture and retain “dissolved” pollutants, but that much of the

effects of the plants will be on nutrients. Metals capture likely will continue to be in the media itself and until the surface media capacity is exhausted, it likely will occur in the top 3 cm of the (bio)(in)filtration system.

## CONCLUSIONS

To address water quality concerns and numeric effluent limits, the designers of (bio)(in)filtration systems will need to integrate water and soil chemistry into the selection of filtration media mixtures. For the “dissolved” metals, designers will need to consider the ratio of valence states as they consider the proportion of ion exchange resins versus organic-based media in the final media mixture. As more of the total metal concentration has either a 0 or +1 valence charge or as more is associated with organic complexes, the smaller the fraction of an ion exchange resin, such as a zeolite, are needed. For metals such as thallium, where few inorganic and organic complexes are formed and where the predominant valence state is +2, increasing the amount of zeolite in the final media mixture is important for improving removal. Therefore, the final media mixture will be based on the pollutants of interest and their water chemistry. As the soil chemistry correlations showed, capacity is directly related to OM and CECe content for many metals. Since organic matter will contribute to CECe, this is not surprising. The organic media, though, provides a wider range of treatment sites. Activating an organic media, such as granular activated carbon, will increase the number of surface active sites for treatment, but this media will not sustain plant growth.

Other trade-offs also have to be considered in a complete analysis of (bio)(in)filtration media. As described briefly in this paper, for the media evaluated in Pitt *et al.* (2010), increasing the amount of the media to improve nitrate removal and retention, but also increases the amount of phosphate released. The tradeoff may be based on an optimization analysis between the damage caused by reduced nitrate treatment and the additional release of phosphate. Finally, there is a lower limit to treatment, given the draindown times required for many bioretention devices.

Slightly improved removals may be achieved with longer contact times for many metals, but the substantial increase in surface area devoted to (bio)(in)filtration may not be cost-effective (given the draindown time requirements). This paper used “dissolved” copper as an example of how to use both soil and water chemistry to design an optimal bioretention media from a subset of potential mixture components.

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## REFERENCES

Abuzald, N.S., and G.F. Nakhla. (1994). Dissolved oxygen effects on equilibrium and kinetics of phenolics adsorption by activated carbon. *Environ. Sci. Technol.* **28**(2):216-221.

Clark, S.E. (2000). *Urban Stormwater Filtration: Optimization of Design Parameters and a Pilot-Scale Evaluation*. Ph.D. Dissertation, University of Alabama at Birmingham, Birmingham, Alabama. 430 pages.

Clark, S.E.; R. Pitt (2010). Integration of site and media characteristics to design (bio)(in)filtration systems. *Proceedings, 2010 World Environmental and Water Resources Conference*. Providence, RI, May 16 – 20, 2010. American Society of Civil Engineers, Reston, VA. CD-ROM.

Clark, S.E.; R. Pitt. (1999). *Stormwater Runoff Treatment: Evaluation of Filtration Media*. EPA 600/R-00/010. U.S. Environmental Protection Agency, Water Supply and Water Resources Division, National Risk Management Laboratory. Cincinnati, Ohio. 405 pages.

Clark, S.E.; R. Pitt. (2009). "Stormwater filter media pollutant retention under aerobic versus anaerobic conditions." *Journal of Environmental Engineering*, Vol. 135, no. 5, pp. 367-371. 2009.

Evangelou, V.P. (1998). *Environmental soil and water chemistry: Principles and applications*. Wiley-Interscience, New York, NY. 600 pages.

Hunt, W.F.; A.R. Jarrett; J.T. Smith; L.J. Sharkey, L.J. (2006). Evaluating bioretention hydrology and nutrient removal at three field sites in North Carolina. *Journal of Irrigation and Drainage Engineering*, 132(6), 600-608.

Johnson, P.D.; Pitt, R.; Durrans, S.R.; Urrutia, M.; Clark, S. (2003). *Innovative metals removal technologies for urban stormwater*. Water Environment Research Foundation. WERF 97-IRM-2. Alexandria, VA.

Long, B.; Clark, S.E.; Baker, K.H.; Berghage, R. (2008). Green roofs – A BMP for urban stormwater quality? *2008 World Environ. and Water Resources Congress Proc.*, Honolulu, HI, May 13 – 16, 2008. American Society of Civil Engineers, Reston, VA. CD-ROM.

Morquecho, R. (2005). Pollutant associations with particulates in stormwater. Ph.D. Dissertation. University of Alabama, Tuscaloosa, Alabama. 220 pages.

Morquecho, R.; Pitt, R.; Clark, S.E. (2005). Pollutant associations with particulates in stormwater. *World Water Congress 2005: Impacts of Global Climate Change – Proc.* American Society of Civil Engineers, Reston, VA. 216.

Pitt, R.; B. Robertson; P. Barron; A. Ayyoubi; S. Clark. (1999). *Stormwater Runoff Treatment at Critical Areas: The Multi-Chambered Treatment Train (MCTT)*. EPA 600/R-99/017. U.S. Environmental Protection Agency, Water Supply and Water Resources Division, National Risk Management Laboratory. Cincinnati, Ohio. 505 pages.

Pitt, R.; S. Clark; B. Steets. (2010). Laboratory evaluations to support the design of bioretention systems in the southwestern U.S. *Proceedings, 2010 World Environmental and Water Resources Conference*. Providence, RI, May 16 – 20, 2010. American Society of Civil Engineers, Reston, VA. CD-ROM.

Pitt, R.; Clark, S.; Field, R. (1999). Groundwater contamination potential from stormwater infiltration practices. *Urban Water*. **1**(3):217-236.

Snoeyink, V.; D. Jenkins. (1980). *Water Chemistry*. John Wiley & Sons. 480 pages.

Suarez, D.L.; Wood, J.D.; Lesch, S.M. (2006). Effect of SAR on water infiltration under a sequential rain-irrigation management system. *Agricultural Water Manage.* **86**:150-164.

Treese, D.P.; S.E. Clark; K.H. Baker. (2010). Effect of soil disturbance in native and engineered soils used in stormwater infiltration systems. *Proceedings, 2010 International Low Impact Development Conference: Redefining Water in the City*. San Francisco, CA. April 11 – 14, 2010. American Society of Civil Engineers, Reston, VA. CD-ROM.

Treese, D.P.; Clark, S.E.; Mikula, J.B.; Baker, K.H. (2009). Pollutant transport within the vadose zone: Interactions of soil horizon chemistry on water quality. *2009 World Environ. and Water Resources Congress*, Kansas City, MO, May 2009. American Society of Civil Engineers, Reston, VA. CD-ROM.

Troeh, F.R.; L.M. Thompson. (2005) *Soils and Soil Fertility*. Wiley-Blackwell. 489 pages. ISBN: 978-0-8138-0955-7

UBC Soil Web. University of British Columbia Soil Web. URL:  
<http://www.landfood.ubc.ca/soil200/interaction/ions.htm>