OPTIMIZING BIORETENTION MEDIA TO TREAT EMERGING CONTAMINANTS

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ABSTRACT

Stormwater treatment is entering a new phase with stormwater management systems being required to meet specific numeric objectives. Meeting numeric discharge requirements will require designers to better understand and apply the physical, chemical, and biological processes underpinning these treatment technologies. This paper uses an example of an industrial site with a numeric discharge permit to illustrate how this theoretical information can be translated into the design of a bioretention/biofiltration treatment system for not only conventional pollutants, but also emerging contaminants such as dioxin, mercury, and radionuclides.

KEYWORDS: stormwater chemistry, treatability, sedimentation, filtration, biological treatment systems

INTRODUCTION

To prevent further degradation and to potentially recover some ecological functionality, it is critical that new and re-developments limit their discharges of stormwater-borne pollutants. In the U.S., these requirements are being enforced typically through National Pollutant Discharge Elimination System (NPDES) permits and Total Maximum Daily Load (TMDL) regulations. Historically, dischargers selected treatment technologies stated to meet specific pollutant percent removals or were the best practical treatment option available. As the need to improve stormwater discharge quality increases, some regulatory agencies are pursuing numeric limits by specifying either effluent concentrations or documentable numeric load reductions. Thus, stormwater site designers must understand how to design systems to achieve these objectives.

Good stormwater design starts first with prevention of excess runoff and pollutant generation through source control and other non-structural measures. However, even sites designed following integrated stormwater management principles have the potential to discharge contaminated runoff. The selected treatment technologies must address appropriately the siteǿs specific pollutants.

CASE STUDY SITE DESCRIPTION

Preferred treatment technologies typically require no electrical power and infrequent maintenance since they are dispersed in the urban environment and treat intermittent flows. This is why bioretention/biofiltration is an attractive option. It combines many unit processes into a single device. To illustrate how bioretention can be optimized to improve treatment performance, the industrial site described in Pitt and Clark (2010) will be used as an example. Site stormwater runoff was required to meet specific permit limits (Table 1). By plotting the data as a probability density function against permit limits, the pollutants for which permit violations would be anticipated were identified (NO_2+NO_3, total zinc, total cadmium, total copper, total lead, total mercury, TCDD) (Pitt and Clark 2010). The treatment processes focused on those problematic pollutants instead of the entire suite of pollutants on the permit.

Table 1. Monitored Stormwater Characteristics, Permit Limits, and Estimated Exceedences if Untreated)

Analytes on Permit	**90th percentile historical stormwater concentration (outfall 1/outfall 2, or combined if no significant difference)**	**Permit Limit (outfall 1/outfall 2 if different permit limits)**	**Expected Exceedence (% of samples exceeding permit limit if untreated)**
Oil and grease (mg/L)	2/3	15	**5**
Chloride (mg/L)	20/30	150	0.1
Sulfate (mg/L)	20/100	300/250	<<0.01
Ammonia N (mg/L)	N/A	10.1	SMALL
Nitrate+nitrite N (mg/L)	8	8	**10**
Zinc (µg/L)	140	159	**10**
Copper (µg/L)	15	14	**10**
Mercury (µg/L)	0.15	0.13	**15**
Lead (µg/L)	25	5.2	**40**
Thallium (µg/L)	ND	2	UNK
TCDD (µg/L)	$5x10^{-6}$	$2.8x10^{-8}$	**40**
Perchlorate	1.5	6	0.1
Suspended Solids (mg/L)	300	N/A	Not on Permit
Copper, filtered (µg/L)	3.5	N/A	Not on Permit
Lead, filtered (µg/L)	0.9	N/A	Not on Permit

N/A: not analyzed
ND: not detected in any of the site samples
SMALL: small likelihood of exceeding permit limits; canôt be better quantified due to lack of adequate monitoring or site data, but available data are well below the permit limits.
Bold type (in exceedence column); exceedence probability values > 1% over the long term.
Not on Permit: These constituents were monitored in order to evaluate treatment options.

TREATMENT OF SUSPENDED SOLIDS

Similar to water and wastewater treatment plants, solids removal must be evaluated as the first step since runoff solids can clog treatment devices and/or block access of the pollutant to treatment sites in chemically-based systems. Droste (1996), based on guidance published by the American Water Works Association, recommends that sedimentation precede filtration unless the water quality meets the following parameters:

- Color < 40 color units
- Turbidity < 5 NTU (deep filters may be used to treat higher turbidity waters)

Because many pollutants are at least somewhat associated with the particulate matter in runoff, sedimentation removes pollutants other than just solids. The effluent concentrations and removal efficiencies of particulate-associated pollutants can be predicted based on the removal efficiency of the solids themselves and the association of the pollutants with the settling solids. Kim and Sansalone (2008) showed that many metals in highway runoff were associated with the larger particles, and that sedimentation would be effective. However, for runoff from more diffuse sources and where large-size particle generation and transport is not likely, many of the pollutants are associated with very-small solids (Morquecho et al. 2005). The selection of the desired particle-size control is critical. High surface overflow rates (SORs) result in basins that do not settle much of the smaller-sized particulates and may result in poor treatment of the particle-associated pollutants. There is also a limit to sedimentation basin efficiency for small solids, given the repulsive charges on the colloidal and clay-sized solids.

For this site, the historical 90th percentile TSS concentration of 300 mg/L indicated that solids treatment should be incorporated as the first step, since this likely results in a turbidity (not monitored) that exceeds the AWWA criteria for stand-alone filtration (Droste 1996). Other studies (Clark, 2000; Pitt and Clark 2010) showed that suspended solids in this range may reduce the treatment effectiveness and lifespan of downstream treatment devices, especially those that use filtration as a primary treatment mechanism. This elevated suspended solids concentration is best treated by sedimentation, either in a standard detention facility or using inclined plate settlers. Since sedimentation is pre-treatment on this site and because the maintenance requirements for chemical-addition systems would be expensive, coagulation was not selected as a means to enhance sedimentation.

TREATMENT OF SOLIDS-ASSOCIATED POLLUTANTS

As can be seen in Table 1, total copper and total lead concentrations were likely to violate the permit limit periodically. However, by monitoring the filtered forms during this period, it can be seen that the concentration of the filtered fraction alone (< 0.45 µm) was not likely to violate the permit. Therefore, removing the particulate-associated copper through a suitably designed sedimentation process should be sufficient to achieve the permit limits, assuming that the copper is associated with particles large enough to be treated by sedimentation. According to Morquecho et al. (2005), approximately 26 and 41% of the total copper and lead, respectively, were removed when particles larger than 20 µm were removed; 30 and 60%, respectively, when particles larger than 5 µm were removed; and 35 and 70%, respectively, when particles larger than 1 µm were removed. For the data presented above, removal of 10 to 20% of the particulate-bound copper would result generally in meeting permit limits; however, for lead, removals must exceed 80%. Filtered zinc was not evaluated; however, the likelihood of exceedence was not great and the 90th percentile value was less than the permit limit. Only small percent removals would be required for zinc and the Morquecho et al. (2005) data show that treatment to 20 µm would achieve 60% removal, which should be sufficient.

For pre-treatment sedimentation, the design particle size for maximum sedimentation could be set at 5 µm. The smallest particle size for which reliable sedimentation can be assumed, and without substantial charge interference of the settling particles, is between 2 and 5 µm (Camp 1952). Because a substantial fraction of the lead is associated with clay-sized and colloidal particles, filtration, likely using a chemically-active media, also will be required. A sand filter could be installed and expected to reduce the solids and lead concentration down to close to the permit limit (70% of 25 µg/L = 17.5 µg/L removed; 7.5 µg/L in solution assuming filtration can remove all particles Ó1 µm). Because this does not achieve the permit limit, particles < 1 µm also must be removed, typically through chemical interactions between the filter media and the particles. This need for chemical interactions requires the incorporation of a reactive media, such as zeolites, activated carbons, and/or organic matter.

TREATMENT OF COLLOIDAL AND IONIC POLLUTANTS THROUGH PHYSICAL AND CHEMICAL PROCESSES IN MEDIA FILTERS

Selecting Treatment Processes for the Pollutants

The pollutants remaining on the treatment list in Table 1 include particulate lead (between 0.45 ï 5 µm), colloidal/ionic lead (< 0.45 µm), NO_2+NO_3, TCDD, mercury, and oil and grease. Many of these can be treated using chemically and biologically active filtration systems. The first step in the selecting of an appropriate filter medium is identifying the pollutant types and forms that require removal. Physical separation for particles greater than colloids and clays can be accomplished using sand filters. Sand without surface amendments such as oxide coatings, though, is considered relatively inert compared to other media and minimal removal likely would occur for the pollutants listed above. Sand often though is incorporated into stormwater media to provide structure and to minimize fluctuations in flow rate through the media (Galli 1990; Lo et al. 1990; Clark 2000). Sand removal efficiencies typically increase as the media/filter ages because the trapping of particles typically decreases the pore openings, especially on the surface, allowing smaller particles to be captured, plus the coating of chemically and biologically active materials on the inert sand particles occurs with time (Metcalf and Eddy 2003). For example, bacteria capture enhances removal of other compounds because of the chemically-reactive organic compounds, exopolymers and others, that many bacteria excrete (Mittelman and Geesey 1985; Geesey et al. 1988; Wolfaardt et al. 1994; Chen et al. 1995; Prado Acosta et al. 2005). The performance of this enhancement has not been quantified, though, and, for this site, cannot be expected to reliably achieve permit limits.

According to Morquecho et al. (2005), lead < 0.45 µm is mostly ionic with a small fraction associated with organic colloids/dissolved organic matter. Clark and Pitt (2011) showed that zeolites can be effective for the fraction of copper in solution that exists as Cu^{2+}. However, the overall effectiveness of zeolites, and potentially other ion-exchange media such as oxide-coated sands, was reduced because much of the copper likely existed in valence forms other than the favored +2. The effectiveness of ion exchange decreases as the valence charge approaches zero. Lead, however, is likely mostly ionic and zeolites are potentially an effective component of the final media. The effectiveness of zeolites and other ion-exchange media will be reduced somewhat because lead does form some complexes with hydroxides and chloride, which have charges ranging between 0 and +2, but the fraction of non-ionic forms is small.

Mercury as a metallic ion exists in the +2 form. However, in the presence of organic matter, it can methylate to form methyl mercury. Methyl mercury is an organometallic compound and is polar, meaning that it will have an unbalanced charge on the molecule. However, because of its size and its organic component, it is not likely to be removed by zeolites, which have both a size exclusion and a preference for strongly charged, small molecules. Mercury also complexes with inorganic ligands in the water, such as chlorides, creating inorganic molecules whose surface charge and/or size may reduce the effectiveness of ion-exchange media (Snoeyink and Jenkins 1980).

Organic compounds and larger, less charged complexes of metals can be chemically attracted to or bonded with a media that can exploit dipole moments and hydrogen bonds, as well as a mixture of negatively and positively charged surface sites. Removal of organic pollutants can be directly related to two equilibrium constants associated with each organic compound, K_{OW} and K_S. K_{OW} will provide an indication of the preference for the molecule to attach to an organic media (peat, compost, GAC) versus remaining in the stormwater runoff. K_S indicates the likelihood that the organic compound will remain dissolved in solution. These constants are qualitatively inversely related, i.e., high K_{OW} compounds typically have low K_S values. For the constituents of concern here ï methylmercury, TCDD, and oil and grease, TCDD has the highest K_{OW} and lowest K_S (Kow = $10^{6.8}$; K_S = 0.1 mg/L for monochloro isomers to 10^{-9} mg/L for octochloro isomers). Therefore, TCDD is preferentially removed by an organic media that can participate in dipole interactions, hydrogen bonding and van der Waals reactions. The low K_S value indicates that it is not likely to resolubilize in the water. Therefore, the transport of TCDD through a media column is likely to be slow with good retention in the media mixture. Methylmercury has a lower K_{OW} and higher K_S (log K_{OW} = 1.7 to 2.5; K_S =1 µg/L), but the K_{OW} still indicates a fairly strong preference for removal by an organic media. Oil and grease behavior is harder to estimate since that is a generic name for many compounds associated with motor oils and other vehicle-associated petroleum products. Oil and grease do not have specific K_{OW} and K_S values. The literature indicates, however, that many of the petroleum-associated products in stormwater runoff are higher molecular weight polyaromatic hydrocarbons (PAHs) (Pitt et al. 1995). These compounds, because of their aromatic ring structure and multiple rings, have high K_{OW} and low K_S values, indicating that an organic media may be very effective for treatment.

Other inorganic cations and anions, specifically nitrate in this example, are problematic because most media have high cation exchange capacities (CEC) and low anion exchange capacities (AEC). CEC and AEC provide an estimate of the potential for exchanging a less-desirable compound in or on the media with a pollutant whose chemical characteristics are more favorable for an interaction. Fortunately, nitrate is a plant nutrient and it may be removed by biological uptake in the root zone of the vegetated system, assuming that the flow rate through the root zone is within the range for microbial and plant uptake (relatively slow to allow uptake).

Selecting the Filtration Media

In industrial water treatment, granular activated carbon is commonly used to retard the transport of organic pollutants from water through mechanisms such as van der Waals attractions and hydrogen bonding. Granular activated carbon (GAC), though, is expensive. Its use may be justified when the treatment is required to achieve very low permit limits. In this case study, granular activated carbon was considered because of the extremely low TCDD permit limit of 2 x 10^{-8} µg/L. Testing of a virgin coconut-hull GAC from Baker Corp. showed that this GAC was able to remove TCDD below the detection limits, which were approximately equal to the permit limits (Pitt and Clark 2010, 2011). This extensive testing, which evaluated several media and a suite of pollutants (both total and filtered), also showed that the GAC was able to remove metals, including mercury, down to concentrations well below permit limits, likely due to its ability to react with organic and inorganic complexes of these metals which had valence states of -2, 0, +1 and +2 (Clark and Pitt 2011).

GAC is not routinely suggested for incorporation into stormwater treatment media because of its cost and because not all GACs perform equally well for all pollutants; their performance is dependent on their native material and how they are activated (comparison to GAC used in Clark and Pitt 1999). In addition, if the treatment system is vegetated, an organic component that is not activated must be incorporated to provide carbon and other nutrients for the plants.

Two materials that have received attention as an organic component in filtration media are peat and compost. Peat has been extensively studied for its treatment effectiveness in both industrial wastewater and stormwater applications (Allen et al. 1992; Galli 1990; Clark and Pitt 1999). Peat has been shown to be very effective at removing many metals and hydrocarbons, and likely metal complexes, down to very low concentrations because of the variety of binding sites (carboxylic acid, etc.) found in the humic materials and lignins in the peat (Cohen et al. 1991; Kopinke et al. 1995; Lyon 1995; Sharma and Foster 1993). Many of these sites are involved in chemical bonding reactions that are more permanent (chemisorption versus physisorption) compared to the hydrogen bonding and van der Waals forcesôreactions occurring in GAC. According to Cohen et al. (1991), peatôs ability to treat metals can be directly related to its degree of decomposition with *Sphagnum* peat, the least decomposed, being less able to treat metals than *Carex* peat, which is more decomposed and better able to treat metals. However, Clark and Pitt (1999) showed excellent removals of several heavy metals with *Sphagnum* peat, potentially to the level that would meet many permits, and *Sphagnum* peat is readily available at nurseries, as opposed to some other forms of peat. In addition to the release of colored humic and fulvic acids, peatôs primary disadvantage, especially the Sphagnum peat, is that it tends to exchange hydronium ions when it removes metals. The release of hydronium ions reduces the pH of the treated water, often by 1 ï 2 pH units (Clark and Pitt 1999; Clark 2000). This may reduce the pH to a level where many of the metals attached to the media or runoff solids may become more soluble. As an advantage, peat was found by Pitt and Clark (2011) to more effectively remove many of the heavy metals during relatively short contact times (as little as 10 minutes), compared to the other non-organic media tested (which required several hours of contact time). The contact time affects the size of the device with larger and/or deeper devices required to increase the contact time.

Compost, especially that made from municipal leaf waste, also has received much attention in the last decade, especially since it is considered a sustainable material. Compost, like peat, has a variety of potential reaction sites for metals, organics and other pollutants (Sharma and Foster 1993; Guisquiani et al. 1995; McFarland et al. 1992). Unlike peat, it does not tend to drop the pH of the treated stormwater (Carnes and Lossin 1970; Clark and Pitt 1999), but it commonly releases nutrients as it degrades during the first several years of use as a soil amendment for treating stormwater (Pitt, et al 1999), if added at a high concentration. Compostôs ability to treat pollutants and the likelihood that it will release nutrients is directly related to its source material and percentage in the mixture (Hathaway et al. 2008).

In addition, many commercial composts are contaminated with heavy metals and organic toxicants as their source is often from street-side leaf collection operations. Commercial composts are being added to some of the industrial biofilter installations at the site to enhance vegetation growth. As part of the selection process, several nearby compost sources and products were chemically analyzed to ensure minimum import of contaminants targeted by the discharge permit. Initially, a compost certified by the US Composting Council was tested and found to have a low metals toxicity, but it contained levels of dioxin that exceed background levels by about 1.3 times. Three additional composts were then identified and tested along with a retest of the original compost (Table 2 describes the source material of these compost alternatives). These composts were selected because the source materials had the least likelihood of having contaminants.

Table 2. Compost Alternatives Analyzed

Compost Name	Decomposed Wood Fines	Equestrian Shavings	Rice Hulls
100% Organic	X (Douglas fir, byproduct of lumber industry)		
100% organic plus rice hulls (20% by volume)	X (Douglas fir, byproduct of lumber industry)		X
Standard	X	X	
Nitro	X	X	

Table 3 summarizes the testing for these four composts (nutrients were not tested). Each of the tested compost samples exceeded the import criteria levels for the 2,3,7,8-Tetrachlorodibenzodioxin (TCDD) International Toxic Equivalents (TEQ). Of the sampled composts, the 100% Organic Compost had the lowest TCDD TEQ levels and were about 1.7 times higher than the background concentrations. The 100% organic compost samples also generally had the lowest concentrations of the other constituents, and were well under the background levels for all constituents. Several screening levels were exceeded by the 100% organic samples (aluminum, arsenic, cadmium, copper, lead, zinc, and benzo(g,h,i)perylene). The ñStandardò and ñNitroò compost samples were much higher than the background and screening levels for many constituents, with many concentrations being 10 to 100 times higher than the 100% organic samples. As noted, these compost types were selected as having a relatively low contamination potential based on their source materials. It is expected that other commercial composts may be even more contaminated.

Table 3. Commercial Compost Analyses Compared to Background Soil Concentrations

Compound	Background	Lowest characterization risk based screening level*	“100% organic” (average of two sets of analyses)	“100% organic” plus rice hulls	Standard	Nitro
pH	8.9	n/a	8.5	9.1	7.5	7.5
Aluminum (mg/kg)	20,000	12	1,960	3,960	13,900	5,110
Arsenic (mg/kg)	15	0.095	1.1	1.7	10.5	4.2
Cadmium (mg/kg)	1	0.021	0.1	0.3	1.6	2.2
Chromium (mg/kg)	36.8	930	4.2	9.7	28	37
Copper (mg/kg)	29	1.1	5	10.7	210	139
Lead (mg/kg)	34	0.063	2	7.2	106	31
Mercury (mg/kg)	0.09	0.1	<0.01	0.01	0.32	0.36
Selenium (mg/kg)	0.66	0.17	<0.3	0.18	0.42	6.7
Silver (mg/kg)	0.79	0.54	<0.2	0.04	0.73	2.3
Thallium (mg/kg)	0.46	2.9	<0.1	0.08	0.22	0.12
Zinc (mg/kg)	110	21	33	42	452	339
TCDD TEQ (pg/g)	0.87	4.27	1.45	1.45	57.5	12.1
Aroclor 1254 (PCB) (µg/kg)	n/a	78	<18	<4.2	120	<6.1
Aroclor 1260 (PCB) (µg/kg)	n/a	78	<18	<5	82	<7.2
Benzo(a)pyrene (µg/kg)	n/a	60	<8.9	<8.4	160	74
Benzo(ghi)perylene (µg/kg)	n/a	6.4	32	61	120	<61
Bis(2-ethyl hexyl)phthalate (µg/kg)	n/a	4,900	210	190	33,000	6,500
Phenanthrene (µg/kg)	n/a	1,300	26	42	1,300	2,200

* the lowest characterization risk based screen levels are calculated based on default exposure pathways and assumptions as published in the EPAôs ECOTOX database. They can be used to identify contaminants of potential concern, but they are not designed to be used as clean-up goals.

These organic media, like all filtration media, have irreducible concentrations below which no removal occurs. These irreducible concentrations are related to the hydraulic loading (flow rate per unit area) and to the parent material and its background contamination. Slower flow rates increase contact time between the media and the pollutants, providing sufficient time for slower reactions to occur, such as diffusion of the pollutant to an interior location on the media. Pitt and Clark (2010) showed that most metals require contact times of between 10 and 100 minutes for the majority of metals removal to occur. However, both compost and peat release nutrients in the first flush of water from the filter if microanaerobic environments develop in the media between storms, which has been documented to occur when filters are quiescent for extended interevent periods between runoff events (Clark and Pitt 2009b). Therefore, the organic layer should be kept aerobic and should not be left saturated between storms. In addition, minimizing the organic content to the level needed by the plants, rather than the current elevated organic content found in many bioretention media specifications, should reduce the nutrient release both during the early years and between storms (Hunt et al. 2006; Brattieres et al. 2008; Hatt et al. 2008; Davis et al. 2009).

It is anticipated that an organic media will remove these targeted compounds to low levels. Similar to the metals, removal is limited if the native organic material is contaminated. The Pitt and Clark (2010) study showed that TCDD effluent concentrations increased compared to the GAC by itself when peat was added to the media mixture, likely because small quantities of peat were washed from the filter and into the effluent water. The analytical process extracted TCDD from the media, resulting in increased effluent concentrations.

Nitrite and nitrate are difficult to remove from solution chemically. Large removals of nitrate, but with limited chemical capacity, were seen in tests with a virgin coconut-hull GAC (Pitt and Clark 2010). Other commercial anion exchange resins and some native soils and zeolites also may have the potential to sorb nitrogen. AEC values, when compared to CEC values typically specified for media mixes acceptable for use in stormwater treatment, are low, indicating limited lifespan for removing negatively charged pollutants (Evangelou 1998). In addition, because these pollutants have a -1 valence, they are not preferentially taken up if pollutants with higher negative valence charges are in the stormwater runoff to be treated. Removal of nitrite and nitrate typically is best performed by vegetated systems, as shown by Baker and Clark (2011) and Lucas and Greenway (2011). In the Baker and Clark (2011) study, the control (unplanted) systems had no nitrate removal, while the vegetated systems with the plants in an active growth phase had high nitrate removals, down to nearly detection limits (and well below the permit limits for this site). Effective nutrient uptake by plants, however, requires low flow rates through the media, so that the nutrients are not flushed past the root zone before the plants can use them. Biological denitrification has been used by Hunt et al. (2008) in several bioretention systems to treat nitrate. These modified underdrain systems store some of the water passing through the bioretention system until a subsequent storm. During the quiescent time, denitrifiers extract nitrogen from the water and convert the nitrate to nitrogen gas. However, if the organic layer in the media becomes anaerobic, leaching of nitrate would be expected (Clark and Pitt 2009).

Phosphorus was not listed on the permit. Had phosphorus removal been an issue, the particulate associated fraction could be treated with sedimentation and the dissolved/colloidal-bound fraction could be treated either chemically or through uptake by vegetation. Sedimentation would be expected to provide partial removal (about half as predicted by typical phosphorus associations with solids) since phosphorus reacts with the aluminum and iron components of stormwater-borne solids and/or soil. These chemical reactions typically are permanent. Lucas (2009) reviews the treatability of phosphorus based on its reactivity with chemically- and biologically-active media. Lucas and Greenway (2011) and OóNeill and Davis (2011a,b) have demonstrated the effectiveness of aluminum in water treatment residuals to remove and retain phosphorus in laboratory and pilot-scale studies of bioretention media. The reactions of phosphorus with iron and aluminum also have been exploited in stormwater coagulation-sedimentation and iron-enhanced filtration investigations (Trejo-Gayton et al. 2006; Bachand et al. 2010; Erickson et al. 2007; Eberhardt et al. 2006).

Similar to nitrate, phosphorus leaching is a concern. Hunt et al. (2006) investigated the likelihood of phosphorus retention versus leaching in a compost study. The results showed that high P-index (an indication of phosphorus content) values resulted in phosphorus leaching. Because P-index is calculated regionally and the index values may not be transferable, Treese et al. (2010) and Clark et al. (2010) investigated phosphorus retention as a function of initial phosphorus content of the media, measured in mg/kg. While the data analysis is still ongoing, the preliminary results show that if a traditional soil fertility test, where the phosphorus is extracted using a Mehlich 3 extraction, shows that a crop would require phosphorus, then chemical phosphorus retention in the soil is likely. If the phosphorus content is labeled as ñhigh,ò then phosphorus leaching is likely to occur. Phosphorus, like nitrogen, can be released from organic media (peat, compost, soil) if microanaerobic environments develop in the filter between storms (Clark and Pitt 2009b).

Summary of Stormwater Treatability Options

Table 4 addresses the specific pollutants of interest in this example, with a focus on those pollutants that were likely to exceed the permit limits without treatment.

Table 4. Selecting Treatment Technologies to Meet Permit Limits.

Analytes on Permit	**Treatment Technology Options**
Suspended Solids (mg/L)	Sedimentation or Physical Filtration
Ammonia N (mg/L)	Ion-exchange or conversion to nitrate and plant uptake
Nitrate+nitrite N (mg/L)	Ion-exchange or plant uptake
Zinc (µg/L)	Chemically-active filtration (organic media sorption/ion-exchange) after preliminary treatment by sedimentation
Copper (µg/L)	Chemically-active filtration (organic media sorption/ion-exchange) after preliminary treatment by sedimentation.
Lead (µg/L)	Physical filtration of particulates and particulate associated lead after pre-treatment by sedimentation. Chemically-active filtration (organic media sorption and potential zeolite ion-exchange)
TCDD (µg/L)	Chemically-active filtration with strong organic sorption component (GAC) after preliminary treatment by sedimentation. Peat and compost evaluated but potentially have parent material concentrations that are too high to treat TCDD down to permit levels.
Mercury (µg/L)	Chemically-active filtration with sorption for methyl mercury and ion-exchange for inorganic mercury and complexes.
Oil and grease (mg/L)	Chemically-active filtration with strong organic sorption component (GAC) after capture of free-floating material by sorption materials and floatation treatment (oil and grease separators) if concentrations are high. Peat and compost also possible.

As noted, these were not the only parameters on the permit; however, these were the ones for which exceedences and violations were likely. A full evaluation of the proposed treatment system also investigated whether the selection of treatment components, especially of the media in the filtration units, would have negative impacts on the other parameters (change pH out of the required range, release nutrients or metals as part of an ion-exchange reaction) (Pitt and Clark 2010). The final treatment system, given these requirements, first had a sedimentation area to reduce the suspended solids and particulate-bound pollutant concentration. The removal of solids was necessary to reduce the likelihood of clogging and to increase the useful life of the filtration units before necessary maintenance (replacement of the media).

The second unit process in the treatment was the filtration/ion exchange/sorption biofiltration system. As can be seen in Table 4, many of the pollutants can be removed with chemically-active filter media. Suggestions for this media included an ion-exchanging zeolite, GAC, and/or peat, compost, or native soil. Native soil was eliminated because of its clay fraction (likelihood of clogging rapidly) and inconsistent properties across the entire site. This industrial site required multiple, dispersed filtration units, and with the permit requirements, required consistent effluent quality. The low permit limits on TCDD eliminated the use of only peat or compost as the active media. Laboratory testing with these media showed that only the virgin coconut hull GAC was able to achieve the low permit limits consistently. Zeolite was considered because of the lead and ammonia, but testing showed that lead, and ammonia to a lesser degree, also were reduced with peat (Pitt and Clark 2010), which confirms the results of Clark (2000) and others for peat and compost. Zeolite could be eliminated from the media mixture with little detrimental effect. Further ammonia reductions could be achieved by the planted filtration system, which also would address the nitrate. The planted systems would require flow rates slow enough to ensure that the root zone is not bypassed by high flows. Baker and Clark (2011) used flow rates equivalent to 2.7 m/d, which is within the typical design guidance for flow rates through biofiltration systems. Planted systems also have the advantage of reducing clogging since the plant roots continue to break up the soil structure and can penetrate clogged areas as the plants grow and the root zone spreads both horizontally and potentially vertically. Decomposing plant material also replenishes the CEC of the media mixture.

The preceding discussion on the selection of the unit processes to meet numeric discharge permit limits focuses on the removal of specific pollutants to numeric permit limits. Other design factors for filtration devices had to be considered because of their impact on performance and longevity, including the following: sodium adsorption ratio (SAR) and clogging potential. An excess of sodium ions, such as potentially from sodium-based deicing agents, will react with the organic component and disperse soil clays, resulting in a media that is almost impermeable to passing water. Similar to the minimization of organic matter in a filtration media to address nutrient leaching, the percentage of clay in the media mix should be minimized or clay should be removed from the mix, especially in northern climates. If sodium inputs to the treatment device cannot be reduced, then filtration devices may not be the appropriate treatment technology for that drainage area.

Media filters also are subject to clogging due to the solids loading on and in the media. If the appropriate coefficients are known, the Urbonas (1999) equation can be used to estimate the flow rate as a function of media loading. However, these coefficients rarely are known, and the current guidance suggests that clogging, i.e., unacceptably low flow rates and extended drawdown times, will occur in unvegetated systems with cumulative solids loadings between 10 and 25 kg/m^2 (Clark and Pitt 2009; Pitt and Clark 2010). The solids loading to clogging is substantially reduced if the media were compacted during construction and the depth of the media cannot be used for solids retention. Healthy, deep-rooted vegetation, because of the development of a healthy soil structure, can extend the media life before clogging.

CONCLUSIONS

As more stormwater discharges are subject to numeric effluent limitations, it becomes increasingly necessary to design stormwater treatment systems based not on assumed percent removals currently found in many guidance documents, but instead based on an understanding of the performance requirements and the unit processes operating in the various treatment technologies. Understanding both the influent water chemistry and the ability of the treatment unit processes to remove specific forms of pollutants will allow the designer to create a tailored system that addresses the permit requirements. The example used in this paper for designing a treatment system to address a numeric permit illustrates how this can be achieved to select an effective system. The system selected was not uncommon for the stormwater industry (sedimentation followed by bioretention), but use of the chemical and biological unit process theory to support its design and the selection of the media mixture is uncommon.

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