

The Performance of Grassed Swales as Infiltration and Pollution Prevention Practices

A LITERATURE REVIEW

Peter T. Weiss

John S. Gulliver

Andrew J. Erickson

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Table of Contents

List of Figures	- 3 -
List of Tables	- 3 -
INTRODUCTION	- 4 -
SWALE PERFORMANCE	- 4 -
Infiltration Capacity of Swales	- 6 -
Suspended Solids Removal in Swales	- 8 -
Resuspension of Settled Solids	- 12 -
Removal of Other Contaminants Including Infiltration of Dissolved Contaminants	- 13 -
Swales in Cold Climates.....	- 16 -
DISSOLVED NUTRIENT REMOVAL	- 21 -
Nitrogen	- 21 -
Phosphorus	- 25 -
IMPROVING METAL RETENTION	- 26 -
Natural Soils	- 27 -
Activated Carbon	- 29 -
Alumina	- 30 -
Compost	- 30 -
Crustacean Shells	- 31 -
Ferrous Based Materials	- 32 -
Magnesium	- 35 -
Manganese and Manganese Oxide.....	- 35 -
Plant Biomass.....	- 35 -
Zeolites and Clays.....	- 38 -
Other Materials.....	- 39 -
CONCLUSION.....	- 40 -
REFERENCES	- 42 -

List of Figures

Figure 1. Examples of model application to swale performance data from Wang et al. 2006.	- 6 -
Figure 2. Settling velocities of particles investigated by Backstrom (2002a).	- 9 -
Figure 3. Annual and seasonal influent and effluent EMCs for a stone swale and a vegetated/grassed swale. Lines show max and min values, boxes show 75th and 25th percentiles, and the horizontal line in the box indicates the median value (From Roseen et al. 2009).	- 19 -

List of Tables

Table 1. Range of removal efficiencies (%) for a laboratory vegetated swale (from Barrett et al. 1998b). TSS = Total suspended solids, COD = Chemical oxygen demand, TKN = Total Kjeldahl nitrogen, Total P = Total phosphorus.	- 14 -
Table 2. Removal efficiencies of roadside vegetated swales (Caltrans 2004).	- 15 -
Table 3. Annual and seasonal efficiency ratios (ER) and removal efficiencies (RE) for swales (Data from Roseen et al. 2009). RE is calculated as $RE = 1 - (EMC_{outlet}/EMC_{inlet})$ and the reported value is the median of the entire data set. ER is calculated as $ER = 1 - (\text{average } EMC_{outlet}/\text{average } EMC_{inlet})$. TSS = Total suspended solids, TPH-D = Total petroleum hydrocarbons-diesel, DIN = Dissolved inorganic nitrogen (nitrate, nitrite, and ammonia), Total Zn = Total zinc, and Total P = Total phosphorus.	- 20 -

INTRODUCTION

Development and urbanization of watersheds typically increases impervious land cover (e.g. roads, parking lots, buildings) and thus leads to an increase in stormwater runoff peak flow rates, total runoff volume, and degradation of runoff water quality. The degradation in water quality is due to increases in contaminant concentrations in the water and results in increased load to receiving waters. Currently the water contaminants of greatest concern in stormwater are total suspended solids (TSS), phosphorus (P), nitrogen (N), cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn).

Historically, stormwater management focused on flood prevention through mitigation of the increase in peak flow rate by routing the runoff through a detention pond or some other system. Increased runoff volume and degradation of water quality were typically not addressed. With an increase in environmental awareness and more stringent regulations, however, these issues should be considered as part of most stormwater management plans. As a result, stormwater management has shifted to include techniques that reduce runoff volumes and improve runoff water quality in addition to reducing the peak flow rate. Such techniques are called low impact development (LID) practices and are typically designed to reduce runoff through infiltration and/or evapotranspiration as well as improve stormwater runoff quality by retaining or capturing contaminants in the runoff. LID practices include bioretention facilities, infiltration basins and trenches, constructed wetlands, sand filters, grassed swales, etc.

Despite the prevalence of grassed swales within roadway right-of-ways that convey and treat road runoff, data on the performance of swales with regards to infiltration and contaminant capture is relatively sparse. This paper is a review of the available literature on the performance of swales as a stormwater management LID practice.

SWALE PERFORMANCE

Grassed swales have the capability to reduce runoff volume and improve water quality. Volume reduction occurs primarily through infiltration into the soil, either as the water flows over the slope perpendicular to the roadway into the swale or down the length of the swale parallel to the roadway. Pollutant removal can occur by sedimentation of solid particles onto the soil surface, filtration of solid particles by vegetation, or infiltration of dissolved pollutants (with stormwater) into the soil (Abida and Sabourin 2006). When solid particles settle to the soil surface or are captured by filtration on vegetation, the TSS concentration of the runoff is reduced and overall water quality is improved as long as the solids do not become resuspended. As will be discussed later, such resuspension has been determined to be negligible.

The performance of a swale depends on many factors including the health and abundance of the vegetation within the swale. Work by Mazer et al. (2001) on bioswales (not roadside swales), may be helpful in understanding optimum conditions for healthy vegetation within grassed, roadside swales. Mazer et al. (2001) report several causes of poor vegetative cover in swales including standing water in the swale for prolonged periods of time, high flow velocities, large fluctuations in surface water depth and soil moisture, excessive shade, and improper installation. Improper installation could be the result of poor design or poor construction practices. For the eight bioswales in western Washington State

investigated by Mazer et al. (2001) heavy shade was more important than other environmental factors that limited vegetation. The second most important factor was inundation with water. If water was present for more than 35% of the summer the bioswale had significantly less vegetation. Shade may not be a serious problem for most roadside swales because right-of-ways are usually clear from overhanging vegetation due to line-of-sight regulations. It is, however, important to ensure that any swale is not inundated with water for extended periods of time. This may be especially important to consider when developing a horizontal flow filter that will slow the conveyance of water within the swale, as in this study.

With regards to estimating contaminant removal in a swale, Wong et al. (2006) modeled the removal of TSS, total nitrogen (TN), and total phosphorus (TP) along the length of swales using a series of completely stirred tank reactors (CSTR's) and the first order removal equation:

$$q \frac{dC}{dx} = -k(C - C^*) \quad (1)$$

Where q is the hydraulic loading rate ($m^3/m^2\text{-yr}$), x is the fraction of the distance from swale inlet to outlet, C is the concentration of the contaminant, C^* is the background concentration of the contaminant, and k is a fitted decay rate constant (m/year). The results of the model, as compared to data collected by Walsh et al. (1997) on actual swales, are shown in Figure 1.

As summarized by Backstrom (2003), several authors have proposed design guidelines to optimize the performance of swales with respect to stormwater treatment. Ferguson (1988) recommended a swale length greater than or equal to 60 m, water velocities less than 0.15 m/s, and a residence time of at least 9 minutes. Other authors (e.g. Barrett et al. 1998a), however, found that swale length is not an important design parameter as long as the road runoff is allowed to flow directly down the side slope into the swale. The data suggest that under these conditions the side slope acts as a filter strip and removes most of the contaminants before the runoff begins to flow in the swale parallel to the road. Yu et al. (2001) recommend a swale length of 75 m and a bottom slope of no more than 3%. Backstrom (2003), however, suggests that recommending a certain maximum slope may be misleading because, depending on the condition of the vegetation within the swale, small water velocities can exist in swales with moderate slopes.

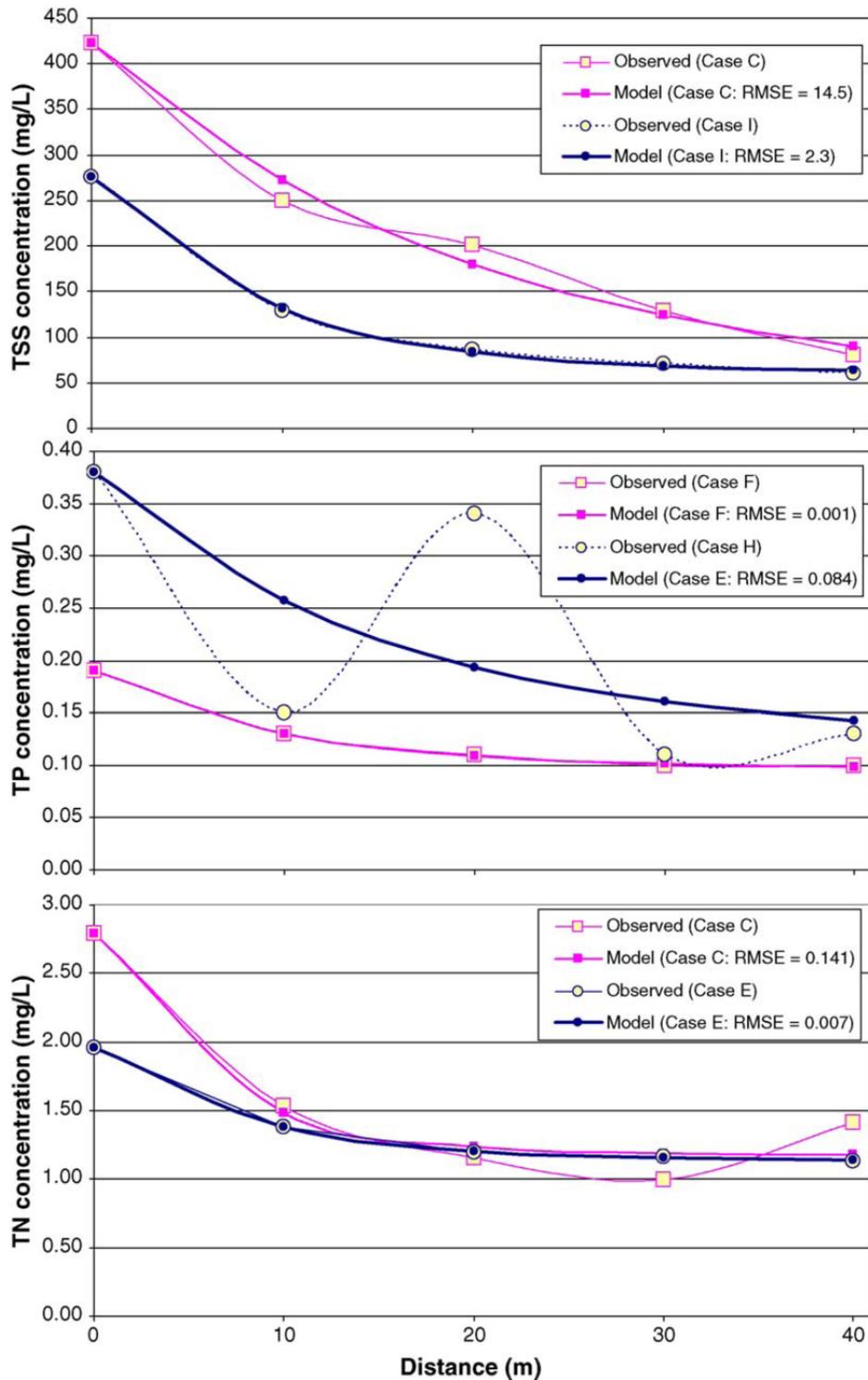


Figure 1. Examples of model application to swale performance data from Wang et al. 2006.

Infiltration Capacity of Swales

In a review of data compiled in the International Stormwater BMP Database, Barrett (2008) found that, if the soil is permeable and the initial moisture content is low, the infiltration achieved by swales can

approach 50% of the runoff volume in semiarid regions. Rushton (2001) found that the installation of swales to carry parking lot runoff in Tampa, FL resulted in 30% less runoff. Using simulated runoff, Yousef et al. (1987) found that swales infiltrated between 9% (input rate of $0.079 \text{ m}^3/\text{m}^2\text{-hr}$) and 100% of the runoff (at $0.036 \text{ m}^3/\text{m}^2\text{-hr}$) with significant variability. Of course the infiltration capacity of each swale will depend on many variables and each swale should be tested individually. Infiltration capacity testing for a single swale can be performed as described in the online manual, *Stormwater Treatment: Assessment and Maintenance* (Gulliver et al. eds 2010) using the Modified Philip-Dunne permeameter (Asleson et al. 2007).

Ahearn and Tveten (2008) investigated the performance of 41 year old, unimproved roadside embankments in the State of Washington for their ability to infiltrate and improve the quality of road runoff. These embankments were not designed for stormwater treatment. Four sites were investigated and at each site monitoring stations were set up at the “edge of pavement” (EOP), 2 meters from the EOP, and 4 meters from the EOP. Runoff volume reductions were 71% to 89% at 2 meters from EOP and 66% to 94% at 4 meters from EOP. The smaller volume reduction at 4 meters was caused by water infiltrating before the 2 meter station and re-emerging as surface flow before the 4 meter station at two of the monitoring locations.

Lancaster (2005) also measured infiltration along a roadside embankment. At one site in Pullman, Washington 36 precipitation events were monitored and in all events all runoff from the roadway had infiltrated within the first two meters from the edge of pavement. At another site in Spokane, Washington 18 precipitation events were monitored. Of these events, five had runoff at 3.1 meters from the edge of pavement and one event had runoff 6.2 meters from the edge of pavement.

Deletic (2001) developed, calibrated, and verified a model to estimate runoff generation (and sediment transport). The model, which is discussed in more detail below, was developed, in part, to estimate runoff volumes from grassed swales. A sensitivity analysis showed that the volume of runoff depends primarily on grass length and soil hydraulic conductivity.

A variable that affects the hydraulic conductivity of a swale is the compaction of the soil within the swale. Gregory et al. (2006) studied the effect of soil compaction on infiltration rates on soils and found that the infiltration capacity of soil decreased as the weight of the heavy equipment driven on the soil increased. Although the results were determined not to be statistically significant with respect to the weight of the vehicle, the study found that soil compacted by a pick-up truck, backhoe, and fully loaded dump truck had infiltration capacities of 6.8 cm/hr, 5.9 cm/hr, and 2.3 cm/hr, respectively. It was also found that that construction equipment or compaction treatment reduced the infiltration capacity of the soil by 70-99%. It can be concluded that the infiltration capacity of a swale will be greatly reduced if subject to heavy equipment loads.

Contrary to the effects of compaction, tree roots have been shown by Bartens et al. (2008) to have the ability to penetrate compact urban soils and increase infiltration. Bartens et al. (2008) studied flooded impoundments and found that those with trees (Black Oak or Red Maple) infiltrated water 2-17 times faster than those without trees. . Placing a tree within a swale may not be practical, but it is possible

that trees near swales could increase infiltration into the surrounding soil. Trees near roadside swales, however, could present a hazard to passing motorists.

In order to determine the infiltration capacity of five grassed swales in Canada, Abida and Sabourin (2006) performed single ring, constant head infiltrometer tests on swales that had perforated pipe underdrains. Although these swales had underdrains that collected infiltrated water and removed it from the soil, the drains were far enough below the ground surface that the authors assumed the drains did not affect infiltration rates over the course of the experiment. The investigators found that the infiltration capacity of the swales decreased exponentially with time until it reached a constant, long-term value. Initial infiltration rates varied from 3-13 cm/hr with constant rates of 1-3 cm/hr achieved after 15-20 minutes.

Jensen (2004) used dye to measure and visualize flow patterns of runoff infiltrating four Danish highway swales. Infiltration capacities of these swales ranged from 5.76 cm/hr to 6.84 cm/hr which were similar to capacities of other authors (1.8 cm/hr to 7.2 cm/hr) that were reviewed by Jensen. The infiltration capacity of the Danish swales was greater than the rate water entered a sub-soil collection pipe. This resulted in a secondary but temporary water table above the collection line. It was also determined that, based on historical Danish rainfall data, the infiltration capacity of the swales would allow for 75% of the annual road runoff to infiltrate.

Jensen also found that infiltrated water had to first pass through a homogenous layer of previously deposited sediment on the ground surface before entering the natural underlying soils. The thickness of the sediment layers was measured at three locations on three out of four swales and was estimated to deposit at a rate of 2-6 mm/year at all but two of the nine measurement locations. Two measurement locations on one swale were estimated to have a deposition rates from 10-16 mm/year. This variability could be caused by differences in traffic volumes, rainfall patterns, or watershed characteristics, etc.

Jensen found the infiltration through these deposited layers was similar and uniform at each site and concluded that these layers could act as filter media. The swale soil that was placed during roadway construction was found to be homogenous at some locations and heterogeneous at other locations. The preferential flow paths that were observed in some swale media was determined to be a result of human influences such as the construction process and not of earthworms or other natural causes. This is relevant because preferential flow paths in swale media could limit contaminant capture and, therefore, should be avoided.

Suspended Solids Removal in Swales

Suspended solids can be removed from stormwater runoff flowing in a grassed swale by two mechanisms, 1) Filtration by vegetation and, 2) Sedimentation and capture on the bottom of the swale (Backstrom 2002b, Schueler 1987, Yu et al. 2001). Documented removal rates vary between close to 100% to large negative values (i.e. export of sediment from the swale). These large discrepancies may be due to many factors including varying TSS influent concentrations, differences in particle size and density, swale design and maintenance, measurement/sampling locations and techniques, and other reasons. For example, Barrett et al. (1998a) states that some studies that have reported swale TSS removal rates

used test sections that had “influent” sampling locations located after much sediment had already been removed by the swale. As mentioned previously, the side slope leading into a swale can act as a filter strip and remove significant amounts of contaminants. Other studies (that are discussed in more detail below) support this notion.

According to Backstrom (2002b), the transport and deposition of particles in swales is dependant primarily on particle size, particle density, soil hydraulic conductivity, and grass density and height. The portion of the plants that are above ground are also thought to induce sedimentation of solids (Mazer et al. 2001). Deletic (2001) reported that, based on several studies by other investigators, the sediment removal effectiveness of grassed swales depends on grass density and thickness of the blades, slope of the surface, soil infiltration and roughness, particle size and density, rainfall intensity and duration, and antecedent sediment and weather conditions.

Backstrom (2002a) investigated a total of nine swales; two artificial turf swales in the laboratory and seven natural grassed swales in the field. Each test used half-hour long, simulated runoff events with synthetic stormwater. The synthetic stormwater was prepared by street sweeping and mixing the collected sediment with water. Sediment fractions used were 0-75 μm (density of 2610 kg/m^3), 75-125 μm (density of 2580 kg/m^3), and 125-250 μm (density not reported).

In order to determine settling characteristics of the particles, settling column experiments were conducted. Particles smaller than 8 μm did not settle during the 1042 minute test and particles larger than 20 μm settled according to Stoke’s Law. Particles between 8 and 20 μm had settling velocities significantly lower than those predicted by Stokes Law. These lower velocities could have been due to lower particle density, non-spherical shape, or electrostatic forces between particles. Figure 2 shows the results of this study.

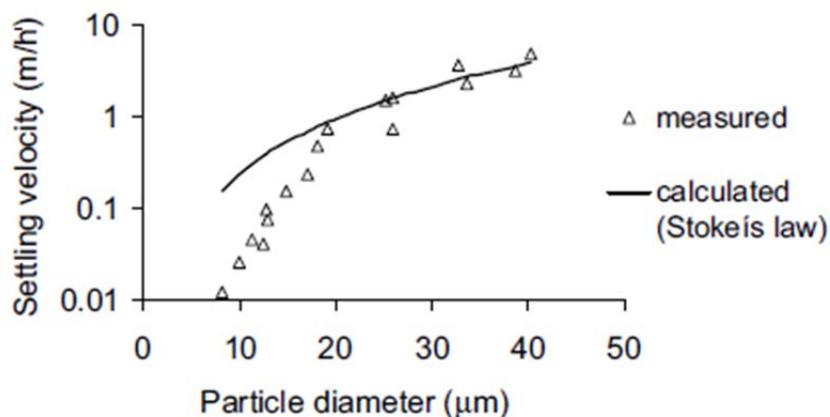


Figure 2. Settling velocities of particles investigated by Backstrom (2002a).

Due to sedimentation of the large sediment fraction (i.e. 125-250 μm) in the synthetic stormwater mixing tank, this size fraction was essentially nonexistent in the synthetic stormwater applied to the swales. Swales with thin turf and short grass had the lowest TSS removal ($\sim 80\%$) whereas swales with fully developed turf achieved TSS removal rates of over 90% for all studies. Thus it was concluded that grass height and spacing are important variables that affect removal efficiency. Also, no relationship was found between swale length and removal efficiency. The authors attributed this lack of correlation to heavy particles dropping out of the water on the upstream portions of the swale.

The laboratory swales were found to capture particles of all sizes equally, perhaps due to large water velocities above the grass. In addition, the laboratory swale with longer grass captured more sediment. Field swales with dense turf and larger infiltration rates removed more sediment and had no signs of sediment resuspension. Based on previous studies, however, Backstrom did report that sediment resuspension and erosion can occur. Field swales also did show a correlation between removal and particle size with large particles experiencing more removal. This lead Backstrom to conclude that, with respect to TSS removal in the field swales, sedimentation was more important than grass filtration.

Backstrom (2002a) developed a model for sediment removal which exhibited a correlation between particle size and trapping efficiency. Swale residence time could not explain all the variation in the data. Backstrom suggests that infiltration rate and swale bottom slope could help explain this variation. It was also suggested that hydraulic residence time could be used as a design parameter for some swales but this would not necessarily be valid for swales with relatively large infiltration rates. Finally, Backstrom proposed the possibility that large particles are captured mostly by sedimentation and relatively small particles are captured by adsorption onto blades of grass.

Deletic (1999) also studied sediment trapping but used artificial turf and synthetic stormwater. The synthetic stormwater was prepared using sediment from an estuary that was mixed with clean water. Two different grass densities, four flow rates, five flow depths, and a range of sediment concentrations were tested. TSS concentrations were found to decrease exponentially with distance along the flow path until a constant value was reached. The rate of the decrease and the constant value were found to be a function of particle size and density along with the flow depth and velocity. The model results did not agree with the Kentucky Model which models the transport of sediment along a grassed surface in four distinct zones; in zone 1 all sediment is transported, in zone 2 some sediment is trapped, in zone 3 all sediment is transported as bed load, and in zone 4 all sediment is trapped. Because results did not fit the Kentucky model a new, simplified model based on a dimensionless fall number, flow depth, and other variables was developed.

In further research, Deletic (2001) modeled runoff generation and sediment transport over grass using a modified form of the Green-Ampt equation for infiltration and a kinematic model for overland flow. The model, which was calibrated and verified against field data, is physically based (i.e. not empirical) and accounts for surface depressions but it does not account for particle infiltration, resuspension, or capture of sediment in ponds. A sensitivity analysis on the model showed that sediment capture depends mostly on grass length and density, soil hydraulic conductivity, and particle size and density. Later, Deletic (2005) developed another equation (the Aberdeen Equation) for capture efficiency on

steady, uniform, overland flow without infiltration. The equation is only applicable for runoff with small to moderate TSS concentrations.

While the previous discussion focused on the theory of sedimentation and filtration processes that occur in swales, other studies have determined the removal efficiency of swales (or the side slope embankment leading to the swales) and the affect of various variables through monitoring of natural and synthetic rainfall and/or runoff events. Backstrom (2003) reviewed and provided an overall summary for three such studies. In the summary, Backstrom states that 79-98% of TSS removal occurred during simulated runoff events. In these studies the parameter that best explained TSS removal was the influent TSS concentration. No significant removal occurred below a TSS concentration of 40 mg/L (which agreed with other studies) and below certain minimum concentrations (not stated), swales can act as a source rather than a sink of sediment. For swales with dense, thick vegetative growth no relationship was found between TSS removal and bottom slope, grass height, side slope, or infiltration capacity but more TSS were removed during the growing season. Also, during the growing season less retention of nutrients was observed. This trend was attributed to decaying plant matter that acted as a source of nutrients.

Barrett et al. (1998a) compared the performance of two roadside medians with different vegetation, bottom slopes, and other variables and found that the medians had similar TSS removal rates of 87% and 85%. As part of this investigation it was noted that, at some locations, there were sediment deposits at the road/median interface that prevented runoff from entering the median. As a result, runoff could not flow freely onto the median and was sometimes diverted by the sediment to a curb and gutter system. It was suggested that this phenomenon could be prevented by ensuring that the soil next to the road surface have a slightly lower elevation than the road and by performing periodic maintenance to remove accumulated sediment. Barrett (2008) reviewed data on 14 swales in the International BMP database and found a median TSS removal of 60% with a range from 6% to 70%. The bioswales (not roadside swales) studied by Mazer et al. (2001) were documented to have TSS removal efficiencies from 60-99%.

In the study by Ahearn and Tveten (2008), which measured contaminant removal along the grassed surface next to the roadway, it was found that TSS removal varied from 59% to 82% at 2 meters from the edge of pavement and from 93% to 96% at 4 meters from the edge of pavement. As Ahearn and Tveten (2008) point out, these removal rates are similar to those found in other studies performed on roadside embankments in Texas and California.

Yonge (2000) studied filter strips adjacent to roadways for their ability to remove typical contaminants found in stormwater runoff. These filter strips were essentially the shoulder of the road that the runoff had to flow over to drain into a roadside swale. Three different test plots, each with a different soil type, were monitored. TSS removal achieved by the filter strips ranged from 20% to 80% with an average value of 72%. Thus, as suggested by other studies, a significant amount of TSS removal from road runoff can occur before the runoff actually enters a roadside swale.

Barrett (2004) also investigated the pollutant removal of two roadside swales in Austin, Texas. As supported by the previously mentioned studies by Ahearn and Tveten (2008) and Yonge (2000), it was determined that most of the pollutant removal occurred along the side slope before the runoff was carried downstream by the swale. Thus, Barrett (2004) suggests that roadside swales be designed with triangular cross-sections with longer side slopes rather than the more common trapezoidal cross-section.

Caltrans (2003) performed a 2-year study in which the performance of vegetative slopes adjacent to roadways was investigated for contaminant removal and infiltration capacity. It was found that these slopes, which were not designed to treat road runoff, performed just as well as buffer strips that were designed and maintained specifically to improve runoff quality. It was found that below 80% vegetative cover on the slope, contaminant removal (of TSS and other contaminants) dropped off significantly, although removal still occurred at vegetative covers of 65%. The vegetative slopes consistently resulted in a significant reduction in the concentration of TSS. In another Caltrans study (2004) swales were found to remove 76% of suspended solids.

Kaighn and Yu (1996) monitored two roadside swales south of Charlottesville, VA. The two swales had differences in slopes (2% vs. 5%) and vegetation characteristics but the biggest difference was that one of the swales had a check dam that slowed the flow of water. The swale with the check dam removed 49% of TSS while the site without the check dam removed 30% of TSS. The difference in removal was attributed to the check dam, not the other differences between the swales.

Kearfott et al. (2005) investigated the performance of vegetated side slopes of rural highways in Texas for their pollutant removal performance. It was determined that the higher the vegetation density the more pollutant removal occurred regardless of the bottom slope and that most TSS removal occurred within the first 2 to 4 meters from the edge of the roadway. A vegetative cover of 90% resulted in the most pollutant removal but significant removal was observed in sites with only 80% vegetative cover.

Liebens (2001) analyzed the sediments found in swales and found that they contain higher fractions of silts and clays and less sand than control sites. One possible explanation is that relatively large particles are captured by grass (and possibly the side slope of the swale) before the runoff reaches the swale flow path. This study also determined that clay content may be associated with larger metal concentrations due to the large surface areas of clays and their ability to capture metal ions through cation exchange processes. In some agricultural areas, however, swales with higher clay content did not have higher metal concentrations. This apparent contradiction may be due to lower metal production rates in agricultural areas or older, more weathered soils in agricultural areas that have lower cation exchange capacities.

Resuspension of Settled Solids

To investigate the potential for resuspension of solids and other factors, Barrett et al. (1998a and 1998b) monitored two highway medians that essentially acted as grassed swales. Data from several rainfall/runoff events were collected and the TSS concentrations of the runoff from the median were found to be less than the concentrations of runoff directly leaving the road. This indicated that, for each storm monitored, there was net TSS removal. The authors did note, however, that one median showed

signs of erosion and, if improperly designed such that erosion occurs, medians (or swales) could be a source of sediment.

Deletic (2005) studied resuspension of sediment in a laboratory using flumes with artificial turf to simulate natural grass. Experiments were performed at different bottom slopes, grass densities, flow rates, sediment concentrations, and sediment densities. The resuspension of previously deposited sediment by clean water flowing on the turf was found to be negligible. This finding did not deviate from the conclusion of Cutierrez and Hernandez (1996) that grass itself tends to constrain detachment of settled solids. Mazer et al. (2001) also mentions that plant roots tend to stabilize sediment deposits. Deletic did find, however, an increase in TSS concentration in the clean water but that was attributed to the washing of sediment off the blades of grass and not resuspension of solids.

Removal of Other Contaminants Including Infiltration of Dissolved Contaminants

By observing data in the International BMP Database, Barrett (2008) investigated the performance of 14 swales. For these swales no significant removal of nitrogen or phosphorus was observed but Barrett suggests that the removal of grass clippings after mowing could remove nutrients from the swale and prevent nutrient release upon decomposition. Significant zinc removal was observed and it was found that the zinc removal efficiency correlated well with the influent zinc concentration. The total zinc removal efficiency had a median value of 60% with a range from 8% to 87%. Dissolved zinc removal efficiency had a median value of 40% with a range from 22% to 58%. Total copper removal efficiencies had a median value of 62% (range -3% to 75%) and dissolved copper had a median value of 24% (range -17% to 54%). Barrett also found that reductions in chemical oxygen demand (COD) were only found when influent COD concentrations were greater than 80 mg/L. Barrett et al. (1998b) discusses possible fates of metals once they have been removed from stormwater by vegetation including vegetation in roadside swales. The potential fates are:

1. Residence in an insoluble form, i.e., attached to particulate matter in the soil matrix;
2. Uptake of soluble metals by plants;
3. Uptake by animals who consume plants with accumulated metals;
4. Leaching of soluble metals from the soil into groundwater;
5. Removal from the filter strip to receiving waters by runoff from subsequent storm events; and
6. Removal from the filter strip by wind action on particulates containing metals.

As part of the same report (Barrett et al. 1998b), the metal deposition rate for zinc and lead on the two highway medians were found to be less than one-tenth of the allowable rate for crop lands. Based on the lead deposition rates, Barret estimated it would take 244 years at one site and 1204 years at the other site for the lead soil concentrations to exceed regulatory limits. It was also estimated that zinc soil concentrations would exceed regulatory limits after 570 years at the first site and 304 years at the other site.

Barrett et al. (1998b) performed experiments at different water depths on vegetated laboratory swales using synthetic stormwater created to represent typical stormwater runoff pollutant concentrations in the Austin, Texas area. Underdrains were used to collect stormwater that infiltrated into and through the swale. Upon reaching the underdrain the water had infiltrated through the top layer of Buffalo grass, 16 cm of topsoil, and 6 cm of gravel. The highest removal efficiencies in the laboratory swales were for suspended solids, zinc, and iron. The ranges of all removal efficiencies (%) for various water depths, given in Table 1, indicate that removal primarily occurs in the first 20 m of the vegetated swale. Dissolved Phosphorus and dissolved metals were not measured.

Table 1. Range of removal efficiencies (%) for a laboratory vegetated swale (from Barrett et al. 1998b). TSS = Total suspended solids, COD = Chemical oxygen demand, TKN = Total Kjeldahl nitrogen, Total P = Total phosphorus.

Contaminant	Distance along swale (m)				Underdrain
	10	20	30	40	
TSS	35-59	54-77	50-76	51-75	73-87
COD	13-61	26-70	26-61	25-79	39-76
Nitrate	(-5)-7	(-5)-17	(-28)-(-10)	(-26)-(-4)	(-8)-(-10)
TKN	4-30	20-21	(-14)-42	23-41	24-41
Total P	25-49	33-46	24-67	34-45	55-65
Zinc	41-55	59-77	22-76	66-86	47-86
Iron	46-49	54-64	72	76	75

The removal efficiencies for the swale at a water depth of 7.5 cm (hydraulic residence time of 8.8 minutes at 40 m) were similar to a swale studied by the Municipality of Metropolitan Seattle (hydraulic residence time of 9.3 minutes). Because these two swales varied in length, slope, and vegetative cover but had similar residence time and removal efficiencies, Barrett claims that this supports the use of residence time as a primary design parameter. The data suggests that a hydraulic residence time of 9 minutes can result in removal of over 80% of TSS over a range of other swale parameters. Removal of TSS was also greater during the growing season than during the winter months but removal of the other contaminants did not appear to be a function of season. The seasonal dependence of TSS removal was attributed to thicker grass density during the growing season. At these times new grass grew amongst the old, dead grass and the combination resulted in a significantly higher grass density.

The removal efficiency of TSS, COD, total phosphorus, and metals increased with length along the swale but this increase in removal efficiency declined as the distance along the swale increased. For these contaminants, most of the removal occurred in the first 20 meters of the swale. For example, over the range of water depths tested (4, 7.5, and 10 cm), the TSS removed in the first 20 meters ranged from 80% to 105% of the total TSS removal at 40 meters.

Barrett et al. (1998b) also found that TSS removal efficiency dropped in the grassed laboratory swale as water depth increased but the removal of other contaminants was not strongly correlated. This suggests that the filtration action of the blades of grass increases removal of solid particles and, as water depth increases above the grass height, this mechanism has less of an effect.

Barrett (2008) also investigated the performance of vegetative buffer strips (as previously stated, Barrett claims that the side slopes of swales perform as buffer strips) by observing the BMP database data and found little relationship between the grass type, grass height, and TSS removal.

A study by Caltrans (2003) found that vegetative slopes next to roadways consistently reduced total metal concentrations and, contrary to Barrett (2004), dissolved metal concentration reduction occurred frequently. Also, dissolved solids concentrations consistently increased and organic carbon concentrations occasionally increased with distance from the edge of the roadway whereas nutrient concentrations remained unchanged with distance from the edge of the roadway. As was found in other studies, total mass loads of all contaminants transported by the runoff decreased with increasing distance from the edge of the roadway due to the infiltration of stormwater.

As shown in Table 2, Caltrans (2004) report that vegetated swales can remove a significant fraction of nitrogen and total and dissolved metals.

Table 2. Removal efficiencies of roadside vegetated swales (Caltrans 2004).

Contaminant	Percent Removal
NO ₃ -N	65
TKN	67
Total Copper	82
Total Lead	85
Total Zinc	89
Dissolved Copper	76
Dissolved Lead	80
Dissolved Zine	87

A study by Kearfott et al. (2005) investigated the performance of vegetated side slopes of rural highways in Texas, and found that significant reductions in lead, copper, and COD all occurred within 8 meters of the roadway edge but no consistent increases or decreases were found for nutrients. Also, total zinc concentrations were found to increase with distance from the roadway but this was thought to be due to the leaching of zinc from the galvanized metal that was part of the collection apparatus.

Lancaster (2005) measured metal concentrations as a function of distance from the edge of the roadway pavement. At this site total zinc concentrations decreased with increasing distance from the edge of pavement, total copper concentrations decreased slightly, and total cadmium and lead concentrations showed no significant change.

Kaighn and Yu (1996) investigated one roadside swale with a check dam and one without, and found that the swale with a check dam removed 3%, 33%, and 13% of chemical oxygen demand (COD), total phosphorus, and total zinc, respectively. In the swale without a check dam COD concentrations increased by 6%, total phosphorus increased by 0.4%, and 11% of total zinc was removed. The difference in COD and phosphorus removal rates between the two swales was attributed to the check

dam. This led the authors to conclude that the use of check dams in roadside swales can increase pollutant removal because the check dam increases both infiltration and particle settling.

Wang et al. (1981) investigated lead (Pb) removal in a grassed swale and found that a 20 meter long swale achieved 60% lead removal and a 60 meter long swale achieved 90% removal.

By monitoring four roadway locations that were 41 years old, Ahearn and Tveten (2008) found that total metal concentrations were reduced as runoff moves from the edge of pavement down the embankment but the dissolved metal and nutrient concentrations often increased. For example, at all monitoring locations dissolved copper concentrations increased from the edge of pavement to either 2 meters or 4 meters from the edge of pavement. When total mass loading is considered, however, the total mass of dissolved metals and nutrients decrease due to the large infiltration rates of the embankments that resulted in less total flow volume.

Mazer et al. (2001) summarizes a handful of studies on bioswales and road side swales and reported metal removal efficiencies of 21% to 91% and phosphorus removal efficiencies of 7.5% to greater than 80%.

It is believed that optimum metal sorption to soil particles occurs between a pH of 5.5 and 7.0 whereas precipitation of metal hydroxides occur at higher pH values. Thus, Muthukrishnan and Oleske (2008) investigated the effect of adding lime to soil on the adsorption of metal from infiltrated stormwater. A 0.5% lime addition by weight resulted in pH change from less than 5.0 to 7.2 after 144 hours. The amount of increase in pH units and the corresponding time required will vary with each soil, but this study shows that stabilization times can be relatively long. It can also serve as a caution with respect to the ease of overdosing before the final, stabilized pH value is obtained.

In other studies Gray et al. (2006) added lime to soil and raised the pH to about 6. Gray found the concentrations of aqueous Zn, Cd, Pb, nickel (Ni), and Cu were reduced by 54%, 36%, 76%, 34%, and 86%, respectively, due to the added lime. Also, Zurayk et al. (1997) added 2% to 4% lime to the soil (by weight) which raised the pH and significantly increased phosphorus removal.

The effect of lime addition and the increase in pH is a function of initial pH, amending agent (i.e. the lime), and the natural resistance of the soil to pH change. Besides pH, other properties that can affect the performance of the swale included soil texture, organic matter, cation exchange capacity, and soil phosphorus status.

When runoff infiltrates into the soil it takes with it the dissolved contaminants. Studies have shown that most dissolved metals become bound to soil media in the first 20-50 cm below the surface (Weiss et al. 2008). Some metals, along with phosphorus and nitrogen, are also used as nutrients by plants and are assimilated into plant biomass.

Swales in Cold Climates

The effect of cold weather on the performance of stormwater BMPs is a concern in cold climates. The impact of frozen soil on infiltration, short-circuiting of ponds caused by ice cover, and ice formation on BMP structures such as inlets and outlets, etc. has caused many to question the ability of stormwater

BMPs to perform as designed during winter months in cold regions. Furthermore, it has been shown that the positive effects of vegetation (i.e. flow retardation and pollutant uptake) have less impact during the winter (Backstrom and Vicklander 2000). These concerns have spurred investigations into the impact of below freezing temperatures on BMPs. Studies related to the performance of swales and their associated removal mechanisms in cold weather are reviewed below.

In addition to the impact of cold weather on the stormwater BMP itself, stormwater and snow melt runoff during the winter in cold regions can vary significantly from warm weather runoff. Backstrom and Viklander (2000) performed a literature review on cold climate BMP performance and found that snowflakes get more polluted in the air than rain drops because of their larger surface area and slower fall velocity which allows the snow to absorb more pollutants. After the snow reaches the ground it can be further polluted by dry and wet deposition and gas adsorption. The snowpack can also act as a filter of fine particles and, one can assume, collect them within the snowpack. This is supported by data that shows suspended solid concentrations in snowmelt can be two to five times greater than in rain runoff. It has also been shown that cold automobile engines pollute more than warm engines. For example, cold engines produce two to eight times more particulates than warm engines.

Al-Houri et al. (2009) investigated the impacts of frozen soils on infiltration. Infiltration capacity and hydraulic conductivity are closely linked to the soil water content at the time of freezing. Using the average soil water content to characterize this phenomenon, however, can be erroneous because of unequal internal distribution of water. During infiltration water preferentially resides in larger pore spaces due to the water surface tension and as a result water is kept out of smaller spaces (Miller 1973). When water drains from the soil, however, it drains more rapidly from the larger pore spaces so that they become filled with air more quickly than small pore spaces. As a result, the longer the time allowed for soil-water redistribution after infiltration ceases and freezing begins, the more air spaces there will be during the next infiltration event. Thus, the time allowed for water-soil redistribution can be used to estimate the soil infiltration capacity of frozen soils.

Al-Houri et al. (2009) studied a loam soil and a sandy loam soil. Both soils were tested under frozen and unfrozen conditions. The soil was allowed to drain for time spans of 2, 4, 8 and 24 hours before freezing commenced. For each specimen, data was collected on three different sections; the top, middle, and bottom sections. The data showed that the loam soil with only a 2 hour drain time before freezing exhibited a decrease in the hydraulic conductivity, K , of the soil by one to two orders of magnitude. Longer drain times resulted in a smaller reduction in hydraulic conductivity, especially for the top sections. For example, the 24 hour drain time specimens had a reduction in K of only 3% to 70%.

For the loam soil, the frozen two hour drain time specimen had an average (of top, middle, bottom sections) hydraulic conductivity that was 5% of the unfrozen specimens. The four and 24 hour tests showed frozen average hydraulic conductivities of 21% and 30%, respectively. The sandy loam soils 24 hour drain time test, by contrast, resulted in an average hydraulic conductivity that was 4% of the unfrozen specimen.

Roseen et al. (2009) compared the annual, summer, and winter contaminant removal efficiencies of various LID practices with respect to influent and effluent event mean concentrations. Roseen determined that, compared to most other LID practices, vegetated swales exhibited larger variations in performance between the summer and winter seasons. Figure 3 shows the annual, summer, and winter influent and effluent event mean concentrations for stone and grass swales. The difference between these two kinds of swales is that the bottom of a stone swale is lined with stones instead of vegetation. Table 3 lists the annual and seasonal removal efficiencies (RE) and efficiency ratio (ER) for the two kinds of swales.

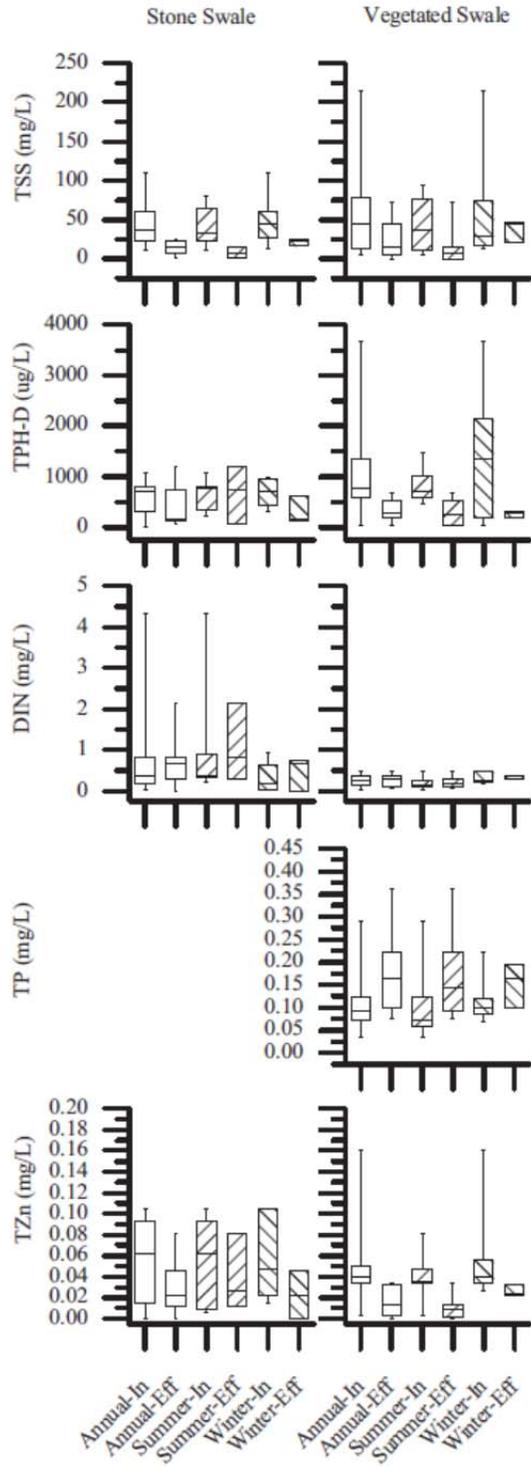


Figure 3. Annual and seasonal influent and effluent EMCs for a stone swale and a vegetated/grassed swale. Lines show max and min values, boxes show 75th and 25th percentiles, and the horizontal line in the box indicates the median value (From Roseen et al. 2009).

Table 3. Annual and seasonal efficiency ratios (ER) and removal efficiencies (RE) for swales (Data from Roseen et al. 2009). RE is calculated as $RE = 1 - (EMC_{outlet}/EMC_{inlet})$ and the reported value is the median of the entire data set. ER is calculated as $ER = 1 - (\text{average } EMC_{outlet}/\text{average } EMC_{inlet})$. TSS = Total suspended solids, TPH-D = Total petroleum hydrocarbons-diesel, DIN = Dissolved inorganic nitrogen (nitrate, nitrite, and ammonia), Total Zn = Total zinc, and Total P = Total phosphorus.

Contaminant	LID Practice	Annual		Summer		Winter	
		ER (%)	RE (%)	ER (%)	RE (%)	ER (%)	RE (%)
TSS	Stone Swale	68	50	85	80	64	8
	Veg. Swale	52	60	69	68	36	13
TPH-D	Stone Swale	28	33	67	9	72	52
	Veg. Swale	53	67	83	60	75	77
DIN	Stone Swale	-2	-72	-81	--	-34	-11
	Veg. Swale	65	-13	61	-5	1	-13
Total Zn	Stone Swale	48	64	18	72	64	56
	Veg. Swale	72	88	73	92	58	17
Total P	Stone Swale	0	61	31	61	--	--
	Veg. Swale	-38	-95	-40	--	--	-64

DISSOLVED NUTRIENT REMOVAL

Stormwater can contain elevated levels of phosphorus and nitrogen Pitt (1996). Sources include fertilizer, animal waste, plant biomass, atmospheric deposition, and motor oil for phosphorus. Dissolved phosphorus and nitrogen are nutrients that have been targeted for removal from stormwater runoff. Nitrate, which is often the limiting nutrient in coastal marine waters, can also cause serious health effects. The Environmental Protection Agency's (EPA) maximum contaminant level for nitrate as nitrogen ($\text{NO}_3\text{-N}$) is 10 mg/L in drinking water. Larger nitrate concentrations can cause a fatal blood disorder in infants called methemoglobinemia or "blue-baby" syndrome. In these cases the oxygen-carrying capacity of blood is severely reduced causing the infants to turn blue. While the EPA has not established regulations for nitrate concentrations in stormwater runoff, human activity has been linked to increases in nitrate levels in ground and surface waters (O'Reilly et al. 2007).

Nitrogen removal can be accomplished through biological activity of bacteria that eventually generates nitrogen gas, ion exchange, reverse osmosis, electrocatalytic, and high temperature and chemical reduction processes (Lin et al. 2008). Bacterial reactions are generally slow, ion exchange and reverse osmosis do not destroy nitrates, and the remaining methods typically have expensive installation and maintenance costs (Lin et al. 2008).

With regards to algae and plant growth in inland fresh water lakes, rivers, and other water bodies that receive stormwater, phosphorus is often the limiting nutrient. Thus, when phosphorus rich stormwater enters the water body, plant growth, which was previously limited by the lack of phosphorus, can increase rapidly. The result is lakes and ponds with an overabundance of plant matter that, upon decomposition, can deplete the dissolved oxygen in the water body. Phosphorus removal in water treatment has conventionally been accomplished through bacterial uptake and chemical precipitation. The uptake of phosphorus by bacteria is typically slow and must occur under controlled conditions. Precipitation is usually accomplished through the addition of alum (i.e. aluminum sulfate) to the water body but adding a metal such as aluminum to a water body to remove phosphorus could be more detrimental than beneficial.

Thus, in order to cost-effectively treat large volumes of stormwater for nitrogen and phosphorus removal, a new, passive method or methods that remove dissolved forms of these nutrients must be developed. The sections below review methods that have been investigated.

Nitrogen

Collins et al. (2010) investigated four different types of permeable pavers for their ability to remove nitrates and nitrites and compared their ability to that of asphalt. The pavers investigated were pervious concrete (PC), two kinds of permeable interlocking concrete pavement (PICP), and concrete grid pavers (CGP) that were filled with sand. The runoff from all of the pavers except CGP had larger nitrate and nitrite concentrations than asphalt, probably due to nitrification occurring in the soil profile, and the concrete grid pavers had the largest total nitrogen concentration. It was theorized that the CGP acted similarly to a sand filter because it had 4 inches of sand base. All of the pavements investigated buffered runoff; probably due to calcium carbonate and magnesium carbonate in the pavement and aggregate. Although some states, such as North Carolina, give no pollution removal credit for permeable pavers

and others, such as Pennsylvania, do, the authors concluded that there was not enough data for permeable pavements to be treated differently by regulators.

Collins et al. (2010) also reviewed other studies, one of which compared the ability of sand, sandy loam, and aggregate to remove nitrogen from aqueous solutions. It was determined that sand and sandy loam were most effective at nitrogen removal due to larger surface areas, allowing more microbes to grow (Henderson et al. 2007). Barrett (2003) found that sand filters were effective in sequestering total suspended solids (TSS) and total Kjeldahl nitrogen (TKN) but nitrate concentrations of the effluent were greater than the influent. A Danish investigation into sand filters found that they removed 30% to 45% of the nitrogen (Nielsen et al. 1993).

Others have found that activated carbon can capture dissolved nitrogen from aqueous solutions. Demiral and Gündüzoglu (2010) investigated activated carbon derived from sugar beet bagasse (the fibrous material remaining after the beets have been crushed to extract their juice) with a surface area of 1826 m²/g and a contact time of up to 400 minutes for its nitrate removal ability. At a nitrate concentration of 300 mg/L NaNO₃, nitrate removal varied between 41.2% and 34.7% as the pH was varied from 3 to 10.5. The increase in nitrate adsorption at low pH was attributed to excess protons reducing the negative charge on the surface of the activated carbon. As a result, the number of positive charged sites increased, which increased the adsorption of the negatively charged nitrate.

Li et al. (2008) used granular activated carbon in a two step process to remove nitrate from water and regenerate the activated carbon for perchlorate removal. The first step involved the activated carbon adsorbing acetate. In the second step, bacteria in a biofilm on the activated carbon completely removed the nitrate in solution in 6 hours. The requirement of pretreatment with acetate and a biofilm may render this process unfeasible for stormwater treatment.

Rezaee et al. (2010) used activated carbon impregnated with MgCl₂ for nitrate removal. At a pH of 6.2, 25° C, and a concentration of 25 mg/L NO₃-N, the nitrate removal rate was 74% compared to only 8.8% for the same activated carbon not impregnated with MgCl₂. Equilibrium for the impregnated activated carbon was attained in 40 minutes. After impregnation, the MgCl₂ was converted to MgO, which has the ability to remove nitrate due to its large surface area, large concentration of low coordinated sites, and structural defects on the surface. Other studies (to be reviewed later) have investigated zero valent iron for nitrate removal. While zero valent iron has been shown to have the ability to remove nitrate, Mg⁰ has a higher reduction potential (2.363 V) compared to Fe⁰ (0.44 V) and may be more effective. Also, other problems with zero valent iron such as long reaction times, the need for anaerobic conditions, and the formation of an iron-hydroxide precipitate on the iron surface which deactivates the iron have been documented.

Choi et al. (2009) investigated the ability of zero valent iron and palladium coated iron to reduce nitrate. The authors found that the palladium coating on the iron increased nitrogen selectivity but did not enhance the degradation rate. All experiments were performed over a pH range of 3.0-4.0 which is significantly below typical values for stormwater runoff and therefore not appropriate for predicting removal from stormwater.

Ugurlu (2009) investigated the ability of fly ash, sepiolite, and heat-activated sepiolite for their ability to remove nitrate from papermill wastewater. Sepiolite is a hydrous magnesium silicate with a surface area of more than 200 m²/g. The average values of contaminant concentration in the wastewater were 0.213 mg/L nitrite, 0.183 mg/L nitrate, 9.88 mg/L ammonium, and 0.176 mg/L phosphate. Concentrations of phenol, lignin, BOD, and COD were also recorded, the average pH was 7.50, and the contact time was 24 hours. Activated sepiolite consistently adsorbed the most nitrate over the range of pH tested (3-11) and the range of particle sizes that were investigated (30-150 μm). The largest adsorption capacity, over 0.09 mg/g, was found for activated sepiolite at a pH of 3. At a pH of 11 the activated sepiolite adsorbed just over 0.004 mg/g. The adsorbent with the smallest nitrate adsorption capacity was found to be fly ash; approximately 0.007 mg/g and 0.002 mg/g at pH values of 3 and 11, respectively. The ability of activated sepiolite to capture more nitrate than the other sorbents was attributed to its high surface area. Finally, all kinetics followed a pseudo-second order model.

Islam and Patel (2010) conducted batch studies to investigate the ability of Zn-Al-Cl layered double hydroxide to remove nitrate from solution. Results showed that the removal of nitrate was 85.5% under neutral pH conditions using 0.3 g of sorbent in 100 mL of solution with an initial nitrate concentration of 10 mg/L and a contact time of 40 minutes. The adsorption of nitrate, which followed first order kinetics, was found to decrease in the presence of competitive anions. The percent nitrate removal increased with decreasing pH and was maximum at a pH of 6, the smallest pH tested. The percent nitrate removal also increased with contact time and increased slightly with temperature. The latter indicates that nitrate adsorption is an endothermic process.

Lin et al. (2008) used zero valent iron nanoparticles to remove nitrites and nitrates from solution. The particles were nearly spherical and ranged in size from 20 to 50 nm in diameter. Removal efficiencies for nitrite and nitrate ranged from 65% to 83% and 51% to 68%, respectively based on three different initial concentrations of 150, 200, and 250 mg/L of nitrate and nitrite. The total contact time was 4 hours although most removal occurred after 2 hours. The authors stated that the removal mechanism appears to be surface precipitation or complexation of nitrite/nitrate with zero valent iron. The zero valent iron used in this study had a surface area of 43 m²/g whereas bulk Fe⁰ has a surface area of about 0.5 m²/g.

Kim et al. (2003) investigated microbial denitrification in a bioretention cell with a continuously submerged anoxic zone and electron donor substrate. It was determined that newspaper was the most effective electron donor compared to alfalfa, leaf mulch compost, saw dust, wheat straw, wood chips, and elemental sulfur. Nitrate mass removal efficiencies ranged from 70% to 80% even after long dormant periods that were introduced to represent the time between runoff events that would naturally occur in practice.

In a literature review, Shrimali and Singh (2001) reviewed a study in which a chemical process using aluminum powder (350 mesh) reduced nitrate to ammonia, nitrogen, and nitrite at pH 9-10.5 (Murphy 1991). No reduction of nitrate occurred at pH 8 because a protective oxide coating formed on the aluminum particles. In another review, Servant et al. (1992) reduced nitrate with iron, aluminum, and stainless steel converting it to nitrite, ammonia, and then into nitrogen. Contact times were not reported and, as with other metals, a film developed on the aluminum and inhibited the reduction

reaction. Summers and Chang (1993) found that Fe(II)-mediated reduction of nitrite and nitrate to ammonia occurred in ocean water with a pH greater than 7.3 and a temperature greater than 25° C in the absence of light. Sato et al. (1996) used a catalyst and UV light to remove nitrate from water and Shrimali and Singh (2001) report that catalysts useful for removing nitrate are rhodium, palladium, and copper. These are usually made into tiny spheres and impregnated with other substances to remove nitrate.

Shrimali and Singh (2001) stated that bacteria with a carbon source can be used to remove nitrate. The carbon source can be methanol, ethanol, acetic acid, sugar, glucose syrup, etc. Garbisu et al. (1991) used *Phormidium laminosum*, a non-nitrogen fixing cyanobacterium (i.e. blue-green algae), to remove nitrate. In batch studies, nitrate concentrations were still in decline after approximately 50 hours. In a continuous flow bio-reactor (1.5 cm inside diameter, 27 cm long, loading rate of 3.5 mL/hr) significant removal of nitrate (data not reported) was achieved from 90 mg/L feed water for 12 weeks. In this study, cells either remained free or were immobilized in one of three ways; 1) In polyurethane foam by absorption, 2) Entrapment followed by polymerization, or 3) By adsorption onto polyvinyl foams. Cells that were entrapped died quickly and did not remove nitrate. Cells that were immobilized through adsorption did not die but removed less than half the nitrate as free cells. Nitrate uptake increased when light and CO₂ increased but the light amount does not account for the difference in uptake rate between free and adsorbed cells. The authors theorized that perhaps the foam acted as a barrier or there was a mucilage layer that formed around the cells. The reduction of nitrate can also be accomplished through immobilized enzymes in a bioreactor with an electrical current (Mellor et al. 1992).

Xuan et al. (2010) sought to develop a new “green” material mix made up of recycled materials to remove nitrates, ammonia, total nitrogen, orthophosphorus, total phosphorus, and biochemical oxygen demand (BOD) from wastewater. Potential sorption media included tire crumbs, tree bark, wood chips, sawdust, newspaper, alfalfa, mulch, cotton, wheat straw, and sulfur/limestone. These materials were selected based on a thorough literature review. The literature review revealed that in one study alfalfa and newspaper achieved 100% nitrate removal and mulch compost achieved only 60% removal. Sawdust, wood chips, and wheat straw obtained greater than 95% removal of nitrate with wood chips achieving consistently greater removal than saw dust. Compost achieved 55% nitrate removal. Materials that were investigated and found to be ineffective for nitrate removal were soil, broken brick, and polystyrene packing material. Another study used sulfur and limestone for nitrate removal in potable water. Sulfur was the electron donor and limestone maintained the pH. At an optimum mixing ratio of 1:1 (sulfur:limestone) nitrate removal was 98%. In a study using granulated tires for nitrate removal it was determined that 48 g of tire removed 16.2 g NO⁻³-N. Other studies found that mulch was very effective in removing nitrate while sand was not. It was concluded that soil with more silt/clay and cations (Mg/Ca/K) might be effective for nutrient removal and that coarse media is not as effective because of its small surface area. Finally, nitrate has also been removed from water using marble chips, limestone, and oyster shells. Oyster shells, which were 98% CaCO₃, were most effective as they removed 80% of nitrate whereas limestone removed 56% of nitrate.

Using the results of their literature search, Xuan et al. (2010) developed a mix of 68% fine sand, 25% tire crumbs, and 7% sawdust that achieved 55% removal of nitrates and 89% phosphorus (with initial concentrations of 0.352 mg/L nitrate and 1.498 mg/L orthophosphorus) in a 24-hour retention time.

In other studies, Wenske (1997) reduced nitrate in water containing hydrogen and Cheng et al. (1997) reduced nitrate to ammonia at room temperature and pressure under aerobic conditions in the presence of iron and either HCl or a pH buffer. In unbuffered solutions no nitrate removal was achieved.

Faucette et al. (2009) investigated the use of socks filled with compost to remove sediment, ammonium, nitrate, fecal bacteria, heavy metals, and petroleum hydrocarbons. Compost sock removal efficiencies were 17% for $\text{NH}_4\text{-N}$ and 11% for $\text{NO}_3\text{-N}$. The addition of NitroLoxx (a flocculating agent) to the compost increased $\text{NH}_4\text{-N}$ removal to 27% but did not affect $\text{NO}_3\text{-N}$ removal.

Some studies have investigated ways to increase nitrate removal. For example, Karimi et al. (2010) studied nitrate adsorption and desorption from modified beet residue. They found that nitrate adsorption in the presence of pyridine increased in the presence of ultrasound at lower temperatures (10°C) and that 90% of the nitrate was removed in less than 10 minutes. The mass of nitrate sorbed was in the range of 70-80 mg/g sorbent. They also found that desorption was larger in the presence of ultrasound through a range of temperatures and that desorption/adsorption was the same after five cycles, indicating the material can be regenerated and reused.

Other studies have shown that for some sorbents nitrate adsorption is significantly delayed in the presence of large molecular weight humic acids (Cacco et al. 2000, Nardi et al. 2000) while for other sorbents it has no effect (Panuccio et al. 2001). Klucakova (2010) found that nitrates may be adsorbed mainly by solid humic particles and a small amount is bonded to dissolved humic macromolecules or aggregates.

As with metal removal, the removal of nitrates in a stormwater filter will require relatively rapid kinetics due to the short contact time between the water and the filter media. Based on the reviewed literature, promising enhancing agents appear to be activated carbon impregnated with MgCl_2 or other magnesium based agents such as hydrous magnesium silicate (sepiolite) and Mg^0 , iron (if the limiting precipitate layer or its effect can be minimized), and Zn-Al-Cl layered double hydroxides. Microbial denitrification with newspaper as an electron donor may also be feasible.

Phosphorus

Dissolved phosphorus removal can occur through adsorption to iron (Fe) and aluminum (Al) hydroxides or oxides under acidic conditions. It has been reported that optimal removal via this mechanism occurs from pH = 5.6 to pH = 7.7 whereas precipitation of phosphates with calcium (Ca) is optimal at pH values of 6 to 8.5 (O'Neill and Davis 2010).

Iron has demonstrated the ability to remove dissolved phosphorus from aqueous solutions. In the work by Erickson et al. (2007) steel wool was used to remove dissolved phosphorus from synthetic stormwater in both laboratory batch and column studies. Based on this work, scrap iron shavings were used as an enhancing agent in a 0.27 acre stormwater sand filter in Maplewood, Minnesota (Erickson et

al. 2010). As a waste product the iron shavings were selected over steel wool due to its smaller cost. The filter is currently being monitored and is removing over 80% of the dissolved phosphorus from the runoff it filters. The iron shavings appear to have most, if not all, of the qualities needed for an optimum enhancing agent that can remove dissolved nutrients. It's inexpensive, safe to handle, does not significantly alter the pH, and, based on the work by Erickson et al. (2007, 2010), appears to have a large capacity such that the life of the iron will outlast the life of the filter.

O'Neill and Davis (2010) investigated the ability of aluminum-based drinking water treatment residual (that contained aluminum and iron), triple-shredded hardwood bark mulch, and washed quartz sand to remove dissolved phosphorus from water. The investigation used laboratory column experiments that were run continuously for 57 days. The columns contained 12 cm of media and had a water loading rate of 15 cm/hr (1.3 mL/min) for the first 28 days. Loading rates were increased to 31 cm/hr (days 29 through 49) and finally to 61 cm/hr (days 49 through 57) to force column breakthrough. At a loading rate of 15 cm/hr, which is typical for stormwater bioretention facilities, quartz sand with 4% water treatment residual reduced the dissolved phosphorus concentration from 0.12 mg/L to, on average, less than 0.02 mg/L for the entire 28 day span (750 bed volumes). Although the effluent concentration increased as the loading rate increased, breakthrough did not occur over the course of the 57 day experiment (2500 bed volumes).

Other materials that have been investigated for phosphorus removal potential include slag, red mud, other iron based components, zirconium, coal fly ash, crab shells, lithium, magnesium or manganese-layered double hydroxides (Chouyyok et al. 2010), aluminum oxide, calcareous sand, limestone, blast oxygen furnace dust (a by-product of the steel making industry), iron oxides, calcite, high calcium marble, clay, diatomaceous earth, and vermiculite (Erickson 2005). While these materials may be effective, steel wool and/or iron shavings have been found to be effective at capturing dissolved phosphorus while meeting other practical requirements such as being relatively inexpensive, easy to place, not clogging the filter, and having a long life. The materials previously mentioned typically have limitations associated with them such as changing the pH of the water to unacceptable values, clogging the filter, dissolving and passing through the filter, etc.

Based on previous work, the most promising enhancing agents for the capture of phosphorus appear to be steel wool, iron shavings, water treatment residual, or other iron based materials. They have already been shown to have relatively high capture rates, be inexpensive, and have a long life.

IMPROVING METAL RETENTION

Urban stormwater runoff typically contains elevated levels of metals in dissolved or particulate form. The metals can originate from vehicle wear, tire and asphalt abrasion, buildings, and other sources (Wu and Zhou 2009). Metals of primary concern (based on toxicity and occurrence) in stormwater are cadmium, copper, lead and zinc (Jang et al. 2005, Rangsvik and Jekel 2005) with up to 50% being in dissolved form (Morrison et al. 1984). Copper, lead, and zinc are detected in urban runoff over 90% of the time (Pitt 1996) and, where erosion is minimal, soluble pollutants can exceed 80% of the total pollutant load (Faucette et al. 2009). The particulate fraction of metals is not readily bioavailable and

can be removed via settling or filtration. Thus, metals that occur primarily in particulate form (such as lead), while toxic, may not typically be of concern in stormwater treatment because they can be removed through settling or filtration. The dissolved fraction, however, typically passes through stormwater treatment devices and into receiving water bodies. With up to 50% of cadmium, copper, and zinc being in dissolved form, attention is being given to the development of methods that can remove these metal ions from stormwater runoff. One possible solution is to add material (i.e. an enhancing agent) to soil or sand filter media that will adsorb or otherwise retain dissolved metal cations.

Metal cation removal from aqueous solution may occur through four different mechanisms; cation exchange, cementation, adsorption, and metal hydroxide precipitation (Rangsvik and Jekel 2005, Zhang et al. 2008). The mechanisms are pH dependent and more than one mechanism can occur at the same time, even on the same sorbent. In cation exchange processes, positively charged ions on the sorbent are displaced by metal cations that have a higher affinity for the site. Thus, metal cations are removed from solution and previously sorbent-bound cations enter solution. At very low pH, metal cations must compete with hydrogen ions for the exchange sites and metal removal tends to be reduced (Kwon et al. 2010). Cementation involves re-dox sensitive compounds being reduced to insoluble forms (Rangsvik and Jekel 2005), surface adsorption occurs when ions are adhered preferentially to the surface of the adsorbent, and metal hydroxide precipitation occurs at high pH values where the metal ions will form a precipitate with free hydroxide ions (OH⁻).

There are many materials with the ability to adsorb metal cations in aqueous solutions including various forms of iron, alumina, activated carbon, compost, mulch, wood bark, grass clippings, and many other plants or plant parts. An ideal enhancing agent for the removal of metal ions from stormwater would:

- Be inexpensive and readily available
- Be easily mixed into the infiltration media without any health or safety issues
- Have relatively fast reaction/sorption kinetics because contact times between the water and enhancing agent are relatively short
- Not alter the pH or other water quality parameters to unacceptable values
- Not dissolve and be washed away or plug the filter media
- Have a high capacity for metal retention
- Not release other contaminants such as phosphorus, nitrogen, or other metals.

After a discussion of dissolved metal removal capabilities of natural soils, studies that have investigated various enhancing agents and their ability to remove metal ions from solution are reviewed below.

Natural Soils

Many natural soils have demonstrated the ability to remove metal ions from solution and most metals adsorb to soil particles in the top 20-50 cm of soil (Mikkelsen et al. 1997, Dierkes and Gieger 1999, Dechesne et al. 2004, Zimmerman et al. 2005, Sun and Davis 2007). Elliot et al. (1986) investigated soil adsorption of Cd, Cu, Pb, and Zn and found that for all metals, a higher pH resulted in more metals being

sorbed by the soil. Possible explanations include the adsorption of metal-hydroxo complexes (Metal-OH⁺), hydrolysis of aluminum on exchange sites, and finally competition between protons and metal cations and acid-catalyzed dissolution of reactive oxide sites that may occur at low pH values.

In batch and column experiments, Plassard et al. (2000) investigated the adsorption of Cd, Pb, and Zn by a soil with a carbonate content of 227 mg/g. In a review of previous studies, Plassard et al. (2000) states that cadmium can be retained by the formation of an ideal surface solution with cobalt carbonate (CoCO₃), and zinc and copper may be precipitated as hydroxides or hydroxycarbonates. Another author found that the reaction between metals and carbonates results in metal incorporation into the solid lattice, not surface adsorption. All of Plassard's experiments were performed at pH = 8.2 with highly buffered soils. In the batch experiments at metal concentrations of 5×10^{-4} mol/L, all metals were bound to the soil after 4 hours, mostly to the acid-soluble fraction of soil. Increases in initial metal concentration, however, lead to weaker retention. For example, in batch experiments at a cadmium concentration of 5000 μmol/L, 27% of Cd remained in solution after 4 hours. Cadmium, it must be noted, behaves differently than other metals as it reacts more slowly and, thus, is typically retained at a lower rate. Metals were removed to a lesser extent in the column experiments, probably due to preferential flow paths and/or shorter contact times. Plassard et al. (2000) concluded that even in situations where the removal rates were high the removal forces (precipitation and cation exchange) were weak and that there is a risk of metal release when conditions change.

Elliot et al. (1986) investigated the effect of organic matter on metal adsorption by performing batch studies with a 24-hour contact time. It was determined that when organic matter was removed from two organic soils, zinc adsorption was greater than cadmium adsorption. When organic matter was not removed, however, cadmium adsorption was greater than zinc adsorption. Based on these results it appears that organic matter prefers adsorption with cadmium, although Elliot et al. (1986) point out that other studies have found equal adsorption tendencies between cadmium and zinc. In some soils all metal adsorption capabilities might be due to organic matter but this is not true for all soils. The investigators also state that for soils without organic matter, the addition of organic matter may increase metal adsorption under acidic conditions and that this will enhance cadmium removal more than zinc.

Blecken et al. (2009) investigated the effect of the saturated (or submerged) zone in soil media on dissolved contaminant removal by the soil. Submerged zones, in combination with organic carbon zones, have been shown by other authors to support nutrient and metal removal, especially copper. Eighteen laboratory biofilters were constructed out of PVC pipe; some filters contained a submerged zone and some did not (Blecken et al. 2009). Lead and zinc removal was large and cadmium was always removed to levels below the detection limit regardless of whether a submerged zone was present. Copper removal, however, was 12% greater in filters with a submerged zone. The authors reasoned that the submerged zone creates anoxic (or partially anoxic) conditions which cause more of these metals to adsorb to sediments. After three weeks of drying, elevated metal concentrations were found in filter effluent but no effect was observed for shorter drying times. Filters with a submerged zone also did not discharge lead, even after long dry periods. Decreased metal removal after drying could be attributed to leaching of metals from the soil, mobilization of fine sediment, and cracking of the soil and creation of

preferential flow paths. Blecken et al. (2009) also observed that metals were removed in the top portion of the soil because below a depth of 20 cm all metal concentrations were below detection limits.

Lassabatere et al. (2004) investigated the effect of geotextiles on contaminant removal, including metal (Cd, Pb, Zn) adsorption, in calcareous soils. It was determined that geotextile fabric can filter particles, trigger development of microorganisms that may interact with contaminants, and modify or control flow. While the geotextile material did not retain metals, it did modify mechanisms of metal retention in the surrounding soil. When geotextile material was placed dry it tended to homogenize the flow. This resulted in better contact between the soil and water and more metal removal. All tests were performed on calcareous sand and the results may not apply to other soil types or other metals.

Activated Carbon

Van Lienden et al. (2010) reviewed the ability of six commercial and six non-commercial activated carbon (AC) materials to remove copper and zinc ions from water. Non-commercial AC included those derived from straw, hulls, and shells of almonds, pistachios, pecans, and walnuts. The performance of each AC was investigated in the laboratory using batch studies with a contact time of 72 hours and a prepared solution containing the metal ions. The batch studies were followed by experiments using actual stormwater runoff samples. Most of the ACs tested, including all of the commercial products, demonstrated a greater affinity for copper than for zinc. The AC that was derived from rice hulls had the largest capacity to remove zinc whereas a commercial AC had the largest copper removal capacity. When tested in actual stormwater, however, the copper sorption dropped by up to 80% due to competition between metal ions and other substances in the water. The authors concluded that 1 kg of AC derived from rice hulls could treat up to 46 m³ of California highway stormwater runoff that contained the 90th percentile concentration of copper. The zinc treatment volume, however, would be 7 m³ and would control the design of a stormwater filter. With regards to copper removal, the rice-derived AC could treat 20.9 times as much California highway runoff than the best commercially AC tested and 4.9 times as much water with respect to zinc removal.

Genc-Fuhrman et al. (2007) tested a host of enhancing agents including a commercially supplied granulated activated carbon (GAC) for their ability to remove arsenic, cadmium, chromium, copper, nickel, and zinc from solution using batch studies with a 48 hour contact time. The GAC in their study ranked behind alumina, bauxolcoated sand, granulated ferric hydroxide, and fly ash in terms of overall removal effectiveness. The fly ash, however, increased pH values to over 9, whereas the GAC increased pH values to between 8 and 9.

The ability of activated carbon impregnated with the surfactants sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), or dioctyl sulfosuccinate sodium (DSS) to remove cadmium ions from solution was investigated by Ahn et al. (2009) using batch studies with a 48 hour contact time. Impregnating the surface increased the number of active cation exchange sites; it was theorized that the new sites could be the heads of the surfactants arranged towards the water. All modified GAC removed Cd well, even at pH =2, with removal rates increasing linearly with pH. It was determined that SDS was the most effective enhancing agent of those tested. Also, the surfactants covered up acid groups and

decreased acidity. Finally, Ahn, et al. concluded that the kinetics of the adsorption reactions are well described by a pseudo-second order kinetic model.

Alumina

Alumina, or aluminum oxide (Al_2O_3), can remove heavy metals from solution by precipitation and adsorption. There are many different grades of alumina but in a batch study experiment (48 hour contact time) by Genc-Fuhrman et al. (2007) that investigated the ability of 11 different sorbents to remove arsenic, cadmium, chromium, copper, nickel, and zinc ions, alumina was determined to have the largest overall removal efficiency of all sorbents. The alumina used by Genc-Fuhrman et al. (2007) was supplied by Haldor-Topsoe in Denmark and was a waste product of their manufacturing process of catalysts (email communication with Professor Anna Ledin, co-author). In this study the alumina outperformed activated bauxsol-coated sand, bark, bauxsol-coated sand, fly ash, granulated activated carbon, granulated ferric hydroxide, iron oxide-coated sand, natural zeolite, sand, and spinel (MnAl_2O_4). It was observed that as the pH and initial metal concentration increased, oversaturated minerals and salts also increased. Thus, precipitation, not adsorption, may have been the primary removal process in these tests. Regardless of the mechanism, the alumina removed all metals to levels below Dutch emission limit values.

The high removal rates of alumina were attributed to the high surface area of alumina and favorable surface reactions with metal ions. Alumina removes cations through mechanisms such as surface complexations with hydroxide groups, pore diffusion, and adsorption. Although alumina was deemed the best overall performer, some sorbents did outperform alumina with respect to removal of certain metals.

Baumgarten and Kirchhausen-Dusing (1997) presented a chemical reaction model to predict the concentration of aluminum ions, other metal ions, and pH as a function of the quantities of alumina, volume of liquid, metal concentrations, and other variables. They also described adsorption with a Henry isotherm.

Compost

Compost, although shown to be effective at removing metal ions, releases or has the potential to release phosphorus and nitrogen into the water. Phosphorus or nitrogen are typically the limiting nutrient for plant and algae growth and therefore are often a target for removal from stormwater. Thus, using an enhancing agent that can release phosphorus and/or nitrogen may be more detrimental than beneficial. A two-stage filter, however, in which the upstream first stage removes metals but releases nutrients followed by a second stage that removes nutrients may be effective.

It is the organic fraction of compost that has the ability to adsorb metal ions from solution. The organic material contains binding sites such as amine, carboxyl, phenolate, and thiol groups that can complex or exchange metals and remove them from water (Nwachukwu and Pulford 2008). Precipitation may also occur, usually by an anion such as phosphate, which forms an insoluble salt with the metal, or by raising the pH to precipitate the metal as its hydroxide.

Nwachukwu and Pulford (2008) tested bonemeal, coir (commercially available blocks of dried coconut husks), compost, green waste compost, peat, and wood bark for their ability to adsorb lead, copper, and zinc in batch laboratory studies with a contact time of one hour. The materials with the three largest metal capacities were, in order of decreasing capacity, green waste compost, coir, and compost. The Langmuir sorption maxima were approximately 87 mg Pb/g (coir and green waste compost), 30 mg Cu/g (compost and green waste compost), and 13 mg Zn/g (compost and green waste compost) all in 0.001 M $\text{Ca}(\text{NO}_3)_2$. The affinity of metals for the compost materials was consistent with other materials tested (in this and other studies) and was in the order of $\text{Pb} > \text{Cu} > \text{Zn}$.

Adsorption was dependent on ionic strength of the solution and competition with other metals. For example, larger background salt concentrations resulted in less lead removal by compost, coir, wood bark, and green waste compost. Also, testing all metals in one combined solution reduced sorption by all materials due to competition. Lead sorption, when in competition, was reduced by about 40-50%, copper was reduced by 60% to 70%, and zinc sorption was decreased by variable amounts under competition.

Seelsaen et al. (2006) used batch studies with a 24 hour contact time to test compost, sand, packing wood, ash, zeolite, recycled glass, and Enviro-media (a manufactured material containing either selected organic matter or a blend of organics, minerals, specialized aggregates, soil and other ingredients) for their ability to remove copper, lead, and zinc ions from solution. The relevance of the Enviro-media mixes is that based on its performance, the authors concluded that a combination of sand and alternative materials could be used to treat stormwater. With regards to metal removal, compost was ranked the best but it also leached large amounts of dissolved organic carbon (DOC) into the water.

Faucette et al. (2009) investigate the use of socks filled with compost to remove sediment, NH_4 , NO_3 , fecal bacteria, metals, and petroleum hydrocarbons. Removal efficiencies for soluble metals tested (Cd, Cr, Cu, Ni, Pb, and Zn) ranged from 17 to 72%.

Composted Manilla grass was investigated by Kahn et al. (2009) to determine whether pH and moisture content (MC) values that create large volume reduction in compost (compost's main purpose), also promote cadmium, copper, lead, and zinc cation removal. The experiments were performed using laboratory batch studies with a contact time of 5 hours. 30% MC and an initial pH of 8 resulted in compost with the largest cation exchange capacity whereas 30% MC and an initial pH of 7 had the maximum volume reduction. Kahn et al. (2009) concluded that 30% MC was optimum for maximizing volume reduction and cation exchange capacity at all initial pH values.

Crustacean Shells

Shells from crabs, shrimp, and other crustaceans are composed of chitin (poly-N-acetylglucosamine), protein, and CaCO_3 and have been shown to have a relatively large capacity to remove heavy metals from aqueous solutions. Chitin complexes investigated by Robinson-Lara and Brennan (2010) removed aluminum ions more quickly (3 days) than lactate (12 days) and spent mushrooms (37 days) and was the only complex able to remove manganese (73% removal). Aluminum removal was consistent with the formation of hydroxides and/or alunite $(\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$. Iron was also removed by chitin which was

consistent with the precipitation of Fe(III) oxides and Fe(II) sulfides, as well as surface adsorption. Finally, the chitin complex increased the pH from 3 to neutral in three days.

Bailey et al. (1999) discuss chitosan, which is a complex that can be produced chemically from chitin, is found naturally in some fungal cell walls, and has a large capacity for metal adsorption. It is estimated that one to four million pounds of chitosan could be produced for \$1-2/lb. Chitosan, however, is highly soluble in water but can be made essentially insoluble by cross-linking it with glutaraldehyde.

The adsorption capacity of chitosan varies with crystallinity, affinity for water, percent deacetylation, and amino group content but studies have found extremely large capacities of 136 to over 500 mg Cd/g, 27.3 mg Cr(VI)/g, several hundred mg Hg/g, and almost 800 mg Pb/g. In other studies N-acylation was shown to increase the porosity of chitosan (which is naturally non-porous) which increased metal capacity by 20% but cross-linking to reduce solubility was shown to decrease capacity by 37%. Other researchers have increased the capacity of chitosan by substitution of functional groups such as organic acids.

Ferrous Based Materials

Iron based enhancing agents, which have the capacity to remove dissolved phosphorus from solution, have also demonstrated the ability to remove metal ions. For example, Namasivayam and Ranganathan (1995a) used Fe(III)/Cr(III) hydroxide, a waste product from the fertilizer industry, to remove cadmium, nickel, and lead ions from solution. In batch studies with contact times of 1 or 5 hours the amount of metals sorbed increased as the sorbent dose increased and particle size decreased. Contrary to some studies (Nwachukwu and Pulford 2008), metal adsorption was not affected by changing the ionic strength of the solution. When all metals were combined in one solution, lead demonstrated the strongest affinity for the sorbent, followed by cadmium and then nickel, due to competition.

Namasivayam and Ranganathan (1995a) also performed fixed bed experiments in which 3 grams of adsorbant was packed into a 1.4 cm inside diameter glass column (2.5 cm bed height) and a solution containing one of the three metal ions (200 mg Pb/L, 80 mg Cd/L, or 50 mg Ni/L) was pumped through the adsorbant at a rate of 10 mL/minute. The breakthrough curves are shown in Figure 4.

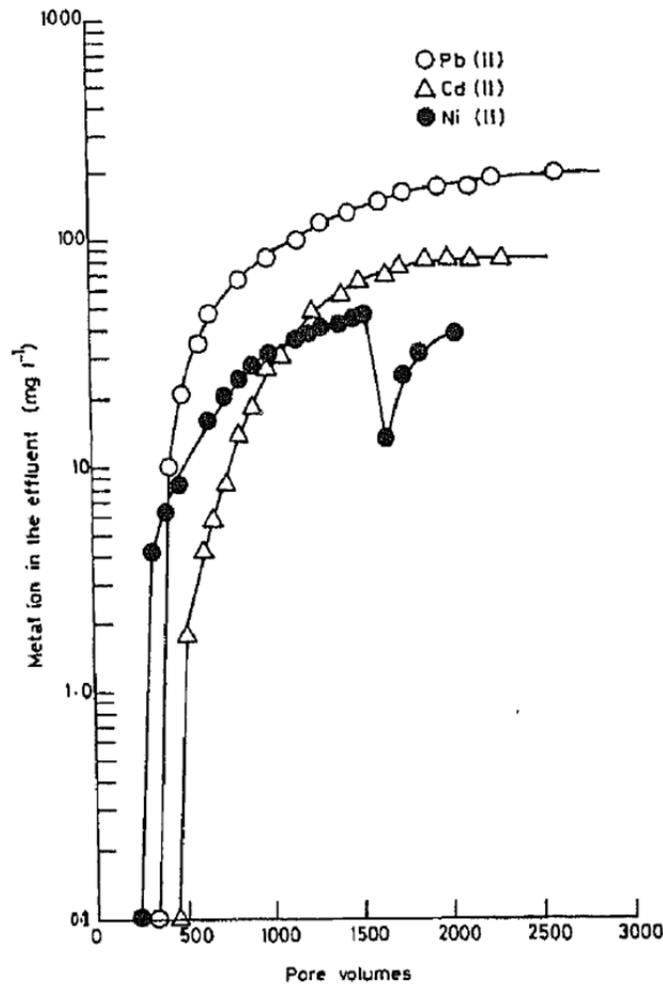


Figure 4. Breakthrough curves for the adsorption of metals on waste Fe(III)/Cr(III) hydroxide (From Namasivayam and Ranganathan (1995a).

In a paper investigating only cadmium ion removal, Namasivayam and Ranganathan (1995b) reported that the mass of cadmium ions removed ranged from approximately 20 to 40 mg Cd/g sorbent as the concentration of the sorbent increased from 50 to 140 mg/L. The time required to reach equilibrium was approximately 300 hours. Adsorption also increased with temperature; equilibrium values of about 25 mg/g were reported at 20° C and about 33 mg/g at 40° C. The effect of temperature was attributed to increased pore sizes in the adsorbent and/or activation of the adsorbent surface. Adsorption also appeared to be endothermic and spontaneous and, as is typical of cation adsorption of metal oxides, increased with pH. Finally, as pH was lowered, previously sorbed metals ions were desorbed; 70% of the cadmium ions desorbed at pH = 3.8, the smallest pH value tested.

Rangsivek and Jekel (2005) used zero valent iron (ZVI), or Fe^0 , to remove copper and zinc ions from solution in batch studies with a contact time of 48 hours. Their ZVI was in the form of scrap iron obtained from an ASTM A284 grade steel cylinder that was 98% Fe^0 and was ground into particles that ranged from 0.4 to 1.25 mm in size. Most of the copper removed was determined to be reduced in a thermodynamically favored reaction by Fe^0 and transformed into insoluble Cu^0 or Cu_2O . Unlike copper, zinc removal required the precipitation of iron oxides that acted as adsorption sites. Zinc removal also increased as dissolved oxygen, ionic strength, pH, and temperature increased but the rate of zinc removal was half that of copper. Metal uptake rates decreased with increasing amounts of dissolved organic carbon as these substances form complexes with metals and Fe^{2+} .

Rangsivek and Jekel (2005) examined the removal processes of ZVI in detail and found that large molecular organics can compete with metal ions for adsorption sites and that the long-term performance of ZVI may be limited or governed by the formation of layers of iron and cuprous oxides. Also, under acid conditions with no dissolved oxygen, only 0.88 mg iron was required to remove 1 mg Cu^{2+} but in stormwater runoff that value increased to about 5 mg of iron. The difference was attributed to iron consumption by dissolved oxygen and accumulated intermediate products such as Fe^{3+} . The presence of DO, however, significantly increased zinc removal as DO increased the corrosion of iron.

Copper removal was not significantly affected by temperature but zinc removal increased by a factor of seven as the temperature increased from 5 to 35° C. The impact of temperature was attributed to increased iron dissolution rates at higher temperatures which resulted in more iron being available to remove zinc. It also appeared that some copper (7% to 9%) formed metal-DOC complexes that could not be removed by the ZVI. The DOC also reduced copper removal rates by a factor of two due to the formation of complexes and competitive adsorption. Zinc removal was reduced by a factor of 4.6 in the presence of DOC. Finally, ionic strength had little impact on copper removal but zinc removal increased from 75% in deionized water to greater than 95% in water with large ionic strength.

In a comparison of 11 different sorbents, Genc-Fuhrman et al. (2007) ranked granulated ferric hydroxide (GFH) only behind alumina and bauxsol-coated sand in terms of overall metal ion removal performance. The GFH was a commercially available product sold under the name Ferrosorp Plus and was later investigated for its ability to remove As, Cd, Cr, Cu, Ni, and Zn from solution (Genc-Fuhrman et al. 2008). The GFH increased the pH of the water from 6.7 to 8.2 and complete breakthrough occurred after 100 days (or about 800 bed volumes). In this study, humic acid was found to reduce the uptake of metals; Cr was most negatively affected with 100 mg/L of humic acid reducing its removal by 81%. Adsorption capacities were also found to decrease in the absence of light because, in the presence of organic matter such as humic acid, light can reduce the Fe(III) in the GFH to Fe(II) .

Wu and Zhou (2009) also investigated the ability of Ferrosorp Plus and Ferrosorp RWR to remove arsenic, cadmium, chromium, copper, nickel, and zinc from solution using batch studies with a contact time of 48 hours. The Ferrosorp Plus leached chromium (14.3 $\mu\text{g/L}$) and zinc (120 $\mu\text{g/L}$) in control batches of clean water. The Ferrosorp products had a large affinity for cadmium, nickel, and zinc but were not as effective at removing copper, arsenic, and chromium. The authors suggested that a Ferrosorp/zeolite mixture could be effective for stormwater treatment; the Ferrosorp would remove cadmium, nickel, and

zinc and the zeolite could remove copper (and possibly other metals). The performance of Ferrosorp, however, could be reduced when used in actual stormwater runoff due to the formation of metal/organic complexes and competition between metal ions and other substances for adsorption sites.

Magnesium

Zhu et al. (2009) used chromatographic silica gel as the host matrix and impregnated it with magnesium chloride. Granules were then dried for 3 hours and calcined at 773° K for 4 hours. The result was a material that had a capacity for metal adsorption 15 to 30 times greater than silicon dioxide. At initial copper and nickel concentrations of 50 mg/L, more than 90% of the metal ions were removed after 8 hours at a pH value of 5 or above. Removal rates decreased as pH decreased below 5 as metal ions had to compete with hydrogen ions for sorption sites. If the metal removal process was all cation exchange, the removal would have been completed in a matter of minutes, not hours. Thus, the authors note that a process that is slower than ion exchange is also involved in the uptake of metals. Adsorption capacities also increased with temperature indicating endothermic adsorption processes are occurring.

Manganese and Manganese Oxide

Shi et al. (2008) used ground, natural manganese ore (rhodochrosite) to remove lead and copper from solution. Like other adsorption studies, pH was found to greatly impact the adsorption process. Adsorption equilibrium was attained within 60 minutes and capacities were on the order of 1-5 mg/g for copper and 1-11 mg/g for lead. The authors concluded that diffusion of the metal ions into the bulk crystal was so difficult that it essentially did not occur and that all adsorbed metal ions were on the surface of the particles.

Manganese oxide coated media (with the coating chemically applied under laboratory conditions) has been shown to remove metal ions from water and has similar adsorption properties as granular activated carbon and iron-oxide coated sand (Liu et al. 2004). Removal mechanisms include adsorption, surface complexation ion exchange, and filtration (Liu et al. 2005). In their study, Liu et al. (2004) coated polymeric media with manganese oxide and found that the coating significantly increased metal removal. Over 50% of the metals (Cd, Cu, Pb, and Zn) were removed in the first 30 minutes with 90% removal occurring within 5 hours. Under conditions where the metals were combined and competing for adsorption sites, the amount of metals adsorbed in decreasing order were Pb > Cu > Cd > Zn. Also, at pH =7 the capacity for Pb removal was found to be several times larger than that at pH = 6.

In a later column study, Liu et al. (2005) compared manganese oxide coated materials (polymeric, cementitious materials, and sand) with iron oxide coated sand, silica sand, granular activated carbon, and cementitious material and found that the manganese oxide coated materials had the best overall behavior for removal of Pb, Cu, Cd, and Zn. In these experiments the loading rates ranged from 20 to 80 L/m²-minute, which is typical for stormwater BMPs.

Plant Biomass

Various plant materials that have been investigated have demonstrated the ability to remove metal ions from aqueous solutions. For example, Al-Asheh et al. (2000) demonstrated that pine bark has the ability to remove Cd, Cu, and Ni ions from water. This study focused on which isotherm models fit best in single

and multi-metal solutions. Freundlich and Sips models most accurately modeled solutions with one metal ion. Solutions containing a combination of two metal ions, however, fit the Extended-Langmuir, Extended-Freundlich, and ideal adsorption solution theory (IAST) best. In general, bark is effective because of its large tannin content. The polyhydroxy polyphenol groups of tannin enable adsorption to occur as ion exchange takes place between metal cations and phenolic hydroxyl groups (Bailey et al. 1999). Tannins can also discolor water by releasing soluble phenols. Pretreatment with acidified formaldehyde, acid, base, or formaldehyde can prevent the water from becoming discolored. Peanut skins, walnut expeller meal, and coconut husks have similar metal removal capacity as bark. Other plant material with demonstrated metal removal capability include seaweed, peat moss, modified orange peel, mulch (from various types of bark), barley straw, manila grass, and dried wheat stem (Bailey et al. 1999, Jang et al. 2005, Pehlivan et al. 2009, Tan and Xiao 2009, Kahn et al. 2009, Feng et al. 2009). The above mentioned orange peel was modified by hydrolysis with a copolymer which increased the adsorption capacity for copper to 289 mg/g which was 6.5 times greater than the non-modified peel (Feng et al. 2009). The results of kinetic experiments on the modified orange peel are shown in Figure 5.

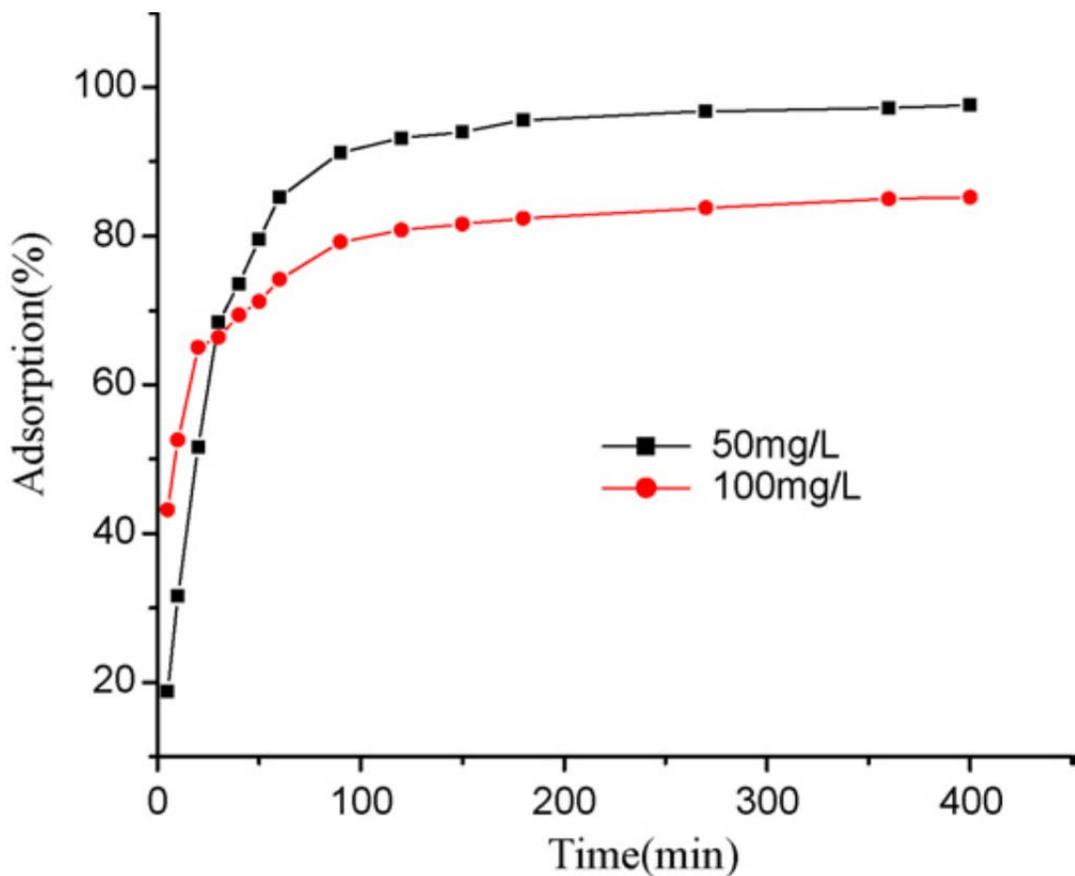


Figure 5. Effect of contact time on the adsorption of Cu (II) at pH = 5.0, temperature = 30 °C, and adsorbent concentration = 2 g/L (From Feng et al. 2009).

The main parameters affecting copper and lead adsorption to barley straw were initial metal concentration, amount of adsorbent, contact time, and pH. The percent lead and copper adsorbed increased with increasing pH with the maximum adsorption occurring at a pH of 6. Equilibrium capacities were 4.64 mg/g for copper and 23.3 mg/g for lead after two hours (Pehlivan et al. 2009). Kinetic experiments performed on the barley straw are shown in Figure 6.

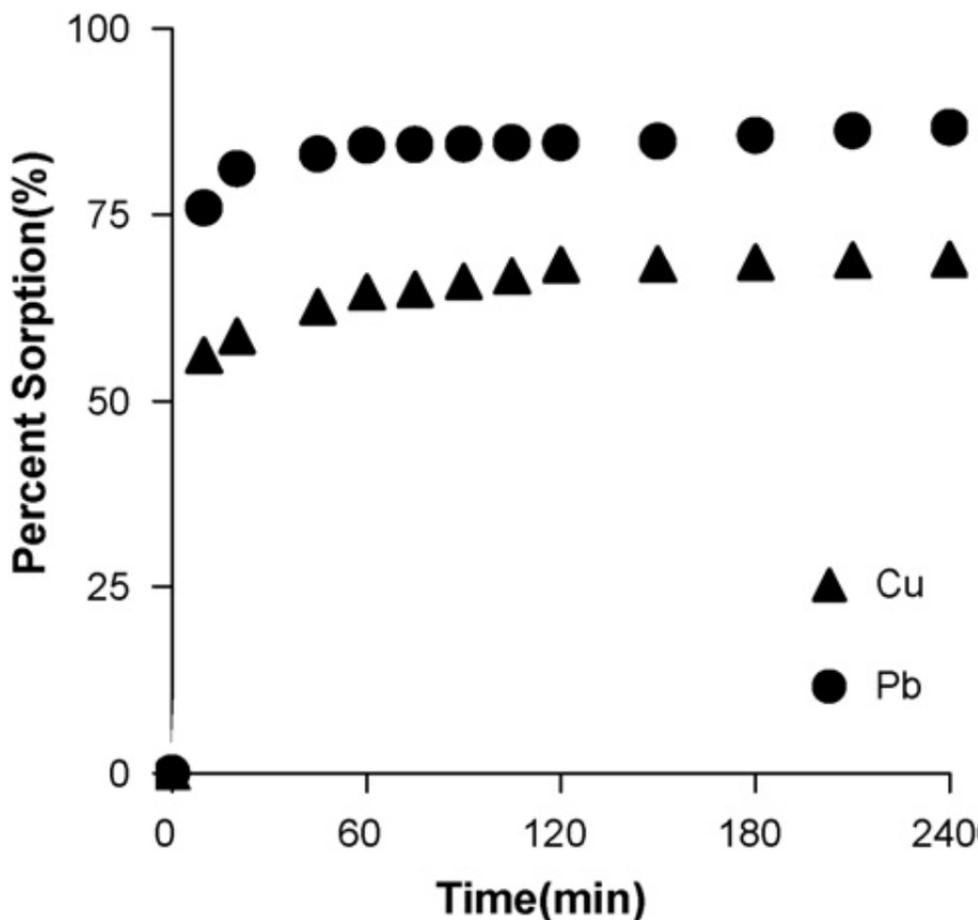


Figure 6. Effect of contact time on the adsorption of Cu (II) and Pb (II) at pH = 6.0, temperature = 25 °C, metal concentration = 1 mM, and adsorbent concentration = 25 g/L (From Pehlivan et al. 2009).

In experiments reviewed by Bailey et al. (1999), seaweed had a capacity of 67 mg Cd/g seaweed and peat moss, due to large cation exchange capacity (CEC), had relatively large metal removal capacities of approximately 5 mg Cd mg/g, 44-119 mg Cr(VI)/g, and 20-230 mg Pb/g.

Algae's (*Synechocystis* sp.) cadmium ion removal capabilities was investigated by Ozturk et al. (2009) who studied dried algae, immobilized and dried algae, and immobilized and live algae. Immobilized algae were in the form of alginate gel beads. Dried algae had the largest capacity (75.7 mg Cd/g) compared to immobilized dried (4.9 mg Cd/g) and immobilized live algae (4.3 mg Cd/g) with equilibrium being established in approximately 15 minutes. The optimum pH and temperature for removal was 7 and 25° C, respectively. Capacities dropped off at temperatures higher than 25° C; a phenomenon that

was attributed to larger temperatures affecting the stability and configuration of cell walls and ionization of chemical functional groups. Also at small pH values, surface ligands are associated with H_3O^+ that restrict the approach of metal cations.

Tan and Xiao (2009) investigated cadmium uptake by dried wheat stems that had been passed through a 100 mesh and were methanol esterified. In these experiments 200 mg of wheat stem was mixed with 50 mL of solution at cadmium concentrations ranging from 0.1 to 1.2 mmol/L. Adsorption increased with increasing pH from 2 to 5 but remained constant at a value of 0.030 mmol Cd/g from pH =5 to pH = 8, the maximum pH investigated. Kinetics were relatively rapid with 90% of cadmium being removed in the first 10 minutes and 95% removed in the first 20 minutes. As with other studies, carboxyl groups (COO^-) were found to be important in the cadmium binding process as were hydroxyl (OH^-) and O^- ions.

Zeolites and Clays

Zeolites and clays have adsorption capabilities that result from a net negative charge on the structure of fine-grain silicate minerals. In zeolites this negative charge results from Al^{3+} replacing Si^{4+} in the tetrahedral (Bailey et al. 1999). The negative charge is neutralized by the adsorption of positively charged species, giving zeolites and clay the ability to attract and hold metals cations. In zeolites, Na^+ , Ca^{2+} , and K^+ occupy spaces within the lattice structure and can be replaced by metals in an ion exchange process. Bailey et al. (1999) reported clay adsorption capacities of 4-16.5 mg Cd/g, 0.5-50 mg Cr(VI)/g, and 0.22 to 58 mg Pb/g with the value for Cr(VI) being the largest reported value for all substances reviewed. Fly ash has also been reported to have metal adsorption capability but a portion of fly ash (about 6%) has been documented to be clay (Zhang et al. 2008).

Genc-Fuhrman et al. (2007) used batch studies (48 hours) to test naturally occurring Clinoptilolite, one of the most abundant of the naturally occurring zeolites, and found that its affinity for metal removal is in the order of $\text{Cu} > \text{Cd} > \text{Zn} > \text{Ni} > \text{As} > \text{Cr}$. Pitcher et al. (2004) investigated the ability of a synthetic zeolite and a natural zeolite, mordenite, to remove Cd, Cu, Pb, and Zn from synthetic stormwater runoff and actual motorway runoff using batch studies with a contact time of 10 minutes. The synthetic zeolite removed greater than 91% of all metals from both solutions but increased sodium levels to 295 mg/L, which is significantly above the freshwater standard of 170 mg/L. The synthetic zeolite also increased the pH to between 8.5 and 9.0 regardless of the starting pH. Finally, the synthetic zeolite also removed calcium. This could be important because hardness is thought to be a factor in reducing the toxicity of metals.

In Pitcher et al. (2004) mordenite was less effective than the synthetic zeolite tested; the mordenite removed 42% to 89% of all metals in synthetic stormwater and only 6% to 44% in motorway runoff. As with many other sorbents the preference for adsorption was $\text{Pb} > \text{Cu} > \text{Zn} \sim \text{Cd}$. Seelsaen et al. (2006) tested seven different sorbents including one zeolite and found that zeolite removed 95% of zinc and 52% of copper in batch tests using synthetic stormwater at concentrations of 5 mg Cu/L and 27 mg Zn/L and a contact time of 24 hours. These concentrations are about 50 times greater than those typically found in stormwater runoff. Thus, the removal efficiencies may not directly correlate to typical stormwater metal concentrations.

Other Materials

Mahmoud et al. (2010) used silica gel coated with chelating agents to remove Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn from solution in batch studies with a contact time of 20 minutes which was long enough for equilibrium to be achieved. Silica gel was used because it is mechanically and thermally stable, experiences less swelling and shrinking, and is less susceptible to microbial effects compared to other organic polymers. It was found that optimum metal recovery occurred in the pH range of 7 to 8.5, except for Cr(III) which experienced maximum removal at pH = 6.

Hu et al. (2010) coated Fe₃O₄ microspheres with SiO₂ to remove lead and mercury ions from industrial wastewater. Lead removal was greater than 95% at a pH of 6 (contact time was not reported). Mercury removal was slightly less than lead removal but still greater than 90%. The microspheres, due to their iron core, can be removed from solution by a magnet and can be regenerated in a weak acidic solution and reused.

Munaf et al. (2009) used columns packed with perlite, a volcanic rock that expands up to 30 times its original size when heated quickly from 800 to 1100° C and has surface hydroxyl groups, to remove Cd, Cr, Cu, and Zn from solution. Chemical analysis of the perlite revealed that it was approximately 72%-77% SiO₂, 13%-17% Al₂O₃, 4%-6% K₂O, with the remaining constituents being miscellaneous materials. Loading rates and contact times were not reported. At a pH value of 6, Cr, Cu, and Zn removal ranged from 75%-90% and Cd removal was 75%. At a pH of 1.0, 83%-99% of all metals desorbed.

Fly ash consisting of 38% SiO₂, 18.4% silt, and 6% clay was used by Zhang et al. (2008) to remove Cu, Pb, and Zn from solution in batch (contact time of 24 hours) and column studies. The columns had a length of 14.3 cm with influent being pumped up through the column at 3 cm/hr. It was determined that a sand/fly ash mixture in a bioretention cell had the capacity to removal heavy metals from stormwater runoff for over 900 years. The mixture with 5% fly ash, however, initially increased the water pH to over 10 and the value remained above 9 after treatment of 240 pore volumes.

Other material reviewed or discussed briefly in the literature includes bonemeal (Nwachukwa and Pulford 2008), sand, recycled glass, packing wood (Seelsaen et al. 2006), sawdust waste, bagasse pith waste from sugar mills, maize cob waste, wool waste, and blast furnace slag (El-Geundi 1997).

Contact times with conventional sand media in stormwater filters can be on the order of one to a few hours. Accounting for the fact that any enhancing agent added to filter media with the intent of capturing dissolved metals will probably be a small fraction (typically <10%) of the media by mass, contact times with the enhancing agent may be as low as three to five minutes (Erickson et al. 2010). Thus, in order to achieve significant levels of dissolved metal removal, removal kinetics must be relatively rapid. As previously discussed, the enhancing agent must also be readily available, cost-effective, and not alter water quality parameters to unacceptable levels. This most likely means that the enhancing agent will not need to be modified in intensive laboratory procedures. Of the materials reviewed, ferrous based materials, alumina, zeolites (if sodium leaching can be minimized), and some activated carbons appear to warrant further investigation.

CONCLUSION

As previously discussed, cost-effective enhancing agents to remove dissolved nitrogen, phosphorus, and metals from stormwater runoff must satisfy requirements that include rapid kinetics, high capacity, and low cost among others. Due to the relatively short contact time between stormwater runoff and the media of a stormwater filter, removal mechanism kinetics must be relatively rapid if significant contaminant removal is to occur. Also, a cost-effective enhancing agent must have a large contaminant capacity, otherwise maintenance costs associated with replacing the media or restoring its capacity will be cost-prohibitive. Finally, the material cost of an enhancing agent must be low enough such that the initial cost and, if replacement of the media will be required over the life of the practice, the replacement cost of the material does not render the use of the material cost-prohibitive.

Potential enhancing agents for the removal of nitrogen appear to include magnesium chloride and magnesium based products along with zinc-aluminum-chloride based hydroxides. These substances removed significant amounts of nitrogen in contact times of 40 minutes which is considerably less than the contact time of many studies. Processes and enhancing agents that require biological or microbial growth would be difficult to maintain in a sand filter, especially a horizontal flow filter that would be necessary in a roadside swale. Although activated carbon showed potential for nitrogen removal, the contact time of these studies were hundreds of hours and nitrogen removal was less than that of the magnesium based products. Iron based products have also shown potential for nitrogen removal but the removal process is precipitation and, as a result, iron based products are limited due to a precipitate layer that forms on the iron surface and hinders removal.

Of the materials reviewed, ferrous based materials, alumina, zeolites (if sodium leaching and increased pH can be minimized), and some activated carbons appear to be the most promising with regards to metal removal. Organic material such as mulch, plant biomass, and activated carbon may also be effective in metal removal but these materials may also leach phosphorus, nitrogen, and other organics into the runoff. Thus, if organic material is to be used to capture metal ions a two-stage filter may be necessary. The organic enhancing agent could be in the upstream or first stage where it would retain metal ions and possibly release nutrient ions. The second stage would contain a material that could capture and retain nutrients, including those released by the enhancing agent in the first stage.

Fly-ash and carbonate based materials that rely on metal precipitation for removal typically either require a high pH environment or raise the pH of the water to levels that would prohibit their use when treating stormwater runoff.

Crustacean shells and similar shell-based enhancing agents tend to dissolve in solution and therefore would be washed away if used in a stormwater filter. Although chemical alteration can reduce their solubility it also reduces their effectiveness and may be cost-prohibitive.

The materials that show the most potential as enhancing agents for dissolved nitrogen, phosphorus, and metal removal will be tested in batch studies to further characterize their performance (i.e. kinetics, capacity, affect on water quality parameters, etc.). Batch study results will be used to select three to five

materials for further testing in column studies. Finally, column study results will be used to develop, optimize and further test filter media and one or more filter designs in a field application.

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