Enhanced Sand Filtration for Storm Water Phosphorus Removal

Andrew J. Erickson¹; John S. Gulliver²; and Peter T. Weiss³

Abstract: Batch studies with an initial phosphorus concentration typical of storm water were conducted at the University of Minnesota on C 33 sand, calcareous sand, limestone, three blast oxygen furnace (BOF) by-products, aluminum oxide, and chopped granular steel wool for the removal of dissolved phosphorus from synthetic storm water runoff. Based on the findings of these batch studies, sand filtration enhanced with steel wool, calcareous sand, or limestone has the potential to be a practical and cost-effective method of removing dissolved phosphorus from storm water runoff. Column studies are then performed on four enhancements with C 33 sand filtration: calcareous sand, limestone, chopped granular steel wool, and steel wool fabric. Synthetic storm water runoff with a variable dissolved phosphorus concentration passed through the columns while the flow rate was measured and effluent samples were taken and analyzed for total and dissolved phosphorus concentration and pH. As found in the batch studies, C 33 sand retained dissolved phosphorus but the capacity was quickly exhausted. Combinations of C 33 sand with limestone or calcareous sand clogged the columns and prevented them from draining completely. Steel wool, however, significantly increased the duration and level of phosphorus retention as compared to C 33 sand alone and did not clog the columns. Between 34 and 81% of the dissolved phosphorus was retained by the six steel-enhanced columns. Fine oxidized iron particles observed in the effluent are too small to be completely captured by typical geotextile fabric and may compromise phosphorus removal performance, but phosphorus adsorbed to iron oxide will be of limited bioavailability. Steel-enhanced sand filtration is modeled with contact time, total mass of phosphorus retained, and influent concentration as variables. Enhancing sand filtration with steel wool fabric would minimally increase installation costs and would increase the material cost by 3–5%. Based on these findings, steel-enhanced sand filtration is a potentially cost-effective treatment for removing dissolved phosphorus from storm water runoff.

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Introduction

Nutrients (phosphorus and nitrogen) are one of many pollutant categories targeted for removal from storm water runoff. The U.S. Environmental Protection Agency (USEPA 1999) reports that excess nutrients can initiate nuisance algae blooms that generate negative aesthetic and eutrophic conditions in receiving lakes and rivers. In temperate fresh waters, dissolved phosphorus is the limiting nutrient (Aldridge and Ganf 2003; Schindler 1977). It exists in the form of phosphates (H₃PO₄, pH < 2.16; H₂PO₄⁻, pH < 7.20; HPO₄²⁻, pH < 12.35 (Stumm and Morgan 1981]) contributed to storm water from sources such as fertilizers on agricultural or residential cultivated land, natural organic material (e.g., leaf litter, grass clippings, unfertilized soils), laundering and commercial cleaning processes, treatment of boiler waters, biological processes instigated by sewage, food residues, and plant material waste, rainfall, among others (APHA/AWWA/WEF 1998; USEPA 1999). Dissolved phosphorus (phosphates) is defined as the amount of phosphorus that passes through a 0.45 μm filter (AHPA/AWWA/WEF 1998), which can be a large fraction of total phosphorus. To efficiently remove dissolved phosphorus from storm water runoff, it must be converted to a solid phase and removed as a particulate in addition to conventional sedimentation and physical sieving processes for solids removal (Jenkins et al. 1971).

New technologies are needed to remove dissolved phosphorus from storm water runoff to efficiently treat storm water runoff while avoiding the high construction and operation costs of a storm water treatment facility or mechanical treatment process. Some storm water management practices rely on vegetation, soil uptake, or both to remove dissolved phosphorus, while others have no mechanism to remove dissolved phosphorus. This paper proposes enhanced sand filtration as a new system to cost-effectively remove dissolved phosphorus from storm water runoff.

The principle of sand filtration is simple. Storm water is collected and delivered to a sand filtration system where it seeps through sand that physically sieves any particulates larger than the soil pore size within the first few centimeters. Sand filters are designed with (from the surface down) approximately 46 cm of ASTM C 33 sand, a layer of geotextile fabric, and a gravel sub-base that supports the system and quickly channels water toward...
a perforated pipe collection system (Claytor and Schueler 1996). The geotextile fabric provides a barrier to prevent the sand from washing into the gravel subbase. The perforated pipe collects the treated storm water and delivers it to the storm water conveyance system or directly to receiving waters. Physical sieving is the primary mechanism for pollutant removal from storm water runoff and any dissolved or particulate pollutants smaller than the pore size of the sand may pass through the filter and into the effluent. The sand filtration system should be sized and placed according to local guidelines with proper pretreatment to settle some influent solids before entering the sand filter.

The objective of this research is to compare several enhancements to sand filtration for the removal of dissolved phosphorus from storm water runoff. Comparison of enhancements will include dissolved phosphorus retention (percent of influent), hydraulic conductivity augmentation, long-term capacity, and pH augmentation.

Chemical Precipitation and Adsorption

Chemical treatment methods for phosphorus removal include precipitation by calcium, aluminum, or iron and surface adsorption to iron oxide or aluminum oxide, which are all a function of pH. Phosphorus precipitation is dominated by iron and aluminum when pH<6 and calcium when pH>6 (Stumm and Morgan 1981). Phosphate adsorption is highest in acidic conditions but ~50% of available phosphate can be adsorbed to iron at pH 10 (Stumm and Morgan 1981). Water quality standards, however, require that pH remain near neutral and are regulated and enforced by each State (e.g., Minnesota) based on suggestions by the USEPA. National secondary drinking water standards (USEPA 2002) suggest that pH values remain between 6.5 and 8.5 and most states have followed this initiative.

Phosphate retention by mineral soils has been summarized as follows (Reddy and D’Angelo 1994): “(1) in acid soils, phosphorus is fixed as aluminum and ferric phosphates, if the activities of these cations are high; (2) in alkaline soils, phosphorus fixation is governed by the activities of calcium and magnesium; and (3) phosphorus availability is greatest in soils with slightly acidic to neutral pH.” Additionally, “there are two other (besides biological uptake) potential sinks for phosphorus, depending on soil type: (1) in mineral soils dominated by iron oxides, phosphorus can be readily immobilized through sorption and precipitation by ferric oxyhydroxide, and formation of ferric phosphate in the oxidized zones at the soil-water interface; and (2) in calcareous systems, phosphorus released into the overlying water column can be precipitated as calcium mineral bound-phosphorus.”

Previous Work

The Water Environment Federation in conjunction with the ASCE (WEF/ASCE 1998) report that the event mean concentration for total phosphorus in urban runoff is 0.33 mg/L and dissolved phosphorus is 0.12 mg/L (USEPA 1983) which corresponds to roughly 36% dissolved phosphorus. Others (Brown et al. 2003) state that a total phosphorus concentration of 0.3 mg/L is adequate to describe both new and old urban development. Total and dissolved phosphorus concentration data for the Twin Cities metropolitan area (Minneapolis and St. Paul, Minn.) (Breznik and Stadelmann 2002), were analyzed to develop a statistical distribution for the dissolved phosphorus fraction of total phosphorus and is shown in Fig. 1. The distribution shown in Fig. 1 indicates that dissolved phosphorus fractions range from 0 to 100% (mean=44%, SD=26%, n=307). It is evident that the dissolved phosphorus fraction varies widely for different sites and storm events, with a mean close to that reported in the literature, but 100% of the total phosphorus concentration can be of the dissolved form in some locations.

Although studies (Arias et al. 2001) have shown that constituents of iron, calcium, aluminum, and magnesium in quartz sand can be sufficient to precipitate or adsorb dissolved phosphorus at pH common to storm water, sand filtration has been found to have limited dissolved phosphorus retention (Anderson et al. 1985; Harper and Herr 1993; Herrera Environmental Consultants 1995). Two enhancements to sand filtration were successfully tested in column studies for phosphorus removal from underground wastewater disposal system leachate (Baker et al. 1997, 1998). The conditions of subsurface wastewater treatment (flow velocity of 10 cm/day and concentration of 3 mg/L) are significantly different from storm water treatment (flow velocity of 100 cm/day and concentration of 0.3 mg/L), and thus the media combinations proposed by Baker et al. (1998) may not be cost effective for storm water treatment. Chopped granular steel wool has been used to enhance sand filtration (Joseph O’Leary, personal communication, May 7, 2003). The steel wool was mixed uniformly throughout the top 15–30 cm of sand but the granular steel wool clumped together, developed Gallionella ferruginea bacteria, and subsequently clogged the filter (for more detailed information, see Erickson 2005).

Batch Studies

Batch studies (Erickson 2005) were used to investigate the effectiveness of eight materials [C 33 sand, calcareous sand, limestone, aluminum oxide, steel wool, and three blast oxygen furnace (BOF) by-products] to remove dissolved phosphorus from storm water runoff and are summarized here. Based on the chemical interactions described above, calcium, aluminum, and iron were used to enhance sand filtration. Sources of calcium, aluminum, and iron used in this study include limestone (CaCO₃), calcareous sand (Ca²⁺ enriched sand, typically, by CaCO₃), aluminum oxide (Al₂O₃), steel wool (Fe), and BOF by-products (Fe and Ca²⁺ constituents) from the steel manufacturing industry.
Materials and Experimental Methods

The batch study experiments utilized standard biochemical oxygen demand (BOD) bottles (~203 mL) and a New Brunswick Scientific model Classic C1 Platform shaker table (12-bottle capacity). A concentration of 0.5 mg/L dissolved phosphorus was chosen to represent high storm water phosphorus loading conditions. Potassium phosphate (KH$_2$PO$_4$) was added to deionized, distilled water to reach a mean concentration of 0.485±0.008 (95% confidence interval, n=66) mg PO$_4^{3-}$/L and mean pH of 5.657±0.295. Equal volumes of this standard phosphate solution (150 mL) were added to the BOD bottles with 10% media by weight. Media consisted of C 33 sand, enhancements (e.g., calcareous sand or steel wool), or both in various combinations. Blanks were also tested. A “blank” refers to an experiment in which only the standard phosphate solution is added to the BOD bottle, without any media. The 12-bottle capacity of the shaker table allowed for six bottles of unique media combinations and six duplicate bottles to be tested simultaneously.

C 33 sand was chosen for these experiments because it is recognized as the standard for sand filtration systems throughout the United States (Claytor and Schueler 1996). It is important to recognize, however, that the ASTM standard for C 33 sand [ASTM C 33-02a (ASTM 2002)] regulates size distribution and organic material but mineralogy could vary based on the source. Fine sand and silica sand were also acquired for these experiments. Grain size distributions were determined by the Research Analytical Laboratory (http://ral.coaes.umn.edu/) at the University of Minnesota on all three sands. The results of this analysis indicate that the pore size of the silica sand is too large to efficiently treat storm water by filtration and, therefore, no batch studies were conducted using this sand. After washing with distilled water, fine sand did not retain dissolved phosphorus when compared to the blank solution and was also eliminated from further experimentation. Materials were tested without washing or other preparation and also after being “washed.” For this paper, washed refers to the material that was retained on a #100 standard sieve (149 µm size opening) after the material was rinsed with distilled water.

Initial samples (corresponding to time zero) were taken for dissolved phosphorus determination, with pH measured prior to addition of media. The media were then added to the bottle and the shaker was turned on. Samples for dissolved phosphorus determination were taken at 0.5, 1.0, 3.0, 5.0, 10.0, and 24.0 h after media addition. pH readings were taken at the same time steps (except for 0.5 h) using a pH meter that was calibrated with pH =4, 7, and 10 standards. Samples were analyzed for dissolved phosphorus according to Standard Methods Section 4500-PE (ascorbic acid) in (APHA/AWWA/WEF 1998) with a minimum detection limit of 10 µg P/L. Dissolved oxygen concentration was not measured because the batch studies are assumed to have ideal mixing and that atmospheric oxygen is readily available.

Results and Discussion

C 33 sand in these batch studies removed approximately 27% of the available phosphorus (0.485 mg PO$_4^{3-}$/L) after 5 h of contact and roughly 40% after 10 h of contact. Both calcareous sand and washed calcareous sand provide dissolved phosphorus removal to below detection limits, but also increased pH between 9.8 and 10.1. While initial experimental combinations of aluminum oxide and calcareous sand with or without limestone exhibited phosphorus removal to detection limits, a series of experiments with only aluminum oxide at varying pH (pH=4 and 6) showed that aluminum oxide alone removed 30–45% of the available phosphorus and only slightly changed the pH. In combination with C 33 sand, however, aluminum oxide provides approximately the same removal and affect on pH as C 33 sand alone. Addition of steel wool to C 33 sand increased phosphorus removal efficiency (~50% for 5% steel wool after 5 h, ~90% after 24 h) as compared to C 33 sand alone (~30% removal after 5 h and ~45% removal after 24 h). BOF by-products removed the phosphorus quickly, but increased pH to approximately 11, which exceeds water quality standards. BOF by-products stained the batch study bottles such that a 10% HCl acid bath could not remove the residue from the glass surface. For these reasons, BOF by-products were presumed to be inappropiate to treat storm water runoff.

Column Studies

Column studies were performed on four enhancements with C 33 sand filtration: calcareous sand, limestone, chopped granular steel wool, and steel wool fabric. Synthetic storm water runoff with a variable dissolved phosphorus concentration passed through the columns while the flow rate was measured and effluent samples were taken and analyzed for total and dissolved phosphorus concentration and pH.

Materials and Experimental Methods

Columns were constructed for the testing of sand filtration media and enhancements to retain dissolved phosphorus. Ten, 5.08 cm inside diameter columns approximately 271 cm long made from clear acrylic pipe were cut approximately 84 cm from the bottom. Threaded unions were attached to the cut ends to allow for easy exchange of media combinations between tests. Reducing caps were also attached to the bottom of the columns to reduce the outflow diameter from 5.08 to 0.635 cm barbed connections. A 568-L elevated reservoir delivered synthetic storm water via gravity through a needle valve used to control influent flow rate and on to a distribution manifold, which distributes flow to the top of the 10 vertical columns. A valve at the base of the reservoir allowed for samples prior to treatment to be taken and analyzed for pH and phosphorus concentration. Dissolved oxygen concentration was not measured because subsurface pipe collection systems are open to the atmosphere and the writers assume that any zones within the filter that become anaerobic would reoxygenate between storm events.

Synthetic storm water was composed of tap water mixed with potassium phosphate (KH$_3$PO$_4$) to various dissolved phosphorus concentrations in order to mimic the variability found in storm water runoff. One objective of these experiments was to determine to what extent, if any, the retention of dissolved phosphorus affected the hydraulic conductivity of the filter media; therefore synthetic storm water was chosen instead of natural storm water to reduce the interference of other constituents found in natural storm water. For example, total suspended solids (TSS) is a primary constituent in natural storm water that would interfere with this determination, and therefore was not incorporated into the synthetic storm water.

Sand filter media was mixed to a total mass of 1,800 g, which corresponded to a media depth of roughly 46 cm. Limestone and calcareous sand mixtures were mixed in buckets with C 33 sand. Limestone was purchased in pellet form (~1 cm in diameter) and
Table 1. Column Mixes, Filter Fabrics, and Designators

<table>
<thead>
<tr>
<th>Column</th>
<th>Mix</th>
<th>Filter fabric</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>Reservoir tank</td>
<td>NA</td>
</tr>
<tr>
<td>A1</td>
<td>50% limestone with C33 sand</td>
<td>Woven generic</td>
</tr>
<tr>
<td>B1</td>
<td>30% limestone with C33 sand</td>
<td>Woven generic</td>
</tr>
<tr>
<td>C1</td>
<td>10% limestone with C33 sand</td>
<td>Woven generic</td>
</tr>
<tr>
<td>D1</td>
<td>50% calcareous sand with C33 sand</td>
<td>Woven generic</td>
</tr>
<tr>
<td>E1</td>
<td>30% calcareous sand with C33 sand</td>
<td>Woven generic</td>
</tr>
<tr>
<td>F1</td>
<td>10% calcareous sand with C33 sand</td>
<td>Woven generic</td>
</tr>
<tr>
<td>D2</td>
<td>2% (36 g) by weight steel wool with C33 sand</td>
<td>Woven generic</td>
</tr>
<tr>
<td>E2</td>
<td>2% (36 g) by weight steel wool with C33 sand</td>
<td>Woven generic</td>
</tr>
<tr>
<td>F2</td>
<td>2% (36 g) by weight steel wool with C33 sand</td>
<td>Woven generic</td>
</tr>
<tr>
<td>G</td>
<td>Steel wool fabric (5.17 g; −0.29% by wt.) with C33 sand</td>
<td>Woven generic</td>
</tr>
<tr>
<td>H</td>
<td>Steel wool fabric (5.49 g; −0.31% by wt.) with C33 sand</td>
<td>150 μm</td>
</tr>
<tr>
<td>I</td>
<td>Steel wool fabric (5.46 g; −0.31% by wt.) with C33 sand</td>
<td>200 μm</td>
</tr>
<tr>
<td>J</td>
<td>Pure C33 sand</td>
<td>180 N</td>
</tr>
</tbody>
</table>

Note: NA = not available.

4Letter indicates the column; 1 indicates first experiment; and 2 indicates second experiment.

calcareous sand was obtained from a local quarry. In experiments with steel wool, the steel wool was placed below the C33 sand, above the filter fabric to prevent migration of steel wool fibers and eliminate surface interaction with any bacteria that may develop. This setup should address documented concerns with steel wool in storm water treatment (Joseph O'Leary, personal communication, May 7, 2003).

Four types of filter fabric were used for these experiments; a generic woven fabric (Morgan et al. 1998), a 150 μm mesh and a 200 μm mesh as specified by the Industrial Fabrics Corporation (http://www.ifcfabrics.com), and 180N-type fabric as specified by Mirafi (http://www.mirafi.com). Global Material Technologies (www.gmt-inc.com) donated chopped granular steel wool (strands of steel wool wire roughly 5 mm in length) and steel wool fabric. The 10 columns and their respective designators for this paper are listed in Table 1.

The columns consisted of approximately 10 cm of gravel subbase at the bottom, a PVC disk with holes for support of the media, a layer of filter fabric, and the filter media, as shown in Fig. 2. Taps were installed 1.02 m above the bottom of the columns (~46 cm above the surface of the media) and the taps of each column were connected by tubing to each other and to a free outfall, which maintained a constant water level within the columns. Each column also had an overflow tap 2.4 m above the bottom of the columns to ensure the water depth did not exceed 1.83 m above the surface of the media. The columns were dry consolidated prior to exposure with synthetic storm water to simulate field installation techniques. The flow from the reservoir was turned on at time zero and the columns were allowed to fill to the level at which the free outfall was set. After influent, effluent, and overflow flow rates equilibrated, volumetric flow rate measurements, head, and effluent samples were taken at various intervals. Effluent samples were taken periodically to ensure adequate mixing had taken place in the reservoir.

The columns were operated similar to a sand filter exposed to storm water runoff. Laboratory-simulated storm events between 1/2 and 2 days duration were run through the columns, after which they were allowed to drain for 1–3 days. Influent concentration was varied between 0.1 and 0.8 mg PO₄³⁻−P/L, to simulate natural runoff conditions.

Analytical Methods

Total phosphorus measurements of the effluent were required because of dissolved-participate transformations in the filter. Samples were analyzed for total phosphorus according to standard methods section 4500-P.B.5 (potassium persulfate digestion) and dissolved phosphorus according to Section E (ascorbic acid) in Standard Methods (APHA/AWWA/WEF 1998) with a minimum detection limit of 10 μg P/L. As recommended (APHA/AWWA/WEF 1998), the persulfate digestion method was verified before it was used exclusively. Prior to column experiments, additional batch studies were conducted to ensure the persulfate digestion could accurately determine total phosphorus concentrations for the synthetic storm water samples that would be collected during the column experiments. Volumes of distilled water with a known mass of toal phosphorus were mixed and sampled for initial concentration confirmation; then the experimental media was added and allowed to mix for 24 h. Samples were taken and analyzed by the persulfate digestion and ascorbic acid methods for total phosphorus and the results were compared to initial phosphorus measurements and known mix concentrations. In addition, actual storm water samples were analyzed for total and dissolved phosphorus concentration. Duplicate samples from the batch studies and actual storm water samples were sent to the Research Analytical Laboratory (RAL) at the University of Minnesota (http://ral.coaes.umn.edu/) for verification. RAL uses a rapid flow analyzer system with potassium sulfate and mercuric sulfate digestion (mercuric) for total phosphorus analysis (RFA Methodology 1986). Comparison of RAL’s mercuric digestion results and persulfate digestion results concluded that the persulfate digestion was accurate (±5% error) for natural storm water samples but not as accurate for samples containing steel wool fibers (i.e., iron) (mean error=27.8%). Based on these results, the persulfate digestion was deemed appropriate if all the iron remained in the column and none exited with the effluent. pH readings were measured using a pH meter that was calibrated to pH=4, 7, and 10 standards.

Effluent samples for the column studies were initially analyzed for total phosphorus to determine if any of the influent dissolved phosphorus was converted into particulate form in the sand filter.
and subsequently released in the effluent. Duplicate samples were sent to RAL for verification, which resulted in less than 10% error (mean=3.9%) in the early stages of the column experiments (early verification). However, duplicate effluent samples sent to RAL after additional experiments (latter verification) revealed discrepancies between persulfate total phosphorus and mercuric total phosphorus, as measured by RAL (mean error=42.3%, n=6). The same samples were then analyzed for dissolved phosphorus concentration by the ascorbic acid method and compared to results from persulfate total phosphorus, which resulted in a mean percent difference of 23.7% for 67 samples. Further analysis of effluent samples was limited to strictly dissolved phosphorus as measured by RAL for estimation of total phosphorus trends. It was postulated that iron bound phosphates may be present in the samples sent to RAL for estimation of total phosphorus trends. It was postulated that iron bound phosphates may be present in the effluent.

With the aid of a microscope, fine oxidized iron particles were observed in the effluent sediments and appeared to be roughly 5 μm in size. Fig. 3 shows a microscopic view of the fine particles found in the effluent.

**Results and Discussion**

As shown in Table 1, various combinations of C 33 sand and limestone or calcareous sand were examined. Initially, these combinations produced hydraulic conductivities of approximately 0.05 cm/s but within one day these columns retained standing water (greater than 5 cm above the surface of the media). The results of a fine particle analysis performed by RAL indicate that more than 50% of the limestone and roughly 11% of the calcareous sand was clay or silt sized particles. Visual observation indicated that fine particles washed through the C 33 matrix and were retained on the filter fabric. The accumulation of fine particles on the filter fabric is believed to cause the clogging observed in the columns. These mixtures would not drain within 48 h and, therefore, were not tested further. Steel wool then became the focus of the column studies.

The batch studies indicated that pH is an important evaluation parameter. Fig. 4 shows that the steel wool media did not increase the pH of the influent synthetic storm water in the column studies beyond the recommended range (USEPA 2002). The influent synthetic storm water was on average less than 0.5 pH units below the effluent of all but one of the seven columns. The standard deviations were roughly 0.1–0.3 pH units for all seven columns and the maximum pH recorded from any of the ten columns was 8.56 (n=183). Additionally, the pH of the effluent indicates that adsorption to oxidized iron is the predominant phosphorus retention mechanism, and not precipitation by ferric phosphate (Stumm and Morgan 1981; see their Fig. 5.18).

The experimental results from the steel wool column studies summarized in Table 2 include mean hydraulic conductivity, mean contact time with steel, total mass of phosphorus retained at the conclusion of the experiments, percent mass of the influent retained, and percent retained per gram of steel wool. The composition of chopped granular steel wool does not contain fine particles like calcareous sand or limestone and, therefore, steel wool enhanced fibers should not clog the filter. A hydraulic conductivity of 0.0013 cm/s or greater is recommended for design for sand filtration systems (Claytor and Schueler 1996). As shown

![](image)

**Table 2.** Mean Hydraulic Conductivity, Mean Contact Time, Total Mass Retained (Total and Dissolved Phosphorus), Mean Percent Retained of Columns, and Percent Retained per Gram of Steel Wool (Sand for Column J)

<table>
<thead>
<tr>
<th>Column</th>
<th>Mean hydraulic conductivity (cm/s)</th>
<th>Mean contact time with steel (s)</th>
<th>Mass of phosphorus retained (mg)</th>
<th>Percent retained by mass (%)</th>
<th>Percent retained per gram steel wool (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2</td>
<td>0.0065</td>
<td>308</td>
<td>25.0</td>
<td>80.8</td>
<td>2.24</td>
</tr>
<tr>
<td>E2</td>
<td>0.0097</td>
<td>206</td>
<td>29.6</td>
<td>61.6</td>
<td>1.71</td>
</tr>
<tr>
<td>F2</td>
<td>0.0114</td>
<td>175</td>
<td>33.8</td>
<td>51.5</td>
<td>1.43</td>
</tr>
<tr>
<td>G</td>
<td>0.0089</td>
<td>167</td>
<td>22.3</td>
<td>47.6</td>
<td>9.12</td>
</tr>
<tr>
<td>H</td>
<td>0.0100</td>
<td>150</td>
<td>18.1</td>
<td>34.2</td>
<td>6.12</td>
</tr>
<tr>
<td>I</td>
<td>0.0091</td>
<td>165</td>
<td>16.3</td>
<td>33.8</td>
<td>6.05</td>
</tr>
<tr>
<td>J</td>
<td>0.0092</td>
<td>4,891a</td>
<td>3.05</td>
<td>2.1</td>
<td>NA</td>
</tr>
</tbody>
</table>

Note: NA=not available.

aContact time with sand.

Fig. 3. Fine particles of oxidized iron found in effluent from columns. The center of oxidized steel particles are black.

Fig. 4. Mean pH±1 standard deviation (n=22, 23, or 24) of column effluent.
in Fig. 5, the mean hydraulic conductivity for the pure C 33 sand column was roughly 0.0092 cm/s, which is a factor of 7 greater than recommended values. Mean hydraulic conductivities (see Table 2) for the columns enhanced with steel wool were found to be in the range of C33 sand. Hydraulic conductivity declined with respect to time in Columns D2, E2, and F2 (as shown in Figs. 6–9) and remained the same in Columns G, H, and I (as shown in Figs. 10–12) but was at least twice the recommended design value (minimum=0.0028 cm/s). Therefore, steel-enhanced filtration does not significantly clog due to dissolved phosphorus retention as compared to pure sand filtration.

The hydraulic conductivity of the pure sand column is shown in Fig. 5. The ordinate in Fig. 5 is hydraulic conductivity, k, as computed according to Darcy’s Law and the abscissa is treated depth (m). Treated depth is calculated by integrating the ratio of flow rate to column cross-sectional area (20.3 cm²) with respect to time. Treated depth for a field application of sand filtration existing or proposed can be similarly estimated given the watershed area, land use with corresponding runoff coefficients, rainfall depth, and a hydrologic method for estimating of runoff volume based on these variables. Dividing the estimated runoff volume (m³) by the sand filter surface area (m²) gives an estimated storm water depth treated (treated depth in meters) for that storm event. An annual treated depth can be estimated similarly with an average (or actual) annual rainfall or runoff volume.

For example, given a 4 ha watershed with 50% impervious cover and 2.5 cm rainfall depth, the design runoff volume (as estimated by Claytor and Schueler 1996) is ≈500 m³. Assuming a 230 m² sand filter is used for this watershed, the treated depth would be (500 m³/230 m²) ≈ 2.2 m for this storm event. If one assumes an average annual rainfall of 0.75 m and that none of the runoff bypasses the filter as overflow, the average annual treated depth for this watershed would be ≈65.2 m. Total treated depths for the column studies ranged from 45 to nearly 220 m.

In order to determine the additional retention within steel wool, a “blank” column with only C 33 sand was constructed and tested for its effectiveness to retain dissolved phosphorus (Column J). Fig. 6 depicts the sum of phosphorus mass retained as a function of treated depth for Columns D2, E2, F2, G, H, I, and J. It is evident that C 33 sand has some capacity to retain dissolved phosphorus but the capacity was exhausted after approximately 50 m of treated depth because minimal positive retention was observed after that depth. The dissolved phosphorus retention in the steel wool enhanced columns continue to increase.

Fig. 5. Hydraulic conductivity for pure C 33 sand: Column J

Fig. 6. Sum of phosphorus mass retained by C 33 sand (Column J) and steel wool enhanced Columns D2, E2, F2, G, H, and I
**Fig. 7.** Hydraulic conductivity, phosphorus retention, and model fit: 2% steel wool, woven fabric, Column D2

**Fig. 8.** Hydraulic conductivity, phosphorus retention, and model fit: 2% steel wool, 150 μm mesh, Column E2

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Fig. 9. Hydraulic conductivity, phosphorus retention, and model fit: 2% steel wool, 200 µm mesh, Column F2

Fig. 10. Hydraulic conductivity, phosphorus retention, and model fit: steel wool fabric, woven fabric, Column G
Fig. 11. Hydraulic conductivity, phosphorus retention, and model fit: steel wool fabric, 150 μm mesh, Column H

Fig. 12. Hydraulic conductivity, phosphorus retention, and model fit: steel wool fabric, 200 μm mesh, column I
from 0 to 50 m of treated depth, and the amount of phosphorus retained is an order of magnitude larger than the C 33 sand column after 70 m of treated depth. Steel wool-enhanced sand filtration, therefore, increases the duration and capacity for dissolved phosphorus retention as compared to C 33 sand alone. Shown in Figs. 7–12 are hydraulic conductivities, mercuri total phosphorus as analyzed by RAL, persulfate total phosphorus, dissolved phosphorus, and the model fit (to be discussed later) for the steel wool enhanced sand filtration columns.

Phosphorus fraction retention was calculated by subtracting the effluent concentration ($C_{\text{out}}$) from the influent concentration ($C_{\text{in}}$) and dividing that difference by the influent concentration. Hydraulic conductivity and phosphorus fraction retained are also shown in each figure to illustrate the inverse correlation between them. The inverse correlation between hydraulic conductivity and phosphorus fraction retained is most evident in Fig. 7; the phosphorus fraction retained increases as hydraulic conductivity decreases. Equilibrium between the iron in the steel wool and the phosphorus in the water can explain this inverse correlation because the amount of time that phosphorus in the water has contact with the iron (i.e., contact time) increases as hydraulic conductivity decreases, which allows for more phosphorus removal.

The additional phosphorus released from the columns and measured by mercuric total phosphorus is likely adsorbed and complexed on fine oxidized iron particles. Due to the size of the particles, it would be difficult to capture all of the particles with conventional geotextile fabric, although the woven fabric appears to capture much of it, as shown in Figs. 7 and 10. The release of oxidized iron with adsorbed phosphorus presents a confounding factor to the use of steel wool to retain dissolved phosphorus. Some of the retained phosphorus will eventually be released from the sand filter in this manner as particulate phosphorus.

The source and bioavailability of particulate and dissolved phosphorus fractions found in fresh waters has been documented (Reynolds and Davies 2001). Iron-bound phosphorus fractions of particulate phosphorus are “conditionally” bioavailable and phosphorus is only available if it is first desorbed and subsequently released as soluble reactive phosphorus. Low redox (i.e., anoxic) conditions will initiate “reduction of amorphous ferric hydroxide to soluble ferrous and the liberation of sorbed and occluded orthophosphate ions into solution.” While anoxic conditions can exist in benthic lake waters, iron oxides can also quickly reoxidize and thus resorb phosphorus. Additionally, exposure of iron-bound particulate phosphorus to benthic anoxic conditions is contingent on whether the particles will settle.

Particle size distinctions between suspended and settling particles in natural waters has also been documented (Gustafsson and Gschwend 1997). Particle sizes “near 10 microns may be retained at steady state in surface water suspension of large lakes.” As shown in Fig. 3, the large iron oxide particles found in the effluent from the columns are roughly 5 μm in size and would likely remain in suspension under this criteria. Due to the conditional bioavailability of phosphorus adsorbed to (and complexed with) oxidized iron and the conditions required to settle the particles, any iron-bound phosphorus is of limited bioavailability to the biota in receiving waters.

The phosphorus measurements may, therefore, be interpreted as follows:

1. The persulfate total phosphorus method was tested against the mercuir total phosphorus method in early verification of the column studies, and deemed equivalent. The persulfate method is effective at measuring precipitates with calcium that originate in the sand of the column.

2. After noticing oxidized iron particles in the effluent, the mercuric total phosphorus method was again compared to the persulfate method for the column effluent (latter verification). Discrepancies between the mercuric and persulfate total phosphorus measurements are attributed to phosphorus attached to fine (~5 μm) oxidized iron particles observed in the effluent which were not digested by the persulfate method.

3. With few exceptions (e.g., Figs. 8 and 10) the persulfate total phosphorus measurements are equivalent to the dissolved phosphorus measurements during and after the latter verification because the calcium available for precipitation originating in the sand of the column had been exhausted.

4. The oxidized iron in the effluent reflects upon the history of the column operation and comparison with current influent concentrations to determine percent phosphorus retention is misleading.

5. The phosphorus attached to oxidized iron is of limited bioavailability. It should only be considered a nutrient under circumstances particular to the application that meet the conditions described above.

Initial observations of the 2% steel wool columns (D2, E2, and F2; Figs. 7–9) reveal that the hydraulic conductivity is relatively constant throughout all three columns for the extent of the experiments. In addition, the initial phosphorus fraction retained is very similar (~40–50%) among all three columns. The fraction of phosphorus retained increases after approximately 5 m of treated depth to between approximately 60 and 90%. As observed in the 2% steel wool columns (D2, E2, and F2), a sudden decrease in hydraulic conductivity may cause an increase in phosphorus fraction retained.

A sudden increase in phosphorus retention may also be explained by an increase in iron oxide sites available for phosphorus adsorption. The hydraulic conductivity and phosphorus retention data shown in Figs. 7–12 are composed of several laboratory-simulated storm events represented by as few as one and as many as 10 data points. Although the columns were allowed to drain between simulated storm events to allow the specific yield to drain, some moisture was retained in the columns due to capillary action. Moisture and oxygen provided conditions conducive for oxidation of the steel wool layer and subsequently a large increase in phosphorus adsorption capacity, which may be reflected by an increase in phosphorus fraction retained.

After the first 10–20 m of treated depth, the 2% steel wool columns exhibited different patterns in phosphorus fraction retained despite sharing relatively constant hydraulic conductivities. Phosphorus fraction retained increased in Column D2 (Fig. 7), remained approximately constant in Column E2 (Fig. 8), and decreased in Column F2 (Fig. 9). The only difference between the three setups was the filter fabric. As listed in Table 2, mean hydraulic conductivity tends to increase from Columns D2 to E2 to F2, which corresponds to a decrease in overall phosphorus retention. Therefore, residence time in the steel wool is the predominant factor in determining phosphorus retention.

All three steel wool fabric columns (G, H and I; ~0.3% steel wool by mass) exhibited consistent hydraulic conductivities, as shown in Figs. 10–12. Phosphorus fraction retained decreases in Columns H and I from approximately 40% retained at 12 m of treated depth to a final retention of approximately 20%. While a decrease in phosphorus retention capacity may be explained by complexation of adsorption sites, the positive retention through-
out the experiments indicates that capacity still exists. The retention capacity is remarkable considering the significant reduction in steel wool mass from 2 to 0.3%.

The total mass of phosphorus fraction retained for 2% steel wool as shown in Figs. 7–9 and listed in Table 2 was 81, 61, and 51%, respectively and the total mass percent retained by steel wool fabric (as shown in Figs. 10–12 and Table 2) was 47, 34, and 34%, respectively. The batch studies concluded that mass of steel wool was directly related to dissolved phosphorus retention. The granular steel wool, however, retained 0.4–2.2% of influent phosphorus per gram of steel and steel wool fabric retained 6.2–8.6% per gram of steel. Comparing 2% steel wool and steel wool fabric (~0.3%) data from the columns indicates that the fabric was more efficient than chopped steel wool at retaining dissolved phosphorus.

The positive phosphorus retention at the conclusion of the experiments indicates that steel wool capacity for phosphorus retention was not exhausted. In addition, phosphorus retention of the steel wool fabric can be increased by increasing the number of layers (i.e., the mass) of fabric. The fraction retained could then be approximated by Eq. (1) where FRₙ = total fraction retained with n layers of fabric; and FRᵢ = fraction retained in each layer of steel wool fabric

\[ \text{FR}_n = 1 - \prod_{i=1}^{n} (1 - \text{FR}_i) \] (1)

Eq. (1) indicates that with three layers of steel wool fabric (0.9% by mass), the columns would have retained between 71% (Column I) and 83% (Column G) of the dissolved phosphorus influent.

Steel wool fabric is approximately twice the cost by mass of chopped granular steel wool (Terry Kane, personal communication, April 6, 2005), and would increase construction costs of C 33 sand filtration systems by roughly 3–5%. Additionally, the small fiber size of chopped granular steel wool makes it difficult to visualize safe and effective placement. Steel wool fabric, as used in the current study, is purchasable in rolls measuring approximately 40 in length and 2.5 m wide, and is designed for easy placement. Steel fabric-enhanced sand filters could improve the dissolved phosphorus retention capacity as compared to standard sand filtration with minimal increase in construction cost.

**Model**

The results of this study show that steel wool-enhanced sand filtration retains more dissolved phosphorus than C 33 sand alone. A mathematical model will be developed to understand phosphorus retention by the iron in steel wool based on contact time, total mass of phosphorus retained, and influent concentration. A bulk phosphorus balance between the water and iron (from the steel wool) can be written as

\[ \text{Vol} \frac{dC}{dt} = -kA(C - C^*) \] (2)

where \( \text{Vol} \) = volume of water available for transfer of phosphorus; \( C \) = phosphorus concentration in the water; \( T \) = time; \( k \) = rate constant (length/time); \( A \) = surface area available for transfer of phosphorus; and \( C^* \) = concentration of phosphorus in the water in equilibrium with iron.

Dividing by volume and designating the surface area per volume (\( A/\text{Vol} \)) as the specific surface area, \( a \), gives

\[ \frac{dC}{dt} = -ka \cdot (C - C^*) \] (3)

Eq. (3) can be rearranged and integrated over the contact time

\[ \int_{C_{in}}^{C_{out}} \frac{dC}{C - C^*} = \int_{0}^{t_{contact}} -ka \cdot dt \] (4)

where \( C_{in} \) = influent phosphorus concentration (mg/L); \( C_{out} \) = effluent phosphorus concentration (mg/L); and \( t_{contact} \) = contact time between water and steel, assumed to be the time required for the water to flow through the steel in the column.

Although \( C^* \) is a weak function of time, it will be assumed to be constant for the contact times \( t_{contact} \) encountered during these experiments. The integration result of Eq. (4) is then

\[ \ln \left( \frac{C_{in} - C^*}{C_{in} - C^*} \right) = -ka \cdot t_{contact} \] (5)

Rearranging and simplifying yields:

\[ C_{in} - C_{out} = (C_{in} - C^*)(1 - e^{-ka \cdot t_{contact}}) \] (6)

According to Eq. (6), the effluent concentration is a function of influent concentration \( C_{in} \), equilibrium concentration \( C^* \), contact time \( t_{contact} \), a rate constant \( k \), and a specific area \( a \).

As iron retains dissolved phosphorus, the equilibrium concentration will asymptotically increase towards the influent concentration until the retention capacity is exhausted. This relationship can be mathematically expressed with an exponential function as given by Eq. (7)

\[ C^* = C_{in}(1 - \beta_0 e^{-\beta_1 \Sigma M}) \] (7)

where \( \beta_0 \) = coefficient related to the phosphorus retention capacity of iron; \( \beta_1 \) = coefficient related to the rate at which \( C^* \) approaches \( C_{in} \) (1/g); and \( \Sigma M \) = instantaneous sum of phosphorus mass retained (g).

Sum of mass retained \( \Sigma M \) is used for simplicity because the reactions governing the phosphorus retention by iron are numerous and complex. Phosphorus retention capacity decreases as phosphorus adsorbs to iron but increases as iron rusts. To eliminate cross correlation of these two dichotomous mechanisms, a single variable (sum of mass retained) is used. If \( C^* \), as given by Eq. (7), is substituted into Eq. (6) and rearranged to solve for dissolved phosphorus fraction retained, then

\[ \text{FR} = \frac{C_{in} - C_{out}}{C_{in}} = (\beta_0 e^{-\beta_1 \Sigma M})(1 - e^{-\beta_2 t_{contact}}) \] (8)

The first term of the model [Eq. (8)] \( (\beta_0 e^{-\beta_1 \Sigma M}) \) is the phosphorus retention capacity of iron where \( \beta_0 C_{in} \) is the initial (or maximum) capacity at \( \Sigma M = 0 \) and \( \beta_1 \) relates to the rate at which \( C^* \) approaches \( C_{in} \). \( \beta_0 \) is related to the mass of iron available for phosphorus adsorption; \( \beta_0 \approx 0 \) indicates little or no phosphorus retention capacity and \( \beta_0 = 1 \) indicates that retention capacity equals or exceeds the initial concentration of phosphorus in the water. \( \beta_1 \) is, therefore, constrained to be less than or equal to 1. \( \beta_1 \) relates to the rate at which \( C^* \) approaches \( C_{in} \) which is affected by rusting (retention capacity increases) and adsorption (retention capacity decreases). Net phosphorus retention was always positive (see Figs. 7–12), so it may be concluded that \( C^* \) was less than \( C_{in} \) throughout the experiments. Therefore \( \beta_1 \) was constrained to be \( \geq 0 \), but was allowed to vary between each column because these studies did not quantitate rusting or adsorption.

The second term, \( (1 - e^{-\beta_2 t_{contact}}) \), is a value between zero and one that represents the rate at which the interaction between phos-
phorus and iron approaches equilibrium. In this derivation, $\beta_1$ is substituted for the product of the rate constant ($k$) and the specific surface area ($a$) where specific surface area is an intensive property of the media (in this case, steel wool) that is independent of the fluid. The gravitational packing of chopped granular steel wool (Columns D2, E2, and F2) will determine its specific area. The fixed woven structure of steel wool fabric (Columns G, H, and I) will produce a differing specific area as compared to chopped fibers. It is assumed that the rate constant ($k$) is constant for the range of contact times observed in this study. Based on these observations and assumptions, $\beta_2$ is a nonnegative constant for chopped granular steel wool and a differing constant value for steel wool fabric.

The model was fit to the persulfate total phosphorus data where the persulfate method was deemed accurate, and otherwise to the dissolved phosphorus data. A standard error function, Eq. (9), was used to compare the results generated by the model to the observed data from the experiments

$$\text{Standard Error} = \sqrt{\frac{1}{n-2} \sum (\text{data-model})^2}$$ (9)

This standard error function was minimized using a nonlinear, Newton method to solve for the coefficients ($\beta_0, \beta_1, \beta_2$) in Eq. (8), with the constraints justified above. The total standard error for all six columns (data weighted average) was 0.0931 ($n=200$). The best-fit coefficients are listed in Table 3, and shown with the data in Figs. 7–12.

The model successfully predicted various trends in phosphorus fraction retained for the six column tests, including an increase in retention capacity (Columns D2), steady retention capacity (E2 and G), and a decrease in retention capacity (F2, H, and I) with steady and dynamic hydraulic conductivities. The model captured trends that related to the capacity of the steel wool to retain phosphorus despite the complexity of processes incorporated into the sum of mass retained term (SM).

As discussed earlier, $\beta_0=1$ represents a retention capacity that equals or exceeds the initial phosphorus concentration and the model fit the data best when $\beta_0=1$, which indicates that retention capacity met or exceeded the amount of phosphorus in the water. The effects of the best fit values for $\beta_1$ on the model are illustrated by the variation in the capacity term, ($e^{-\beta_1 k t}$), at the conclusion of the experiments, as shown in Table 3. Note that the SM term varies for each column. The larger $\beta_1$ for steel wool fabric as compared to chopped granular steel wool indicates a faster reduction in adsorption capacity due to the mass of steel wool available (0.3 versus 2 or 5%). According to $(1-e^{-\beta_2 (\text{contact})})$, an increase in $\beta_2$ will increase the rate at which equilibrium is approached when $t_{\text{contact}}$ is constant. Therefore, steel wool fabric ($\beta_2=0.0017$ s$^{-1}$) approaches equilibrium at a slower rate than chopped granular steel wool ($\beta_2=0.0028$ s$^{-1}$). This difference could be caused by preferred flow paths through the chopped granular steel wool.

As shown in Table 3, $\beta_1$ values increase as filter fabric type is changed from generic woven to 150 micron mesh to 200 µm mesh. If the generic woven filter fabric captures more fine oxidized iron particles than either mesh, the captured particles could continue to retain phosphorus and therefore delay the rate at which retention capacity is reduced (i.e., lower $\beta_1$ values). The tortuous path of the filter fabric could cause it to retain a greater percentage of the fine oxidized iron particles.

Based on the data shown in Figs. 7–12 with the interpretations of these measurements given, the columns with the smallest values of $\beta_1$ correspond to the columns with the least difference between mercuric total phosphorus and dissolved measurements. In other words, the columns that release the least amount of oxidized iron seem to maintain the largest capacity for phosphorus adsorption and therefore have the smallest value of $\beta_1$. This indicates that a proper choice of filter fabric can make a difference in the performance of a steel-enhanced sand filter in the removal of dissolved phosphorus from storm water.

### Table 3. Resultant Coefficients from Model Fit to Data for Each Column

<table>
<thead>
<tr>
<th>Column</th>
<th>Column description</th>
<th>$\beta_0$</th>
<th>$\beta_1$ (l/g)</th>
<th>$\beta_2$ (l/s)</th>
<th>$\beta_0 e^{-\beta_1 k t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2</td>
<td>2% steel wool with generic filter fabric</td>
<td>0.983</td>
<td>0.000</td>
<td>0.0028</td>
<td>0.101</td>
</tr>
<tr>
<td>E2</td>
<td>2% steel wool with 150 micron mesh</td>
<td>0.983</td>
<td>12.164</td>
<td>0.0028</td>
<td>0.109</td>
</tr>
<tr>
<td>F2</td>
<td>2% steel wool with 200 micron mesh</td>
<td>0.983</td>
<td>17.151</td>
<td>0.0028</td>
<td>0.089</td>
</tr>
<tr>
<td>G</td>
<td>Steel wool fabric with generic filter fabric</td>
<td>1</td>
<td>0.000</td>
<td>0.0017</td>
<td>0.079</td>
</tr>
<tr>
<td>H</td>
<td>Steel wool fabric with 150 µm mesh</td>
<td>1</td>
<td>18.651</td>
<td>0.0017</td>
<td>0.106</td>
</tr>
<tr>
<td>I</td>
<td>Steel wool fabric with 200 µm mesh</td>
<td>1</td>
<td>40.742</td>
<td>0.0017</td>
<td>0.074</td>
</tr>
</tbody>
</table>

Note: Constraints: $\beta_0=1$; $\beta_1 \geq 0$; $\beta_2$ is equal for Columns D2, E2, and F2 and $>0$; and $\beta_2$ is equal for Columns G, H, and I and $>0$.

### Conclusions

The results of the batch studies show that C 33 sand alone retains some dissolved phosphorus but steel wool, calcareous sand, and limestone enhancements increased dissolved phosphorus removal which can be applicable to storm water treatment. C 33 sand enhanced with aluminum oxide removed approximately the same amount of dissolved phosphorus as C 33 sand alone. C 33 sand enhanced with steel wool removed more than either C 33 sand alone and C 33 sand enhanced with aluminum oxide. Increases from 1 to 5% by weight of steel wool mixed with C 33 sand increased the dissolved phosphorus removal from approximately 60 to 90%. BOF by-products by far removed the most phosphorus quickly but increased pH to approximately 11, which exceeds water quality standards.

Column studies were then used to further investigate enhanced sand filtration. C 33 sand removed 2.1% of the dissolved phosphorus from the synthetic storm water during these column experiments, and its capacity was quickly exhausted. Batch studies indicated that limestone or calcareous sand retained phosphorus effectively, but the fine grain size of precipitates clogged the filter fabric and prevented the columns from draining.

Steel-enhanced, sand-filter columns retained between 25 and 99% of dissolved phosphorus and enhanced the quantity and duration of phosphorus retention as compared to C 33 sand alone. Based on sand filtration design guidelines and a pure sand col-
umn, dissolved phosphorus retention did not clog the steel enhanced sand filter columns. Additionally, enhancing sand filtration with steel wool fabric would only increase construction costs by approximately 3–5%.

A model was developed to describe the processes occurring in steel enhanced sand filter columns. Based on mass balance between phosphorus and iron, this model used contact time, total mass of phosphorus retained, and influent phosphorus concentration to predict effluent concentration. The overall standard error between the model and the data was 0.0931 for all nine columns (n=200).

As with other sand filtration systems, steel-enhanced sand filters should be sized and placed according to local guidelines with proper pretreatment to settle some influent solids prior to the sand filter. Steel wool fabric could be laid in multiple layers, increasing the residence time in the steel wool and subsequently dissolved phosphorus removal, and is therefore a cost effective enhancement to sand filtration for retaining dissolved phosphorus.

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