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GRADUATE SCHOOL

Enhanced Sand Filtration for Storm Water Phosphorus Removal

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Overview

The U.S. EPA. (2000) reports that “approximately 40 percent of surveyed U.S. waterbodies are still (as of 1996) impaired by pollution” and a “leading source of this impairment is polluted runoff.” While storm water management has historically been focused on the *quantity* of urban storm water runoff, recent legislation pursuant to the Clean Water Act of 1972 has forced many municipalities and communities to begin regulating the *quality* of their runoff as well. Sand filtration is one management technique designed to remove pollutants associated with storm water runoff. It treats runoff by physically sieving suspended particulates and the associated pollutants from the water. While this process may remove particulates and debris, it has no mechanism to remove dissolved contaminants, such as phosphorus. To remove dissolved phosphorus, sand filtration must be enhanced with materials that possess chemical adsorption or precipitation processes to pull dissolved phosphorus from the storm water runoff.

This thesis is composed of two manuscripts focused on treatment of storm water runoff by enhanced sand filtration. The first manuscript uses batch studies to examine several potential enhancement materials to sand filtration for the removal of dissolved phosphorus. Based on the results of these batch studies, the second manuscript examines steel wool, calcareous sand, and limestone in column studies and characterizes the dissolved phosphorus removal by steel wool from these column studies with a mathematical model.

Chapter 1, entitled “Phosphorus Capacity of Enhanced Sand for Storm Water Filtration,” provides an experimental evaluation of sand filtration enhancements for the

removal of dissolved phosphorus from storm water. This preliminary evaluation quickly assessed several sand filtration enhancements under ideal conditions with batch studies, which are designed to determine phosphorus removal capacity and therefore allowed for the more focused column study research (Chapter 2). In addition to the results of this evaluation, Chapter 1 also contains a detailed review of the chemical precipitation and adsorption processes that govern dissolved phosphorus removal by enhanced sand filtration and a literary review of previously published batch study results. The manuscript will be submitted for publication to the Journal of Environmental Quality.

Chapter 2, entitled “Enhanced Sand Filtration for Storm Water Phosphorus Removal,” uses the preliminary results found in Chapter 1 to evaluate three sand filtration enhancements with column studies: calcareous sand, limestone, and steel wool. Using the data from these column studies and a mass balance of phosphorus and steel wool, a model was developed to describe the processes of dissolved phosphorus removal in the sand filtration columns enhanced with steel wool. The manuscript will be submitted for publication as a companion to the Journal of Environmental Quality.

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Chapter 1: Phosphorus Capacity of Enhanced Sand for Storm Water Filtration

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ABSTRACT

Of utmost concern in storm water treatment today is the removal of dissolved phosphorus. One method to effectively determine the phosphorus removal capacity of different media for sand filtration is controlled, well mixed experiments called batch studies. 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. After evaluation, our conclusions are: (1) C 33 sand alone can remove some dissolved phosphorus but batch studies are inconclusive about longevity of removal and pH affects; (2) calcareous sand and limestone removed significantly more dissolved phosphorus as compared to C 33 sand alone; (3) C 33 enhanced with aluminum oxide removed little, if any, additional phosphorus as compared to C 33 sand alone; (4) chopped granular steel wool removed significantly more phosphorus than C 33 sand alone after 10 hours of contact; (5) increases in mass of steel wool increased dissolved phosphorus removal; and (6) BOF by-products exhibited the most dissolved phosphorus removal, but produced alkaline pH conditions that exceed nationally suggested and state enforced standards. Based on these findings, sand filtration enhanced with steel wool, calcareous sand, or

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limestone has the potential to be practical and cost effective, but must be investigated further in laboratory column experiments or field sand filtration applications to ensure clogging or pH effects are not detrimental to the sand filter's functionality and to determine the long-term effectiveness of these enhancements.

INTRODUCTION

Nutrients (phosphorus and nitrogen) are one of the many pollutant categories being targeted for removal from storm water runoff. The U.S. EPA. (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 as reported by Aldridge and Ganf (2003); Schindler (1977). It exists in the form of phosphates (H_3PO_4 , $pH < 2.16$; $H_2PO_4^-$, $pH < 7.20$; HPO_4^{2-} , $pH < 12.35$, Benjamin (2002); Stumm and Morgan (1981)) contributed to storm water from laundering and commercial cleaning processes, treatment of boiler waters, fertilizers on agricultural or residential cultivated land, biological processes instigated by sewage, food residues, and/or plant material waste, etc. (A.P.H.A. *et al.* (1998); U.S. EPA. (1999)). Dissolved phosphorus (phosphates) is defined as the amount of phosphorus that passes through a 0.45 micron filter (A.P.H.A. *et al.* (1998)). To remove it from storm water runoff, it must be converted to a solid phase and removed as a particulate (Jenkins *et al.* (1971)).

Efficient phosphate removal is only possible if chemical treatment methods are employed for dissolved phosphorus fractions along with conventional sedimentation

processes (Jenkins *et al.* (1971)). Possible chemical treatment methods include precipitation by calcium, aluminum, or iron and surface adsorption to iron oxide or aluminum oxide. Phosphorus precipitation is dominated by iron and aluminum in acidic to neutral conditions and calcium in neutral to alkaline conditions. Surface adsorption to iron decreases as pH increases but can still occur in pH as high as 11 (Stumm and Morgan (1981)). Sources of calcium, aluminum and iron used in this study include limestone ($CaCO_3$), calcareous sand (Ca^{2+} enriched sand typically by $CaCO_3$), aluminum oxide (Al_2O_3), steel wool (Fe), and Blast Oxygen Furnace (BOF) by-products (Fe and Ca^{2+} constituents) from the steel manufacturing industry.

Chemical phosphorus removal and pH are interrelated and must be balanced to provide cost effective removal of dissolved phosphorus. The U.S. EPA. (2002), through published national secondary drinking water standards, suggests that pH values remain between 6.5 and 8.5 and most states have followed this initiative. The Minnesota Pollution Control Agency, for example, mandates that pH values remain between 6.5 and 8.5 for class 2A waters: aquatic life and recreation (MN P.C.A. (2003a)) and between 6.0 and 8.5 for class 4A waters: agriculture and wildlife (MN P.C.A. (2003b)).

The value of batch studies is paramount to storm water treatment. Batch studies determine a quantified capacity under ideal contact conditions that can be replicated and allow for the quick examination of many mix combinations and quantities. They can be used to determine baseline data and preliminary removal rates prior to laboratory or field experiments. This paper investigates the potential effectiveness of eight materials (C 33 sand, calcareous sand, limestone, aluminum oxide, steel wool, and three BOF by-

products) with regard to their ability to remove dissolved phosphorus from storm water runoff using results from batch studies conducted at the University of Minnesota.

PREVIOUS WORK

Based upon a publication by the U.S. EPA from 1983, the Water Environment Federation in conjunction with the American Society of Civil Engineers (W.E.F. and A.S.C.E. (1998)) report that the event mean concentration for total phosphorus in urban runoff is 0.33 mg/L and “soluble” phosphorus is 0.12 mg/L. A more recent report by Brown *et al.* (2003) based upon three different studies (~500, 107, and >3,783 storm events, respectively) states that a total phosphorus concentration of 0.3 mg/L is adequate to describe both new and old urban development. Urban runoff in the Twin Cities Metropolitan Area (Minneapolis and St. Paul, MN) exhibits event mean concentrations for total and dissolved phosphorus, respectively, as a function of climatic season: 1.37 and 0.37 mg/L for winter, 0.85 and 0.53 mg/L for spring, 0.59 and 0.21 mg/L for summer, and 0.55 and 0.21 mg/L for fall as described by Brezonik and Stadelmann (2002).

Baker *et al.* (1998) performed batch studies on the removal of phosphorus from subsurface sewage with concentrations of 10 ± 2 mg $PO_4^{3-} - P$ /L and pH ranging from 5.5-6.0 to simulate onsite wastewater disposal system effluent. Their experiments studied calcareous and non-calcareous sands, limestone, iron oxides, and aluminum oxides for dissolved phosphate and pH modification over a maximum exposure time of 10 hours. From the graphical results it is evident that the 100% (by weight) silica sand and 100%

non-calcareous sand did not exhibit any phosphorus removal or pH modification. Also, 100% calcareous sand and 50% limestone (with 50% silica sand) both removed dissolved phosphorus (by ~41% and ~88%, respectively) and caused slight pH increases (to 8.1 and 9.1, respectively).

Baker *et al.* (1998) also found that BOF (Blast Oxygen Furnace) by-products, iron oxide compounds, and aluminum oxide compounds successfully removed phosphorus during their batch studies. Some mixtures (BOF oxide, BOF slag, and red mud) also contributed a substantial pH increase (effluent pH ~11-12). Chemical composition analysis reported by Baker *et al.* (1998) show that BOF by-products contain iron, calcium, magnesium, manganese, silicon, and zinc or aluminum.

While their experiments provide background for the utilization of these materials to remove dissolved phosphorus, the mixtures they propose will likely not be cost-effective for storm water treatment because of vastly differing inflow concentrations and flow rate conditions as described further in Erickson *et al.* (2005a).

Arias *et al.* (2001) conducted isotherm studies on 13 different sands from Denmark for their phosphorus adsorption capabilities. Mineral content analysis revealed many of the sands contained amounts of phosphorus (mean = 0.25 mg P/g), iron (4.27 mg Fe/g), calcium (28.43 mg Ca/g), aluminum (1.88 mg Al/g), and magnesium (1.1 mg Mg/g) prior to experiments, and the average pH of the sands in tap water was 8.39.

Results from Arias *et al.* (2001) show that quartz sand is relatively inert with very low mineral content and low capacity for phosphorus removal and that phosphorus removal by other sands could be related to calcium content, texture-related variables, and

pH variables. Based upon their Langmuir isotherm experiments, it is reported that “the amount of removed P varied between 0.27 mg g⁻¹ dry weight for quartz sand and 3.94 mg g⁻¹ dry weight for Darup sand.” However, Arias *et al.* (2001) conclude that Langmuir isotherm experiments do not accurately estimate capacity for sands due to the number of complex reactions that occur between dissolved phosphorus and the calcium, magnesium, iron, and aluminum that may be present in sands.

Additional results from column experiments that incorporated calcite, marble (high calcium content), light-expanded-clay-aggregates (LECA), diatomaceous earth, and vermiculite were also reported by Brix *et al.* (2001). Results from those isotherms show that calcite (240 mg Ca/g) and marble (389 mg Ca/g) removed more phosphorus than the Darup sand while the LECA, diatomaceous earth, and vermiculite all performed approximately the same as the quartz sand.

Field scale vertical flow wetland experiments with calcite filters were conducted by Arias *et al.* (2003) to examine phosphorus removal but, “the nominal residence time of the water in the calcite filters ranged between 28 to 99 minutes.” They attribute enhanced phosphorus removal to both low hydraulic loading rates, which resulted in increased residence time, and higher inlet concentrations. The capacity was determined to be approximately 2.2 kg P/m³ calcite. The data presented by Arias *et al.* (2003); Arias *et al.* (2001); and Brix *et al.* (2001) would also not be indicative of results expected for storm water treatment because inflow concentrations used in these studies are considerably higher than typical storm water values.

CHEMICAL PRECIPITATION AND ADSORPTION

Reddy and D'Angelo (1994) summarize previous research in phosphate retention by mineral soils into three general conclusions: “(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.” They also state that “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.” They identify the mechanisms for phosphorus retention by soils as precipitation by calcium/magnesium (alkaline) or a combination of adsorption and precipitation with iron/aluminum (acidic).

Stumm and Morgan (1981) use a phase solubility diagram to illustrate the dominate phosphate precipitates throughout the pH range:

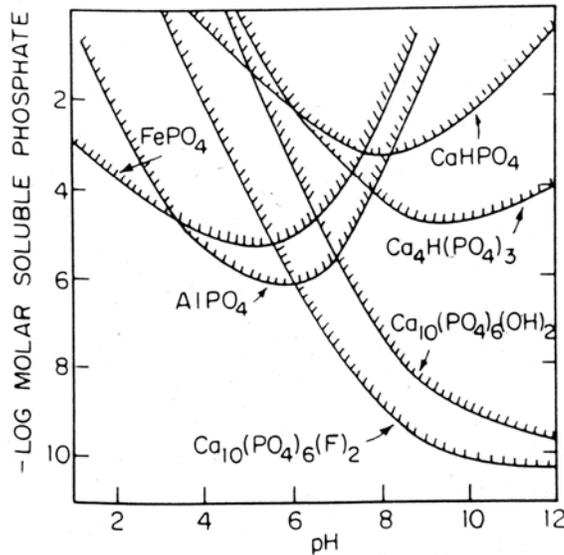
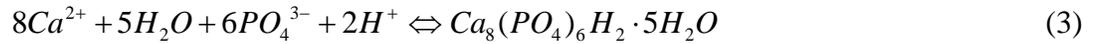


Figure 1: Solubility of the metal phosphates. The solubility of $AlPO_4$ and $FePO_4$ has been calculated on the basis of equilibria, assuming that $FePO_4(s)$ or $AlPO_4(s)$ can be converted incongruently into $Fe(OH)_3(s)$ [or $\alpha\text{-}FeOOH(s)$] or $Al(OH)_3(s)$. The solubility of the calcium phosphate phases has been calculated under the assumption that $[Ca^{2+}] = 10^{-3} M$ and that F^- is regulated by the solubility of $CaF_2(s)$. (Stumm and Morgan (1981))

It is apparent from figure 1 that iron and aluminum precipitates dominate the regions below $pH \sim 6$ and that calcium phosphates dominate above $pH \sim 6$. Iron can combine through precipitation with phosphates to form strengite ($Fe(PO_4) \cdot 2H_2O$) and vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) (see table 5.1 of Stumm and Morgan (1981)). Aluminum can form both variscite ($Al(PO_4) \cdot 2H_2O$) and wavellite ($Al_3(OH)_3(PO_4)_2 \cdot 5H_2O$) (Kadlec and Knight (1996)).

Calcium in limestone and calcareous sand can form cation precipitates with phosphate such as apatite ($Ca_{10}(PO_4)_6(F)_2$) and hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$) as reported by Kadlec and Knight (1996). Baker *et al.* (1998) used the geochemical speciation model MINTEQA2, to determine the following calcium phosphate phase changes:





Equations (1), (2), and (3) list calcium phosphate precipitates that occur in neutral to alkaline pH conditions in order of increasing solubility. In figure 1, Stumm and Morgan (1981) assume that there is enough fluorine in solution for phosphates to precipitate as apatite, but Baker *et al.* (1998) make no statements about fluorine availability when they applied their speciation model.

In general, solutions of high pH and high total phosphorus concentrations will have precipitation of Ca^{2+} and PO_4^{3-} while solutions with low pH and low total phosphorus concentrations will remain as calcite and not precipitate with PO_4^{3-} . Benjamin (2002) explains that increases in pH are also caused by the simple abiotic oxidation of ferrous iron, which removes protons. Baker *et al.* (1998) explain how BOF by-products, which are a waste product from the steel manufacturing process, also cause increases in pH by “the dissolution of portlandite” as described by equation (4), where calcium ions are incorporated into phosphate precipitates:



Iron and aluminum also possess the ability to adsorb phosphorus to their surfaces. Patrick and Khalid (1974) determined that “ferric oxyhydroxide is capable of binding dissolved phosphate ions more firmly than the ferrous form, but probably has less surface area exposed to the solution P than the gel-like hydrated ferrous oxide or ferrous

[†] where beta (β) most likely represents the most stable crystalline morphology of tricalcium phosphate.

hydroxide.” Their study also determined that “considerably more amorphous iron oxide” was available to react with phosphorus under reducing conditions (vs. oxidized) and that P concentrations were lower in reduced soil conditions (vs. oxidized). Stumm and Morgan (1981) illustrate the dependence of binding capacity on pH for iron oxide and phosphate species. They report that total phosphate adsorption is highest in acidic conditions but ~50% of the total available phosphorus can still be adsorbed to iron at a pH as high as 10.

Caraco *et al.* (1993) found that surface water sulfate concentrations had a strong impact on iron: phosphorus ratios and that higher sulfate concentrations can increase the magnitude of phosphorus released from bottom sediments. In anaerobic sediments, the presence of sulfides can reduce phosphorus retention in soils by forming ferrous sulfides.

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). Based on typical storm water phosphorus concentrations stated earlier, a concentration of ~0.5 mg/L dissolved phosphorus was chosen for these experiments to represent extreme phosphorus loading conditions. A standard phosphorus solution was mixed with potassium phosphate (KH_2PO_4) to a mean concentration of 0.485 ± 0.008 (95% confidence interval, n = 66) mg $PO_4^{3-} - P$ /L and mean pH of 5.657 ± 0.295 (95% confidence interval, n = 66).

Equal volumes of standard phosphate solution (150 mL) were added to the BOD bottles with 10% media by weight. The media combinations of initial experiments were chosen using knowledge gained from Baker *et al.* (1998) and further experiments were conducted based upon the results of our initial experiments. Tables 1, 2, and 3 list all the individual batch study experiments and combinations of media that were investigated, excluding the blanks, and table 4 lists the elemental composition of these media. For this paper, a 'blank' refers to an experiment in which only the standard phosphate solution was added to the BOD bottle, without any media. The 12 bottle capacity of the shaker table allowed for six bottles of unique media combinations as described in tables 1, 2, and 3 and six duplicate bottles to be tested at one time.

Table 1: Experiments with sands and limestone.

Pure Sand (15g)	Combinations (wt% of 15g)
C 33 Sand	90% Calcareous Sand 10% Limestone
Calcareous Sand	70% Calcareous Sand 30% Limestone
Fine Sand	50% Calcareous Sand 50% Limestone
Washed Calcareous Sand	90% C 33 Sand 10% Limestone
Washed C 33 Sand	70% C 33 sand 30% Limestone
	50% C 33 Sand 50% Limestone

Table 2: Experiments with Metal Oxides (Steel Wool and Aluminum Oxide).

Steel Wool (wt% of 15g)	Aluminum Oxide (wt% of 15g)
1% Steel Wool 99% Calcareous Sand	1% Aluminum Oxide 99% Calcareous Sand
3% Steel Wool 97% Calcareous Sand	3% Aluminum Oxide 97% Calcareous Sand
5% Steel Wool 95% Calcareous Sand	5% Aluminum Oxide 95% Calcareous Sand
1% Steel Wool 49.5% Calcareous Sand 49.5% Limestone	1% Aluminum Oxide 49.5% Calcareous Sand 49.5% Limestone
3% Steel Wool 48.5% Calcareous Sand 48.5% Limestone	3% Aluminum Oxide 48.5% Calcareous Sand 48.5% Limestone
5% Steel Wool 47.5% Calcareous Sand 47.5% Limestone	5% Aluminum Oxide 47.5% Calcareous Sand 47.5% Limestone
1% Steel Wool 99% C 33 Sand	1% Aluminum Oxide 99% C 33 Sand
3% Steel Wool 97% C 33 Sand	3% Aluminum Oxide 97% C 33 Sand
5% Steel Wool 95% C 33 Sand	5% Aluminum Oxide 95% C 33 Sand
5% Steel Wool @ pH = 2.0	5% Aluminum Oxide @ pH = 2.0
5% Steel Wool @ pH = 6.0	5% Aluminum Oxide @ pH = 6.0
5% Steel Wool @ pH = 4.0	5% Aluminum Oxide @ pH = 4.0

Table 3: Experiments with Blast Oxygen Furnace (BOF) by-products.

Old BOF Dust (wt% of 15g)	New BOF Dust (wt% of 15g)
1% Old BOF Dust 99% Calcareous Sand	1% New BOF Dust 99% Calcareous Sand
3% Old BOF Dust 97% Calcareous Sand	3% New BOF Dust 97% Calcareous Sand
5% Old BOF Dust 95% Calcareous Sand	5% New BOF Dust 95% Calcareous Sand
1% Old BOF Dust 49.5% Calcareous Sand 49.5% Limestone	
3% Old BOF Dust 48.5% Calcareous Sand 48.5% Limestone	
5% Old BOF Dust 47.5% Calcareous Sand 47.5% Limestone	
1% Old BOF Dust 99% C 33 Sand	
3% Old BOF Dust 97% C 33 Sand	
5% Old BOF Dust 95% C 33 Sand	
5% Old BOF Dust @ pH = 2.0	
5% Old BOF Dust @ pH = 6.0	
5% Old BOF Dust @ pH = 4.0	
	BOF Slag (wt% of 15g)
	1% BOF Slag 99% Calcareous Sand
	3% BOF Slag 97% Calcareous Sand
	5% BOF Slag 95% Calcareous Sand

Table 4: Elemental composition in experimental media (mg/g dry weight)

Material	Element Analysis (mg/g dry weight)							
	Al	Ca	Fe	K	Mg	Mn	Na	P
New BOF Dust	0.27	74	29	1.6	12.4	0.66	0.44	0.22
Old BOF Dust	0.42	81	38	0.01	9.6	1.25	0.03	0.45
BOF Slag	2.72	177	16	0.02	7.9	3.5	0.08	1.6
Steel Wool	0.06	0.22	716	< 0.02	0.37	6.8	0.02	0.18
Aluminum Oxide	0.73	0.45	0.11	0.17	0.13	0.04	0.03	0.01
C33 Sand	0.21	2.0	0.38	0.02	0.57	0.03	0.01	0.14
Calcareous Sand	0.02	106	0.01	0.03	60	0.38	0.09	0.01
Limestone	0.06	346	1.5	0.09	12.4	0.26	0.91	0.09

C 33 sand was chosen for these experiments because it is recognized as the standard for sand filtration systems throughout the United States. Fine sand and silica sand were also acquired for these experiments. Grain size distributions were determined by the Research Analytical Lab (<http://ral.coafes.umn.edu/>) at the University of Minnesota on all three sands (figure 2) and the results of this analysis indicates that the pore size of the silica sand is too large to efficiently treat storm water by filtration. Thus no batch studies were conducted using this sand.

After washing with distilled water, fine sand was found to be relatively inert when compared to the blank solution and was also eliminated from further experimentation. Materials were tested without washing or other preparation except those experiments listed (in tables 1, 2, or 3) as ‘washed.’ For this paper, ‘washed’ refers to the material that was retained on a #100 standard sieve (149 micron size opening) after material was rinsed with distilled water.

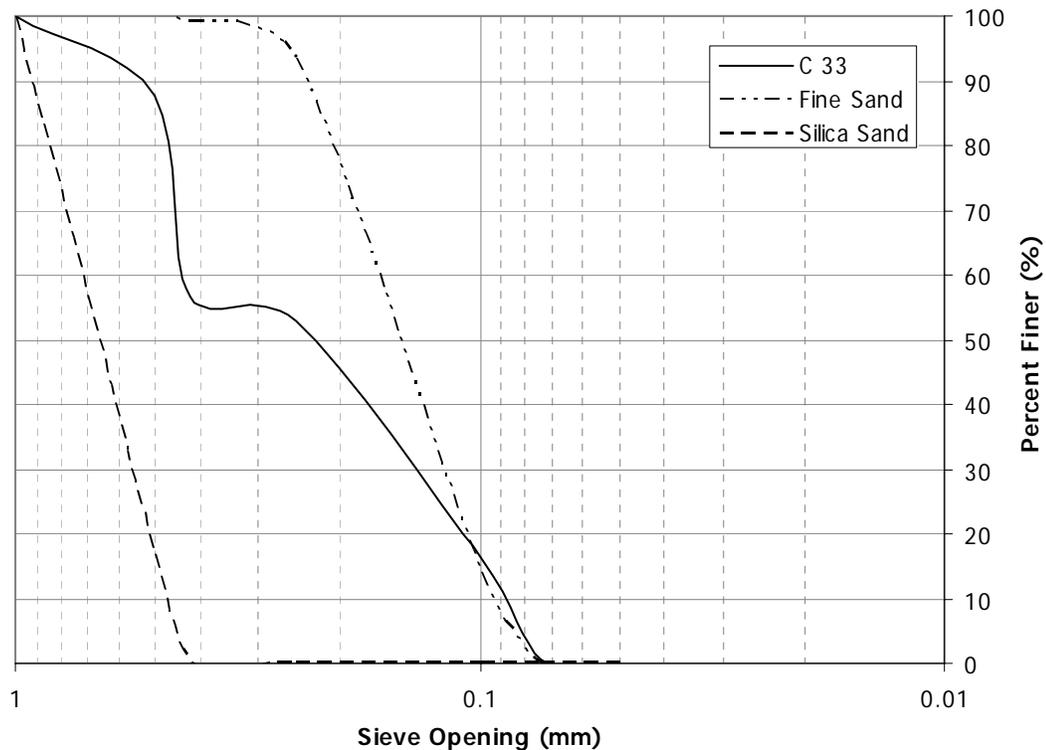


Figure 2: Grain size distribution of C 33, fine, and silica sands

Initial samples (corresponding to time zero) were taken for dissolved phosphorus determination, with pH measured prior to addition of media. The media to be examined was then added to the bottle, except in the case of blank phosphate solution in which no media was added, 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 hours after media addition and pH readings were taken at the same time steps (except for 0.5 hours) to determine how pH was affected. Samples were analyzed for dissolved phosphorus according to standard methods section 4500-P E (Ascorbic Acid) in A.P.H.A. *et al.* (1998) with a

minimum detection limit of 10 µg P/L. pH readings were measured using a pH meter that was calibrated with pH = 4, 7, and 10 standards.

RESULTS AND DISCUSSION

Results were normalized to a blank phosphate solution experiment (as shown in figure 3). Media with normalized concentrations greater than 1.0 are contributing phosphorus, while those with values below 1.0 are removing phosphorus from the solution. pH measurements were not normalized.

Sands

As reported by Arias *et al.* (2001), some sands have the capacity to remove phosphorus from storm water. For 15 grams of sand, the capacity results of Arias *et al.* (2001) correspond to a potential removal of 4.05 to 59.1 mg -P; equivalent to completely removing a dissolved phosphorus concentration of 27 to 394 mg $PO_4^{3-} - P$ /L. C 33 sand in these batch studies removed approximately 27% of the available phosphorus (0.485 mg $PO_4^{3-} - P$ /L) after 5 hours of contact and roughly 40% after 10 hours of contact, as shown in figure 3. Washing the C 33 sand caused no significant change in the phosphorus removal, but limestone and calcareous sand alone and in combination with C 33 can remove significantly more dissolved phosphorus than C 33 sand alone (See figure 4).

C 33 sand increased the batch solution pH from approximately 5.7 to about 10. These results are higher than the U.S. EPA. (2002) recommended upper limit of 8.5; even after the C 33 sand was washed, the pH still increased to about 9.5. As will be shown in

the companion paper by Erickson *et al.* (2005a), C 33 sand alone does not significantly increase the pH of the influent storm water as it passes through a sand filter column. The high pH results exhibited by the batch studies may be attributed to the small volume of water used in the batch studies (150 mL) which could allow small impurities in the sand to have strong impacts on pH. The blank phosphate solution's pH did not change with respect to time.

Both calcareous sand and washed calcareous sand provide dissolved phosphorus removal to below detection limits, but also increased pH to between 9.8 and 10.1. These pH results are not significantly different than those found for the C 33 sand alone, but due to the small volume of water used during the batch studies it is difficult to estimate the longevity of the pH effects. Only column or field experiments would give an accurate indication of how long pH levels would be affected by calcareous sand, limestone or C 33 sand.

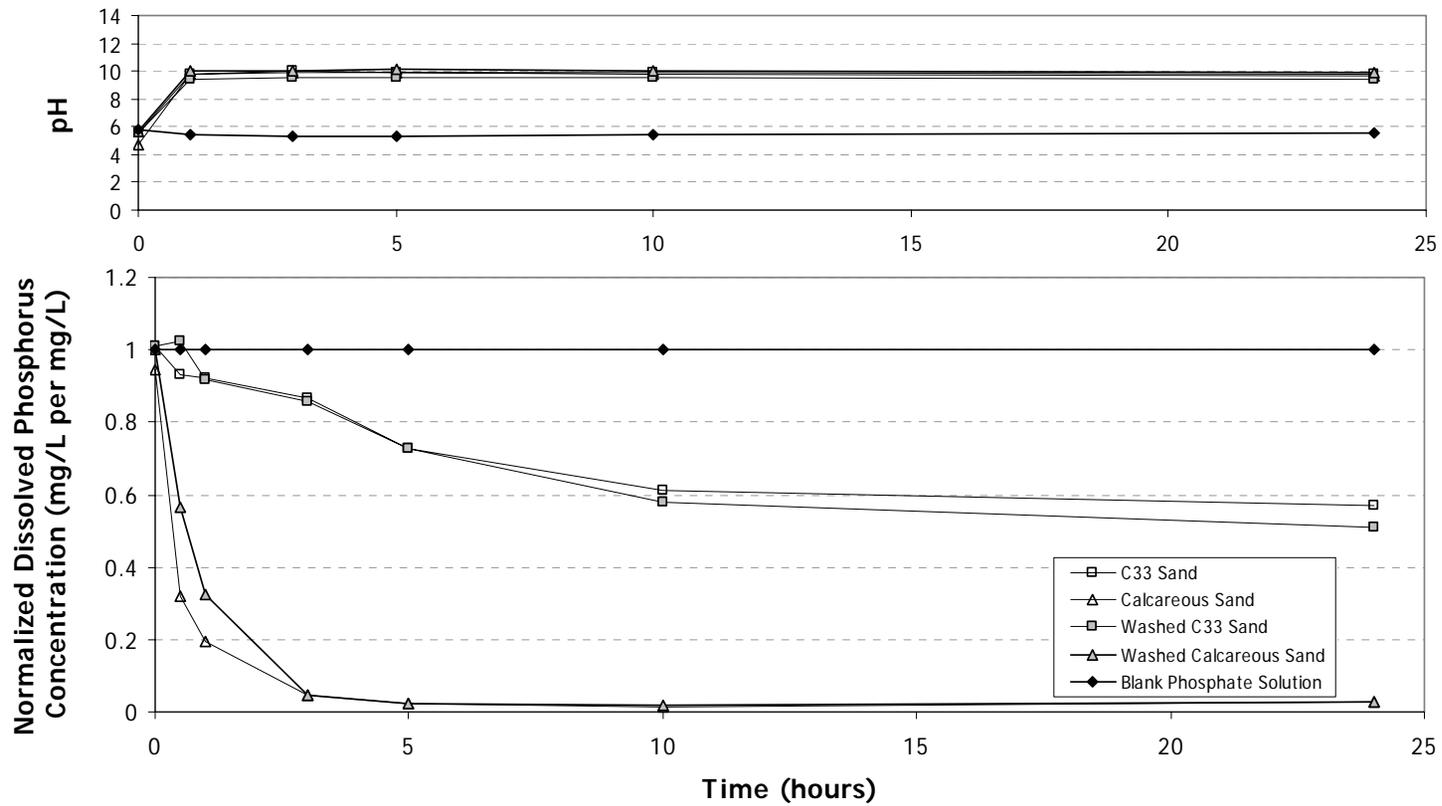


Figure 3: Phosphorus removal by sands.

15 g of media were placed in 0.15 L of standard phosphate solution with initial concentration of 0.485 mg $PO_4^{3-} - P$ /L. Normalized dissolved phosphorus concentration = 0 at 100% removal.

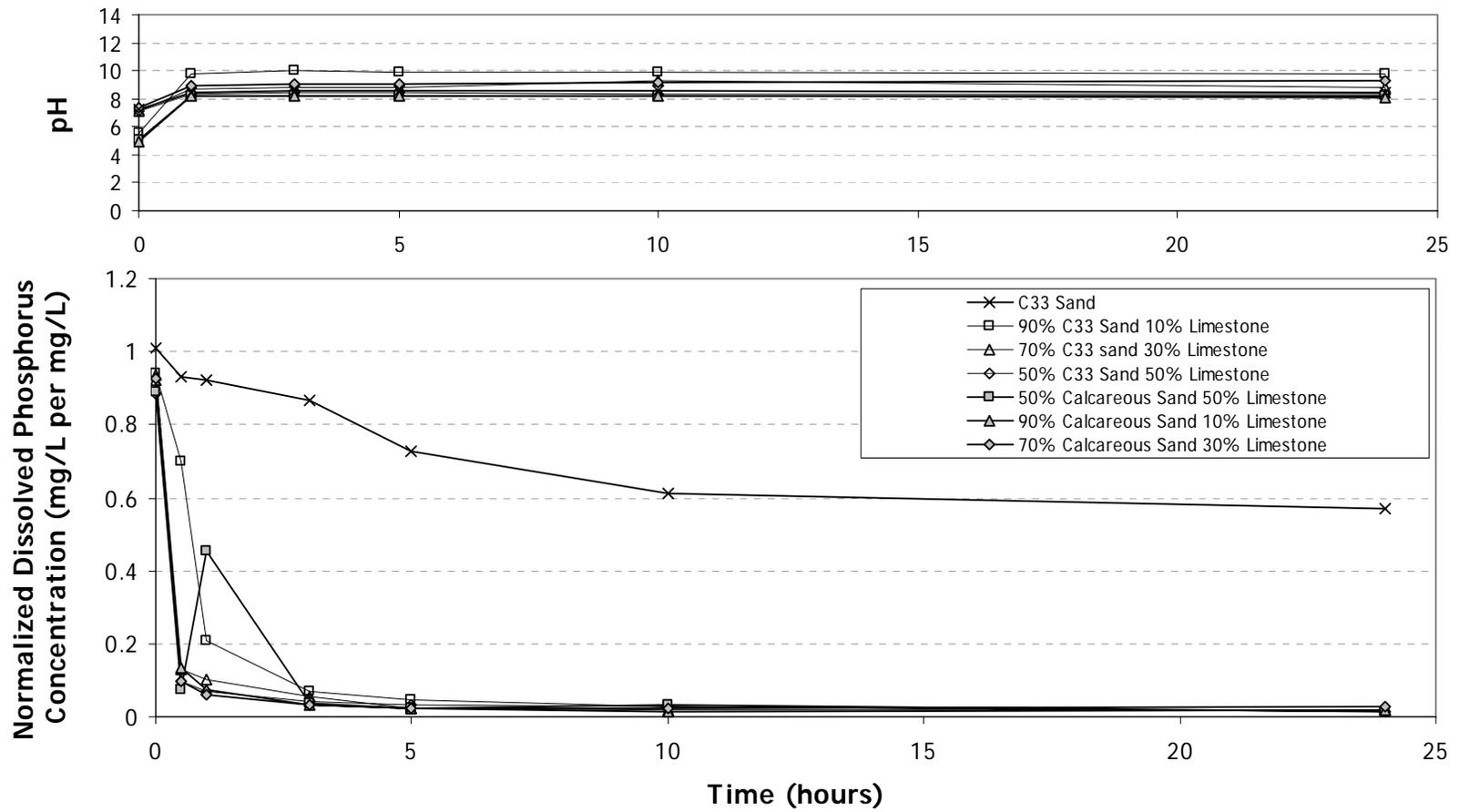


Figure 4: Phosphorus removal by limestone with calcareous sand or limestone.

Limestone and calcareous sand are primarily composed of fine particles that became suspended in the batch study solution and quickly clogged the 0.45 micron filter used in the dissolved phosphorus analysis. Fine particle analysis was performed at the Research Analytical Lab on both the calcareous sand and limestone media used in these experiments (see table 5).

Table 5: Fine particle analysis for limestone and calcareous sand

	% Sand	% Silt	% Clay
Calcareous Sand	88.85	9.05	2.1
Limestone	45.8	42.0	12.2

The fines may also cause clogging problems in sand filtration applications or alternatively, these fine particles may not be captured by the sand filter at all and produce turbidity and calcium phosphate precipitates in the effluent, negating the purpose of using these enhancers. Proper application in sand filtration systems and pH concerns need to be addressed before calcareous sands and limestone can be effectively and efficiently applied in storm water treatment.

Metal Oxides

While initial experimental combinations of aluminum oxide and calcareous sand with or without limestone exhibited phosphorus removal to detection limits (see figure 2), 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. However, in combination with C 33 sand, aluminum oxide provides approximately the same removal and affect on pH as C 33 sand alone (see figure 5). In addition, the increases in pH to between 8 and 10 exhibited by combinations of

aluminum oxide with C 33, limestone, and/or calcareous sand shown in figure 5 can be attributed to calcareous sand, limestone, or C 33 because the pure aluminum oxide experiments (pH = 4 and 6) show no evidence that aluminum oxide alone has any significant affect on pH. While aluminum oxide alone removed some dissolved phosphorus, the addition of aluminum oxide to C 33 sand did not increase phosphorus removal as compared to C 33 sand alone. Figure 1 indicates that $AlPO_4$ precipitation is most significant at a pH of approximately 6, and still more important at pH = 4, but is not important at higher pH values, which corresponds to the lack of additional removal in combination with C 33 sand.

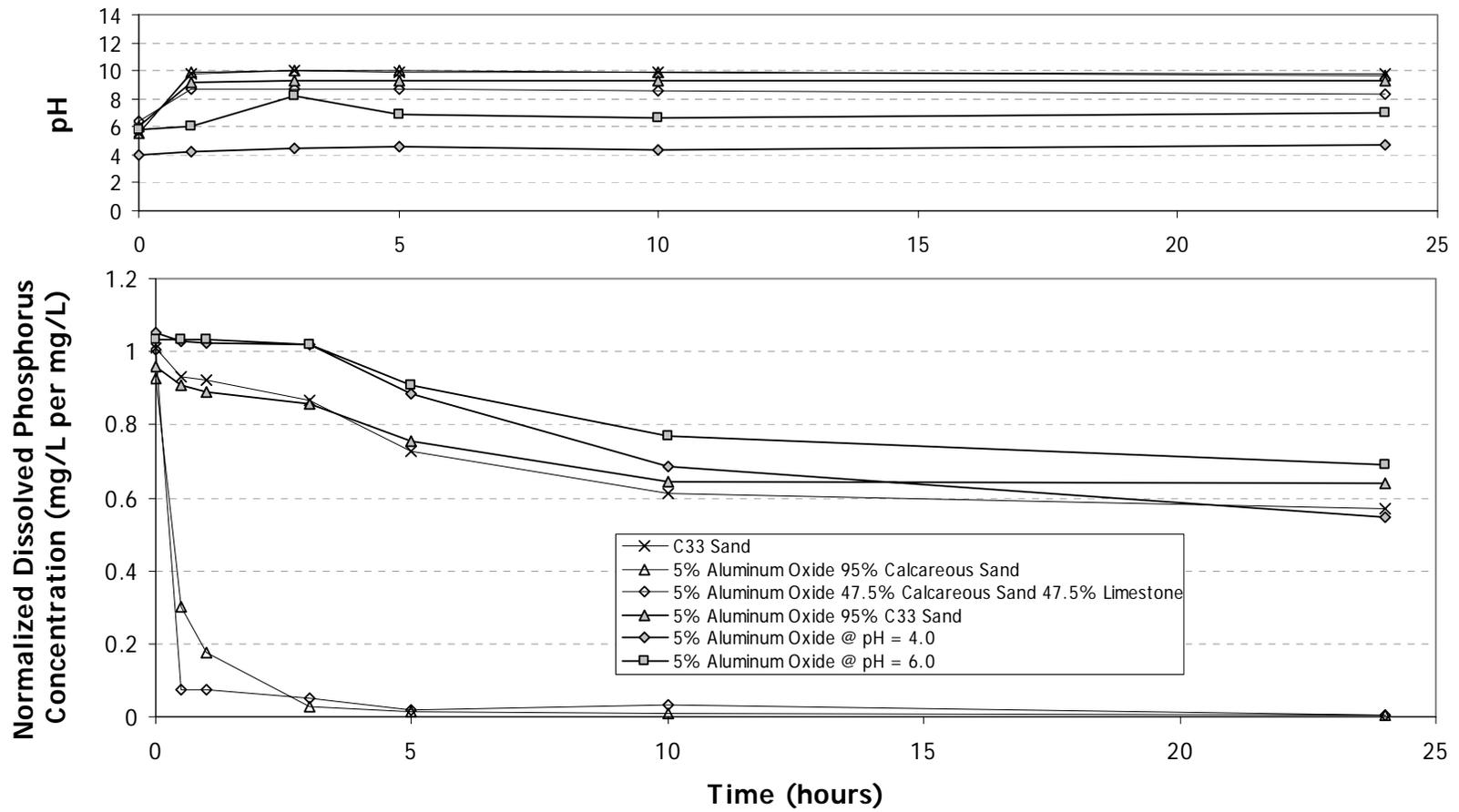


Figure 5: Phosphorus removal by Aluminum Oxide with Calcareous Sand/Limestone. 5% = 0.75 g in weight.

Addition of steel wool to C 33 sand increased phosphorus removal efficiency as compared to C 33 sand alone given enough time (~50% for 5% steel wool after 5 hours, ~90% after 24 hours), as shown in figure 6 (versus ~30% removal after 5 hours and ~45% removal after 24 hours for C 33 sand). Figure 6 also illustrates that steel wool exhibits better phosphorus removal capabilities than aluminum oxide and that as steel wool mass increases, overall dissolved phosphorus removal increases. Based on these facts, no further investigation of aluminum oxide was deemed warranted.

Steel wool and aluminum oxide mixes both increased pH to between 9.1 and 9.5 and figure 7 shows that steel wool mixed with calcareous sand with or without limestone increases pH to between 8 and 10. These results are consistent with other C 33 sand, calcareous sand, and limestone mixes. The lack of significant $FePO_4$ precipitation between pH = 8 and pH = 10 (see figure 1) and the slower rate of phosphorus removal indicates that adsorption to oxidized iron is the primary source of additional dissolved phosphorus removal by steel wool.

The consistent increase in removal efficiency with time can be explained by the visual oxidation observed during these batch studies, although quantifying the extent and rate at which oxidation of the iron occurred was not possible during the experiments. Knowing the extent at which the iron is rusted at any given point in time could be used to estimate a 'capacity' for adsorption of phosphates to the iron oxide and the rate at which the steel rusts could be used to estimate a rate of change in 'capacity.'

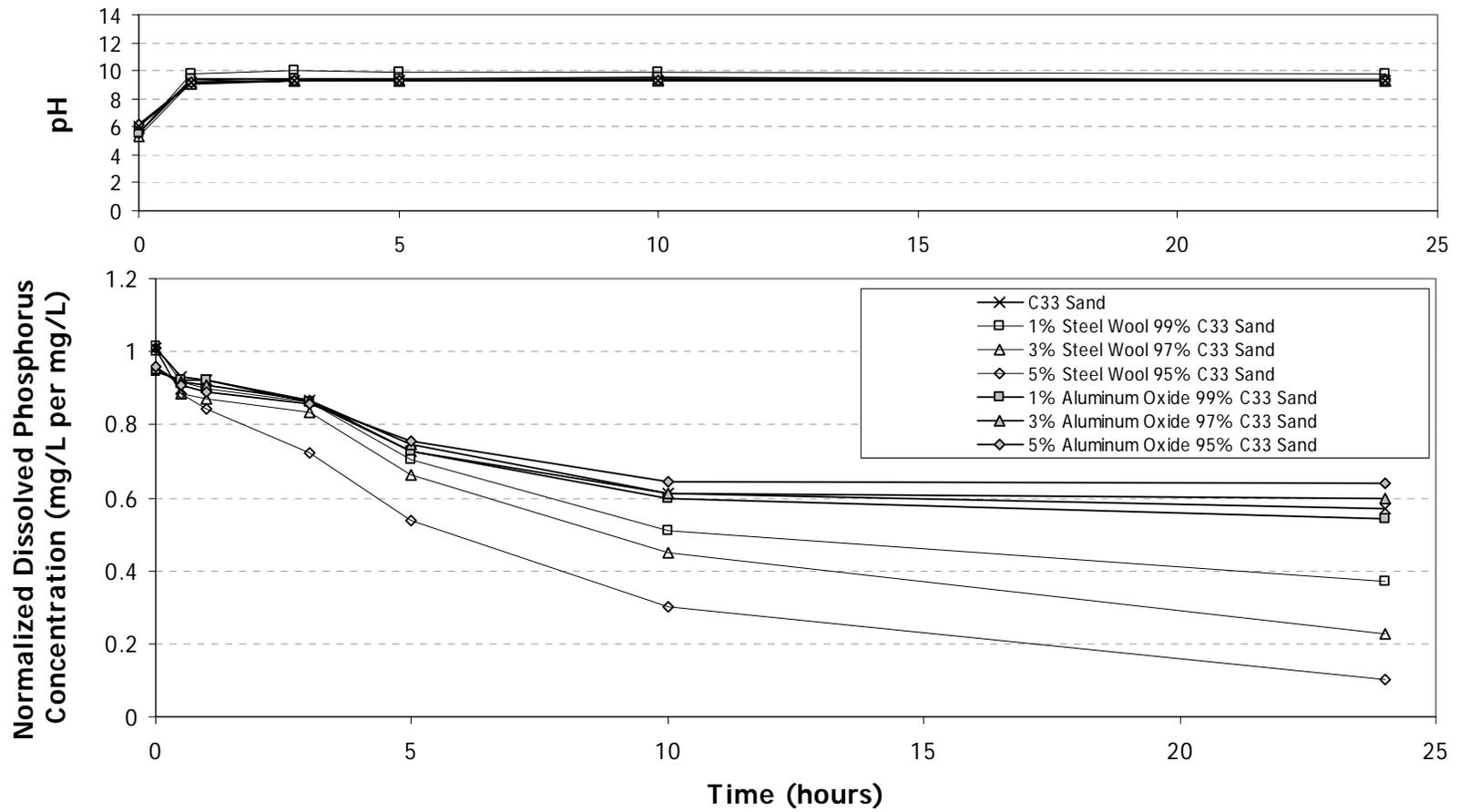


Figure 6: Phosphorus removal by Steel Wool and Aluminum Oxide with C 33 sand.

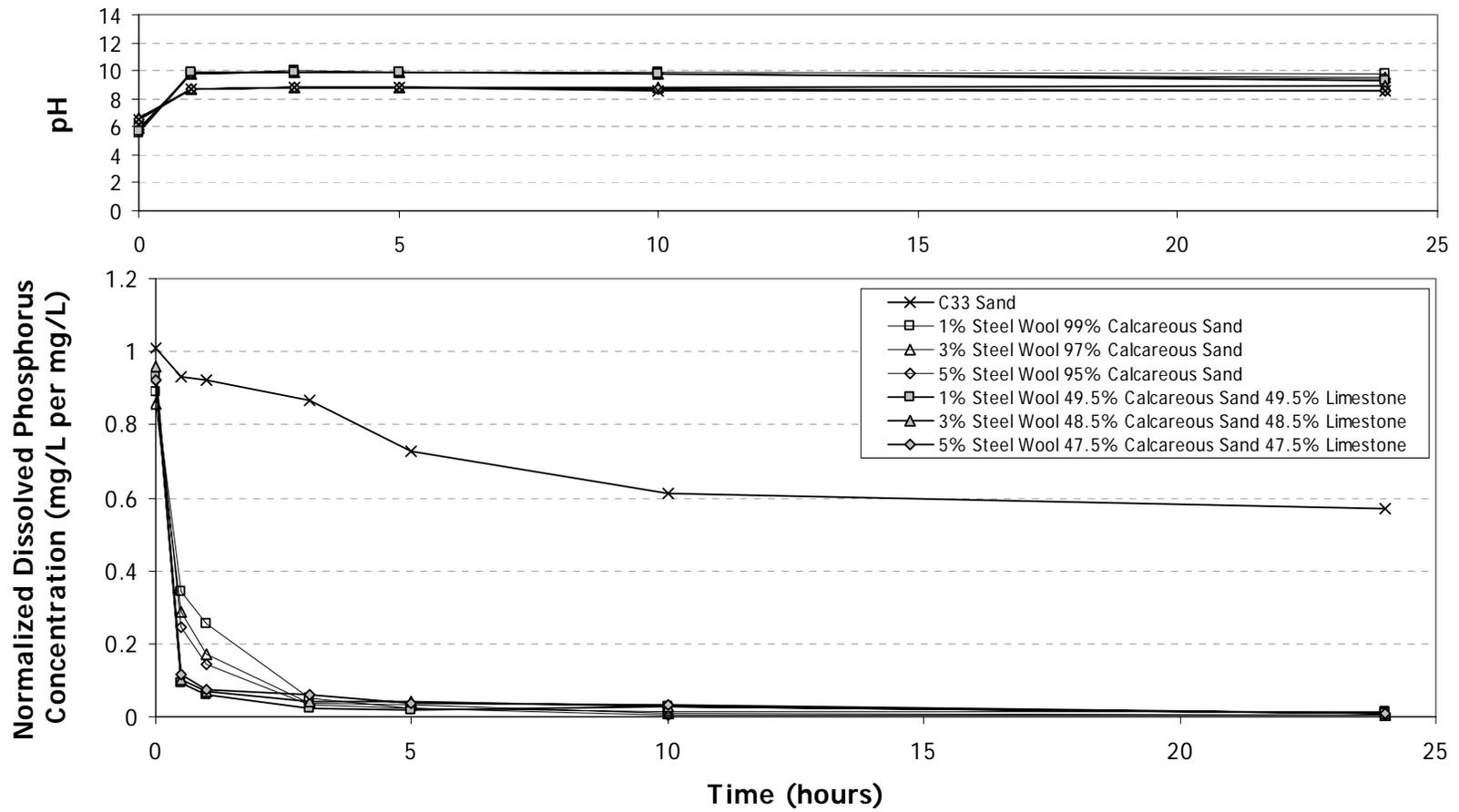


Figure 7: Phosphorus removal by Steel wool with calcareous sand with/without limestone.

Blast Oxygen Furnace (BOF) by-products.

Three by-products from the steel manufacturing process were attained from International Steel Group (ISG, Inc.): BOF slag, BOF dust land filled for ~5 years (labeled “Old BOF Dust”), and more recent BOF dust (labeled “New BOF Dust”). All three products were difficult to handle while dry and tended to cling to all surfaces of contact. In addition, the BOF by-products stained the BOD test bottles used in the batch studies so that a 10% HCl acid bath could not remove the residue from the glass surface.

While it is difficult to visualize effective and safe placement of these products in the field, the BOF by-products were studied in combination with sand and/or limestone to determine their dissolved phosphorus removal capacity and pH modification. The BOF products removed 90 – 100% of the dissolved phosphorus (see figure 8) throughout a range of pH values ($2 < \text{pH} < 12$) but also caused a significant increase in pH to the effluent from an average initial value of 5.6 to between 10 and 12. BOF products at 1 mg/L concentration can generate a pH increase from an initial 2.0 to 11.5 within 30 minutes of contact and therefore can not feasibly be used as a storm water treatment media in their current state. If these products could be neutralized to eliminate their ability to alkalize the effluent and pelletized to facilitate field placement, they could possibly become a cost effective method to capture a large portion of dissolved phosphorus.

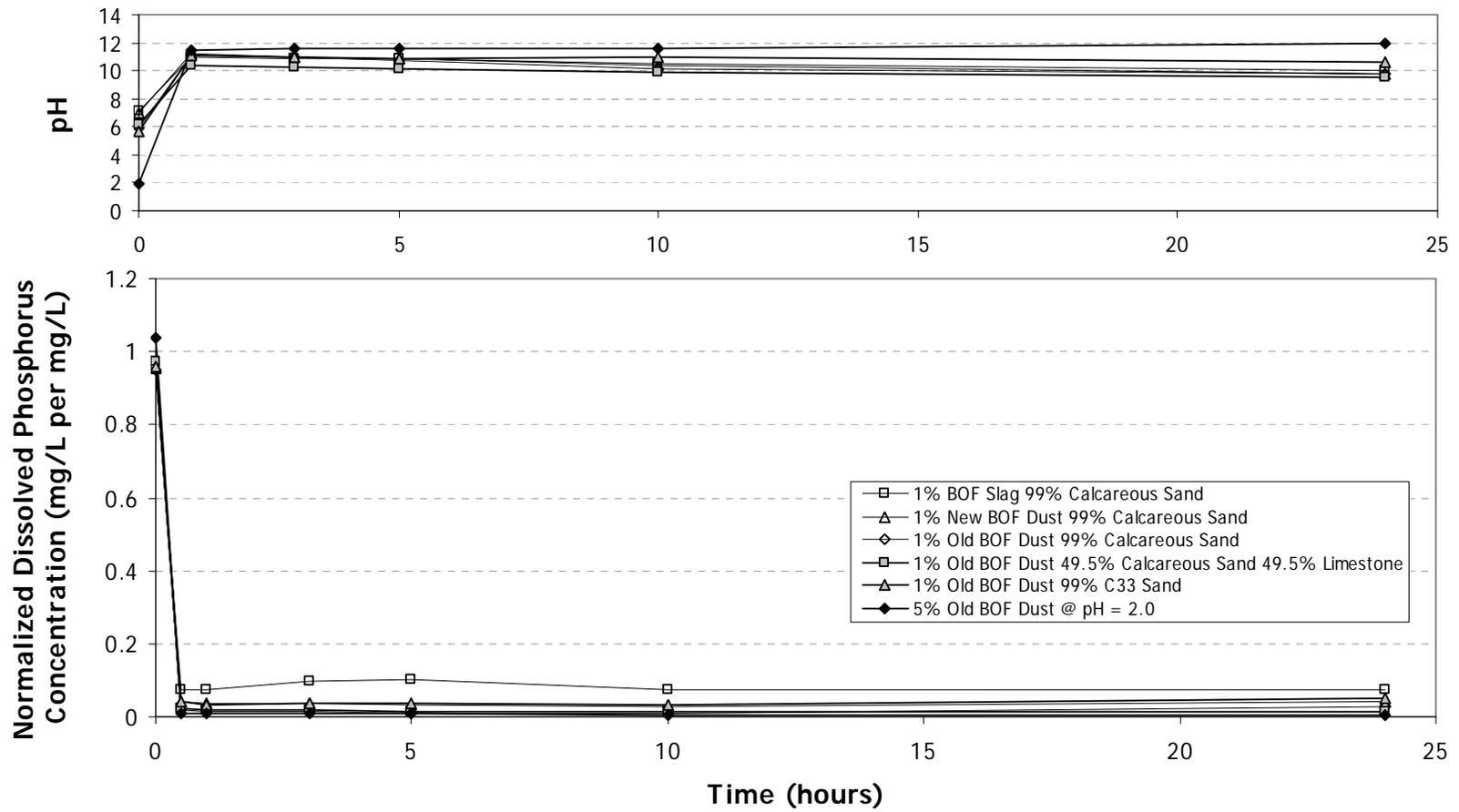


Figure 8: Phosphorus removal by BOF by-products.

CONCLUSIONS

While C 33 sand alone removed some dissolved phosphorus during these batch studies, the steel wool, calcareous sand, and/or limestone enhancements to sand filtration systems for storm water treatment demonstrate potential for significant additional removal of dissolved phosphorus. Calcareous sand and limestone efficiently removed dissolved phosphorus through precipitation during these batch studies but the fine grain size of the media may pose potential difficulties due to clogging of the filter. C 33, calcareous sand, and limestone all increased pH in the 0.15 L solution to levels that exceed standards recommended by U.S. EPA. (2002), but the small volume of phosphate solution utilized in the batch studies may not truly indicate the pH effect in a field sand filtration application.

While aluminum oxide alone removed phosphorus, 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 or C 33 sand enhanced with aluminum oxide. The results of these batch studies also show that 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%. O'Leary (2003) reports that chopped granular steel wool has been used in sand filter applications in which it was mixed uniformly throughout the top 15 to 30 cm of sand. In this configuration, the filter experienced difficulties with clumping of the steel wool, subsequent clogging by the migration of the steel wool particles, and the development of *Gallionella Ferruginea* bacteria. BOF by-products by far remove the most phosphorus in

the shortest amount of time but their ability to alkalize the effluent and tendency to cling to contact surfaces prohibits their current use for storm water treatment.

Since batch studies do not accurately simulate flow rate and contact conditions as experienced in a field application, column studies or other scaled laboratory experiments are required to determine the ability of these enhancers to remove phosphorus in storm water filtration applications and to determine their longevity and impact on filter clogging and effluent pH. A companion paper by Erickson *et al.* (2005a) will examine combinations of steel wool, calcareous sand, and/or limestone with C 33 sand in column experiments to determine the best enhancement media to remove dissolved phosphorus with sand filtration.

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Chapter 2: Enhanced Sand Filtration for Storm Water Phosphorus Removal

by A.J. Erickson³, P.T. Weiss⁴, and J.S. Gulliver¹

ABSTRACT

Column studies were performed on four enhancements to sand filtration treatment systems for storm water runoff: combinations of C 33 sand enhanced with calcareous sand, limestone, chopped granular steel wool, or steel wool fabric. Synthetic storm water runoff with a variable dissolved phosphorus concentration passed through the columns while the flow rate was monitored and effluent samples were tested for total and/or dissolved phosphorus concentration and pH. Our conclusions are: (1) C 33 removed dissolved phosphorus but its capacity was quickly exhausted; (2) Combinations of C 33 sand with limestone or calcareous sand clogged the columns and prevented them from draining completely; (3) Steel wool significantly increased duration and level of phosphorus removal as compared to C 33 sand alone; (4) Phosphorus removal by steel wool adsorption/precipitation did not clog the columns; (5) Enhancing sand filtration systems with steel wool fabric would minimally increase installation costs and would increase the material cost by 3-5%; (6) Fine oxidized iron particles from the steel wool observed in the effluent are too small to be captured by typical geotextile fabric or settle out in receiving lakes or rivers; (7) Phosphorus attached to oxidized iron particles in the effluent is relative to phosphorus removed from the influent during a previous time; and (8) Steel enhanced sand filtration can be modeled with contact time, total mass of

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phosphorus removed, and influent concentration as variables. Based on these findings, steel enhanced sand filtration is a potentially cost effective treatment solution for dissolved phosphorus removal from storm water runoff.

INTRODUCTION

To meet new storm water effluent regulations while avoiding the high construction and operation costs of a storm water treatment facility or mechanical treatment process, new technologies must be developed to remove dissolved phosphorus from storm water runoff. Current storm water management options such as sand filtration, constructed wetlands, wet detention basins, and bioretention filters are used for the quality control of storm water runoff, but these practices either rely on vegetation and/or soil uptake as the primary removal mechanisms for dissolved phosphorus, or have very little potential to remove dissolved phosphorus. In addition, these processes are unpredictable and difficult to control. This paper proposes a new, potentially cost effective technology built upon the framework of sand filtration to remove dissolved phosphorus for storm water runoff.

The principle of sand filtration is simple. Storm water is collected and delivered to the sand filtration system where it seeps through the sand that physically sieves any particulates larger than the soil pore size within the first few centimeters. For sand filter design, Claytor and Schueler (1996) propose, from the surface down, ~ 46 cm of sand (often specified as 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. The geotextile fabric provides a barrier which prevents the sand from washing through to the gravel sub-base and the perforated pipe collection system collects the

treated storm water and delivers it to further storm water treatment practices or directly to receiving waters. Based on this design, the only significant mechanism to remove contaminants from storm water runoff is physical sieving and any dissolved or particulate contaminants, including phosphorus, smaller than the pore size of the sand may pass through the filter and potentially be delivered to receiving waters.

Dissolved phosphorus can be a large percentage of the total phosphorus concentration. For example, data on total and dissolved phosphorus used by Brezonik and Stadelmann (2002), were further analyzed to develop a statistical distribution for the dissolved phosphorus fraction (of total phosphorus) for the Twin Cities Metropolitan Area (Minneapolis and St. Paul, MN), as shown in figure 9.

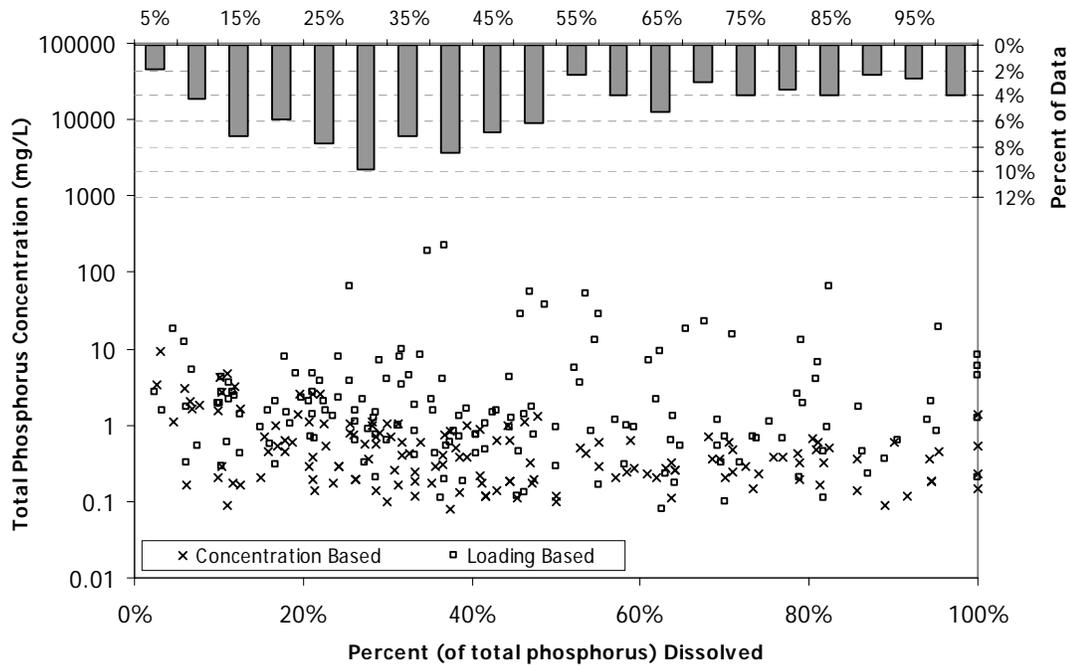


Figure 9: Dissolved phosphorus fraction for Minneapolis and St. Paul, MN metropolitan area. Concentration based mean = 43%, n = 147; loading based mean = 44%, n = 160; all data mean = 44%, n = 307

The Water Environment Federation in conjunction with the American Society of Civil Engineers (W.E.F. and A.S.C.E. (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 (citing U.S. EPA (1983)) which corresponds to roughly 36% dissolved phosphorus. The distribution shown in figure 9 indicates that dissolved phosphorus fractions range from 0 to 100% (mean = 44%, std. dev. = 26%, n = 307). The terms “Concentration Based” and “Loading Based” refer to the calculation methodology for removal data collected by Brezonik and Stadelmann (2002). It is evident from this data that ‘mean’ dissolved phosphorus fraction may not accurately represent the phase in which phosphorus occurs at any given site during a given storm event. Therefore, sand filtration would benefit from enhancements to remove dissolved phosphorus that would not reduce its effectiveness to remove particulate matter.

PREVIOUS WORK

Harper and Herr (1993) performed pilot scale and full scale monitoring studies in Florida for the removal of several storm water contaminants. Through these studies, they found that typical sand filters can remove approximately 40-50% particulate and total phosphorus, but at most only five percent dissolved phosphorus. In addition, silica sand filter exhibited better results for total and dissolved phosphorus (55 and 35% respectively) but contributed particulate phosphorus to the effluent. Harper and Herr (1993) state that the silica sand is considerably coarser than the sand media used in their other experiments, which would allow fine particles to travel through the media.

Contributions of particulate phosphorus in this case may be due to precipitation of dissolved phosphorus with constituents in the sand that then were passed to the effluent through the large pore size of the coarse silica sand. They also conducted experiments on four types of sod placed on top of a typical sand filter and they report that all but one sod covering contributed dissolved phosphorus to the effluent, and removal rates for particulate or total phosphorus were at most 54%.

The full scale monitoring performed by Harper and Herr (1993) encompassed many water quality and quantity characteristics of their detention with filtration pond. Using mass balance procedures, they report that the pond removed approximately 30-40% ortho-phosphorus, 80% particulate, and 60% total phosphorus over a six-month monitoring period. The basin they monitored incorporated both infiltration and filtration practices, which they term a “wet detention basin.” Due to this configuration, a permanent pool developed allowing for the growth of algae. The authors attribute the high removal rates of ortho-phosphorus to algae uptake in the biomass while particulate phosphorus retention is attributed to the filtration processes.

Herrera Environmental Consultants (1995) conclude from their sand filter column study that their sand filters provided little (0 - 28% total, 0 - 38% dissolved) capacity for phosphorus removal. Anderson *et al.* (1985) monitored more than a dozen intermittent sand filters for the U.S. EPA for several water quality parameters and also found that pure sand filter media provides “only limited removal of phosphorus.”

Enhancements such as peat or compost have been studied for their ability to remove contaminants from storm water runoff. Galli (1990) suggests the use of a peat-sand filter

for urbanized runoff treatment and predicted 70% removal of total phosphorus for peat species that contain minimal, if any, phosphorus content. The U.S. EPA. (1999) monitored a filter built to Galli's design specifications and report that two out of four storm events with outflow contributed total phosphorus (-70%, 26%, -5%, and 17% total phosphorus removal, respectively) and one of four contributed ortho-phosphorus (-474%, 79%, below detection, and >90% removal, respectively). Koerselman *et al.* (1993) report from their study on peat soils that the type of peat used, temperature, water chemistry, and water level all affect nutrient (phosphorus and nitrogen) release. Their results indicate that peat soils release two to three times more nutrients after being frozen for one week; thus peat enhanced sand filtration may release more phosphorus in cold climate areas. Stewart (1992) reports results from leachate tests performed by the University of Washington on leaf compost and mixed yard debris targeted for a "physical and molecular filter". The tests exposed the compost yard debris to a volume of distilled water followed by a volume of artificial storm water. The results (section 3, table 12) show that the leaf compost leached 1.14, 2.05, and 1.66 mg/L of phosphorus into the triplicate distilled water samples and increased the triplicate artificial storm water samples from 0.52 mg $PO_4^{3-} - P$ /L to 1.52, 2.17, and 1.56 mg $PO_4^{3-} - P$ /L, respectively. These studies indicate that peat and compost are not reliable as enhancements of sand filtration for dissolved phosphorus removal, and often add dissolved phosphorus to the effluent.

Baker *et al.* (1997) used long-term dynamic flow for a laboratory column study on a "mixture containing 50 wt% silica sand, 45 wt% crushed limestone, and 5 wt% metal

oxide” to investigate the removal of phosphorus from wastewater disposal systems with permeable reactive curtains. The alkaline metal oxide (BOF oxide) used comes from steel manufacturing processes that produce by-products from a blast oxygen furnace. Using an influent concentration of 3.30 mg $PO_4^{3-} - P$ /L over the course of 3.6 years, or the equivalent of 1250 pore volumes, Baker *et al.* (1997) report an average effluent concentration of 0.27 mg $PO_4^{3-} - P$ /L, which corresponds to greater than 90% removal.

Baker *et al.* (1997) also conducted pilot scale and *in situ* experiments of their reactive mixture. The pilot scale experiments (133 days, or ~ 101 pore volumes) at a municipal wastewater treatment facility and the *in situ* experiments (779 days) in a “well-characterized septic system plume” reinforced findings of their laboratory column study. The pilot scale experiment reduced phosphorus concentrations from an average of 3.93 mg $PO_4^{3-} - P$ /L (2.50 mg/L ortho-P) to 0.14 mg $PO_4^{3-} - P$ /L (0.05 mg/L ortho-P) and the *in situ* experiments similarly reduced plume concentrations from 2-3 mg/L to an average effluent of 0.19 mg $PO_4^{3-} - P$ /L. They neglected to monitor or report the pH conditions of the effluent in any of the three experiments conducted on the steel manufacturing by-products. As shown in Erickson *et al.* (2005b), steel manufacturing by-products can significantly increase the pH with only 1% metal oxide (by weight) in 30 minutes or less, which excludes them as viable enhancements to storm water treatment applications in their current state.

Baker *et al.* (1998) later reported additional results from the same column study mentioned above (4 years, or ~ 1450 pore volumes), batch studies, and a second column

study containing 50 wt % silica sand, 40 wt % limestone, and 10 wt % activated aluminum oxide over a two year period (~413 pore volumes). The silica sand/limestone/BOF oxide column operated at an average column velocity of 24.9 ± 6.3 cm/day (20 cm long, 6.35 cm diameter column) corresponding to an average contact time of 21.6 ± 4.8 hours. Over the four year test period (1450 pore volumes) the column reduced phosphorus concentrations from 3.31 ± 0.09 to 0.27 ± 0.20 mg $PO_4^{3-} - P$ /L and initially modified pH from 5.3-5.6 in the influent to 9.8, which eventually dropped to 8.5-9.3 by the end of the experiment. The silica sand/limestone/aluminum oxide column study had an average column velocity of 9.0 ± 0.5 cm/day corresponding to an average contact time of 40.8 ± 2.4 hours. Over the two year test period (413 pore volumes) the column reduced phosphorus concentrations from 3.31 ± 0.09 mg $PO_4^{3-} - P$ /L to (or below) detection limits (0.01 mg $PO_4^{3-} - P$ /L) and modified pH from 5.3-5.6 in the influent to 7.6 initially, and then increased pH to approximately 9.0 by the end of the experiment. While their experiments provide background for the utilization of these materials to remove dissolved phosphorus, the mixtures they propose will likely not be cost-effective for storm water treatment because of vastly different inflow concentrations and flow rate.

The reactive curtains designed by Baker *et al.* (1998) treat groundwater plumes as they flow down gradient from leaking underground wastewater disposal systems. Ground water flow velocities (column one = 24.9 ± 6.3 cm/day, column two = 9.0 ± 0.5 cm/day) are substantially lower than recommended storm water sand filter flow rates

(~107 cm/day, Claytor and Schueler (1996)). This difference in flow rate equates to a substantial reduction in contact time between contaminants in the water and the sand filter media, therefore reducing the expected removal efficiency. Baker *et al.* (1998) used an average influent phosphorus concentration of 3.31 ± 0.09 mg $PO_4^{3-} - P$ /L to simulate a subsurface wastewater pollutant plume, where 0.1 to 0.5 mg $PO_4^{3-} - P$ /L dissolved phosphorus is more appropriate for storm water runoff. Thus, the media combinations proposed by Baker *et al.* (1998) may not be cost-effective for storm water treatment because of these differences.

Arias *et al.* (2001) conducted isotherm and column studies on 13 different sands from Denmark for their adsorption capabilities for phosphorus (see discussion of isotherm experiments in Erickson *et al.* (2005b)). They found that the “maximum apparent P-sorption capacities estimated using the Langmuir-isotherm plots did not correspond to or correlate with the actual amount of P removed in the columns.” In fact, nine out of the thirteen sands tested in column studies exhibited P removal capacities between 20% and 160% larger than the capacity predicted by the Langmuir isotherm. Arias *et al.* (2001) conclude that Langmuir isotherm experiments do not accurately estimate capacity for sands due to the number of complex reactions that occur between dissolved phosphorus and the calcium, magnesium, iron, and aluminum that may be present in sands.

In contrast to Baker *et al.* (1997, 1998) and Anderson *et al.* (1985), Arias *et al.* (2001) shows that some forms of sand have the ability to remove phosphorus from water. Even the relatively inactive quartz sand used by Arias *et al.* (2001) had constituents of

iron (1.21 mg Fe/g), calcium (0.6 mg Ca/g), aluminum (0.32 mg Al/g), and magnesium (0.08 mg Mg/g). Arias *et al.* (2001) did not exhaust the phosphorus adsorption capacity for some soils after 12 weeks (loading ~0.2 mg -P/g sand dry weight).

MATERIALS AND EXPERIMENTAL METHODS

Columns were constructed for the testing of sand filtration media and enhancements to remove 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 attached to the bottom of the columns to reduce the outflow diameter from 5.08 cm to 0.635 cm barbed connections. A 568-liter 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 ten vertical columns. Synthetic storm water was mixed with potassium phosphate (KH_2PO_4) and tap water to various dissolved phosphorus concentrations to mimic the variability found in storm water runoff. As one objective of these experiments was to determine to what extent, if any, the removal of dissolved phosphorus affected the hydraulic conductivity of the filter media, synthetic storm water was chosen over 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 was therefore not incorporated into the synthetic storm water. A valve at the base of the

reservoir allowed for samples to be taken and analyzed for pH and phosphorus concentration.

Sand filter media was mixed to a total mass of 1800 grams, 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 (~ one cm in diameter) and calcareous sand, which was similar to C 33 sand but had more fines and significantly more moisture content, was obtained from a local quarry. In experiments with steel wool, the steel wool was placed above the filter fabric and below the C 33 sand. O'Leary (2003) reported difficulties with steel wool clumping and development of *Gallionella Ferruginea* bacteria in a sand filter with chopped granular steel wool roto-tilled into the top 15 to 30 cm of sand. The setup used in this study proposes that the steel wool be placed in a layer beneath the 46 cm of sand and above the filter fabric and gravel subbase. This setup eliminates the possibility of steel wool migration as documented by O'Leary (2003) and any development of *Gallionella Ferruginea* bacteria that may form within the steel wool layer is covered by 46 cm of sand, which eliminates physical contact with the bacteria from the surface.

Four types of filter fabric were used for these experiments; a generic fabric used and specified by Morgan *et al.* (1998), a 150 micron mesh and a 200 micron mesh as specified by 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 five mm in length) and steel wool fabric. Table 6 lists the 10 columns and the designators used to describe them throughout this paper.

Table 6: Column mixes, filter fabrics, and designators with a letter indicating the column and 1 or 2 indicating first or second experiment

Column	Mix	Filter Fabric
T	Reservoir tank	N/A
A1	50% limestone with C 33 sand	Generic
B1	30% limestone with C 33 sand	Generic
C1	10% limestone with C 33 sand	Generic
D1	50% calcareous sand with C 33 sand	Generic
E1	30% calcareous sand with C 33 sand	Generic
F1	10% calcareous sand with C 33 sand	Generic
A2	5% by weight steel wool with C 33 sand	Generic
B2	5% by weight steel wool with C 33 sand	150 micron
C2	5% by weight steel wool with C 33 sand	200 micron
D2	2% by weight steel wool with C 33 sand	Generic
E2	2% by weight steel wool with C 33 sand	150 micron
F2	2% by weight steel wool with C 33 sand	200 micron
G	Steel wool fabric (0.29% by wt.) with C 33 sand	Generic
H	Steel wool fabric (0.31% by wt.) with C 33 sand	150 micron
I	Steel wool fabric (0.31% by wt.) with C 33 sand	200 micron
J	Pure C 33 sand	180 N

Holes were drilled in a PVC disk that had a diameter slightly less than the inside diameter of the columns. PVC supports, approximately 3 cm in height, were constructed to support the disk, approximately 10 cm of gravel sub-base in the bottom of the columns, a layer of filter fabric, and the filter media. Taps were installed 102 cm 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 240 cm above the bottom of the columns to ensure the water depth did not exceed 183 cm above the surface of the media. 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. Influent samples were taken periodically to ensure adequate mixing had taken place in the reservoir.

Analytical Methods

Samples were analyzed for total phosphorus according to standard methods section 4500-P B.5 (Potassium Persulfate Digestion) and dissolved phosphorus according to E (Ascorbic Acid) in A.P.H.A. *et al.* (1998) with a minimum detection limit of 10 µg P/L. Some samples were also analyzed by Research Analytical Lab at the University of Minnesota (<http://ral.coafes.umn.edu/>) for verification of our analysis procedure. The Research Analytical Lab (RAL) uses a rapid flow analyzer system with potassium sulfate and mercuric sulfate digestion (mercuric) for total phosphorus analysis as described by the RFA Methodology (1986). pH readings were measured using a pH meter that was calibrated to pH = 4, 7, and 10 standards.

As recommended by A.P.H.A. *et al.* (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 for the synthetic storm water samples that would be collected during the column experiments. Volumes of distilled water with a known mass of total phosphorus were mixed and sampled for initial concentration confirmation; then the experimental media was added and allowed to mix for 24 hours. 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 to these samples, actual storm water samples were also analyzed for total and dissolved phosphorus concentration. Duplicate samples from the batch studies and actual storm water samples were sent to RAL for secondary verification. Comparison of RAL's mercuric digestion results and persulfate digestion results indicated that the persulfate digestion was accurate ($\leq 5\%$ error) for natural storm water samples but not as accurate for samples containing steel wool fibers (*i.e.* iron) (mean = 27.8% error). Based on these results, the persulfate digestion was deemed appropriate if all the iron remained in the column and none exited with the effluent.

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 = 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. It was cost-prohibitive to send all the effluent samples to RAL for total phosphorus analysis so further analysis of effluent samples was limited to strictly dissolved phosphorus analysis by the ascorbic acid method with periodic samples sent to RAL for estimation of total phosphorus trends.

RESULTS AND DISCUSSION

As shown in table 6, various combinations of C 33 sand and limestone or calcareous sand were examined. Initially, these combinations produced hydraulic conductivities of approximately 0.05 cm/sec but when left to drain overnight, these columns retained standing water (greater than five cm above the surface of the media). The results of a fine particle analysis performed by RAL (table 7) indicate that more than 50% of the limestone and roughly 11% of the calcareous sand was clay or silt sized particles.

Table 7: Fine particle analysis for limestone and calcareous sand

	% Sand	% Silt	% Clay
Calcareous Sand	88.8	9.0	2.1
Limestone	45.8	42.0	12.2

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 be the cause of the clogging observed in the columns. These mixtures would not drain within 48 hours and therefore were not tested further. Based on the results found in the batch studies companion paper (Erickson *et al.* (2005b)), steel wool was then examined as a media enhancement.

The batch studies (Erickson *et al.* (2005b)) illustrated that pH effects should be closely monitored during any experiments that utilize these media enhancements. The column experiments, however, show that the steel wool media did not increase the pH of the influent synthetic storm water beyond the range recommended by U.S. EPA. (2002) (figure 10).

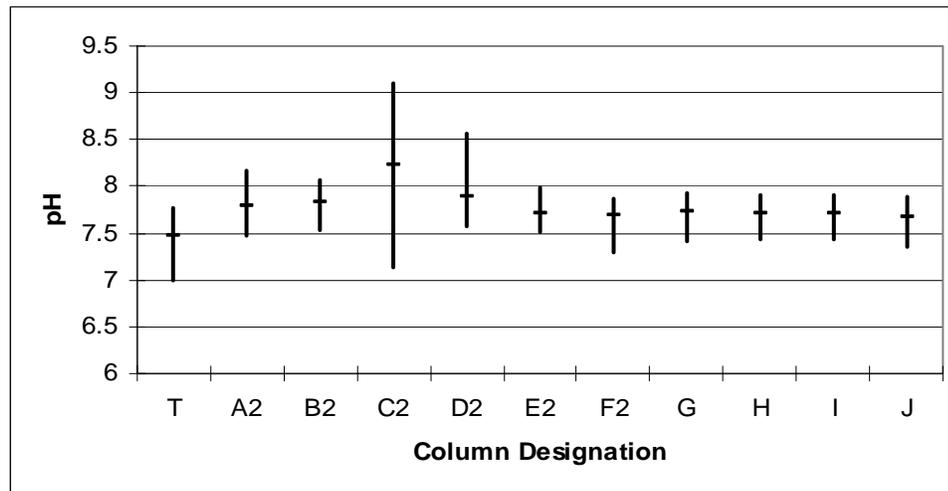


Figure 10: Mean pH \pm 1 standard deviation (n = 22, 23, or 24) of column effluent

The influent synthetic storm water (designated ‘T’) was on average less than 0.5 pH units below the effluent of all but one of the 10 columns, and only 0.76 pH units below the highest column average. The standard deviations were roughly 0.1 to 0.5 pH units for all ten columns and the highest pH recorded from any of the ten columns was 9.11 (n = 255). The results from these experiments show that the mean pH levels did not exceed the maximum levels recommended by the U.S. EPA, as outlined in Erickson *et al.* (2005b). Additionally, the pH of the effluent indicates that adsorption to oxidized iron is the predominant phosphorus removal mechanism, as opposed to precipitation by ferric phosphate as described by Stumm and Morgan (1981).

To summarize the experimental results from the steel wool columns studies, table 8 lists the mean hydraulic conductivity, mean contact time with steel, the total mass of phosphorus removed at the conclusion of the experiments, and the mass removed as a percent of the influent.

Table 8: Mean hydraulic conductivity and contact time, total mass removed (total and dissolved phosphorus) and mean percent removal of columns

Column	Mean hydraulic conductivity (cm/sec)	Mean contact time with steel (sec)	Mass of phosphorus removed (mg)	Percent removed by mass
A2	0.034	78	57.4	35.3%
B2	0.029	84	73.5	42.4%
C2	0.030	233	66.5	54.5%
D2	0.0084	148	29.9	80.7%
E2	0.012	88	33.1	60.6%
F2	0.015	64	36	51.2%
G	0.012	55	21.1	44.7%
H	0.014	49	18.3	34.0%
I	0.012	53	16.7	33.9%
J	0.012	1652*	2.4	1.6%

*Contact time with sand

The composition of chopped granular steel wool does not contain fine particles like calcareous sand or limestone so steel wool enhanced filters should not encounter the same clogging problems. Claytor and Schueler (1996) recommend a design hydraulic conductivity for sand filtration system of approximately 1.1 m/day (0.0013 cm/sec). As shown in figure 11, the mean hydraulic conductivity for the pure C 33 sand column was roughly 0.012 cm/sec, which is roughly an order of magnitude larger than the recommended values. Table 8 summarizes the mean hydraulic conductivities for the columns with steel wool enhancements, which shows that all columns had hydraulic conductivities higher than that recommended for design and all, with the exception of column D2, were higher than the mean hydraulic conductivity found in the pure sand column (J). This shows that steel enhanced columns did not significantly clog due to dissolved phosphorus removal as compared to pure sand filtration.

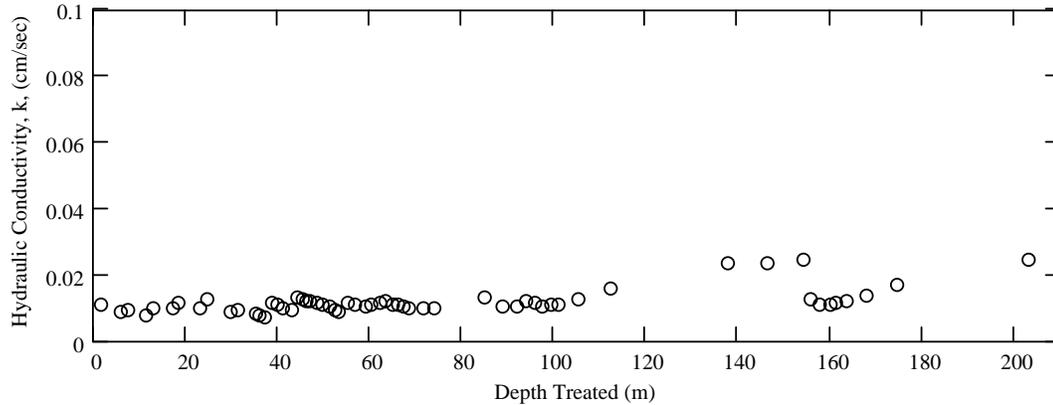


Figure 11: Hydraulic conductivity for pure C 33 sand: column J

Figure 11 gives the hydraulic conductivity of pure sand. The ordinate is hydraulic conductivity, k , as computed according to Darcy's Law. The abscissa in figure 11 is treated depth (m), which is calculated by the integration with respect to time of the flow rate divided by the cross-sectional area a column (20.3 cm^2). Treated depth for a field sand filter (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 upon these variables. Dividing the estimated runoff volume by the sand filter surface area gives an estimated storm water depth treated (treated depth) for that storm event. A cumulative sum of storm event treated depths can then be used to estimate the annual treated depth.

For example, given a 4 hectare watershed with 50% impervious cover and 2.5 cm rainfall depth, the runoff volume as estimated by Claytor and Schueler (1996) is $\approx 500 \text{ m}^3$. Assuming a 230 m^2 sand filter is used for this watershed, the treated depth would be $(500 \text{ m}^3 / 230 \text{ m}^2) \approx 2.2 \text{ m}$ 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 m to nearly 220 m.

The primary objective of this research is to determine the effect of enhancements upon the ability of sand filtration to remove dissolved phosphorus. In order to determine that effect, a 'blank' column with only C 33 sand was constructed and tested for its effectiveness to remove dissolved phosphorus (column J). Figure 12, which shows sum of phosphorus mass removed versus treated depth for columns B2 and J, illustrates how C 33 sand used in this study has some capacity to remove dissolved phosphorus, but that capacity was exhausted within approximately 70 meters of treated depth after which no positive removal was observed. The capacity for dissolved phosphorus removal in the steel wool enhanced column (B2), as shown in figure 12, continues to increase throughout the experiments and is 35 times larger than the capacity found in the C 33 sand column upon completion of the experiment. This illustrates that steel wool enhanced sand filtration can increase the duration and capacity for dissolved phosphorus removal as compared to C 33 sand alone.

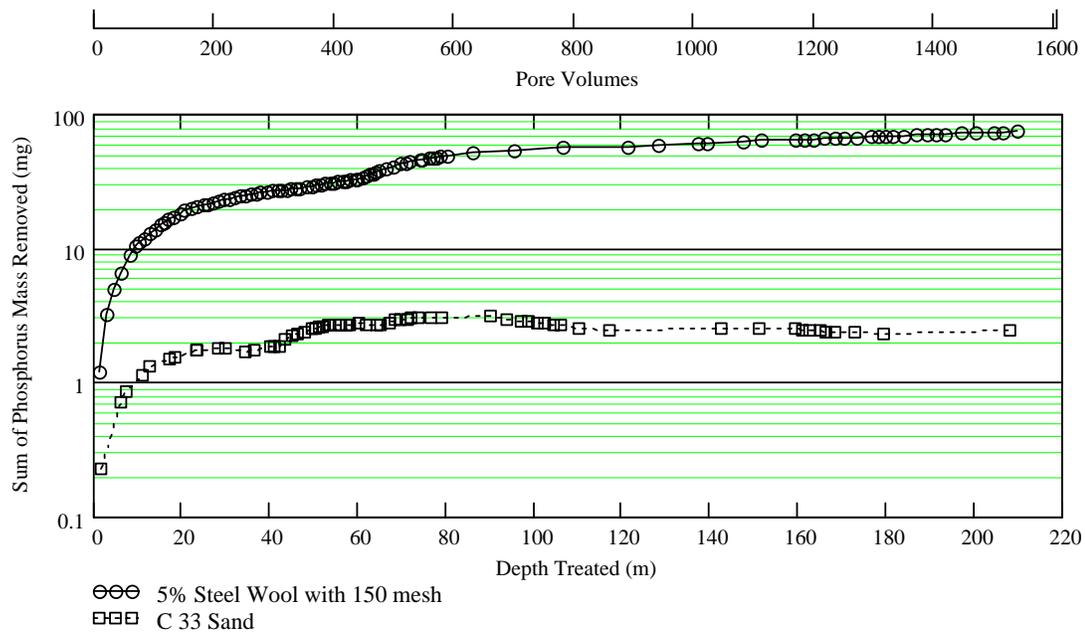


Figure 12: Sum of phosphorus mass removed by C 33 sand (column J) and 5% steel wool enhanced sand (column B2)

Shown on figures 14 through 22 are hydraulic conductivities, mercuric total phosphorus as analyzed by RAL, persulfate total phosphorus, dissolved phosphorus, and the model fit (to be discussed later) for the steel wool columns. Phosphorus fraction removed was calculated by subtracting the effluent concentration (C_{out}) from the influent concentration (C_{in}) and dividing that difference by the influent concentration. Hydraulic conductivity and phosphorus fraction removed are shown in each figure to illustrate the inverse correlation between hydraulic conductivity and phosphorus removal. The correlation between hydraulic conductivity and phosphorus fraction removed is most evident in figure 16; for treated depths greater than 60 meters and less than 110 meters, the phosphorus fraction removed increases as hydraulic conductivity decreases. After approximately 110 meters of treated depth, the hydraulic conductivity begins to increase and the fraction removed significantly decreases. Equilibrium between the iron in the

steel wool and the phosphorus in the water explains this inverse correlation between hydraulic conductivity and phosphorus fraction removed. As hydraulic conductivity decreases, the time that phosphorus in the water is in contact with the iron (i.e. contact time) increases, and therefore approaches closer to equilibrium causing more phosphorus removal.

Figures 14, 15, and 16 show the hydraulic conductivity and phosphorus fraction removed versus treated depth results from the 5% steel wool enhanced sand filter columns. These three columns were the first of the ten columns to begin filtration and suffered initially from incomplete dry consolidation, as shown by the high initial (< 20 m treated depth) hydraulic conductivity. The uncharacteristically high initial hydraulic conductivities coupled with high phosphorus removal prompted investigation into the consolidation conditions in the columns. The first two columns (A2 and B2) were consolidated after approximately 100 and 70 meters of treated depth, to determine if the large hydraulic conductivities could be attributed to unconsolidated filter media. Consolidation had an impact on the flow conditions in the columns, as shown by the respective drop (A2) and jump (B2) in hydraulic conductivity and corresponding changes in phosphorus fraction removed, respectively. Column C2 was not consolidated to allow for observation of unconsolidated conditions.

The consolidation procedure appears to have caused the erratic behavior in the persulfate total phosphorus measurements in column A2 (see figure 14) at 100 meters of treated depth by creating new flow paths through the steel wool which resulted in the spike in phosphorus fraction removed. The columns with 2% steel wool and steel wool

fabric (columns D2 through J, figures 11 and 17 through 22) were dry consolidated prior to exposure with synthetic storm water to simulate field installation techniques. These columns did not exhibit the same trends as columns A2, B2, or C2 in initial hydraulic conductivity. This gives evidence that the anomaly observed during the first 20 meters of treated depth in columns A2, B2, and C2 can be attributed to unknown factors related to the consolidation techniques used during their installation.

As discussed in the analytical methods, discrepancies were observed (early verification) between the mercuric total phosphorus determination as reported by RAL and the persulfate total phosphorus performed for this study. As shown in figures 14 through 22, the only apparent trend or correlation in the discrepancies between mercuric total phosphorus, persulfate total phosphorus, and dissolved phosphorus measurements is that mercuric total phosphorus concentrations are always larger than both persulfate total phosphorus and dissolved phosphorus concentrations. Batch studies performed prior to the column experiments for method verification concluded that persulfate digestion was accurate for effluent samples that do not contain particulate iron, so it was postulated that iron bound phosphates may be present in the effluent. With the aid of a microscope, fine grain oxidized iron particles were observed in the effluent and appeared to be roughly five microns in size. Figure 13 shows a microscopic view of the fine particles found in the effluent.

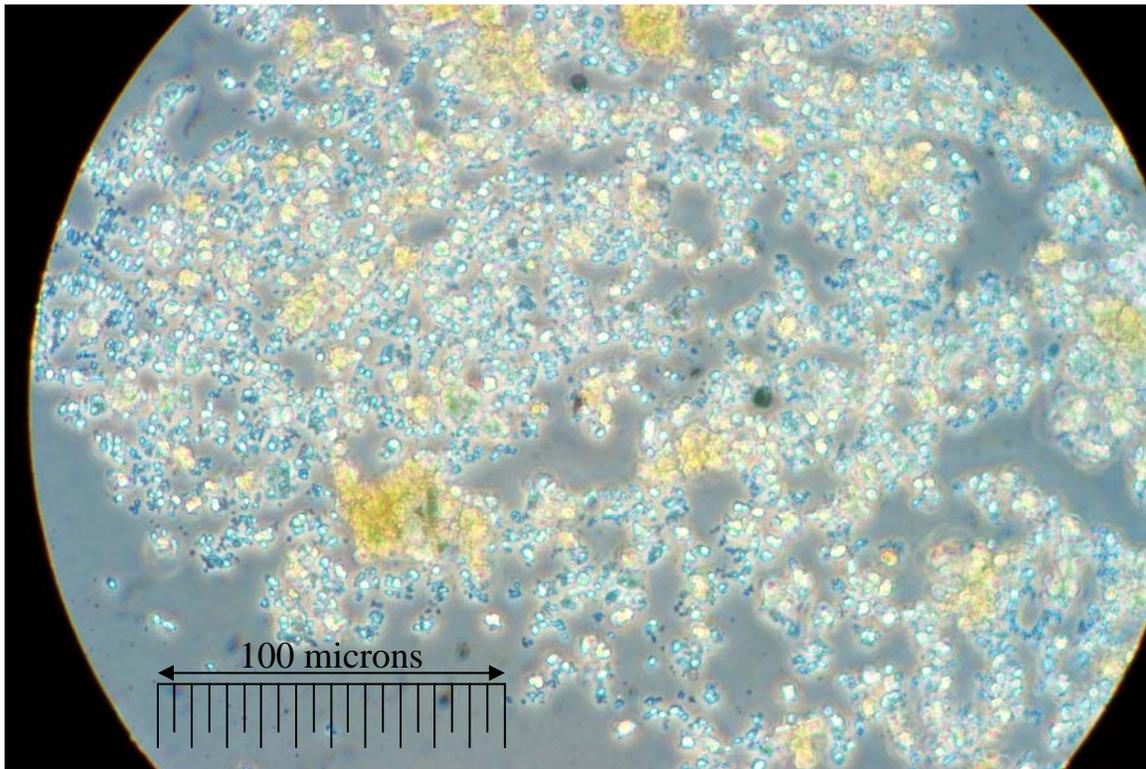


Figure 13: Fine particles of oxidized iron found in effluent from columns

The additional phosphorus released from the columns and measured by mercuric total phosphorus is likely adsorbed and complexed on these small oxidized iron particles. Due to the small size, it would be difficult to capture the particles with conventional geotextile fabric. The release of oxidized iron with adsorbed phosphorus presents a confounding factor to the use of steel wool to remove dissolved phosphorus. Some of the removed phosphorus will eventually be released in this manner as particulate phosphorus.

Reynolds and Davies (2001) discuss the source and bioavailability of particulate and dissolved phosphorus fractions found in fresh waters. They classify iron-bound phosphorus fractions of particulate phosphorus as ‘conditionally’ bioavailable and explain that the 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 these conditions can exist in lake bottom waters, iron oxides can quickly re-oxidize and readily re-sorb phosphorus, making it mostly available to ‘anoxic-tolerant benthic resting cells and propagules” and only “remotely” available to phytoplankton. The fine particles observed in the effluent from the current study would have to settle to the bottom of receiving lake or river for these processes to occur and subsequently release any iron-bound phosphorus.

Gustafsson and Gschwend (1997) discuss observed limits distinguishing between suspended and settling particles in natural waters. They concluded that particle sizes “near 10 microns may be retained at steady state in surface water suspension of large lakes.” As shown in figure 13, the iron oxide particles found in the effluent from the columns are roughly 5 microns in size and would likely remain in suspension in most receiving lakes and rivers. This evidence shows it is unlikely that any phosphorus attached to the fine iron oxide particles would become de-sorbed under normal freshwater conditions.

The phosphorus measurements may therefore be interpreted as follows:

1. The persulfate total phosphorus method was tested against the mercuric 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 small (~5 micron) oxidized iron particles observed in the effluent which were not digested by the persulfate method.
3. With some exceptions (e.g. figures 18 and 20) 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 removal is misleading.
5. The phosphorus attached to oxidized iron is conditionally bioavailable. It should only be considered a nutrient under circumstances particular to the application that meet the bioavailability conditions described above.

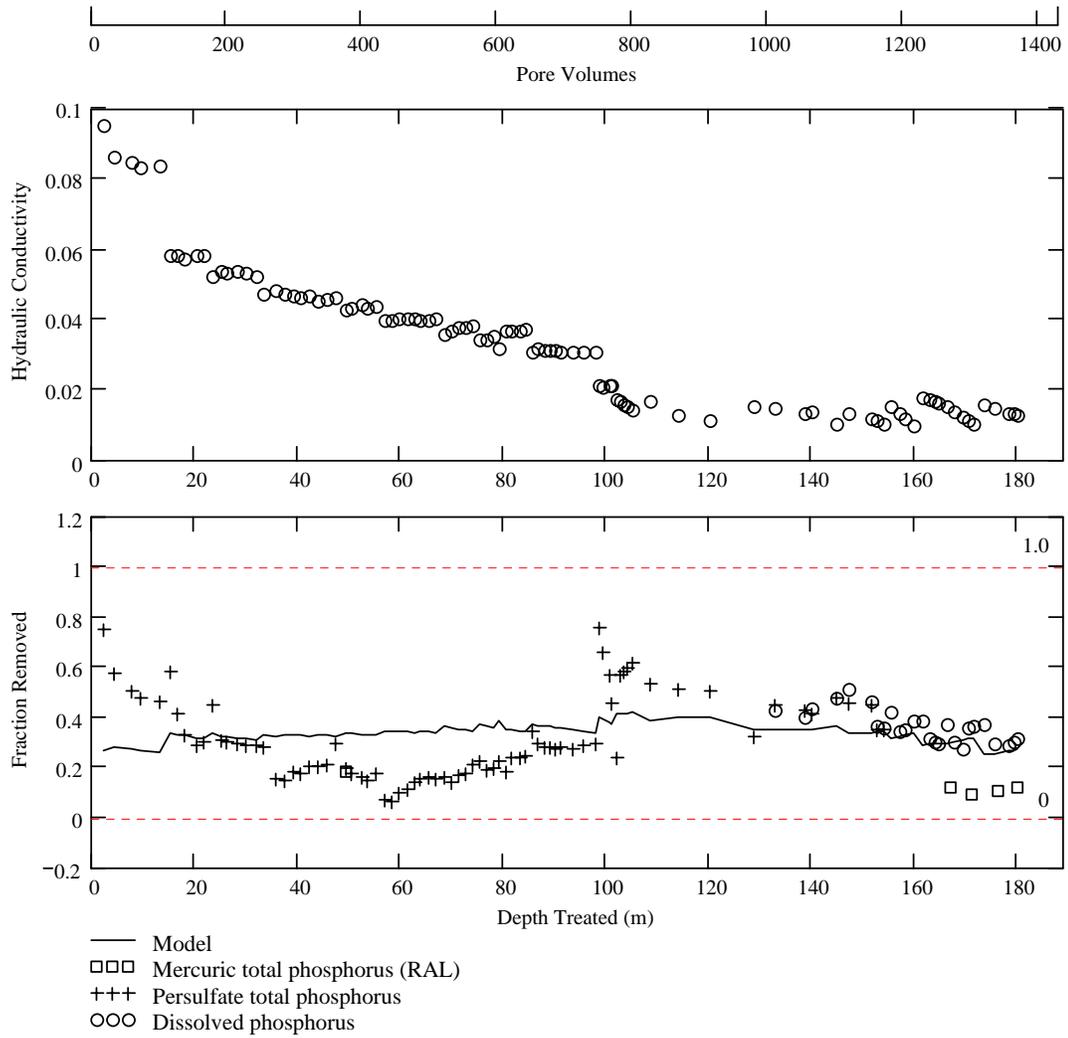


Figure 14: Hydraulic conductivity, phosphorus removal, and model fit: 5% steel wool, column A2

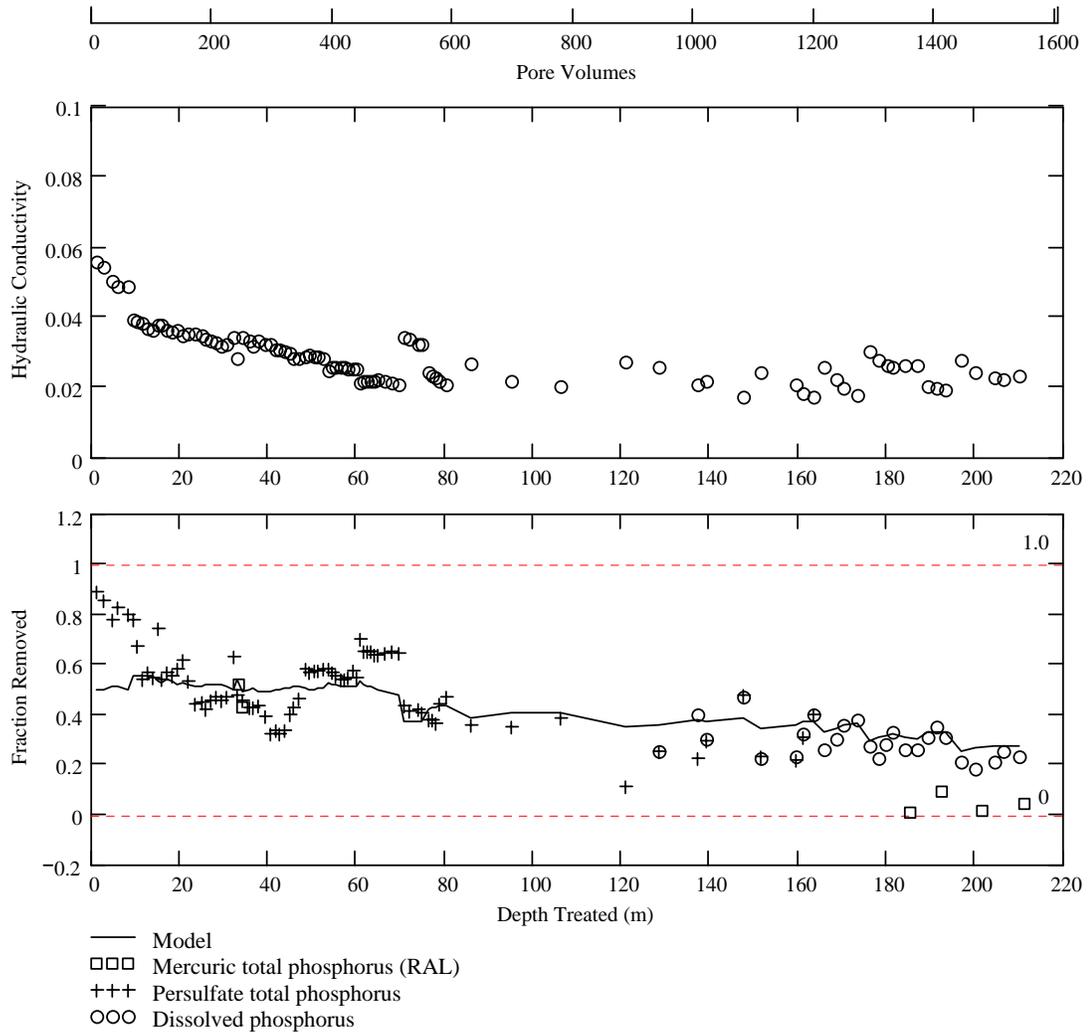


Figure 15: Hydraulic conductivity, phosphorus removal, and model fit: 5% steel wool, column B2

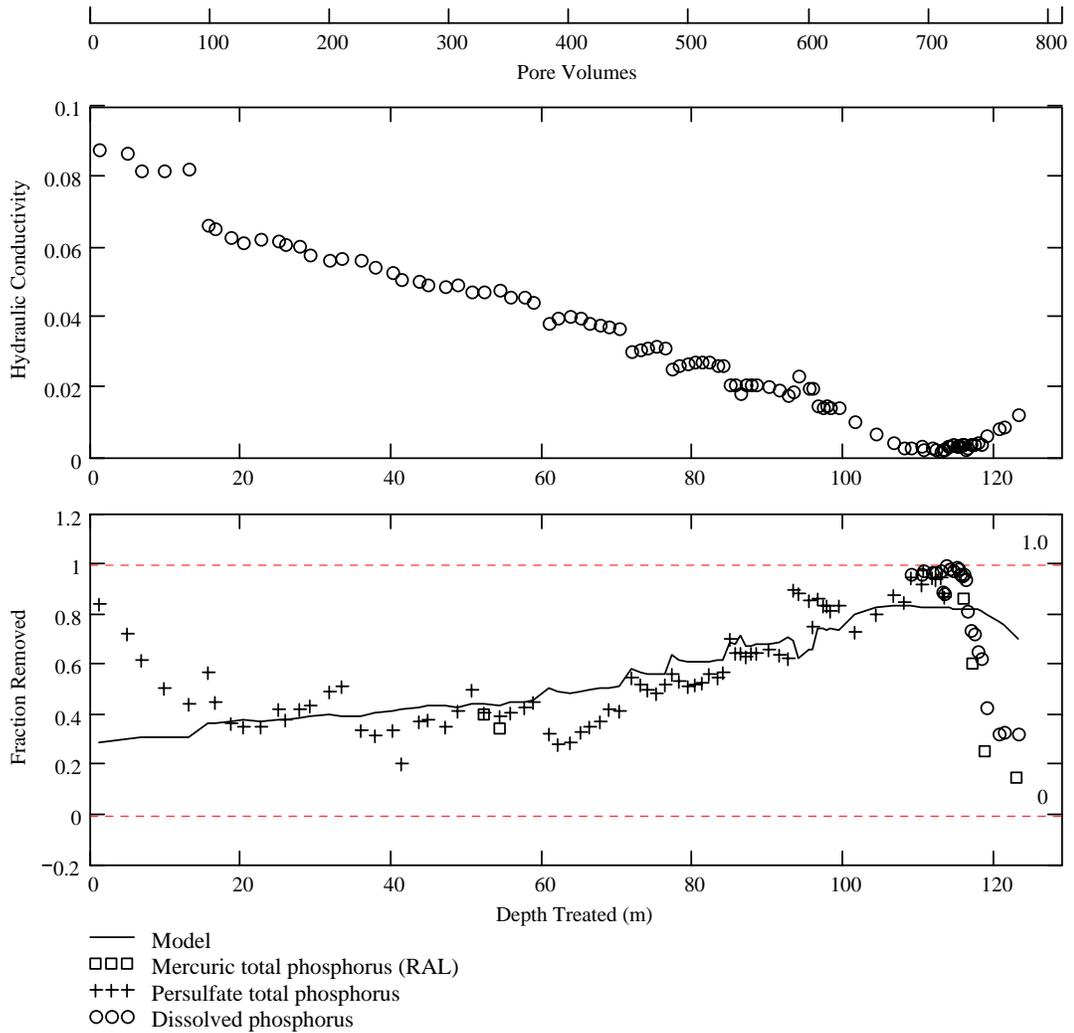


Figure 16: Hydraulic conductivity, phosphorus removal, and model fit: 5% steel wool, column C2

Initial observations of the 2% steel wool columns (D2, E2, and F2; figures 17, 18, and 19) reveal that the hydraulic conductivity is relatively constant throughout all three columns for the extent of the experiments, which indicates that the consolidation techniques used during their installation was successful. In addition, the initial phosphorus fraction removed is very similar (~ 40 to 50%) among all three columns. All increase after approximately 5 meters of treated depth to between approximately 60 and 90% fraction removed. As seen in the 5% steel wool columns (A2, B2, and C2), this

sudden increase in phosphorus fraction removed may be caused by the sudden, if only slight, decrease in hydraulic conductivity.

In addition to the decrease in hydraulic conductivity, the sudden increase in removal may also be explained by the increase in iron oxide sites available for phosphorus adsorption. The hydraulic conductivity and phosphorus removal data shown in figures 14 through 22 is composed of several laboratory-simulated storm events represented by as few as one and as many as 10 data points. The columns were allowed to drain long enough between simulated storm events to remove the specific yield but the moisture that was retained in the columns after the first simulated storm event provided conditions conducive for oxidation of the steel wool layer. The oxidation of iron provided a large increase in phosphorus adsorption capacity, which may be reflected by the approximate 20% increase in phosphorus fraction removed.

After the first 10 to 20 meters of treated depth, the 2% steel wool columns exhibited different patterns in phosphorus fraction removed despite sharing relatively constant hydraulic conductivities. Phosphorus fraction removed increased in column D2, remained approximately the same in column E2, and decreased in column F2, respectively, as treated depth increased beyond 20 meters of treated depth. However, as listed in table 8, an increasing trend in relative hydraulic conductivity is observed in columns D2, E2, and F2, which corresponds to a decreasing trend in overall phosphorus removal from column D2 to E2 to F2.

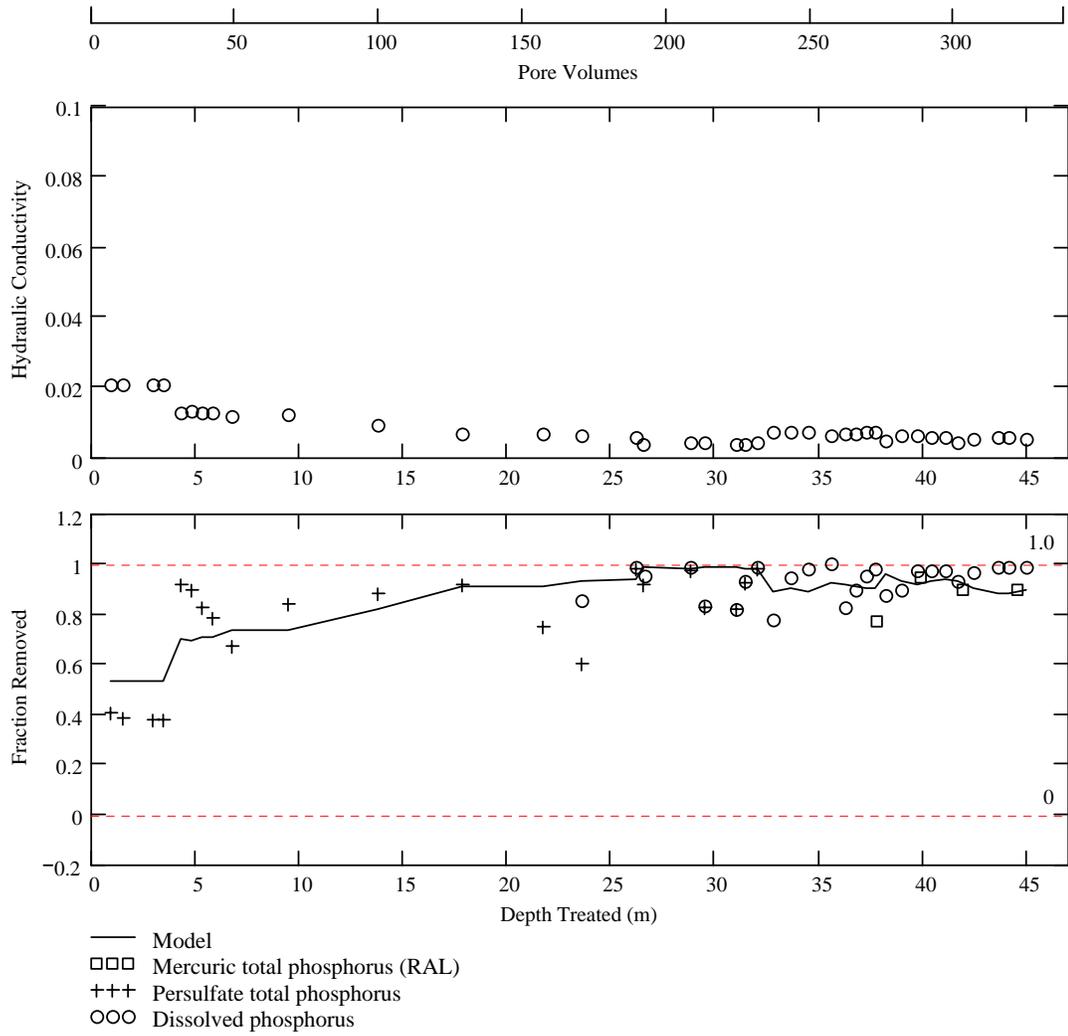


Figure 17: Hydraulic conductivity, phosphorus removal, and model fit: 2% steel wool, column D2

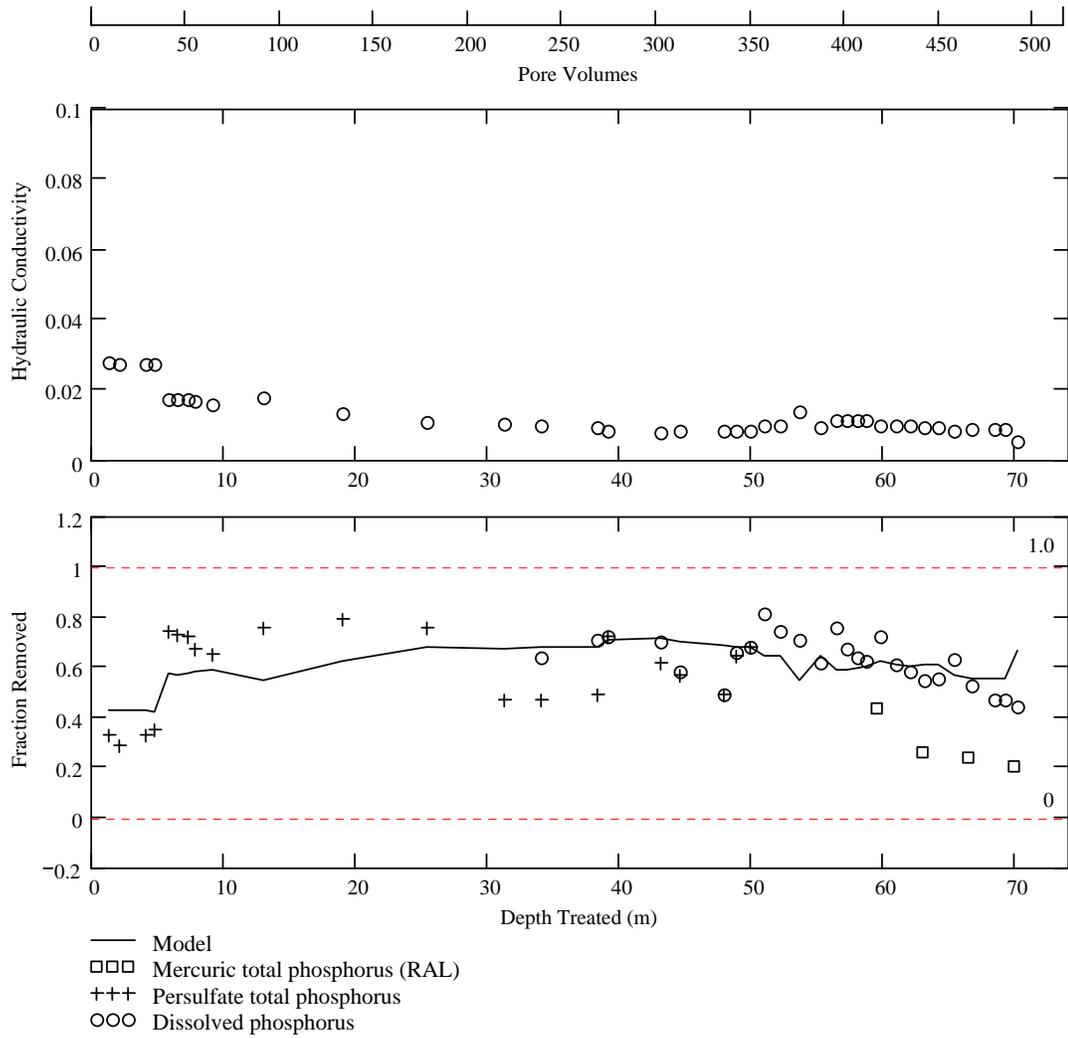


Figure 18: Hydraulic conductivity, phosphorus removal, and model fit: 2% steel wool, column E2

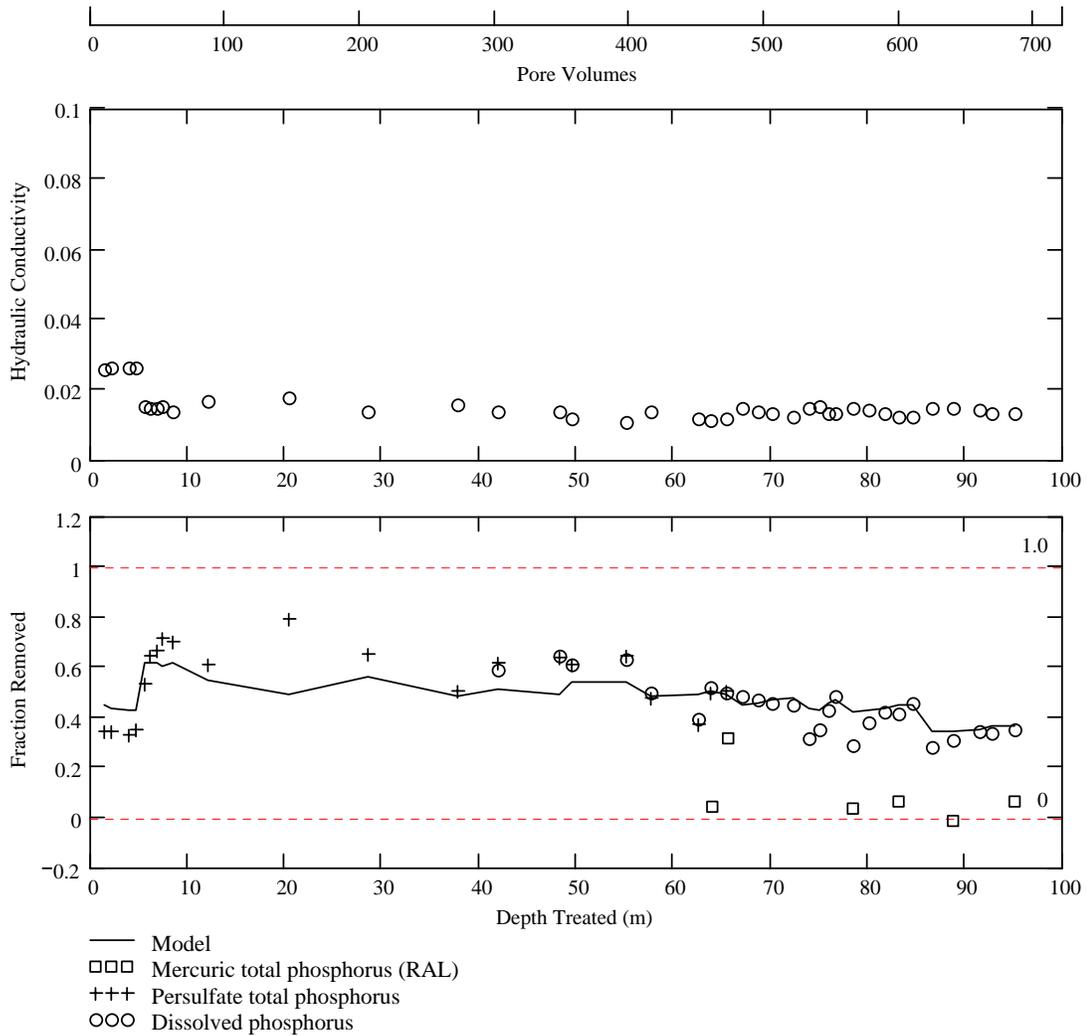


Figure 19: Hydraulic conductivity, phosphorus removal, and model fit: 2% steel wool, column F2

Figures 20, 21, and 22 show evidence of consistent hydraulic conductivities for all three steel wool fabric columns (G, H and I; ~0.3% steel wool by mass). However, columns H and I demonstrate a decreasing trend in phosphorus fraction removed from approximately 40% removal at a treated depth of about 12 meters to a final removal of approximately 20%. This trend may indicate a decrease in phosphorus removal capacity due to adsorption sites filling, but the positive removal at completion of the experiments indicates that capacity still exists.

The phosphorus fraction removed for 2% steel wool shown in figures 17, 18, and 19 reflect the total mass percent of phosphorus removed of 81%, 61%, and 51%, respectively, as listed in table 8. Figures 20, 21, and 22 also reflect the total mass percent removed by steel wool fabric of 44%, 34%, and 34%, respectively. The batch studies, Erickson *et al.* (2005b), concluded that the mass of steel wool was directly related to the dissolved phosphorus removal. The comparison of 2% steel wool and steel wool fabric (~0.3%) supports the claim that the mass of steel wool is directly related to phosphorus removal capacity. However, the steel wool fabric had more than half of the removal with only one sixth of the mass as compared to the 2% chopped granular steel wool columns. When compared to the 5% steel wool columns, steel wool fabric removes roughly the same mass percent of phosphorus, as shown in table 8. A much longer study would be required to determine the total capacity for phosphorus removal of chopped granular steel wool and steel wool fabric. While not verified during these column experiments, it is expected that two layers of steel wool fabric would increase the phosphorus removal by a substantial amount as compared to a single layer used in these column studies.

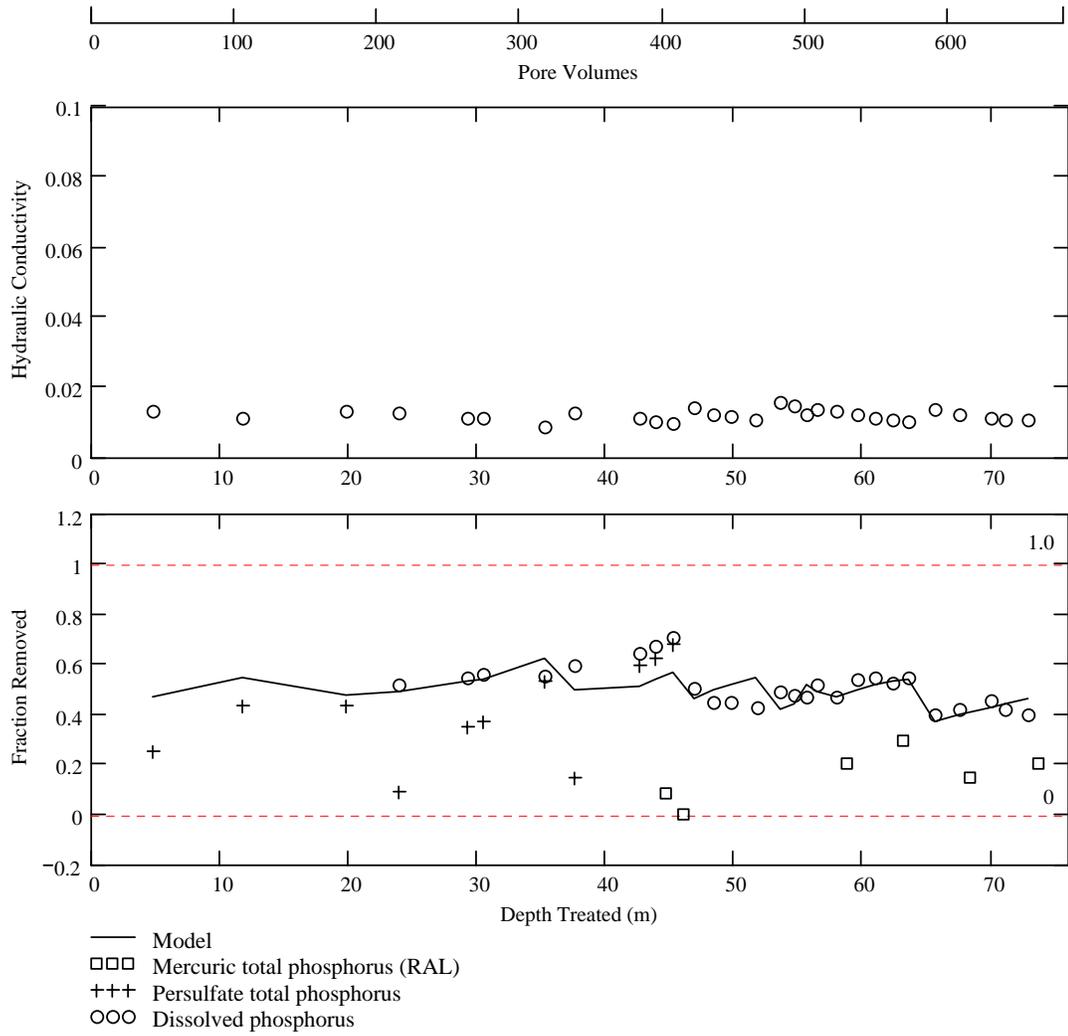


Figure 20: Hydraulic conductivity, phosphorus removal, and model fit: steel wool fabric, column G

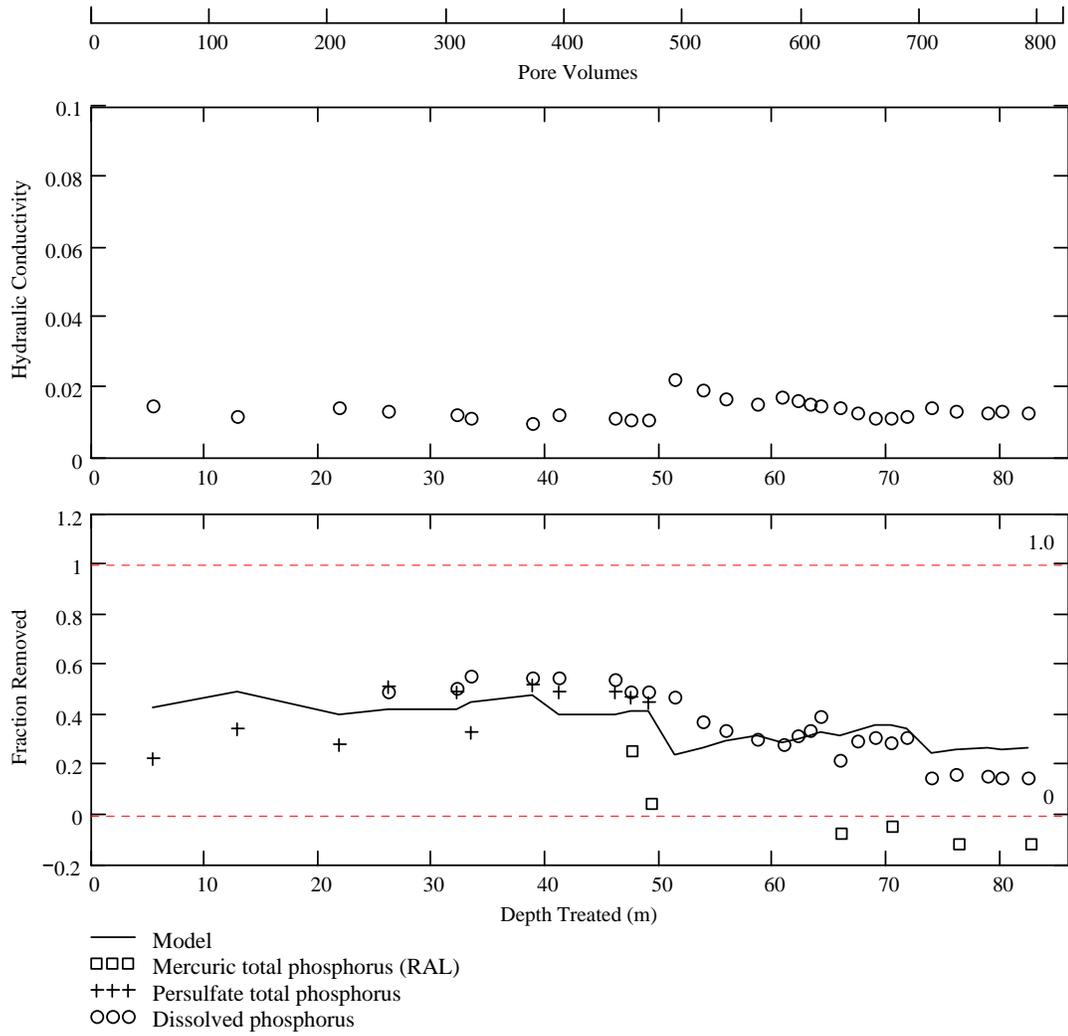


Figure 21: Hydraulic conductivity, phosphorus removal, and model fit: steel wool fabric, column H

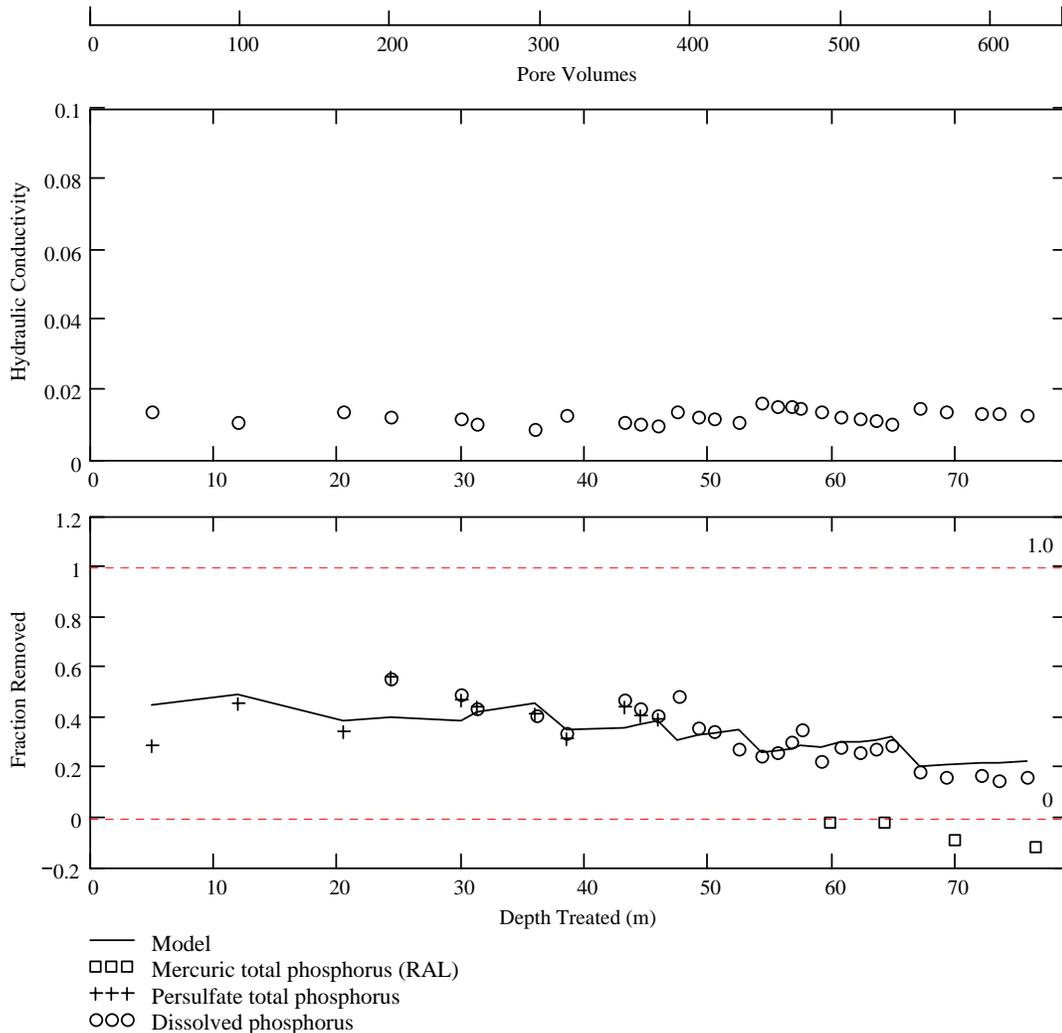


Figure 22: Hydraulic conductivity, phosphorus removal, and model fit: steel wool fabric, column I

The steel wool fabric used in these experiments is purchasable in rolls measuring approximately 40 meters in length and 2.5 meters in width. Field installation of a sand filtration system with steel wool fabric enhancement would only require rolling out the steel wool fabric rolls over the installed geotextile fabric before the 46 cm of C 33 sand is applied (see Claytor and Schueler (1996) for sand filtration design). Steel enhanced sand filters would only minimally increase the installation labor required over a standard sand filter and would improve the removal effectiveness for dissolved phosphorus. An

estimate by Kane (2005) shows that chopped granular steel wool is approximately 51% of the cost of steel wool fabric for the same mass, but it is difficult to visualize effective and safe placement of chopped granular steel wool, while steel wool fabric would increase construction costs of a C 33 sand filtration system by roughly 3-5%. In addition, the percent phosphorus mass removed per mass of steel wool can be calculated from the percent mass removed in table 8 and the mass of steel wool listed in table 6. Performing this calculation reveals that steel wool fabric removed approximately 6.1 to 8.6 percent per gram steel wool as compared to the 2% steel wool columns, which only removed approximately 1.5 to 2.25 percent per gram steel wool. Therefore, it is recommended that steel wool fabric (versus chopped granular steel wool) be utilized to enhance sand filtration for the removal of dissolved phosphorus.

MODEL

The results of this study show that steel wool enhanced sand filtration removes more dissolved phosphorus than C 33 sand alone. A mathematical model to better understand the mechanics driving phosphorus removal by the iron in steel wool will be developed. The variables for this model include contact time, total mass of phosphorus removed, and influent concentration. A bulk phosphorus balance between the water and iron (from the steel wool) can be written as:

$$Vol \frac{dC}{dt} = -kA(C - C^*) \quad (5)$$

where: 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
 C^* = equilibrium concentration of phosphorus in the water

Dividing by volume, designating the surface area per volume (A/Vol) as the specific area, a , gives:

$$\frac{dC}{dt} = -ka \cdot (C - C^*) \quad (6)$$

Equation (6) can be rearranged and integrated over the contact time:

$$\int_{C_{in}}^{C_{out}} \frac{dC}{C - C^*} = \int_0^{t_{contact}} -ka \cdot dt \quad (7)$$

where: C_{in} = influent phosphorus concentration (mg/L)
 C_{out} = effluent phosphorus concentration (mg/L)
 $t_{contact}$ = 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 during the contact time ($t_{contact}$) encountered during these experiments. The integration of (7) is then:

$$\ln\left(\frac{C_{out} - C^*}{C_{in} - C^*}\right) = -ka \cdot t_{contact} \quad (8)$$

After rearrangement and simplification of equation (8), one gets:

$$C_{in} - C_{out} = (C_{in} - C^*)\left(1 - e^{-ka \cdot t_{contact}}\right) \quad (9)$$

Equation (9) is a function of influent concentration, equilibrium concentration, and contact time. The equilibrium concentration, C^* , will tend to increase as more dissolved phosphorus is removed and will ultimately approach the influent concentration, C_{in} . This

tendency can be mathematically expressed with an exponential function as illustrated by figure 23 and equation (10):

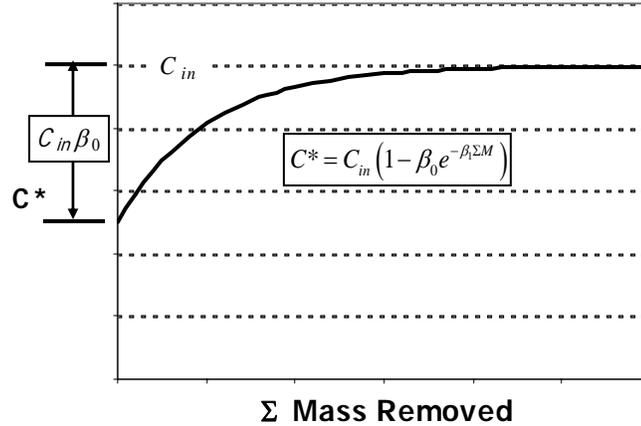


Figure 23: Equilibrium concentration, C^* , assumed for steel wool. $\beta_0 = 1 - C^*/C_{in}$ at $\Sigma M = 0$.

$$C^* = C_{in} \left(1 - \beta_0 e^{-\beta_1 \cdot \Sigma M} \right) \quad (10)$$

where: β_0 = coefficient related to capacity of iron for phosphorus removal
 β_1 = coefficient related to rate at which C^* approaches C_{in} (1/g)
 ΣM = sum of phosphorus mass removed at a specific depth or time (mg)

The rationale to use sum of mass removed (ΣM) stems from the complexity and multitude of the reactions governing the removal of phosphorus by iron. Sum of mass removed incorporates the depletion of capacity by the adsorption of phosphorus to the steel wool and the increase in capacity due to the continued rusting of the iron. The use of a single variable to describe both of these processes avoids the cross-correlation of two fitting parameters with opposing trends. If C^* , as described by equation (10), is substituted into equation (9) and rearranged to provide fraction removed, then:

$$FR = \left(\frac{C_{in} - C_{out}}{C_{in}} \right) = \left(\beta_0 e^{-\beta_1 \cdot \Sigma M} \right) \left(1 - e^{-\beta_2 \cdot t_{contact}} \right) \quad (11)$$

The first term of the fraction removed model, $(\beta_0 e^{-\beta_1 \Sigma M})$ as given by equation (11), is the capacity of iron with regards to phosphorus where $\beta_0 C_{in}$ is the initial (or maximum) capacity at $\Sigma M = 0$ and β_1 relates to the rate at which C^* approaches C_{in} , as shown in figure 23. β_0 is related to the mass of iron available for phosphorus uptake; $\beta_0 \sim 0$ indicates little or no phosphorus removal capacity and $\beta_0 = 1$ indicates that removal capacity equals the initial concentration of phosphorus in the water. β_0 is therefore constrained to be less than or equal to 1. While β_0 could vary between the columns, it should remain constant for columns with the same mass of steel wool. Thus, when determining the best fit values for β_0 , columns A2, B2, and C2 were required to have the same value for β_0 with similar constraints on D2, E2, and F2 and G, H, and I. β_1 relates to the rate at which C^* approaches C_{in} and therefore combines the effects of rusting, which increases removal capacity, with the effects of adsorption sites filling, which reduces removal capacity. Because there was no evidence of phosphorus contribution (i.e. net negative removal) in the data collected, it may be concluded that C^* was $\leq C_{in}$ throughout the experiments, and therefore β_1 was constrained to be ≥ 0 . Since these studies did not quantify the effects of rusting or the filling of adsorption sites and each column could react independently, β_1 is variable for each column.

The second term, $(1 - e^{-\beta_2 t_{contact}})$, is a value between zero and one that determines the rate at which the interaction between phosphorus and iron approaches equilibrium. β_2 is the product of the rate constant and the specific area, ka , in this derivation. The specific surface area, a , is an intensive property of the media (in this case, steel wool) that is also

independent of the fluid. Chopped, granular steel wool (columns A2, B2, C2, D2, E2, and F2) has a specific area that is different than steel wool fabric (columns G, H, and I) due to packing of a granular material as opposed to a woven fabric. While the boundary layer thickness around the steel wool fibers changes as the interstitial fluid velocity changes (inversely related to contact time) it is assumed that k is constant for the range of contact times observed in this study for all columns. Based on these observations and assumptions, β_2 should be a non-negative constant for chopped granular steel wool and a different constant value for steel wool fabric.

The model was fit to the persulfate total phosphorus measurements and later to the dissolved phosphorus measurements given in figures 14 through 22. A standard error function, (12), was used to compare the results generated by the model to the observed data from the experiments.

$$\text{Standard Error} = \sqrt{\frac{1}{n-2} \cdot \sum (\text{data-model})^2} \quad (12)$$

This standard error function was minimized using a non-linear, Newton method to solve for the coefficients (β_0 , β_1 , β_2) in equation (11), with the constraints justified above. The total standard error for all nine columns (data weighted average) was 0.1237 ($n = 501$) as fit to both total and dissolved phosphorus. The results of the model with the best-fit coefficients are listed in table 9 and are shown against the collected data in figures 14 through 22.

Table 9: Resultant coefficients from model fit to data for each column.
Constraints: $\beta_0 \leq 1$. Equal β_0 for columns A2, B2, and C2; columns D2, E2, and F2; and columns G, H, and I. Equal β_2 for columns A2 through F2; and G, H, and I.

	Column Description	β_0	β_1 (1/g)	β_2 (1/sec)	Standard Error	$(\beta_0 e^{-\beta_1 \Sigma M})$
A2	5% Steel wool with generic filter fabric	1	19.9	0.017	0.15	0.32
B2	5% Steel wool with 150 micron mesh	1	13.5	0.017	0.12	0.37
C2	5% Steel wool with 200 micron mesh	1	3.1	0.017	0.16	0.81
D2	2% Steel wool with generic filter fabric	1	0	0.017	0.10	1.00
E2	2% Steel wool with 150 micron mesh	1	9.4	0.017	0.12	0.73
F2	2% Steel wool with 200 micron mesh	1	14.5	0.017	0.09	0.60
G	Steel wool fabric with generic filter fabric	1	0	0.012	0.08	1.00
H	Steel wool fabric with 150 micron mesh	1	21.7	0.012	0.11	0.67
I	Steel wool fabric with 200 micron mesh	1	34.9	0.012	0.07	0.56

As shown by the standard errors for the individual columns (table 9) and the overall standard error of 0.1237, the model fit the data well in some instances, and poorly in others. The anomaly found in the 5% steel wool columns during the first 20 meters of treated depth was not modeled well, most likely because incomplete consolidation created conditions of incomplete contact between the iron in the steel wool and the phosphorus in the synthetic storm water influent. The model assumes complete contact with no preferential flow paths through the media and therefore could not capture this anomaly. Changes in flow path are also presumed to explain the change in hydraulic conductivity, and subsequently fraction removed, observed in figure 14 before 100 meters of treated depth and figure 16 after 110 meters of treated depth.

However, the model successfully predicted phosphorus fraction removed for columns B2 through I, including positive (columns C2 and D2), steady (E2 and G) and negative (B2, F2, H, and I) slopes or trends for both steady and changing hydraulic conductivities. This indicates that the model captured trends that related to the capacity

of the steel wool to remove phosphorus despite the complexity of processes associated with the sum of mass term (ΣM).

A closer inspection of the coefficients listed in table 9 reveals further insight to the model. As discussed earlier, β_0 relates to the mass of iron available for phosphorus uptake and $\beta_0 = 1$ indicates that removal capacity equals the initial concentration of phosphorus in the water. Since the best-fit determination found that $\beta_0 = 1$, this means that the amount of steel wool meets or exceeds the capacity of phosphorus in the water. Additionally, β_1 relates to the rate at which C^* approaches C_{in} and the best-fit determination found eight different values for the nine sand filtration columns. The right hand column of table 9 contains the 'capacity term,' $(\beta_0 e^{-\beta_1 \Sigma M})$, calculated at the conclusion of the experiments. This indicates the magnitude of the effect, if any, that β_1 has on the total capacity. $\beta_1 = 0$ indicates no substantial loss in capacity over the course of one experiment, and the capacity term = 1.0, as shown in table 9. Comparing columns A2, B2 and C2; a 32% decrease in β_1 from A2 to B2 causes a 16% increase in total capacity and a 77% decrease in β_1 from B2 to C2 causes a 219% increase in total capacity. It is evident from this analysis that the results for column A2, $\beta_1 = 19.9$, are not substantially different from $\beta_1 = 13.5$ for column B2, but $\beta_1 = 3.1$ for column C2 is different from β_1 for both A2 and B2.

The larger β_1 for steel wool fabric relates to a more rapid decrease in adsorption capacity, which would occur with the weight of steel wool available (0.3% versus 2% or 5%). The capacity terms also reflect the sum of phosphorus mass removed in the

experiment. Therefore, the effect of β_1 differences versus steel wool content is not as apparent in the capacity terms.

The differences in β_2 also illustrate the differences between chopped granular steel wool and steel wool fabric. For the same contact time, a larger value of $\beta_2 \sim ka$ translates to a larger rate to approach equilibrium, $(1 - e^{-\beta_2 t_{contact}})$, and therefore a larger fraction removed.

For the 2% steel wool and steel wool fabric, table 9 gives increasing β_1 values with filter fabric, 150 micron mesh, and 200 micron mesh, respectively. It is possible that the filter fabric captures a greater percentage of the iron oxide particles shed from the steel wool as compared to the mesh. These captured iron particles would still be available for adsorption of dissolved phosphorus. The anomaly of the β_1 trend for the 5% steel wool columns could be attributed to the flow paths that were set up through the steel wool during the incomplete consolidation.

Finally, comparison of mercuric total phosphorus and dissolved phosphorus in figures 14 through 22, with the interpretations of these measurements given, indicates that the lowest differences between mercuric total phosphorus and dissolved measurements correspond to the lowest values of β_1 . In other words, the columns that release the least amount of oxidized iron seem to maintain the largest capacity for phosphorus adsorption and have the smallest value of β_1 .

CONCLUSIONS

C 33 sand removed 1.6% of the dissolved phosphorus during these column experiments, but its capacity was quickly exhausted. Also, while combinations of C 33 with limestone or calcareous sand were expected to remove more dissolved phosphorus than only C 33 sand, the fine grain size of calcareous sand and limestone caused clogging of the filter fabric that ultimately prevented these columns from draining and excludes them as a potential sand filtration enhancement.

With steel enhanced sand filter columns achieving removal rates between 25% and 99%, it is evident that steel wool enhances the ability of sand to remove dissolved phosphorus in regards to quantity and duration. Using sand filtration design guidelines and a baseline pure sand column for comparison, steel enhanced sand filter columns did not significantly clog due to dissolved phosphorus removal. Despite the presence of fine iron oxide particles in the effluent from the steel wool enhanced columns, evidence from the literature shows that these particles would likely remain suspended in most receiving lakes and rivers and the subsequent bioavailability of any phosphorus that may be attached to these particles is low, if any. An estimate of costs shows that construction cost would increase by roughly 3-5% by enhancing the sand filter with steel wool fabric.

Interpretations of the mercuric sulfate total phosphorus, persulfate total phosphorus, and dissolved phosphorus measurements are that persulfate total phosphorus digests phosphates precipitated with calcium but not phosphates bound to iron. Phosphorus attached to the fine oxidized iron particles present in the effluent represents phosphorus that was removed from a preceding and possibly differing influent concentration.

Therefore, calculating phosphorus removal with influent concentration measurements at the same time step that the iron-bound phosphorus is present in the effluent samples is misleading.

A model was developed to describe the processes occurring in the steel enhanced sand filter columns. Starting with the a mass balance between phosphorus in the water and iron in the steel wool, this model incorporated contact time between the steel wool and the water, the total mass of phosphorus removed by the column, and the influent phosphorus concentration as variables. The overall standard error between the model and the data was only 0.1237 for all nine columns (n = 501).

In summary, the batch studies and column studies both give evidence that C 33 sand alone can remove some dissolved phosphorus, but that capacity is quickly exhausted. The batch studies and column studies also show that steel wool successfully removed more dissolved phosphorus as compared to C 33 alone, did not clog the filter, did not increase the pH beyond U.S. EPA guidelines, and would not significantly increase the construction cost. Based on the results of this study, it is apparent that steel wool fabric could be used to enhance sand filtration by effectively removing dissolved phosphorus from storm water runoff.

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