Using Denitrification Bioreactors and Phosphate Adsorption Media to Remove Nutrients from Agricultural Subsurface Drainage

Annual Report

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This report summarizes the activities undertaken during Year 1 of the project, from July 1, 2014 to June 30, 2015.

Executive Summary

Subsurface (tile) drainage has increased substantially in eastern South Dakota over the last several years. This project seeks to demonstrate the utility of using woodchip denitrification bioreactors and phosphorus adsorption beds as a conservation drainage practice to remove nitrate-nitrogen and phosphorus from tile drain water. Data collected from laboratory experiments and field installations are being used to evaluate the performance of the installations, track installation costs and estimate the cost per pound nitrate-nitrogen and phosphorus removed. Initial results showed that the maximum phosphate adsorption capacity varied from 0.087 to 0.262 mg P/g for the three minerals at three temperatures (5, 20, and 30 ºC). Steel slag showed maximum phosphate adsorption capacity between 0.960 and 2.416 mg P/g. Steel byproducts showed maximum phosphate adsorption capacity ranging from 1.530 to 5.359 mg P/g at different temperatures. Lab experiments suggest that locally available steel byproducts are highly efficient phosphate adsorbents. Field activities are currently been performed for continued monitoring of the three existing bioreactors (Arlington, Montrose, and Baltic), and design, installation and evaluation of phosphorus adsorption bed.

1.0 Introduction

Subsurface (tile) drainage on agricultural land with poor natural drainage allows timelier field operation access and contributes to improved crop yields. While properly designed and installed subsurface drainage typically reduces sediment and particulate-bound phosphate losses, studies show that subsurface drainage may enhance exports of nitrate-nitrogen and dissolved phosphorus to surface waters. Nitrate-nitrogen and dissolved phosphorus have a very high bioavailability and elevated levels of nutrients in natural waters may lead to a number of adverse effects including algal blooms, depletion of dissolved oxygen in the water, and decline in aquatic life populations. While improved management of fertilizer and animal manure is one important method for reducing nitrate-nitrogen and dissolved phosphorus losses, it is often not enough; therefore, water quality goals for nitrate-nitrogen and dissolved phosphate require additional, edge-of-field drainage water and nutrient management methods. This creates a critical need for strategies that minimize nitrate-nitrogen and phosphorus losses through subsurface drainage from agricultural land.

The objective for this project is to demonstrate and evaluate practices placed at the edge of fields to reduce nitrate-nitrogen and phosphorus loads from subsurface drainage systems to receiving waters in eastern South Dakota and disseminate this information to stakeholders. Our hypothesis is that phosphate adsorption media can be used in conjunction with woodchip bioreactors for simultaneous removal of nitrate-nitrogen and phosphorus from subsurface drainage.

This project consists of laboratory tests and field installation and maintenance of a phosphorus adsorption bed. The goals of laboratory tests are to evaluate the phosphate adsorption capacity of several cost-effective materials, and provide recommendations on the materials used for the field installation. The phosphorus adsorption bed will be monitored to evaluate its effectiveness for agricultural water management.

2.0 Laboratory Scale Experiments

2.1 Literature Review

Artificial subsurface drainage is a widely used drainage control strategy to improve the agricultural productivity. However, it has been recognized that this practice may adversely affect the water quality of the receiving water. Nitrate contamination resulted from the agricultural drainage has caused significant water quality concerns. Studies have shown that subsurface drainage can transport a significant amount of nitrate to surface waters and result in detrimental water quality impacts (Rabalais et al., 1996, Dinnes et al., 2002, Schilling, 2005, Schipper et al., 2010).

A number of agricultural practices and technologies have been developed to reduce the nitrogen loss from the field. Biological denitrification is an emerging technology being investigated to reduce nitrate concentrations in the drainage water (Christianson et al., 2009, Robertson et al., 2009, Schipper et al., 2010). The type of carbon source for the denitrifying bioreactors is one of the important considerations for the biological denitrification system. A variety of carbon sources have been tested in laboratory experiments and field trials for denitrification. These carbon substrates include wood, cardboard, wheat straw, corn, maize cobs, and others (Greenan et al., 2006, Schipper et al., 2010). Wood particles such as woodchips are the most widely used carbon substrate for denitrifying bioreactors in field trials because of the cost, hydraulic conductivity and longevity (Schipper et al., 2010). A woodchip bioreactor is typically constructed as excavated trenches filled with the wood materials and placed along the edge of a field. Control structures are used to divert the drainage water to the bioreactor for treatment before the water enters the receiving water body. Full-scale woodchips bioreactors have demonstrated their ability to provide long-term effective nitrate removal for agricultural drainage waters.

A large number of studies have indicated the importance of surface runoff in phosphorus transport from agricultural fields to surface waters (Sharpley et al., 1999). However, phosphorus transport in subsurface drainage can be an important pathway as well (Dils and Heathwaite, 1999). Recent studies suggest that subsurface drainage contributes substantially to the total phosphorus loads to the agricultural watersheds. Agoazany et al. (2007) evaluated the phosphorus transport through subsurface drainage and surface runoff from a relatively flat watershed. The results showed that although subsurface drainage phosphorus concentrations are typically lower than surface runoff phosphorus concentrations, annual phosphorus loads from drainage exceed the loads from the surface pathways. Gentry et al. (2007) also identified that subsurface drainage is a significant pathway to transport phosphorus to receiving water bodies. The woodchip bioreactors are designed to remove nitrate from the water and they are not effective in removing phosphate. To protect surface water quality, it is necessary to develop a system that can remove nitrate and phosphate simultaneously from subsurface drainage.

Enhanced biological phosphorus removal has been used in municipal wastewater treatment to reduce the phosphorus concentrations in treated effluents. This technology requires an activated sludge system with alternating anaerobic and aerobic zones, and complex structures and control systems. Therefore, biological phosphorus removal currently is not a practical method for in-situ treatment of agricultural drainage waters. Emerging phosphate removal technologies are being developed to reduce phosphorus pollution using low-cost adsorption materials. These phosphorus adsorbents include natural minerals, synthetic filtration byproducts, and industrial byproducts (steel slag, steel wool and turnings, fly ash, drinking water treatment residuals and others) (Buda et al., 2012, Stoner et al., 2012). These phosphorus adsorption materials provide metal cations (iron, aluminum, or calcium) to bind with dissolved phosphorus to form an insoluble compound (Buda et al., 2012, Chardon et al., 2012, Weng et al., 2012). The steel byproducts (steel slag, wool, and turnings) are cost-effective and practical materials for agricultural drainage treatment. These byproducts can also provide sufficient hydraulic conductivity and longevity for phosphate removal in the fields (McDowell et al., 2008). Studies have shown that these steel byproducts are highly efficient phosphate adsorption materials (Goodwin 2012).

Table 2.1 presents a summary of the particle sizes and phosphorus adsorption capacity of natural minerals and products from literature. Table 2.2 shows the particle sizes and phosphorus adsorption capacity of industrial byproducts from literature. The phosphorus adsorption capacity of several proprietary commercial products is summarized in Table 2.3. The natural minerals and products typically showed phosphorus adsorption capacity less than 1 mg P/g. Limestone, olivine, shell sand and wollastonite had higher phosphate adsorption under certain experimental conditions. A wide range phosphate adsorption (0.014 to 83 mg P/g) was reported for different industrial byproducts including acid mine drainage residual, drinking water treatment residual, steel slag, fly ash, cement and iron filings. A majority of these materials showed phosphate adsorption that was higher than 1 mg P/g. Several commercial products have also been used for phosphate removal, such as Filtra P and granular activated carbon. The phosphate adsorption capacity of these materials is similar to that of industrial byproducts.

Table 2.1. Phosphorus adsorption capacity of natural minerals and products

Material	Testing Method	Particle Diameter	Phosphorus Adsorption capacity	References
Calcite	Batch	0.7 mm	0.017 mg P/g	Reddy et al., (2013)
Limestone	Batch	0.05-4 mm	0.07-1.55 mg P/g	Mortula et al. (2007), Lyngsie et al., (2014), Johansson, (1999), Wium-Andersen et al., (2012)
Olivine	Batch	n.d.	1.55 mg P/g	Wium-Andersen et al., (2012)
Opoka	Batch	0.9 mm	0.10 mg P/g	Johansson, (1999)
Oyster Shell	Batch	1.5 mm	0.833 mg P/g	Seo et al., (2005)
Sand	Batch	0.6 mm	0.010 mg P/g	Reddy et al., (2013)
Sandstone	Batch	0.70 mm	0.167 mg P/g	Mann, (2007)
Sea Shells	Batch	0.05-4 mm	0.55 mg P/g	Lyngsie et al., (2014)

Shell Sand	Batch	n.d.	1.20 mg P/g	Wium-Andersen et al., (2012)
Wollastonite	Column	1-3 mm	0.467-1.80 mg P/g	Gustafsson et al., (2008)
Zeolite	Batch	1.2 mm	0.012-0.10 mg P/g	Reddy et al., (2013), Wium-Andersen et al., (2012)

Table 2.2. Phosphorus adsorption capacity of industrial byproducts

Material	Testing Method	Particle Diameter	Phosphorus Retention	References
Acid Mine Drainage Residual	Column	<0.5 mm	26 mg P/g	Stoner et al., (2012)
Alum Sludge	Batch	1.25 mm	0.300-1.787 mg P/g	Mortula et al., (2007)
Basic Oxygen Furnace Slag	Batch	0-10 mm	50 mg P/g	McDowell et al., (2008)
Basic Oxygen Furnace Slag	Column	6-50 mm	1.01-1.05 mg P/g	Barca et al., (2014)
Blast Furnace Slag	Batch	0.1-15 mm	0.15-6.37 mg P/g	Mortula et al. (2007), Mann, (1997), Johansson, (1999), Oguz, (2004)
Blast Furnace Slag	Column	0-4 mm	1.00-3.11 mg P/g	Gustafsson et al., (2008)
Cement Kiln Dust	Batch	<0.1 mm	0.469 mg P/g	Mortula et al., (2007)
Drinking Water Treatment Residual	Column	<5 mm	29-30 mg P/g	Stoner et al., (2012)
Electric Arc Furnace Slag	Batch	0-5 mm	6.56 mg P/g	McDowell et al., (2008)
Electric Arc Furnace Slag	Column	5-40 mm	0.81-29 mg P/g	Stoner et al., (2012), Barca et al., (2014)
Flue Gas Desulfurization Gypsum	Column	<5 mm	45 mg P/g	Stoner et al., (2012)
Fly Ash	Batch	0.012-1.0 mm	0.625-6.65 mg P/g	Mann, (1997), McDowell et al., (2008)
Fly Ash	Column	0.025-5.0 mm	21-32 mg P/g	Agyei et al., (2002), Stoner et al., (2012)
Iron Filings	Batch	0.9 mm	0.014 mg P/g	Reddy et al., (2013)
Iron Sludge	Batch	2.0 mm	1.64 to 4.06 mg P/g	Chardon et al., (2012)
Ordinary Portland Cement	Column	0.021 mm	83 mg P/g	Agyei et al., (2002)
Steel Slag	Column	0.031 mm	60 mg P/g	Agyei et al., (2002)

Steel Slag	Batch	15.0 mm	0.380 mg P/g	Mann, (1997)

Table 2.3. Commercial products used as adsorption materials for phosphorus removal

Material	Testing Method	Particle Diameter	Phosphorus Retention	References
Bone Char	Batch	0.45 mm	0.55 mg P/g	Mortula et al., (2007)
Filtralite P	Batch	0.05-4 mm	3.10-4.80 mg P/g	Lyngsie et al., (2014)
Filtra P	Column	2-13 mm	2.47-19.4 mg P/g	Gustafsson et al., (2008)
Filtra P	Batch	4-13 mm	4.3 mg P/g	Herrmann et al., (2012)
Granular Activated Carbon	Batch	1.25 mm	0.35 mg P/g	Mortula et al., (2007)

2.2 Phosphate Adsorption Materials Selection

A total of eight phosphate adsorption materials were selected for this project. These materials include three natural minerals (limestone, zeolite, and calcite), steel slag, iron filings, and three steel byproducts (large turnings, small chips, and fine chips). All of these materials have good phosphate adsorption capacity and are cost-effective and practical materials for agricultural drainage treatment. It should be noted that the steel byproducts selected for this study were obtained from machine shops in Sioux Falls region. These steel byproducts are readily available for agricultural drainage treatment in South Dakota.

Table 2.4 presents the size and the producer of each of the selected phosphate adsorption material. Table 2.5 shows physical and chemical properties of each material. The selected materials showed similar dry densities and hydraulic conductivities. The pHs of the three natural materials were slightly alkaline and the pHs of the steels were slightly acidic. The steel slag showed the highest pH value among the selected materials.

Figures 2.1 and 2.2 present the pictures of the selected phosphate adsorption materials.

Table 2.4. Phosphorus adsorption materials selected for this study

Material	Size (mm)	Producer
Limestone	0.85 - 2.0	Martin Marietta, Fort Dodge, IA
Zeolite	0.85 - 2.0	Bear River Zeolite, Preston, ID
Calcite	0.85 - 2.0	Fresh Water Systems, Greenville, SC
Electric Arc Furnace Steel Slag	0.85 - 4.75	Nucor Steel, Norfolk NE
Fine Carbon Steel Chips	0.1 – 1.0	Rural Manufacturing, Freeman, SD
Iron Filings	0.5 – 5.0	Connelly-GPM Inc., Chicago, IL
Small Carbon Steel Chips	1.0 – 5.0	Prairie Manufacturing, Sioux Falls, SD
Large Carbon Steel Turnings	30 - 60	Prairie Manufacturing, Sioux Falls, SD

Table 2.5. Phosphorus adsorption materials selected for this study

Material	Dry Density (g/cm³)	Hydraulic Conductivity (cm/s)	pH	Moisture Content	Organic Content
Limestone	1.40	0.34	8.3	0%	0.4%
Zeolite	0.97	0.10	8.0	3.20%	4.7%
Calcite	1.55	0.27	8.4	0%	0.8%
Electric Arc Furnace Steel Slag	1.85	0.58	10.9	0.70%	2.0%
Iron Filings	2.52	0.24	6.5	0%	0%
Fine Carbon Steel Chips	2.30	0.11	6.3	0%	0%
Small Carbon Steel Chips	1.05	0.71	6.4	0%	0%

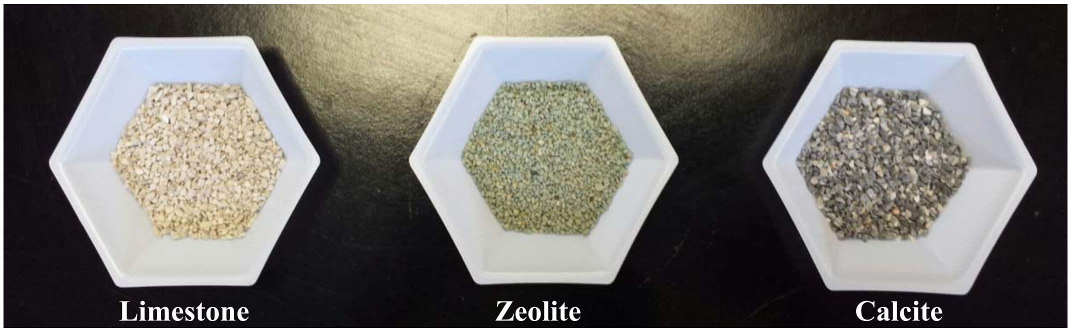

Figure 2.1. Selected Natural Minerals for Bench Scale Testing

Figure 2.2. Selected Industrial Byproducts for Bench Scale Testing

2.3 Batch Adsorption Experiments Design

Batch adsorption experiments were conducted to determine the phosphate adsorption isotherms (capacity) and kinetics of the selected materials. A temperature controlled shaker was used for the adsorption experiment. Figure 2.3 shows the experimental design for phosphate adsorption isotherms. The phosphate adsorption isotherms experiments were conducted using 250 mL Erlenmeyer flasks, 100 mL phosphate solutions (0-40 mg P/L), and varying initial adsorption materials mass loadings. A 2 g mass loading was used for minerals. A 1 g mass loading was used for steel slag, steel turnings and small chips, and a 0.5 g mass loading was selected for steel fine chips and iron filings. The selection of these experimental conditions for these materials was based on the projected phosphate removal efficiencies.

After adding 100 mL phosphate solutions and adsorption materials, the Erlenmeyer flasks were subjected to mixing in an orbital shaker at 100 rpm for 24 hours at three different temperatures (5, 20 and 30 °C). The phosphate concentration of each sample was measured using ion chromatography after 24 hour adsorption.

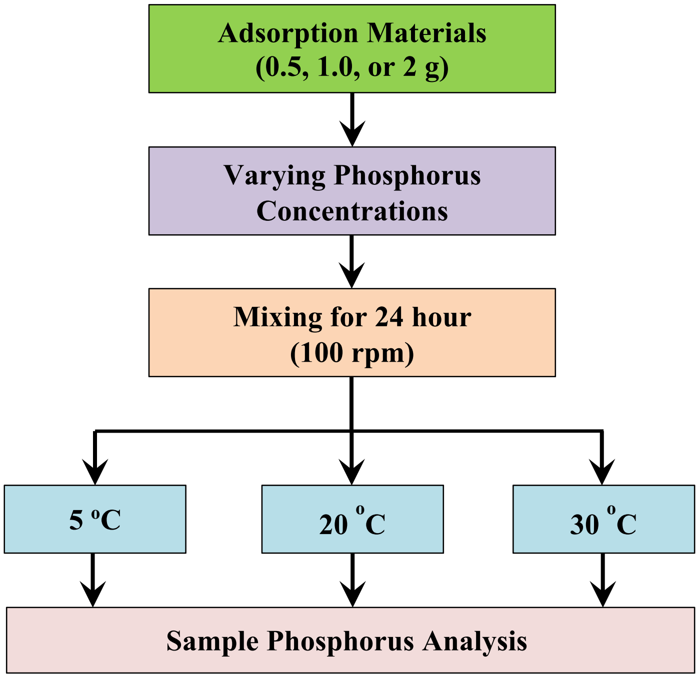

Figure 2.3. Experiments Design for Phosphate Adsorption Isotherms

Figure 2.4 presents the experimental design for phosphate adsorption kinetics. The initial phosphate concentration was 5 mg/L and 30 mg/L for minerals, and steel materials, respectively. The initial mass loadings were same as the isotherm tests. After adding 100 mL phosphate solutions and adsorption materials, the Erlenmeyer flasks were subjected to mixing in an orbital shaker at 100 rpm for 24 hours at a fixed temperature of 20 °C. Samples were taken at various time intervals (1 minute – 24 hours). The phosphate concentration of each sample was measured using ion chromatography.

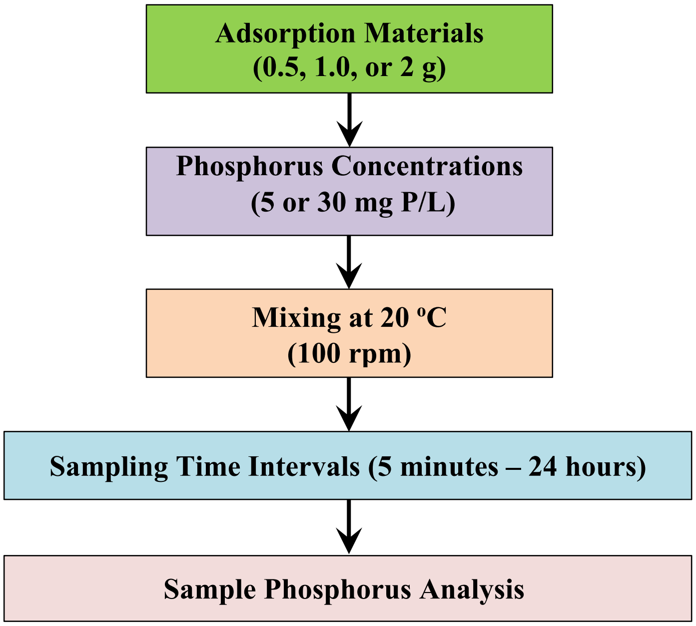

Figure 2.4. Experiments Design for Phosphate Adsorption Kinetics

2.4 Batch Adsorption Experiments Results and Discussion

Figure 2.5 shows the adsorption isotherms for five industrial byproducts tested at 20°C. It is clear from Figure 2.5 that the size of the steel byproduct had a significant impact on phosphate adsorption capacity. The phosphate adsorption of the three steel byproducts follows the order of fine chips > small chips > large turnings. Iron filings exhibited a similar capacity as steel fine chips, and steel slag showed a lower capacity than steel large turnings. Figure 2.6 presents the adsorption isotherms for three minerals tested at 20°C. It was found that limestone and calcite showed precipitation when phosphate equilibrium concentrations were higher 3 mg/L. This precipitation is likely caused by the reactions between calcium and phosphate ions. No apparent precipitation was observed for zeolite. The three minerals showed very similar phosphate adsorption capacity when the phosphate equilibrium concentrations were less 3 mg/L.

Steel slag and small steel chips were used as examples to illustrate the impact of temperatures on the phosphate adsorption capacity (Figures 2.6 and 2.7). It was observed that high temperatures promoted higher the phosphate adsorption capacity of the two materials. Steel slag showed approximately 3 times more phosphate adsorption when the temperature was increased from 5 to 30 ºC. The corresponding increase of small steel chips was about 2 times.

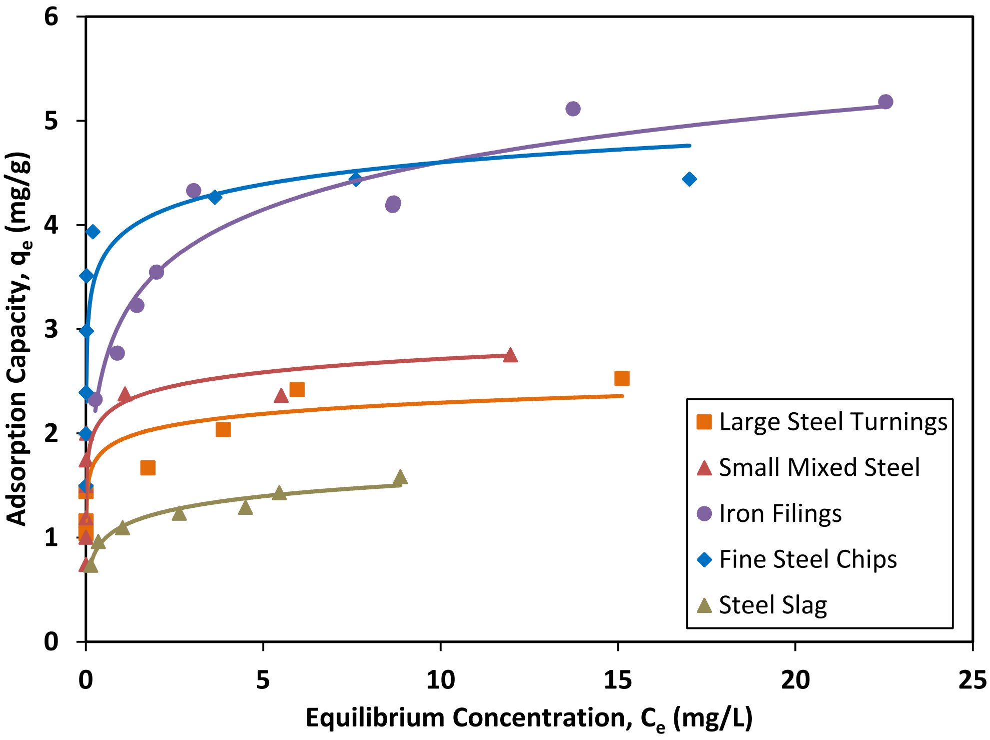

Figure 2.5. Adsorption isotherms for five industrial byproducts tested at 20°C

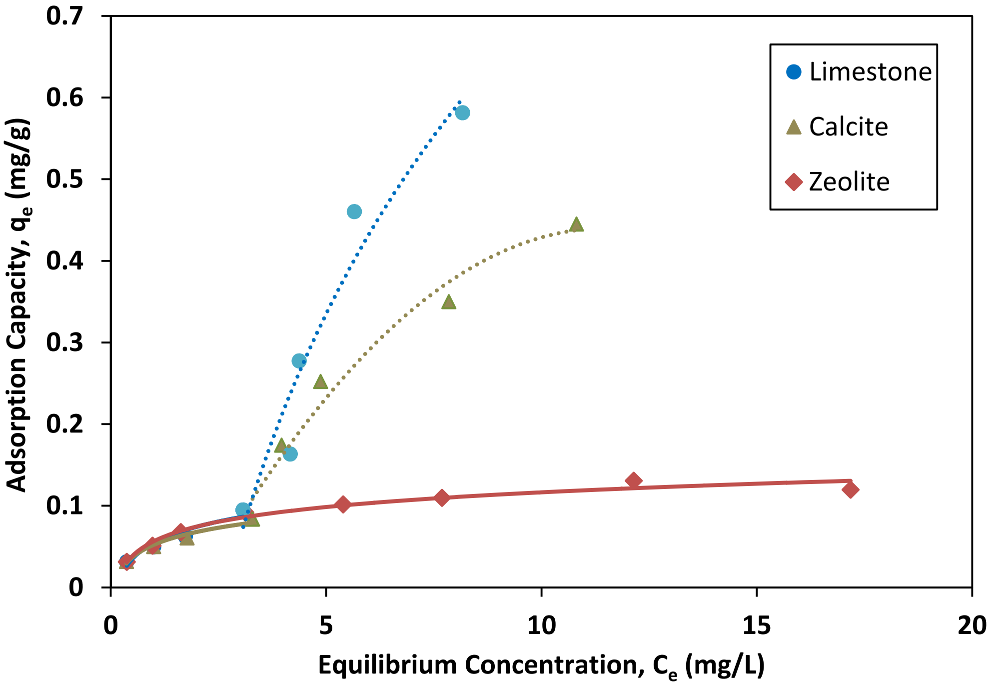

Figure 2.6. Adsorption isotherms for three minerals tested at 20°C
(Limestone and calcite showed precipitation at $C_e > 3$ mg/L, denoted by dotted line).

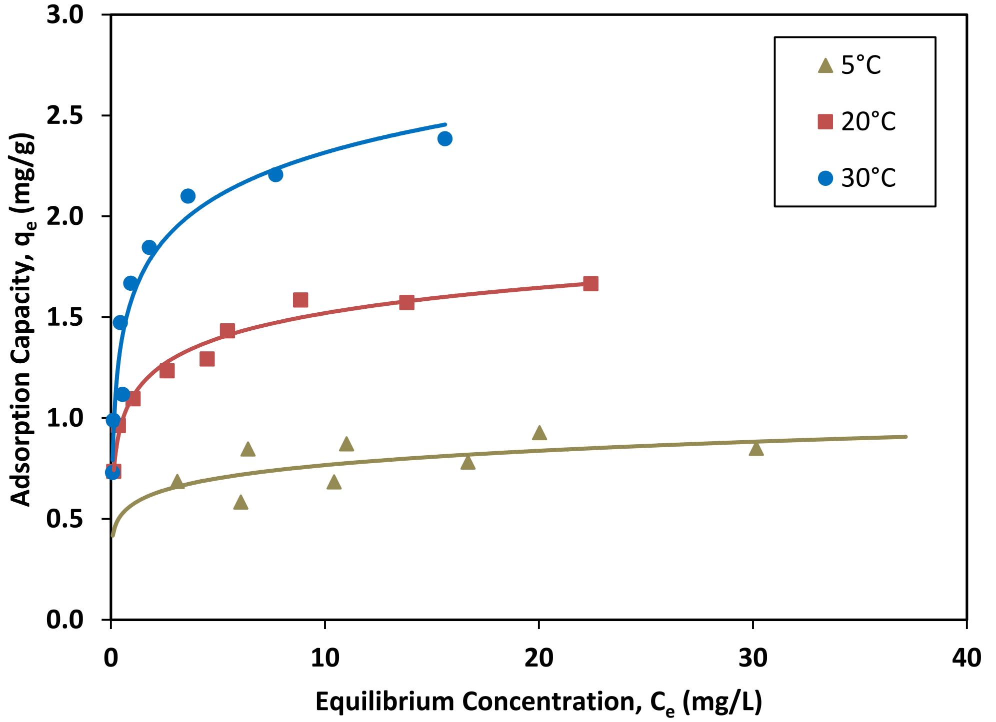

Figure 2.7. Effect of temperature on the adsorption capacity of steel slag

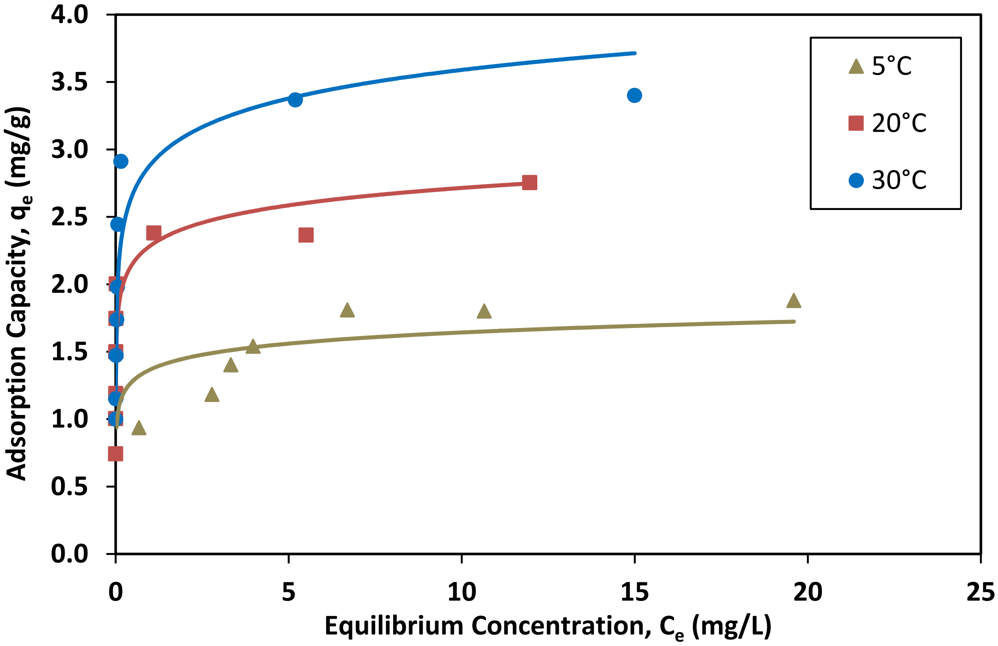

Figure 2.8. Effect of temperature on the adsorption capacity of small steel chips

Table 2.6. Summary of phosphorus adsorption isotherms of selected materials

Material	Temp. (°C)	q_{max} (mg/g)	R^2	Material	Temp. (°C)	q_{max} (mg/g)	R^2
Limestone	5	0.096	0.9920	Fine Steel Chips	5	3.123	0.9591
	20	0.135	0.9089		20	4.442	0.9999
	30	0.262	0.8848		30	5.330	0.9998
Zeolite	5	0.087	0.9848	Iron Filings	5	4.575	0.9897
	20	0.134	0.9925		20	4.921	0.9953
	30	0.191	0.9906		30	5.359	0.9906
Calcite	5	0.083	0.9920	Small Mixed Steel	5	1.956	0.9933
	20	0.107	0.9681		20	2.697	0.9954
	30	0.158	0.9036		30	3.381	0.9999
Steel Slag	5	0.960	0.9337	Large Steel Turnings	5	1.530	0.9935
	20	1.689	0.9969		20	2.546	0.9938
	30	2.416	0.9983		30	2.737	0.9648

Table 2.6 presents a summary of the phosphorus adsorption isotherms of selected materials. The maximum phosphate adsorption q_{max} (mg/g) was determined using the Langmuir isotherm model. The model correlation coefficients of each material were also presented in the table. In general, the five industrial byproducts exhibited one order of magnitude higher phosphate adsorption capacity than three minerals. There was no significant difference in phosphate adsorption among the three minerals. The steel byproducts typically showed higher phosphate adsorption compared to steel slag.

Figure 2.9 shows the phosphorus adsorption kinetics (Ct/Co) for four selected materials. Steel slag, small steel chips, and fine steel chips showed a fast adsorption stage within several hours followed by a relatively slow adsorption stage up to 24 hours. Fine steel chips (0.5 g) and small steel chips (1 g) removed approximately 80% of the initial phosphate concentration (30 mg/L) at 24 hour adsorption. Steel slag (1 g) removed about 50% of the initial phosphate (30 mg/L) at 24 hour adsorption. Limestone exhibited the fast phosphate adsorption kinetics among the four materials tested. The adsorption reached equilibrium after approximately 10 minute contact time for limestone. Figure 2.10 shows the phosphate adsorption capacity at different contact times. The adsorption capacity of limestone reached its maximum after 10 minutes. Steel slag and steel chips showed a more gradual increase in phosphate adsorption with increasing times.

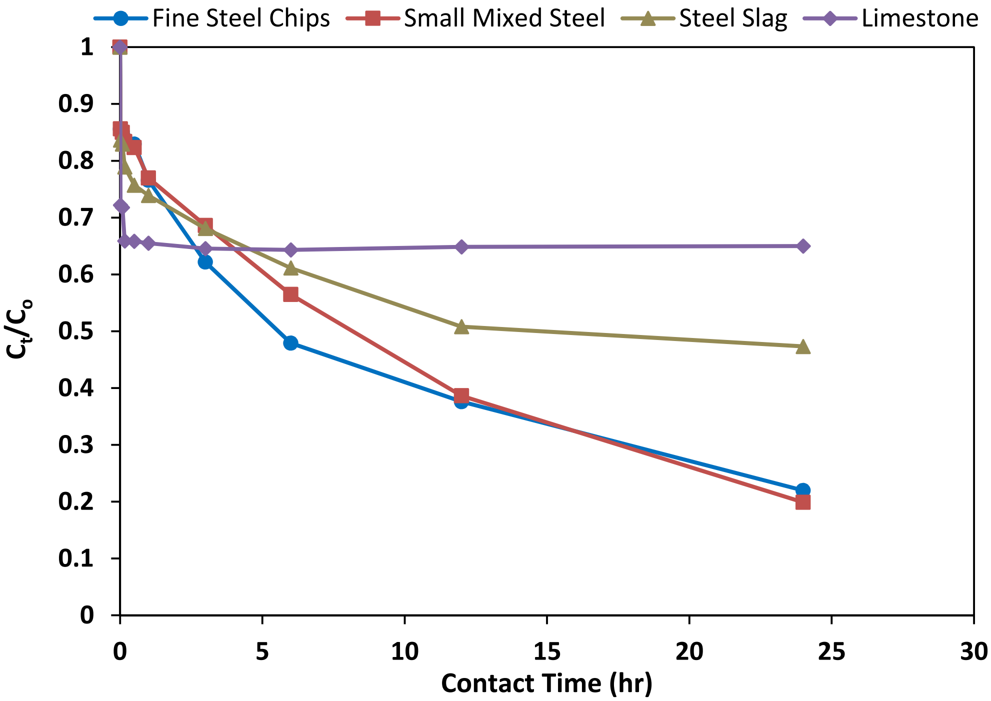

Figure 2.9. Phosphorus adsorption kinetics (C_t/C_o) for four selected materials (C_t: phosphate concentrations at time t; C_0: initial concentration)

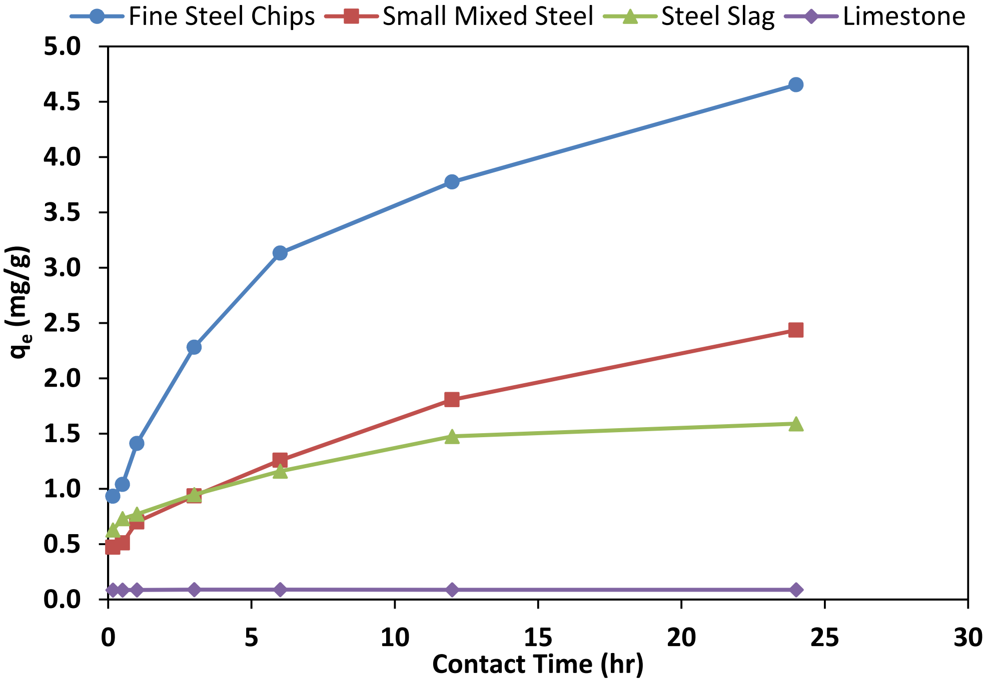

Figure 2.10. Phosphorus adsorption capacity as different contact times

2.5 Conclusions

A variety of materials have been evaluated for phosphate adsorption for environmental applications in the literature, including natural minerals, commercial filtration products, and industrial byproducts. Industrial byproducts and commercial filtration products typically showed higher phosphate adsorption capacity than natural minerals according to literature.

A total of eight materials were selected for agricultural subsurface drainage treatment for this study based on their phosphate adsorption capacity, cost and availability. These materials included three natural minerals (limestone, zeolite, and calcite), steel slag, iron filings, and three steel byproducts (large turnings, small chips, and fine chips).

The adsorption isotherm experiments results showed that the maximum phosphate adsorption capacity varied from 0.087 to 0.262 mg P/g for the three minerals at three temperatures (5, 20, and 30 ^{o}C). Steel slag showed maximum phosphate adsorption capacity between 0.960 and 2.416 mg P/g. Steel byproducts showed maximum phosphate adsorption capacity ranging from 1.530 to 5.359 mg P/g at different temperatures. The phosphate adsorption of the three steel byproducts follows the order of fine chips > small chips > large turnings. The results of the batch adsorption experiments suggest that locally available steel byproducts are highly efficient phosphate adsorbents.

2.6 Experimental Plan for Year 2

The following batch and column experiments are planned for the second project year to meet the project objectives.

(1) Perform batch adsorption experiments to determine the impact of pH, nitrate, sulfate and organic matter on phosphate adsorption of selected materials.
(2) Perform batch desorption experiments to determine the phosphate desorption kinetics of selected materials.
(3) Build column reactors and perform column experiments to determine the phosphate adsorption characteristics of selected materials under continuous flow conditions.

3.0 Field Scale Experiments

3.1 Literature Review

Phosphorus in Agriculture
In agroecosystems, phosphorus increases the biological production, accelerates N and P uptake, increases nitrogen biofixation, improves root growth, and increases soil organic matter water holding capacity (Crites, 1977; Smil, 1999; Smil, 2000).

Phosphorus in Water
However, phosphorus can contribute to eutrophication of lakes (Hem, 1985). Therefore, in aquatic environments attempts are based on maintaining very low phosphorus concentrations to diminish the negative impacts of organic reactions (Crites, 1977). Nutrient presence in water can be problematic, causing faster plant growth. Phosphorus as a limiting factor in lake eutrophication at very low rates (Hem, 1985; Hecky & Kilham, 1988; Hellstrom, 1998; Smith, 1984; Tyrrell, 1999). Although dissolved P is a small portion of total P export from agricultural lands (Sharpley et al., 1993), it is instantly used by algae and eutrophication begins (Vollenweider and Kerekes, 1982; Kronvang et al., 1993).

Phosphorus and Eutrophication
In order to feed a growing population, humans tend to apply more commercial fertilizers, including phosphorus particularly from mid of 19th century to 20th century (Smil, 2000). Through 1960 to 1980, nutrient enrichment significantly degraded aquatic coastal environments globally, especially in Europe, Asia, North American and Oceania (Boesch, 2002). Nutrient over-enrichment is one of the main factors in impairing water quality in the aquatic ecosystems and eutrophication (Garnier et al., 2005; Carpenter et al., 1998; Vitousek et al., 1997).
Eutrophication is defined as a condition in which biological productivity of clean water switches to highly biological productivity and growth of algae (Litke et al., 1999). Cultural eutrophication, which occurs in streams, estuaries, lakes, reservoirs, is caused by nutrient loadings related to anthropogenic causes (Hutchinson, 1969; Ketchum, 1969; Litke et al., 1999). Streams rich in nutrients can potentially promote plant growth; however, as final substitution of nutrient has not been done, it is not appropriate to use eutrophication for flowing streams (Hynes, 1969).
According to EPA (1992), lakes and reservoirs in the US are in danger of excess of nutrients and degrading water quality. The hypoxic condition in the Gulf of Mexico, one of the critical water quality concerns, is driven mainly by N and P discharge into the system. Consumption of oxygen by accelerated algae blooms, change in taste and odor of water, threatened aquatic habitats, and decreased quality of water for fishery and recreational applications are results of eutrophication (Mueller and Helsel, 1996; Litke, 1999; Crites, 1977; Carpenter et al. 1998). Eutrophication also changes the ecosystem function (Rabalais et al., 2001).

Furthermore, over-enrichment of N and P in water disrupts the natural balance of aquatic inhabitants through water strata. As a result, due to hypoxic zones, survival of organisms can be endangered at greater depths while food and oxygen are abundant at shallow depths (Jansson & Dahlberg, 1999; Smil, 2000). Historically, nitrogen was considered as a primary cause of freshwater eutrophication (Johnstone, 1908; Nixon, 1995; Ryther & Dunstan, 1971; Vince & Valiela, 1973; Rockwell et al., 2005; Schindler et al., 2008). But recent studies have indicated that P can also contribute to hypoxic conditions (Dodds, 2006). Some studies reported that, in the

Gulf of Mexico in deep marine coastal ecosystems, phosphorus may have a more important role in hypoxic conditions than once it was assumed, (Conley, 1999; Sylvan et al., 2006). In addition, while some studies noted that both nitrogen and phosphorus control the eutrophication process (Correll, 1998; Goldman et al., 1990; Howarth et al., 2000; Howarth & Marino, 2006; Paerl, Valdes, Joyner, Piehler, & Lebo, 2004), increases in phosphorus concentrations can accelerate growth of algae blooms more when compared to other nutrients (Wetzel, 1975). Furthermore, when primary production is P-limited, biomass production is mostly regulated by N rather than P; however, increase in P concentrations can promote oxygen depletion issues in water bodies with nutrient over-enrichment, especially in deep parts of these systems (Conley, 1999; Glibert and Pitcher, 2001; Malone et al., 1996; Malone et al. 1996; Rabalais et al. 2002a,b; Conley, 2000). Relative contribution of N and P in driving coastal eutrophication can differ seasonally in some marine coastal ecosystems (Rabalais et al., 2002).

On the other hand, Smil (2000) stated eutrophication is mainly likely to be driven by nutrient loading rather than N and P concentrations in water. As a rule of thumb, if P delivery to surface water does not exceed 10 Kg/ha/year, the water body is not threatened by eutrophication (Jaworski, 1981). Besides nutrient loading rate, a reservoir's characteristics can be contributing factors in the process of eutrophication (Vollenweider, 1975). For instance, the quotient of average depth and hydraulic resistance time determines the threshold of P loading in estuaries to develop eutrophication (Vollenweider, 1976).

Natural Cycling of Phosphorus

Phosphorus in rocks is mainly insoluble. About 95% of the Earth's crust is composed of calcium phosphate minerals with poor solubility (Smil, 2000). Even dissolved P, a product of weathering, is immediately transformed into immobile phosphorus (Khasawneh et al., 1980).

Human Intensification of Phosphorus Flows

Human activities, application of fertilizer and manure, use of phosphate detergents, wastewater treatment discharge and industries are some of the sources of phosphates in waterways (Gianessi & Peskin, 1984; Litke et al., 1999; Parry, 1998; Smil, 2000). Phosphorus loading can be increased by land use change (forests and grasslands to croplands and urbanized areas), subsurface drainage, runoff from animal feedlots, release of urban sewage, generation and reuse of organic wastes, use of commercial laundry detergents, and inorganic fertilizers (Parry, 1998). During the 1950's, the volume of phosphate discharged was increased because of the increase in the use of detergents. However, in 1960's because of public awareness of the dangers of phosphorus in causing eutrophication in aquatic environments, use of phosphate in detergents was limited (Hem, 1985).

The main origin of phosphorus and nitrogen delivered to the Gulf of Mexico is central and eastern parts of Mississippi and Atchafalaya River Basin (MARB) reaches (Alexander et al., 2008, Figure 3.1). The nine states with largest contributions to nutrient depletion to the Northern Gulf are Illinois, Iowa, Indiana, Missouri, Arkansas, Kentucky, Tennessee, Ohio and Mississippi. These states account for about 1/3 of the total area of MARB reaches but more than ¾ of total nutrient loading to the Gulf (Alexander et al., 2008).

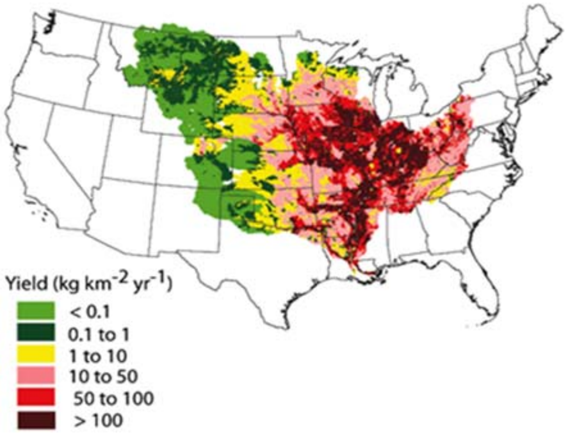

Figure 3.1. Total phosphorus load delivered to the Gulf of Mexico from incremental drainage of MARB reaches (Alexander et al., 2008).

Nutrient loading into the MARB watershed mainly originates from animal manure and cultivated crops, mainly corn and soybean (Alexander et al., 2008; Figure 3.2). An estimate with the SPARROW water quality model revealed that animal manure on pasture and rangelands (37%), crop cultivation (43%) and urban by-products (12%) are major origins of phosphorus delivery into the Gulf of Mexico (Alexander et al., 2008). Moreover, the contribution of agricultural sources in P export to the Maumee River is accounted for 49% by SPARROW modeling (Robertson and Saad, 2011).

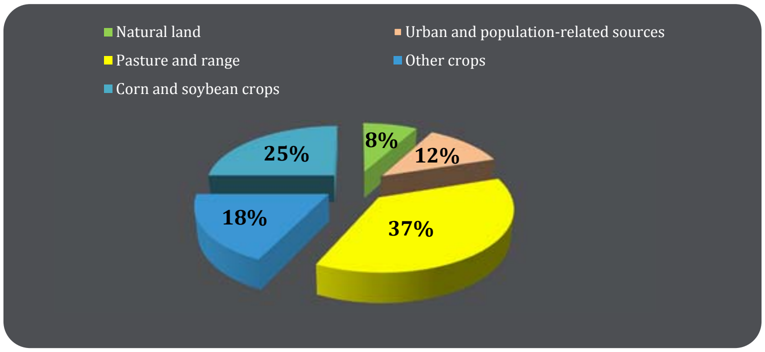

Figure 3.2. Sources of phosphorus delivered to the Gulf of Mexico (Alexander et al., 2008)

Nutrient Reduction Strategies

Due to negative consequences of phosphorus presence in water, regulatory agencies limited the permissible concentration of phosphorus in all wastewater effluents (USEPA, 2000*a*). In the 1960s, phosphorus drew the attention of pollution control agencies in the US in a way that resulted in less attention paid to nitrogen control and effects on hypoxia in fresh waters and coastal ecosystems (Federal Water Pollution Control Administration 1968; EPA 2001).

To improve nutrient management in aquatic systems, it is important to identify the nutrient sources contributing to the problem (Alexander et al., 2008; Boesch, 2002; Howarth & Marino, 2006; Rabalais et al., 2002; Scavia & Donnelly, 2007).

Permissible P Concentrations in Water

The critical P concentrations to prevent eutrophication may vary by space and time (King et al., 2015a) and by surface water bodies (USEPA, 2014). However, the critical concentration to drive eutrophication is 0.01 to 0.03 mg L^{-1} (Daniel et al., 1998; Heathwaite and Dils, 2000; King et al., 2015a). Because phosphorus is the main factor leading to eutrophication, EPA established permissible total phosphorus concentrations of 0.05 mg/L and 0.1 mg/L in streams at the point of delivery and flowing waters, respectively (Litke et al., 1999; US Environmental Protection Agency, 1982).

Forms of Phosphorus

Classification of phosphorus in water is mainly based on fractionations of phosphorus, i.e., orthophosphate, total phosphorus in filtrate, and total phosphorus in the unfiltered water, rather than chemical analyses of phosphorus (Figure 3.3) (Vollenweider et al., 1970).

<table>
<tr><td colspan="2">Dissolved P</td><td colspan="3">P in suspension</td></tr>
<tr><td>Orthophosphate (PO_4^{3-})</td><td>As organic colloids and/or combined with and adsorptive colloid</td><td>As mineral particles (i.e., apatite) and/or adsorbed on inorganic complexes such as $Fe(OH_3)$</td><td>Organisms</td><td>Adsorbed on detritus and/or present in organic compounds</td></tr>
<tr><td colspan="2">Dissolved inorganic P
← Total P in filtrate →</td><td colspan="3"></td></tr>
<tr><td colspan="5">Total P content of unfiltered water
← →</td></tr>
</table>

Figure 3.3. Forms of phosphorus present in surface and waste waters total P
(from Vollenweider et al., 1970)

The product of decomposition of phosphoric acid (H_3PO_4) can be any of solute species of H_3PO_4 (aq), $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}, which the latter, orthophosphate, is the final dissociation product (Figure 3.4).

Knowing the pH, the proportions of dissolved phosphate can be estimated (Figure 3.4). For instance, at pH of 7, the ratio of $H_2PO_4^-$ to HPO_4^{2-} is 1. At any specific pH in this graph, at most two solute species could be available simultaneously since trivalent and neutral ions can be found out of pH ranges of neutral fresh water (Hem, 1985). The most abundant and thermodynamically stable form of P^{5+} in natural water is the orthophosphate species. However, the final water analyses are commonly based on total phosphorus, not separate species (Hem, 1985). Phosphorus (P) in forms of phosphate, sediment-bound P, and organic P compounds in aquatic ecosystems, is the primary factor in unpleasant prevalence of algal blooms (Downing et al., 2001; Davis et al., 2009).

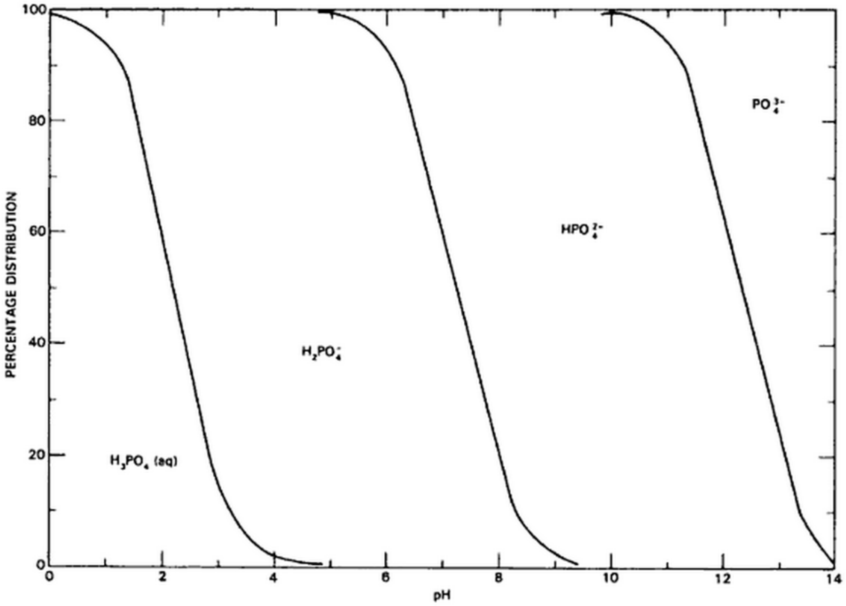

Figure 3.4. Percentage of dissolved phosphate species activity as a function of pH at 25°C and 1 atmosphere pressure (Hem, 1985).

Status of Subsurface Drainage in the Midwest

In United States and Canada, approximately 25% of the cropland could not be as productive without subsurface (tile) drainage (Skaggs et al., 1994). Due to high fertility of Midwestern soils, extensive arable lands are located in this area. Subsurface drainage is required in the Midwest to maintain economical crop production (Madramootoo et al., 2007; Skaggs et al., 1994) because of the cool climate of the region, water table variations (Smith et al., 2015), precipitation being greater than crop demand (King et al., 2015a), and to remove surplus soil water content (Fausey et al., 1987).

In the Midwestern United States, the first subsurface drainage system was installed in the 1800s to drain the excessive water from wetlands (King et al., 2015a). About 37% of croplands in the Midwest are drained with subsurface drainage systems (Zucker and Brown, 1998).

Contribution of Subsurface Drainage to P loss

Historically, because of the high fixation of phosphorus in soils compared with NO3-N and subsequently less P export through subsurface drainage (Sims et al., 1998; Hansen et al., 2002; Smith et al., 2015; Baker et al., 1975; Kladivko et al., 1991), most studies focused on N transport to drains. In addition, surface runoff was considered as primary P export pathway from agricultural fields. Therefore, most P reduction studies attempted to reduce soil erosion (King et al., 2015a). Because of low P concentrations in subsoils, P loss through subsurface flow was generally disregarded (Baker et al., 1975).

However, some studies have indicates that subsurface drainage is an important contributor to P loss (Gilliam et al., 1999; Beauchemin et al., 1998; Culley et al., 1983; Gaynor and Findlay, 1995; Sharpley and Seyers, 1979a, 1979b; Sims et al., 1998). For instance, Ryden et al., (1973) argued that substantial P loss can occur in association with surface water bodies enrichment.

Subsurface drainage reduces the possibility of surface runoff occurrence (Sommers et al., 1979; Cooper and Gilliam, 1987; Stone and Mudroch, 1989). Consequently, the amount of P transport with surface runoff is decreased as well (Bengtson et al., 1995). On the other hand, subsurface drainage increases the potential of P loss through subsurface flow and in some cases is even higher than surface runoff flow (Jamieson et al., 2003; Zhang et al., 2009; Reid et al., 2012). The ranges of P loss through subsurface drainage in the agricultural Midwest ranged from 0.01 to 0.11 kg soluble P ha^{-1} in Indiana and 0.05 to 1 kg soluble P ha^{-1} and 0.2 to 1.3 kg total P ha^{-1} in Illinois (Kladivko et al., 1991). Farmers in the central Ohio watershed are cautious of applying fertilizer as needed and P concentrations in subsurface drainage water accounted for less than 2% of applied fertilizer; however, this concentration is substantially higher than the threshold of algae growth and nuisance algae (King et al., 2015b).

About 70% of total P export to Lake Erie is associated with tributaries discharging into the lake; in particular, nonpoint sources (Dolan and McGunagle, 2005). In the western Lake Erie Basin, to prevent unpleasant conditions due to algal blooms, the critical total P loads should not exceed 0.6 to 1.1 kg ha^{-1} year^{-1} (Ohio P Task Force, 2013). Zhao et al. (2001) indicated up to 24% of soluble P (SP) and up to 21% of total phosphorus (TP) can be transported through subsurface drainage. In a study by Ruark et al. (2012) in Wisconsin, they reported that 17-41 % of cumulative TP transport is from subsurface drains. In a study by Smith et al. (2015) where P loss from four fields in the St. Joseph River watershed was measured, they observed that relative discharge from subsurface drainage accounted for 49% of SP and 48% of TP. Likewise, King et al. (2015b) reported that subsurface drains contributed to 48% and 40% export of dissolved P and TP from Big Walnut Creek watershed in Ohio.

Contributing Factors in P loss from Subsurface Drainage

Subsurface drainage influences water storage capacity of soil, timing, shape and peak flow, and total water yield of previously undrained lands (Skaggs and Broadhead, 1982; Schilling and Helmers, 2008). King et al. (2015a) noted the P loss through subsurface drainage is a function of soil characteristics (e.g. preferential flow, phosphorus sorption capacity, redox conditions), drainage design (e.g. drainage depth and spacing), management practices (e.g. tillage, cropping system, soil test phosphorus concentration, phosphorus application rate and timing), climatic and hydrologic factors (e.g. season and baseflow and event flow).

Some other studies discussed that P movement through subsurface drainage can be controlled by P concentrations in soil, type and structure of soil, P sorption capacity, preferential flow, and organic matter content (Sharpley et al., 1993; Sims et al., 1998; Gilliam et al., 1999; Hansen et al., 2002; Smith et al., 2001; Culley et al., 1983). Algoazany et al., (2007) indicated that P export from agricultural fields can be also influenced by vegetative cover, drainage intensity, hydrology of the watershed, form and availability of P. In addition to low P sorption capacity of soil (Gburek et al., 2005), hydrological connectivity to drainage network makes it prone to P leaching (Schoumans and Breeuwsma, 1997). In a study by Olli et al. (2009) on drainage reaches in the Swedish island of Färingsö, they discussed that increasing water flow caused decrease in the P retention rate. Furthermore, SP loss predominantly occurs during growing season; in particular from February until August for both subsurface flow and surface runoff. During dormant seasons, because of les flow relative to the growing season, P loss is undetectable (Algoazany et al., 2007). Laubel et al. (1999) indicated macropores in agricultural soils increase particulate matter loss as well as associated harmful substances. During the initial phase of storm events, the rate of particulate matter and particulate phosphorus transport to the drains is high (Laubel et al., 1999). The phenomenoon of translocation of fine particulate matter and hence pariculate phosphorus from topsoil to drains can take from hours to decades (Laubel et al., 1999). Artificial drainage of such soils conncects topsoil to surface waters.

Phosphorus Control Measures

There are different strategies to reduce nonpoint source pollutants to aquatic ecosystems such as controlling P discharge from point sources as well as P applied in organic and inorganic fertilizers (Smil, 2000), application of fertilizer in the field based on soil sampling and spatial nutrient deficiency (Wollenhaupt et al., 1994), indirect P-reducing practices including soil management practices to inhibit erosion, trapping uncontrolled runoff originated from animal manure, increasing phosphates solubility using acid-producing bacteria (Smil, 2000), and raising algae-grazing fish in aquatic ecosystems with algae blooms issues (Drenner et al., 1997). In a mesocosm study by Tyler at al. (2012), three aquatic macrophyte species, cutgrass (Leersia oryzoides), cattail (Typha latifolia) and bur-reed (Sparganium americanum), were assessed for their phosphate removal capabilities from simulated storm runoff enriched with phosphate (PO_4^{3-}) (10 mg L^{-1}). They concluded that the rate of dissolved phosphorus mitigation by L. oryzoides and T. latifolia was the most efficient and rapid at the initial stage of exposure to PO_4^{3-}-enriched water. However, these organisms were still effective even after 1 week.

P Removal Techniques

Phosphorus removal materials rich in Fe, Al, Ca or their combination showed promising results in phosphorus sorption and the resulting prevention of algae growth (Hickey and Gibbs, 2009; Hupfer and Hilt, 2008). These materials include iron oxide mine tailings, blast furnace slag, coconut shell–activated carbon, flue gas desulfurization gypsum, zeolite, goethite, bone char, and dolomite sand (King et al., 2015a). Coprecipitation, adsorption, and uptake by biota are some control methods of phosphorus solubility (Hem, 1985). Spears et al. (2013) under a laboratory experiment compared the P sorption characteristics of six industrial by-products—black iron ochre, red iron ochre, gypsum, mag dust, sander dust, vermiculite—and one commercially available modified lanthanum(La) bentonite product—Phoslock®. Except the gypsum, all products achieved significant P sorption with capacities varying from 4 mg P g^{-1} dry weight for ‘black ochre’ to 63 mg P g^{-1} dry weight for ‘sander dust’. Aluminum and iron based salts (i.e., $Al_2(SO4)_3$ and $FeSO_4$) can adsorb phosphorus from solution under particular environmental condition (for instance, pH and alkalinity of receiving waters, and lake morphology) (Cooke et al., 1993; Perkins and Underwood, 2001; Huser, 2012).

In-stream and edge-of-field Treatments

Because of the high sensitivity of algae growth to P presence in water, especially in shallow water bodies, even very low concentrations of P can lead to oxygen depletion eutrophication (Smil, 2000). Although best agricultural practices such as cropping without fertilizer or land use conversion from agricultural lands to prairie can lower P loss, they are not effective enough to prevent of eutrophication in sensitive waters (Smil, 2000). Therefore, to prevent the negative consequences of P enrichment in water bodies, the best approach is to minimize the initial P concentrations discharged into aquatic ecosystems.

Under lab-scale experiments, P sorption capacity using dolomite sand (Pant et al., 2001), surfactant-modified zeolite and high calcium oxide–high carbon fly ash materials (Allred, 2010), or clinoptilolite/alumina/activated carbon cartridge (King et al., 2010) showed to be above 50%. However, materials with high P removal capacity in laboratory-scale may not be necessarily effective in field-scale due to seasonal precipitation change and high flow during storms (King et al., 2015a). P removal capacity may vary due to variations in P removal capacity of different materials, environmental conditions, P loading, and chemical composition (King et al., 2015a). Changes in pH, media size, and phosphate concentrations leads into variation in P adsorption rate (Eckenfelder 2000).

To select the best technology to treat wetland and municipal runoff, cost plays an important role in selection of P-sorbing material (USEPA 2000*b*; Lin and Yang 2002; Gray et al. 2000). Inserting a porous sock of slag mix in the drain outlet was successful in removing 70% of dissolved reactive phosphorus (McDowell et al., 2008). P-sorbing rate in a field-scale experiment compared with a lab-setting scale (Brix et al., 2001) and during storm event compared with low-flow through structure (Penn et al., 2007) using the same material can be 10 times lower.

3.2 Field Monitoring

Each bioreactor had two control structures. One controlled the water level at the inlet of the structure and the other controlled the water level at the outlet of the structure. Together, they controlled the flow rate through the bioreactor. The Arlington bioreactor also had four monitoring wells installed within the bioreactor. The wells were equally-spaced along the flow path of the bioreactor. They were placed midway between the two sides of the bioreactor.

Water samples were collected manually from each of the two control structures and the monitoring wells on the dates shown in the tables. Water was sampled from within the bioreactor by bailing water from the monitoring wells. Water from upstream and downstream of the bioreactors was sampled by lowering a bottle into the water in the control structure. The samples were quickly delivered to the Civil and Environmental Engineering laboratory on the SDSU campus and analyzed for nitrate-nitrogen concentration and ortho-phosphate concentration. Results from sampling during 2015 are shown here. Because of the dry conditions, there were no samples to collect during 2014 after June 30.

3.3 Preliminary Results

The bioreactors have had water flowing since late April to early May. The winter and early spring were drier than normal so drainage systems and bioreactors did not have water flow until late April or early May. Flow rate data are still being analyzed and are not presented in this report.

After a relatively dry, open winter, spring 2015 also started dry. The Baltic site received only 0.65 inches of rain between March 1 and April 24 (Figure 3.5). Between April 25 and May 17, the site received 6.16 inches. Between May 18 and June 22, rainfall measured 2.52 inches. The total rainfall received at the site was 8.73 inches from 1 March to 30 June. Rainfall at the other sites followed similar patterns but had different amounts.

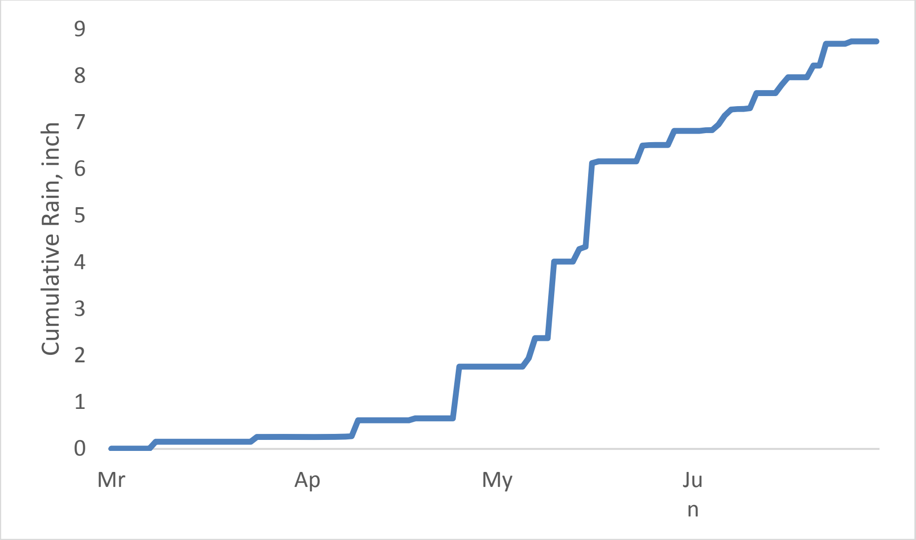

Figure 3.5. Cumulative rainfall at the Baltic bioreactor site for March through June 2015 (http://climate.sdstate.edu/awdn/archive/archive.asp). Note: the March rainfall may be slightly underreported because of freezing conditions during precipitation on March 24.

Nitrate-nitrogen concentrations measured before and after the wood chip bioreactors still show significant nitrate-nitrogen reductions (Tables 3.1 and 3.3). Orthophosphrus concentrations measured before and after the wood chip bioreactors showed no trends (Tables 3.2 and 3.4). This was not surprising because wood chip bioreactors are not designed to reduce phosphorus concentrations. Most concentrations (15 of the 23 measured concentrations, Tables 3.2 and 3.4) measured in the water before it enters the bioreactor were less than 10 µg P/L. The ortho-P concentrations show potential for reduction with the addition of a phosphorus removal structure. Installation of a field-test phosphorus control structure is planned for 2015 as part of this project. Nitrate-nitrogen concentrations show consistent decrease as the water moves through the bioreactor (Table 3.3). When there is bypass flow (that is, the drain flow rate is greater than the bioreactor design flow rate so not all of the drain water passes through the bioreactor), the downstream NO_3-N concentration is actually greater than the concentration in the last monitoring well within the bioreactor (15 May, 1 June, and 12 June, for example).

Table 3.1. Nitrate-nitrogen concentrations at the Baltic, Hartford, and Montrose bioreactors, mg N/L

	Baltic		Hartford		Montrose	
Date	Upstream	Downstream	Upstream	Downstream	Upstream	Downstream
8 May 2015	-	-	-	-	10.9	<0.1
15 May 2015	43.8	17.4	11.5	1.7	14.8	1.7
20 May 2015	-		13.1	3.4	-	-
22 May 2015	35.1	25.6	-	-	9.1	5.2
1 June 2015	55.1	40.2	11.9	1.6	14.8	2.1
5 June 2015	36.1	19.7	11.6	7.6	-	-
12 June 2015	42.1	17.6	12.1	3.7	14.1	4.7
26 June 2015	-	-	12.3	1.2	14.3	<0.1

A blank cell indicates that no sample was collected on that date.

Table 3.2. Orthophosphorus concentrations at the Baltic, Hartford, and Montrose bioreactors, µg P/L

	Baltic		Hartford		Montrose	
Date	Upstream	Downstream	Upstream	Downstream	Upstream	Downstream
8 May 2015	-	-	-	-	13.5	16.3
15 May 2015	7.7	8.3	5.9	67.6	6.3	6.6
20 May 2015	-	-	4.4	141	-	-
22 May 2015	17.5	9.0	-	-	11.3	7.4
1 June 2015	6.8	7.4	21.8	25.5	7.7	8.2
5 June 2015	10.7	7.9	10.1	42.1	-	-
12 June 2015	8.1	7.2	6.6	8.5	8.9	28.9
26 June 2015	-	-	6.5	26.5	19.6	7.4

A blank cell indicates that no sample was collected on that date.

Table 3.3. Nitrate-nitrogen concentrations before (upstream), after (downstream), and within the Arlington bioreactor, mg N/L. The four monitoring wells were equally spaced along the flow path within the bioreactor.

Date	Upstream	Well 1	Well 2	Well 3	Well 4	Downstream
8 May 2015	13.5	-	-	-	-	ND
15 May 2015	15.7	13.3	6.3	0.4	<0.1	3.5
22 May 2015	14.2	25.2	18.6	4.1	4.0	2.3
1 June 2015	18.7	17.5	15.5	5.1	1.9	10.5
5 June 2015	7.4	10.7	5.9	5.2	3.9	3.3
12 June 2015	17.2	15.4	12.1	6.2	5.1	13.2

A blank cell indicates that no sample was collected on that date. ND means the concentration was less than the detection limit.

Table 3.4. Nitrate-nitrogen concentrations before (upstream), after (downstream), and within the Arlington bioreactor, µg P/L. The four monitoring wells were equally spaced along the flow path within the bioreactor.

Date	Upstream	Well 1	Well 2	Well 3	Well 4	Downstream
8 May 2015	7.0	-	-	-	-	5.1
15 May 2015	61.4	6.3	7.4	4.8	6.8	6.9
22 May 2015	6.5	8.3	8.4	6.7	4.2	6.4
1 June 2015	6.5	5.0	7.4	6.9	4.5	5.8
5 June 2015	6.9	5.1	5.0	6.2	6.5	7.2
12 June 2015	6.6	5.4	8.0	15.4	7.4	4.7

A blank cell indicates that no sample was collected on that date.

3.4 Field Implementation and Monitoring Plan for Year 2

The following field efforts are planned for the second project year to meet the project objectives.

(1) Continue field monitoring and water sampling at all bioreactor sites.
(2) Complete the experimental design for field implementation and install a phosphorus removal bed at the Baltic site.
(3) Perform field monitoring of the phosphorus removal bed to determine phosphate reduction from the media.

(4) Continue information transfer through outreach and education.

4.0 Conference Presentations

This project led to the following presentations:

Sellner, B., Hua, G., Amiri, S., Trooien, T., Hay, C., Ahiablame. L., Kjaersgaard, J., 2015, Using low-cost adsorption materials to remove phosphorus from agricultural subsurface drainage, Western South Dakota Hydrology Meeting, Rapid City, SD, April 15. (Poster Presentation)

Amiri, S., Trooien, T., Hay, C., Ahiablame, L., Hay, C., Kjaersgaard, J., Hua, G., Sellner, B., 2015. Phosphorus removal media: A potential alternative to prevent phosphorus loss from agricultural drained lands. Poster presented at the SD 2015 Gamma Sigma Delta Achievement Day and Awards Banquet and Initiation Ceremony, Brookings, SDSU, SD, April 2, 2015.

Sellner, B., Hua, G., Kjaersgaard, J., Trooien, T., Hay, C., Ahiablame. L., 2015, Phosphorus removal in agricultural subsurface drainage using low-cost adsorbents, the 4th Annual Student Water Conference, Stillwater, OK, March 25-27. (Poster Presentation, this poster won an Outstanding Graduate Student Poster Award).

Sellner, B., Hua, G., Trooien, T., Hay, C., Ahiablame. L., 2014, Low-cost filtration materials for phosphorus removal, Eastern South Dakota Water Conference, Brookings, SD, October 29. (Poster Presentation, this poster won the 2nd place Student Poster Award).

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