# EXAMINATION OF SYNERGISM IN NITRATE AND ORTHOPHOSPHATE REMOVAL IN BIOREACTORS

BY

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THESIS

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# ABSTRACT

The use of fertilizer on agricultural cropland to replenish soil nutrients removed by crops is one of the most important steps to continually producing healthy, high yielding crops. However, the historic overuse of these fertilizers has had a detrimental effect on the receiving waters of agricultural watersheds. Due to their important role in plant nutrition, the two main nutrients generally associated with these impacts are nitrogen and phosphorus due to high application rates as well as high potential for transport to receiving waters. For these reasons, there is a demand for better management practices and remediation techniques to reduce and potentially eliminate the transport of nutrients from agricultural lands. To aid in this effort, this study evaluated materials suitable to convert orthophosphate into a non-bioavailable form as well as examine the synergistic effects of using this material in conjunction with a woodchip bioreactor known to have a high affinity for nitrate-N removal.

The evaluation of materials was conducted via a bench-top batch study and led to the selection of a locally available iron-based scrap steel material, which was able to remove over 99% of orthophosphate from solution at the 24 hour retention time. A laboratory-scale column reactor was then constructed using the iron-based material and woodchips as reactor media. Synergism was displayed as a result of alternating media arrangement with the observation of 25% higher reduction in nitrate-N concentrations, on average, as a result of interaction with woodchips when woodchips were downstream of steel turnings as opposed to upstream. This was also demonstrated in the orthophosphate results, where woodchips reduced orthophosphate concentrations by 8.54% on average when upstream of steel turnings, but yielded a net increase in orthophosphate concentration (23.8% of initial concentration on average) by converting bound phosphate back to orthophosphate when downstream of steel turnings. This led to a final experiment where the steel turnings were placed both upstream and downstream of woodchips. This confirmed earlier findings of enhanced nitrate-N removal by woodchips downstream of iron, while showing that the second iron section downstream of woodchips could once again remove orthophosphate from solution down to non-detectable concentrations.

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# CHAPTER 1: INTRODUCTION

In the past 50 years there have been substantial advancements in nearly every aspect of row crop agriculture, including seed technology, fertilizer and pesticide development and delivery systems, as well as tillage and land management practices. These advancements have led to vast increases in yield over the years, and have made farming practices much more efficient, allowing producers to grow more now than at any point in history.

While the advancements in agricultural have led to growth in production, it has not come without a price, particularly to the environment. The use of fertilizers has led to a net increase in the amount of nutrients in many soils. Nitrogen (N) and phosphorus (P) have been identified as the two most problematic nutrients. While N and P are both macronutrients that are essential for crop growth, each presents a unique problem when certain forms of these nutrients begin to accumulate in the environment. Past studies have identified these nutrients as being primarily responsible for the eutrophication of surface waters as well as the large hypoxic zone present in the Gulf of Mexico. In the case of nitrogen, some derived compounds have also been shown to have adverse health effects on humans above certain concentrations.

Although excess fertilizer application can lead to nutrient runoff from agricultural lands, the delivery mechanism is also a key issue. Subsurface drainage is a technique that has been used by agricultural producers for over 150 years to remove excess water from farmland. Among other benefits, this practice can allow farmers to enter fields earlier for spring planting, which provides them a larger window in which to ensure a good crop. It also allows for the rapid transport of water from poorly drained soils to prevent ponding, which can lead to crop losses throughout the growing season. Improvements in the effectiveness and efficiency of subsurface drainage systems have led to more economical production of crops. However, while subsurface drainage benefits crops, it can in turn have a detrimental effect on waters that receive drain outflow, since subsurface drains effectively act as a direct conduit for water-soluble nutrients. As a result, buildup of these nutrients can occur, degrading water quality and causing undesirable effects such as eutrophication.

Best Management Practices (BMPs) include a number of approaches that have been developed to minimize the negative effects of agriculture practices, as well as those of other industries, on the environment. In the case of agriculture, there are a number of BMPs that can be applied to slow or potentially prevent excess nutrient loading to receiving waters. While many of these practices are good in theory, there is a lack in research quantifying their ability to prevent or improve environmental externalities from agricultural practices. In many cases, existing BMPs have shown promise, but there is a need for further investigation, particularly to improve nutrient removal efficacy and to characterize synergistic effects.

This research is an attempt to address the need for more effective nutrient management practices. Outlet treatment approaches have been a topic of increasing interest for addressing nutrient loss through subsurface drainage. The use of biological and chemical substrates has shown potential in reactors or pseudo-filters for the removal of nutrients such as N and P from subsurface drainage waters. This study is an examination of the efficacy of two substrates to remove soluble N and P from solution on a laboratory scale.

# CHAPTER 2: OBJECTIVES

The overall goal of this study is to enhance the ability of bioreactors to remove nitrate-N and orthophosphate from agricultural drainage water. This specific study aims to contribute to this overall goal by providing baseline data to be used to select a material capable of reducing orthophosphate concentrations in solution and evaluate the synergistic effects of using it in conjunction with woodchips as a multi-stage bioreactor used to remove orthophosphate and nitrate-N from solution.

Under the specific objectives of this study, the following tasks were formatted:

1. Examine the change in orthophosphate concentration as a result of varying contact time with different materials known to have a capacity to adsorb or bind orthophosphate via bench-top beaker batch experiments.
2. Observe the changes in orthophosphate and nitrate-N concentration as well as other water quality parameters to observe the synergistic effects by alternating media placement of the material selected based on the results of task 1and woodchips in a two-stage laboratory-scale bioreactor.
3. Incorporate the results obtained from tasks 1 and 2 into a recommendation for future bioreactor research.

# CHAPTER 3: REVIEW OF LITERATURE

## 3.1 Non-Point Transport of Nitrogen and Phosphorus to Surface Waters

Non-point source pollution is generally considered to the result of several discrete inputs combining to produce a source of contamination. While separately the sources might be considered insignificant, together they can pose a greater threat than many point sources due to the inability to target the source and apply a treatment. A classic example of this is the export of fertilizers such as nitrogen and phosphorus from agricultural land.

### 3.1.1 Row Crop Agriculture

The use of fertilizers to replace soil nutrients taken up by crops has been practiced for many decades. Although this has helped increase crop yields over the years, fertilizers are often applied in quantities in excess of crop uptake. This practice has led to a net increase in certain nutrient concentrations such as Nitrogen (N) and Phosphorus (P) in soils in many crop production areas throughout the world (Carpenter et al., 1998; Brown et al., 1997). This increase in soil nutrient concentrations, along with a variety of other factors (e.g. tillage practices, landscape, timing of fertilizer application, weather patterns, soil type, and other environmental factors), has led to long-term adverse effects on the receiving waters of agricultural watersheds. Although it is important to note that (rowcrop) agriculture is not the only contributor of N and P discharge to receiving waters, over the past two decades it has been shown that cropland alone is responsible for as much as 48% and 37% of all nonpoint N and P discharges to surface waters in the United States, of which nonpoint sources accounted for 82% and 84% of the total N and P discharges to surface waters, respectively (Carpenter et al., 1998; Havens and Steinman, 1995; Gianessi et al., 1986). A more recent simulation study conducted in the Mississippi River Basin estimated that agricultural watersheds accounted for 70% of the total N and P delivered to receiving waters, with corn and soybean acres alone accounting for 52% of the total N delivered and 25% of the total P delivered (Alexander et al. 2007).

### 3.1.2 Nitrate and Phosphate

Nitrogen (N) and Phosphorus (P) occur in a number of different forms in a row crop agriculture setting. However, nitrate and phosphate tend to attract greater attention due to their unique properties. Although there are other forms of N and P that occur in agricultural soils and drainage waters, nitrates and phosphates are the most water soluble. Because nitrate and phosphate are also the forms most readily available for crop uptake, many agricultural fertilizers either already contain some form of nitrate or phosphate, or contain compounds that are readily converted to these forms in the soil.

Nitrate is the most water soluble form of nitrogen (N) in agricultural soils and therefore makes up the largest percentage of N transported from agricultural lands (USGS, 1996). In most areas of the United States, this leads to greater nitrate concentrations in groundwater as compared to surface water, with the exception of the vastly cultivated Midwest. Here, the presence of highly fertile, but poorly drained soils oftentimes requires artificial subsurface drainage to remove excess water from fields and ensure a good crop. However, frequently, an externality of this practice is the transport of nitrates to surface waters (USGS, 1996).

Phosphates are only moderately soluble as compared to nitrates. Phosphate is commonly found bound to soil particles and exists as particulate P (USGS, 1996). This form of P is typically not readily available for plant uptake except under certain conditions of pH and dissolved oxygen in solution (Evangelou, 1998). In agricultural areas, P can be found in both the soluble phosphate and particulate P forms. In most cases particulate P tends to dominate the ratio and be the main fraction transported, but under certain conditions soluble phosphate can dominate (Sharpley and Smith, 1990; Kronvang et al., 1997; Heathwaite and Dils, 2000).

### 3.1.3 Distribution and Usage Trends in the United States

While the application of fertilizers containing plant nutrients to crops is a practice that has been used for decades, the amounts of those fertilizers applied has varied greatly over time. From 1964 to 2010, the amount of nitrogen and phosphate applied to corn, cotton, soybeans, and wheat acres increased by 212% and 94%, respectively (Figure 3.1). Over this same time period, the total number of acres planted for these crops only increased by just over 40%, giving a net increase of 128% and 41% in the amount of nitrogen and phosphate applied on a per acre basis. It is important to note, however, that there has been a significant increase in yield for these crops over this time span (corn: 142%, cotton: 57%, Soybeans: 91%, and Wheat: 79%) (USDA, 2012). While this has led to an improved nitrogen balance and phosphorus deficit in soils in recent years in many watersheds, areas still exist where the amount of nutrients applied are greater than the amount of nutrients removed by the harvested crop (Figure 3.2 and Figure 3.3).

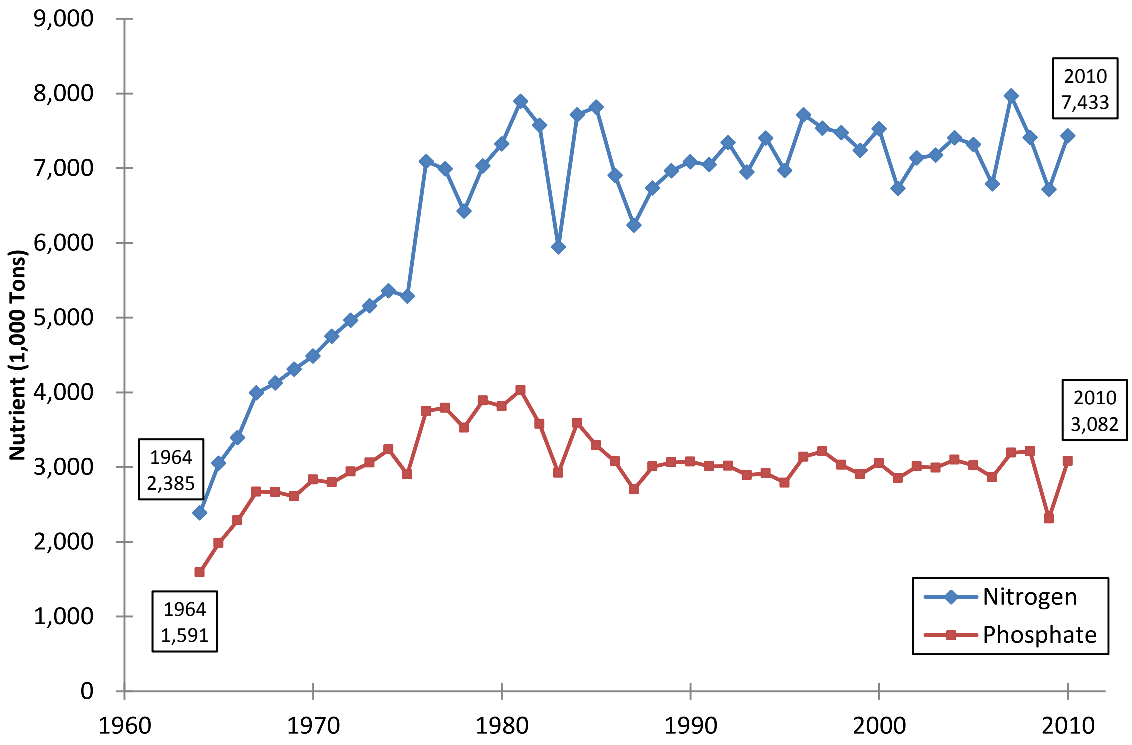

Figure 3.1. U.S. Consumption of Plant Nutrients (for Corn, Cotton, Soybeans, and Wheat): 1964-2010 (Source: USDA/NASS, 2012)

Figure 3.2. Watershed N Balance for the United States. (Source: IPNI, 2012)

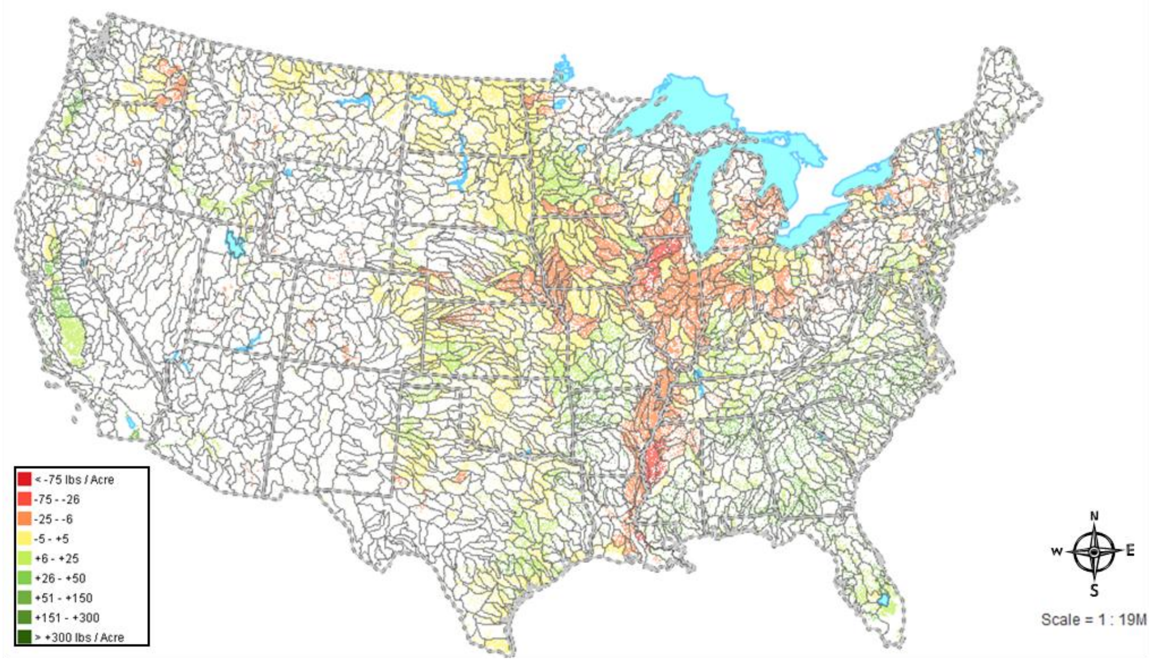

**Figure 3.3. Watershed P Balance for the United States. (Source: IPNI, 2012)**

### 3.1.4 Loss Quantification and Variability

A number of factors can contribute to the amount of N and P lost from agricultural lands. These losses can be widely variable due to timing and form applied, method of application, soil type, season, timing of rainfall events, tillage/incorporation, artificial drainage, vegetative cover, and other environmental factors (Carpenter et al., 1998). It has been shown that the various combinations of these factors can lead to N losses from 10% to 80% of initially applied fertilizer from agricultural lands (Howarth et al., 1996). P is much less soluble than N, and P losses are generally more closely linked to the P content of the soil in agricultural fields as opposed to environmental and human-induced factors. However, certain conditions can lead to significant P loss. Gentry et al. (2007) observed an event that resulted in 40% of the total average annual phosphorus loss occurring over a seven day span. Cooke et al. (2004) observed that most of the phosphorus lost from several subsurface drainage systems occurred in a few discrete events that typically occur after extended dry periods.

### 3.1.5 Pathways

Three main pathways have been identified as contributing to N and P losses from agricultural croplands to receiving waters. Those pathways are surface or overland transport, subsurface or artificial drainage transport, and leaching or deep seepage transport to groundwater. The first two pathways, surface and subsurface, discharge N and P to surface waters, which can be generally classified as drainage ditches, streams, rivers, ponds, lakes, and other open surface water bodies. The third pathway, leaching, is responsible for contributing N and P to groundwater. Although losses of N and P can be transported through all of the different pathways, due to their differences in chemical properties, studies have found trends in which pathways tend to dominate the transport of each. Varying combinations of factors affecting N and P loss from agricultural croplands allow for these losses to occur via different pathways. Different combinations of these factors determine which pathway will contribute the greatest loss.

Nitrogen (N) tends to be transported via subsurface drainage and leaching. As reported by the USGS (1996), nitrate is the most common contaminant of groundwater in the United States. This is due to the negatively charged nitrate molecules being repelled by the mostly negatively charged clay and organic matter in the soil column. This dynamic, combined with the gently sloping, poorly drained soils throughout much of the intensely cultivated Midwest has led to leaching and subsurface drainage being the predominate pathways for nitrate transport (Zhao et al., 2001). Although subsurface transport and leaching of N are the two most prevalent pathways, surface transport does also take place, particularly of ammoniacal forms of N. Although ammonium ions are quickly converted to nitrate by the soil in general, they can remain near the surface. These positively charged ions can become bound to soil particles and, therefore, can be transported via surface runoff to receiving waters (Dodds and Oakes, 2008).

The predominate phosphorus (P) transport pathways are significantly different from those for nitrogen (N). A review of literature on the loss pathways for this nutrient show that the dominant transport pathway can vary depending on the conditions of the study location. A wide range of results have been reported, citing the dominant pathways being both surface and subsurface depending on site characteristics. The common consensus in many reports over the past 40 years was that due to its low mobility in soils, P is predominately transported in surface runoff (Baker et al., 1975; Sharpley et al., 1993; Sims et al., 1998; Heathwaite and Dils, 2000; Hansen et al., 2002; Algoazany et al., 2007). Based on this belief, studies during this period were largely focused on quantifying P transport in surface runoff and neglected to investigate the subsurface fraction of P transport (Sims et al., 1998; Hansen et al., 2002; Algoazany et al., 2007). However, some studies over the past decade have made an attempt to quantify the subsurface portion of P transport. In a study in East Central Illinois monitoring four sites over a seven year period for soluble P concentrations in surface runoff and subsurface flow, Algoazany et al. (2007) found that the average and annual flow-weighted soluble P concentrations at all four sites were higher in surface runoff than in subsurface flow. However, due to the topography of the study area, nearly eight times as much of the annual precipitation was removed via subsurface drainage than surface runoff. This led to a substantially greater annual average soluble P mass load occurring in the subsurface flow (Algoazany et al., 2007).

### 3.1.6 Tile Drainage

The implementation of artificial subsurface (tile) drainage has greatly increased the agricultural productivity of poorly drained soils throughout the Midwestern United States and other parts of the world. However, the same mechanisms that allow for the increase in land productivity have an adverse environmental effect on the receiving waters of tile drained agricultural lands (Skaggs et al., 1994; Fausey et al., 1995; Shirmohammadi et al., 1995; Kladivko et al., 2001; Algoazany et al., 2007). While tile drainage increases infiltration it also decreases soil-water retention time and decreases the amount of storm water that occurs as surface runoff. This effect has altered the interaction between soil, water, and nutrients and led to a significant change in the way that nutrients previously behaved in agricultural fields.

## 3.2 Impacts of Nutrient Contamination

The effects of nutrient contamination represent a broad array of conditions that impact the environment in different ways depending on severity. In many cases, effects are generally mild an unnoticed by the majority of people, however, eutrophication can take place in areas where water bodies are subject to prolonged exposure. This effect is often detrimental to the general water quality in that area and can threaten aquatic species as well as humans in some instances.

### 3.2.1 Eutrophication and Hypoxia

Eutrophication, in relation to water quality, is the term used to identify the process by which excessive algae and algal blooms form in a water body due to an outside source of nutrients. Agroecosystems and/or discharged human waste from settlements, as caused by nutrient enrichment through runoffs that carry down overused fertilizers typically being the largest contributors (Khan and Ansari, 2005). Although eutrophication can occur naturally over the lifespan of a water body, human activity can greatly accelerate the rate at which this process takes place (Khan and Ansari, 2005). All types of surface water bodies are susceptible to eutrophication; streams, rivers, ponds, estuaries, lakes and even coastal waters have been distinctly affected by eutrophication in various locations all over the world (Yang et al., 2008). The degradation of surface waters by eutrophication poses a large threat to global water resources (Anderson et al., 2002). This is especially true in areas of large population where surface water reuse is essential to sustain life.

A variety of human-related activities contribute to the accelerated rate of eutrophication seen in surface waters. Excessive nutrient loadings to surface waters are a result of both point and non-point pollution and can be the consequence of industrial activities, municipal sewage, domestic animal waste, and runoff from production agriculture (Anderson et al., 2002; Yang et al, 2008). The primary nutrients responsible for the eutrophication of these surface water bodies are nitrogen (N) and phosphorus (P), and non-point sources tend to be a greater contributor on an annual basis (National Research Council 2000). Of the two nutrients, P tends to be limiting for algal growth, although both contribute and can be limiting (Mainstone and Parr, 2002). According to

Zhao (2004), 80% of lake and reservoir eutrophication is limited by phosphorus, 10% by nitrogen and 10% by alternate factors.

Phosphorus is considered to be the main limiting nutrient with regard to primary production leading to the eutrophication of fresh waters (Sharpley et. al., 1994; Correll, 1997; Smith et. al., 1999). Although there are many sources that contribute to this, the overuse of commercial fertilizer from production agriculture has been identified as one of the most significant (Sharpley et. al., 1994; Foy et. al., 1995). In the United States, agricultural contributions alone have been deemed responsible for the impairment of 55% and 58% of the river length and lake area surveyed, respectively (Sharpley et. al., 1994).

The effects of eutrophication are problematic on a variety of different levels. In areas where water bodies, such as lakes, are used for recreation, eutrophication can degrade the water quality and make recreation undesirable and in some cases unsafe. Alternatively, in regions where these waters are necessary to sustain a population as a source of food and/or drinking water, the impacts can be more catastrophic. The release of toxins by certain species of algal blooms can cause death in both aquatic life and humans (Yang et al, 2008). More commonly reported impacts, however, are related to general environmental and economic concerns such as shifts in the equilibrium of aquatic ecosystems by depletion of dissolved oxygen and a decline in aquatic life populations used to sustain seafood markets (Yang et al, 2008).

The most widespread example of the effects of human-influenced eutrophication on a large scale is the oxygen-depleted hypoxic or “dead” zone in the Gulf of Mexico. Suffering from the aforementioned impacts, this zone averaged an area of approximately 5,200 square miles between 1985 and 2009, reaching an area of nearly 8,500 square miles in 2002 (Rabalais et al., 2010). Occurring between the months of February to November, the size of the hypoxic zone is closely related to the nitrate load of the Mississippi River when it is at its peak in mid-summer (Turner et al., 2006). As the US Geological Survey has shown the primary areas that contribute nitrogen and phosphorus to the Mississippi River to be primarily agricultural watersheds throughout the Midwest, it is recommended that they be the targets of control measures in order to mitigate hypoxia in the Gulf of Mexico (Rabalais et al., 2010; USEPA, 2008; Alexander et al., 2008).

### 3.2.2 Other Effects

Aside from eutrophication and hypoxia, a number of other adverse effects have resulted from nutrient contamination, with elevated nitrate levels in drinking water being one of the most common. Nitrate tends to attract attention due to the associated human health impacts. High nitrate levels in drinking water used to make baby formula have been shown to induce methemoglobinemia, more commonly known as “blue baby syndrome”, in young infants (USEPA, 1991). This syndrome can lead to many adverse health effects in exposed children including coma and death in some cases (USATSDR, 2001). Although there is no unanimity in the literature, some studies have shown long term high nitrate exposure is linked to various types of cancer, brain tumors, leukemia, and nasopharyngeal tumors in humans ranging from children to adults (Preston-Martin et al., 1982; USEPA, 1991; Dusdieker et al., 1994; McCredie et al., 1994; Sarasua and Savitz 1994; Preston-Martin et al., 1996; Ward et al., 2000; Pogoda and Preston-Martin, 2001; Sanchez-Echaniz et al., 2001; Volkmer et al., 2005; USEPA 2007).

Although exposure to high nitrate can come from various sources, drinking water from private groundwater wells has been shown to be one of the most common. These wells tend to be shallower than most public water supply wells and therefore more susceptible to nitrate contamination from sources such as agriculture. In a survey by the USGS (1996), approximately 12% of private groundwater wells contained nitrate levels higher than the USEPA maximum contaminant level (MCL) for drinking water of 10 mg/L of nitrogen in the form of nitrate (nitrate-N).

## 3.3 Best Management Practices (BMPs)

Best Management Practices (BMPs) are various practices implemented to reduce the negative externalities of various industries on an environmental system to help increase their sustainability. In the case of agriculture, a review of the literature indicates a strong need for the continued use and development of BMPs to reduce nutrient transport from agricultural fields. With the variability inherent to nutrient transport from agricultural fields, it can be concluded that a multitude of management techniques need to be utilized in order to control the problem. Some of these techniques include controlling excess use of fertilizers, implementing conservation tillage practices, utilizing terraces and vegetative filter strips, and in the presence of subsurface drainage, implementing wetlands and using an end of the pipe treatment approach.

Research indicates that wetlands can be an effective means of reducing nutrient concentrations and improving water quality parameters of waters leaving agricultural lands. This is demonstrated by a study near Bloomington, IL, where volume-weighted concentrations of NO3-N in runoff entering Lake Bloomington were reduced by 42% and 31% in two trial scale wetlands and combined P mass retention was 53% (Kovacic et al., 2006). However, an extrapolation of the results indicated that a 450 hectare wetland costing between \$3 and \$3.5 million would be necessary in order to reduce N loading to

Lake Bloomington by 46%. Other wetland research indicates that soil amendments must often be added to increase the sorption capacity of the soil in order to extend the wetlands effectiveness to remove soluble P (Ann et al., 2000). Although it is known that the cost of implementation is far less expensive than current water treatment plant nutrient removal methods, less expensive alternatives that remain effective and do not remove land from agricultural production are desirable.

### 3.3.1 Outlet Treatment Approach

An outlet treatment approach is increasing in popularity for use as a subsurface drainage nutrient removal BMP. This method typically consists of a diversion structure which intercepts the subsurface drainage tile outlet and diverts flows through a filter media (biological or chemical) before the water is allowed to enter the receiving water body. In contrast to wetlands, current designs of these systems are installed parallel to receiving streams and take little to no agricultural land out of production. While no standard filtration media yet exist, woodchips and other carbon containing substrates have shown great promise for promoting denitrification and have greatly reduced NO3-N loads in several studies (Blowes et al., 1994; Cooke et al., 2001; Greenan et al., 2006; Chun et al., 2007; Jaynes et al., 2008; Robertson et al., 2009). With NO3-N being the primary contaminant transported through artificial subsurface drainage, the early focus of this approach was to promote denitrification through the introduction of an additional carbon source. However, the achievement of highly reduced NO3-N loads has increased interest to investigate this method using other types of media to remove other nutrients and contaminants such as pesticides and soluble P. In most studies, testing of materials for their ability to remove soluble P from solution had been focused towards waste water treatment application (Bastin et al., 1999; Jeon et al., 2002; Zeng et al., 2004; Genz et al., 2004; Boujelben et al., 2007; Xiong et al., 2007; Dobbie et al., 2009) or improving soil amendments for wetland application (Drizo et al., 1999; Brooks et al.; 2000, Seo et al., 2005; Leader et al., 2005; Leader et al., 2008), but recently, some have focused on the treatment of tile drainage waters (McDowell et al., 2008; King et al., 2010).

With respect to materials used for the removal of soluble P from solution in a tile outlet treatment application, most research trials have explored industrial waste products as sorbents, generally containing large percentages of natural minerals such as calcium (Ca), aluminum (Al), and iron (Fe) in various forms (McDowell et al., 2008; King et al., 2010). McDowell et al. (2008) found that using a mix of 90% melter slag and 10% basic slag (steel and energy industry by-products) as a backfill around tile drains decreased P loss by approximately two-thirds on a load basis as compared to the control drain. It was also found that when using this mixture of media in a porous mesh and locating it in the end of the drain that up to 70% of reactive P was removed as compared to the control. Similarly King et al. (2010) found that using a blend of clinoptilolite (a type of zeolite), alumina (aluminum oxide), and activated carbon (a well-known contaminant sorbing compound) reduced dissolved reactive phosphorus loads by an average of 51.6% for lab simulated tile flow rates up to 1.9 L/s with removal rates being inversely proportional to flow rate.

While existing research has begun to address efficient and cost effective approaches for controlling contaminant release from tiled drained agricultural lands, current methods and materials are far from refined. Although King et al. (2010) were able to cut dissolved reactive phosphorus loads in half, N03-N removal rates were negligible at 4.7% on average.  This allows for a large increase in removal efficiency of both nutrients before the methods behind this approach could be considered ideal.  Based on the results of existing research, the goals of this study was to conduct beaker trails and lab scale column experiments to test the efficacy of using woodchips and a steel by-product from a local steel forge for their ability to remove NO3-N and soluble P from solution for use as a subsurface tile drainage BMP.

# CHAPTER 4: BENCH-TOP BATCH EXPERIMENTS

## 4.1 Methods and Materials

Bench-top batch experiments were conducted at the Agricultural Engineering Sciences Building at the University of Illinois campus in Urbana-Champaign. The purpose of these experiments was to evaluate different materials for their potential use in a larger scale, column reactor trial. The media chosen for the batch trials were based on their ability to remove soluble phosphorus from solution in trials in the literature, or their similarity to material that was successfully used for this purpose in previous trials. Based on this criterion, as well as characteristics including porosity, cost, and availability, aluminum oxide (an industrial blast grit cleaning product and commercial adsorbent), steel wool (a refined steel product for sanding and polishing), and steel turnings (a by-product of industrial milling and fabrication) were chosen. Aluminum oxide was chosen based on similar research conducted by Genz et al. (2004), where this material showed a high affinity for phosphorus sorption. Steel wool and steel turnings, both sharing very similar chemical compositions, were selected based on multiple studies that showed iron oxides and hydroxides as having a high capacity to adsorb soluble phosphorus (James et al., 1992; Zeng et al., 2004; Genz et al., 2004; Boujelben et al., 2007).

Batch trials were conducted to investigate the effect of contact time with the different materials on the concentration of orthophosphate remaining in solution. In these trials, the media was placed in a glass beaker with 500 mL of de-ionized water spiked with $KH_2PO_4$ for different retention times. All of the trials were conducted at room temperature (approximately 24-25 degrees Celsius) and contained a control in which no media was placed in solution. At the end of each time period, the solution was shaken by hand, and a 30 mL sample of the 500 mL volume was collected and immediately vacuum filtered using 0.45 micron pore size filters and stored at 4 °C until being analyzed for orthophosphate according to EPA Method 365.1. An example of the beaker setup during a portion of the steel turnings and aluminum oxide trials is pictured in Figure 4.1.

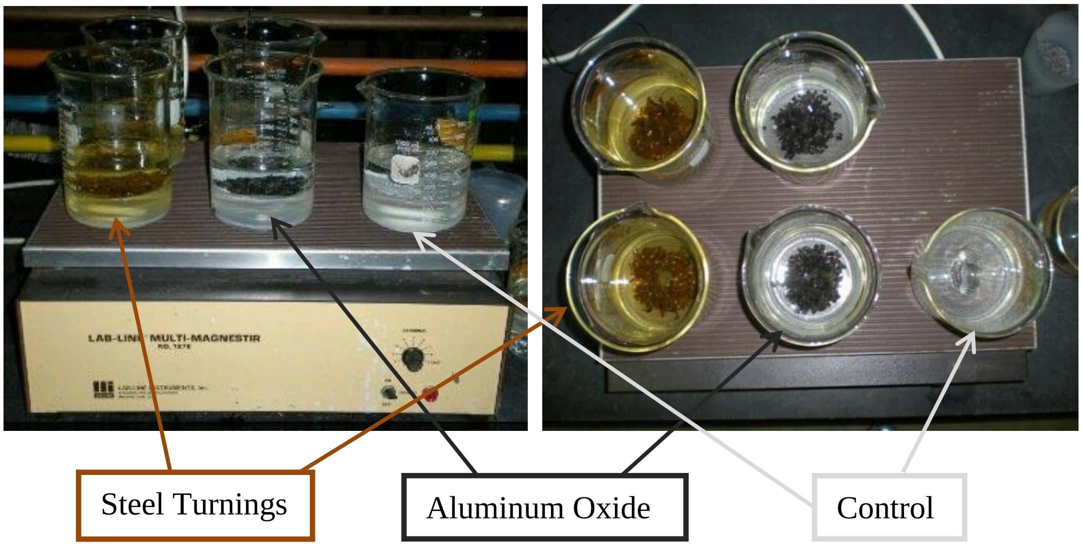

Figure 4.1 Beaker trials for steel turnings and aluminum oxide

### 4.1.1 Steel Wool Experiments

Steel wool was chosen for use in batch trials based on its high iron content and large surface area. The steel wool selected was very fine (#0000 grade), and was previously untreated in any way before being used in these beaker trials. In each trial, 25.0 g of steel wool was weighed and placed in a beaker. Orthophosphate spiked solution was then added to the beaker entirely inundating the mass of steel wool. The beakers were hand shaken at the beginning and end of each time period, but were not agitated between the beginning and end of the experiment.

Two different concentrations of orthophosphate solution were tested in the presence of steel wool; 25 mg-P/L and 5 mg-P/L. 500 mL of each orthophosphate solution was measured out and poured into a separate beaker for each retention time tested. The retention times examined were 0.02, 0.08, 0.25, 0.5, 0.75, 1, 2, 4, 6, 8, 10, 12, 16, 20, 24, and 48 hours (the 0.02, 0.75, 16 and 48 hour retention times were not tested for the 5 mg-P/L trial). The 25 mg-P/L initial concentration was selected in order to insure the observation of a reaction and the 5 mg-P/L concentration was indicative of a likely “worst case” scenario from agricultural drainage outflow. The 25 mg-P/L trial was conducted in triplicate, while the 5 mg-P/L was conducted in duplicate.

### 4.1.2 Steel turnings Experiment

Steel turnings were obtained from Kurland Steel Company located in Urbana, IL. The turnings are a by-product of a CNC (Computer Numeric Control) milling machine. Prior to being used in the trial, the turnings were sieved by hand using a #4 sieve to achieve an approximately uniform particle size. Due to lubricant present on the turnings, they were washed in a non-phosphate soap solution and rinsed several times with de-ionized water prior to being used in the trials. In each trail, 50g of the steel turning material was placed in a beaker for each retention time period investigated. Orthophosphate spiked solution was then added to the beaker, fully inundating the material. Since the steel turning material had a much smaller surface area than the steel wool, the volume occupied by the media was much less in these trials as compared to the steel wool trials. Because of this, each beaker was magnetically stirred to ensure the uniformity of the solution.

For each retention time tested, 500 mL of 5 mg-P/L phosphate solution was added to 50 g of turnings in each beaker and reacted for times of 0.5, 2, 6, 12 and 24 hours.

### 4.1.3 Aluminum Oxide Experiment

Aluminum oxide media, #6 particle size, was purchased from AGSCO Corp. for use in a trial. Prior to the trial, the media was untreated. For each retention time tested, 50 g of the media was measured and entirely inundated in orthophosphate spiked solution. The beakers were magnetically stirred to ensure consistency in the solution throughout the experiment, also because the volume occupied by the media was small in comparison to the volume of the beaker.

For each retention time tested, 500 mL of 5 mg-P/L phosphate solution was added to 50 g of aluminum oxide in each beaker and reacted for time periods of 0.5, 2, 6, 12 and 24 hours.

## 4.2 Results and Discussion

### 4.2.1 Steel Wool

The results of the steel wool retention trials displayed significant reduction of orthophosphate in solution for both the 25 mg-P/L and 5mg-P/L initial concentration trials. In the 25 mg-P/L experiment, the concentration of soluble phosphorus remaining in solution was 5.04 mg-P/L at the longest retention time tested (48 hours). The range of percentage of orthophosphate removed from solution was from 1.13% in 0.2 hours (shortest retention time) to 80.83% removed after 48 hours (longest retention time). During the 5 mg-P/L experiment, a residual concentration of only 0.34 mg-P/L remained after the 12 hour retention period, with the percentage of orthophosphate removed ranging from 0.00% at the 0.25 hour retention time to 93.79% at the 12 hour retention time. Table 4.1 depicts the full range of retention times, average residual concentrations, and average reduction percentages observed across all trials. Various irregularities in residual concentration of orthophosphate remaining in solution were observed throughout some of the retention times tested for both the 25 mg-P/L and 5 mg-P/L trials (i.e. some longer retention times had significantly greater orthophosphate concentrations remaining than some of the shorter retention times tested), however this was much more pronounced in the 5 mg-P/L trial. Although this occurred, high removal rates were observed and the inconsistency is likely due to the lack of agitation of the solution which possibly introduced non-uniformity within the reactions in some of the trial times tested. One negative percent reduction was observed during the trials indicating a higher orthophosphate concentration at a retention time greater than zero. It is assumed that this was due to general error in the experiment and the limitations of accuracy in the analytical method.

Sorption percentages of initial concentration observed in these beaker trials were similar to those found by James et al. (1992) during beaker trials with preformed rust (iron oxides) created from steel wool. It is important to note, however, that any differences in sorption rates as compared to James et al. (1992) can be attributed to their use of preformed rust instead of unaltered steel wool (elemental iron). Delayed rates of sorption were observed in this study because of the time needed for iron oxides to develop from the elemental iron.

**Table 4.1. Average concentration and percent reduction for steel wool batch trials.**

| Retention Time (hrs.) | 5 mg-P/L Initial Concentration | | 25 mg-P/L Initial Concentration | |
|---|---|---|---|---|
| | Avg. Conc. (mg-P/L) [a] | Avg. Reduction (%)[a] | Avg. Conc. (mg-P/L) [b] | Avg. Reduction (%)[b] |
| 0.00 | 5.41 | 0.00 | 26.30 | 0.00 |
| 0.02 | *NT* | *NT* | 26.00 | 1.13 |
| 0.08 | 5.36 | 0.88 | 23.71 | 9.84 |
| 0.25 | 5.41 | 0.00 | 22.39 | 14.85 |
| 0.50 | 5.28 | 2.34 | 21.36 | 18.77 |
| 0.75 | *NT* | *NT* | 21.53 | 18.12 |
| 1.00 | 5.03 | 7.08 | 19.87 | 24.44 |
| 2.00 | 4.81 | 11.10 | 16.02 | 32.50 |
| 4.00 | 1.93 | 64.29 | 11.95 | 54.57 |
| 6.00 | 0.99 | 81.75 | 11.75 | 55.33 |
| 8.00 | 0.72 | 86.68 | 12.75 | 51.51 |
| 10.00 | 3.33 | 38.48 | 10.94 | 58.39 |
| 12.00 | 0.34 | 93.79 | 9.74 | 62.98 |
| 16.00 | *NT* | *NT* | 9.13 | 65.28 |
| 20.00 | 2.36 | 56.37 | 7.99 | 69.61 |
| 24.00 | 1.08 | 80.10 | 8.53 | 67.57 |
| 48.00 | *NT* | *NT* | 5.04 | 80.83 |

*NT = Not Tested*

[a] Average of two trials

[b] Average of three trials

### 4.2.2 Steel Turnings

The Steel Turnings also demonstrated a high capacity for removing soluble phosphate from solution. The 5 mg-P/L initial concentration was reduced to 0.01 mg-P/L (99.72% removed) at the end of the 24 hour time period. Table 4.2 shows the full range of retention times tested, average concentration remaining in solution, and average percent reduction over the two trials.

Similar to the steel wool beaker trial results, the sorption rate observed is likely the combination of the time needed for iron oxides to form from the steel turnings (elemental iron) as well as the time needed for sorption of the soluble P to the iron oxides to take place. Results observed for these trials were more consistent than those from the steel wool trials (i.e. longer retention times produced greater percent reductions of orthophosphate). This is likely because these trials were magnetically stirred which ensured uniformity in the solution throughout the experiment.

**Table 4.2. Average concentration and percent reduction for Steel Turnings.**

| | 5 mg-P/L Initial Concentration | |
|---|---|---|
| Retention Time (hrs) | Avg. Conc. (mg-P/L) [a] | Avg. Reduction (%)[a] |
| 0 | 4.98 | 0.00 |
| 0.5 | 4.87 | 2.11 |
| 2 | 4.18 | 16.11 |
| 6 | 2.74 | 44.91 |
| 12 | 0.19 | 96.28 |
| 24 | 0.01 | 99.72 |

[a] Average of two trials

### 4.2.3 Aluminum Oxide (Alumina)

The aluminum oxide displayed mixed results over the variety of retention times. Over the five retention times tested in two separate trials, three of the five from one of the runs was returned displaying residual orthophosphate concentrations in solution below the minimum detectable limit (MDL). All of the other retention periods were returned showing no effect on the initial concentration of 5mg-P/L. These results are displayed in Table 4.3 and do not contain the average reduction percentage due to irregularities in the data. These results are far different than those observed by Baker et al. (1998), where aluminum oxide was used in similar batch experiments resulting in greater than 99% removal of dissolved reactive phosphorus from solution within one hour of contact time.

Due to wide variability in the results from trials using this material, as well as the cost and availability of the material (more expensive than other materials tested and not locally available), use of this material in further beaker trials or larger scale experiments was not pursued.

**Table 4.3. Average concentration for both batch trials with aluminum oxide.**

| Retention Time (hrs) | 5 mg-P/L Initial Concentration | |
|---|---|---|
| | Trial 1 Conc. (mg-P/L) | Trial 2 Conc. (mg-P/L) |
| 0 | 4.98 | 4.98 |
| 0.5 | 4.96 | <MDL |
| 2 | 4.96 | <MDL |
| 6 | 4.93 | <MDL |
| 12 | 4.96 | 4.98 |
| 24 | 4.93 | 4.99 |

<MDL = Below Minimum Detection Limit

### 4.2.4 Effect of Retention Time

The effect of retention time on the residual orthophosphate concentration in solution was observed in these beaker trials. Figure 4.2 shows a plot of the results for both steel wool experiments (25 mg/L-$PO_4$ and 5 mg/L-$PO_4$ initial concentration) and the steel turnings experiment (5 mg/L-$PO_4$ initial concentration). An analysis of these results indicates that retention time (contact time between media and solution) did directly affect the concentration of orthophosphate remaining in solution at the end of each trial time tested for all experiments. However, variation in the results between percent reductions of orthophosphate versus time curves displayed in Figure 4.2 is likely due to multiple factors that varied among trials, which will be discussed in further detail in the following paragraphs.

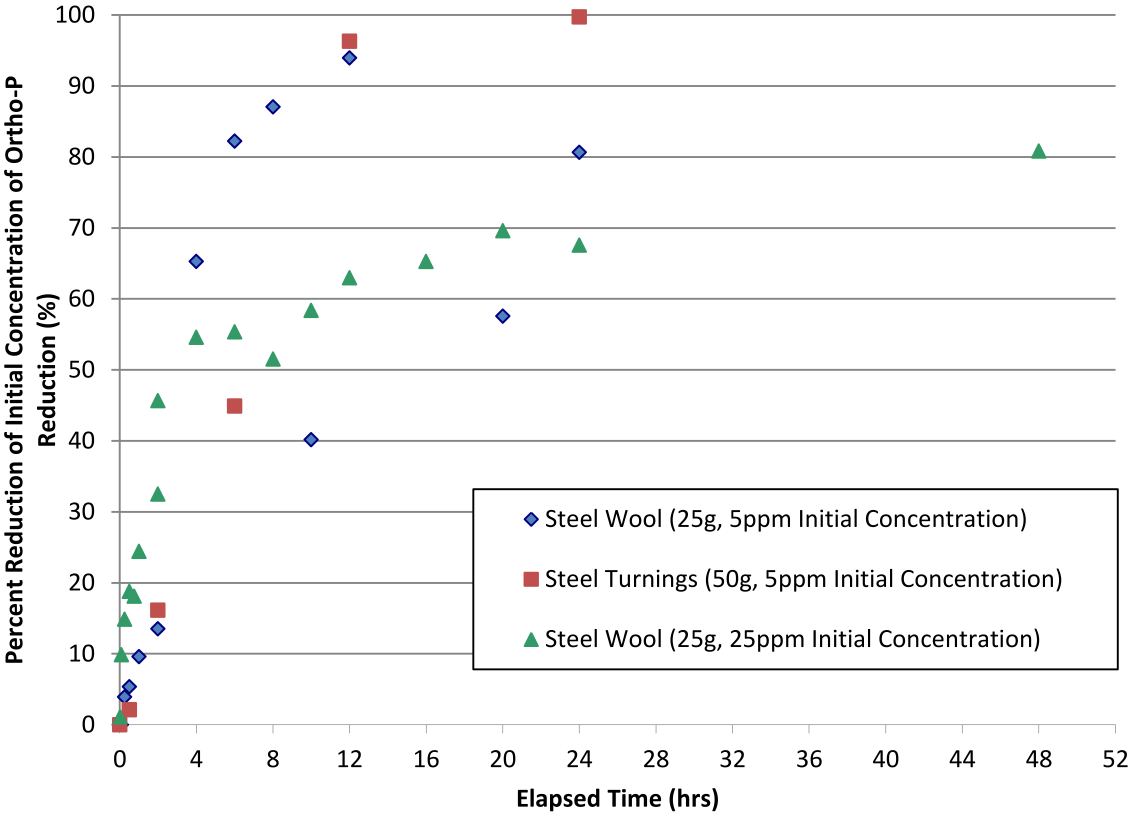

**Figure 4.2. Percent reduction PO4-P Vs. Time plots for all batch trials.**

### 4.2.5 Oxidation

The process of oxidation of the elemental iron in both the steel wool and the steel turnings to form iron oxides is likely the rate limiting process being observed in the percent reduction of soluble P vs. time plots. Justification of this can be explained by the results found by Boujelben et al. (2008), where iron oxide coated sorbents were tested for their ability to remove soluble P from solution. During the kinetic study portion of their batch experiments, they found that equilibrium (equilibrium being between approximately 75% to 95% soluble P removal) was reached after 15 to 60 minutes of contact time for all of the sorbents tested.

### 4.2.6 Surface Area

The percent reduction of soluble P versus time plots is also an indicator of the effect of surface area on the rate of reduction of soluble P by the steel wool and steel turnings. It can be noticed that in both of the steel wool experiments that the initial rate of reduction is greater than the rate of reduction during the steel turnings experiment even though double the mass (50g instead of 25g initial mass of media) was used during the steel turnings experiment. This can be attributed to the larger surface area providing more oxidation sites for the formation of iron oxides.

### 4.2.7 Initial Soluble P Concentration

Another factor that was observed to have an effect on the initial rate of reduction is the initial soluble P concentration. When examining the reduction versus time plot for the beginning two hour period of the experiment, the rate of reduction in the 25 mg/L-$PO_4$ initial starting concentration experiment was faster than that observed in the 5 mg/L-$PO_4$ initial concentration trial. Because no factors except initial concentration of $PO_4$ ions were varied between the steel wool trials, it can be assumed that this effect is directly related to that variable. It can also be inferred that this observation occurs due to the extra $PO_4$ ions in solution and initially present at the beginning of the trial. This observation can also explain the similarities between the reduction rates observed from 0 to 2 hours for the steel wool and steel turnings trails that were conducted with the 5 mg/L-$PO_4$. It can then be assumed that surface area becomes limiting for oxidation to occur, thus allowing steel wool (having more surface area) to more quickly adsorb the remaining soluble P as compared to the steel turnings.

## 4.3 Summary and Conclusions

Three different materials (steel wool, steel turnings, and aluminum oxide) were tested in beaker trials for their ability to remove soluble phosphorus from solution. The materials varied in terms of cost, availability, chemical composition, size, density, and surface area. In these trials, each material tested was reacted for differing lengths of time. The results of the trials were used to produce reduction versus time plots, which yielded a curve for each material tested. From these results, observations were made to evaluate each material for suitability in a larger scale column reactor trial.

Conclusions of the beaker trials included:

- Retention time had a direct effect on the concentration of soluble P remaining in solution for all of the materials tested except aluminum oxide. It remains unknown as to the why the results of the aluminum oxide trial were inconsistent, but due to the limitations of the study, further trials with the material were not conducted.
- Due to differences in reduction times between this trial and similar research (Boujelben et al., 2008), it can be concluded that the rate of reduction observed in these trials was rate limited by the oxidation of the steel materials and not by the reaction of the orthophosphate and iron oxide.
- The difference in surface area between the steel wool and steel turnings had an effect on the rate of oxidation of the iron in each material. This resulted in a faster initial rate of reduction in orthophosphate concentration observed in the steel wool trials.

- The effect of initial concentration of $PO_4$ ions in solution on the $PO_4$ reduction rate from 0 to 2 hours was observed. It can be concluded that a higher initial concentration of $PO_4$ in solution allows for an increased rate of those ions coming into contact with sorption sites, thus increasing the initial rate of reduction.

Based on the evaluation criteria and the findings from the beaker trials, steel turnings were selected for use in the larger scale column reactor trial. The displayed ability of the turnings to reduce orthophosphate at rates similar but slightly lower to those observed for the steel wool indicated that the oxidation of the steel turnings was limited to a lower rate, likely due to differences in surface area. However, after oxidation had taken place, the surface area overall was not limiting with regard to the total observed reduction of orthophosphate. These were the basis behind the decision as well as other factors including local availability of the material and its relative inexpensiveness (material was donated).

# CHAPTER 5: LABORATORY-SCALE COLUMN REACTOR

## 5.1 Methods and Materials

### 5.1.1 Construction of Column Reactor

A laboratory-scale column reactor was constructed at the Agricultural Engineering Sciences Building located on the University of Illinois campus in Urbana. The reactor was designed to test a steel turnings material for its capacity to remove soluble phosphorus from tile drainage water, while simultaneously examining the effect of the steel media on woodchip media used for nitrate removal. To allow for simultaneous experimental repetitions, the reactor consisted of four identically constructed horizontal PVC columns 0.1524 m (0.5 ft) in diameter. Each column consisted of two sections, one a 1.327 m (4.33 ft) long section filled with steel turnings, and one a 5.689 m (18.66 ft) long section filled with woodchips. Material was secured in the columns by PVC plates with drilled holes (1.905 cm, 0.75 in diameter), covered by a non-reactive mesh at each end. Figure 5.1 depicts an image of this end cap.

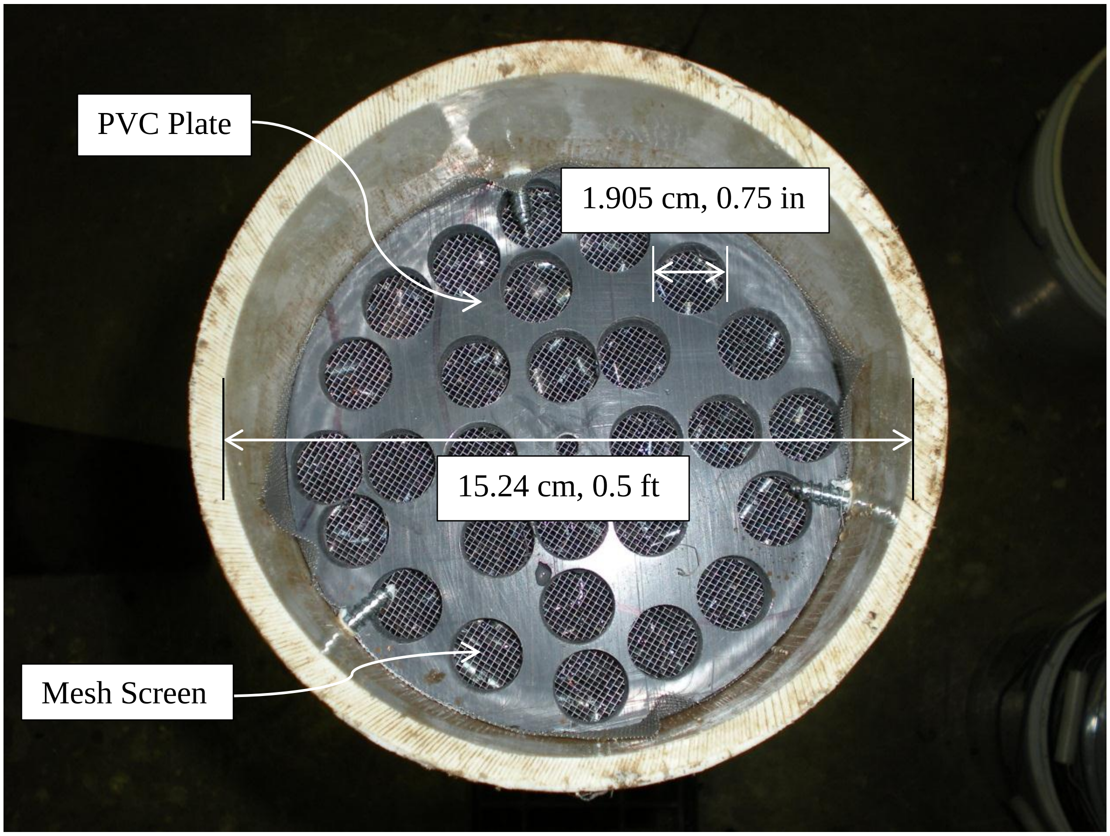

**Figure 5.1 PVC end cap and mesh mounted in a column.**

Flow through the columns was regulated using a controlled drainage structure connected to a manifold, which diverted the flow equally and served as the inlet for each of the four columns. Figure 5.2 shows an image of this assembly as well as the influent tank and pump.

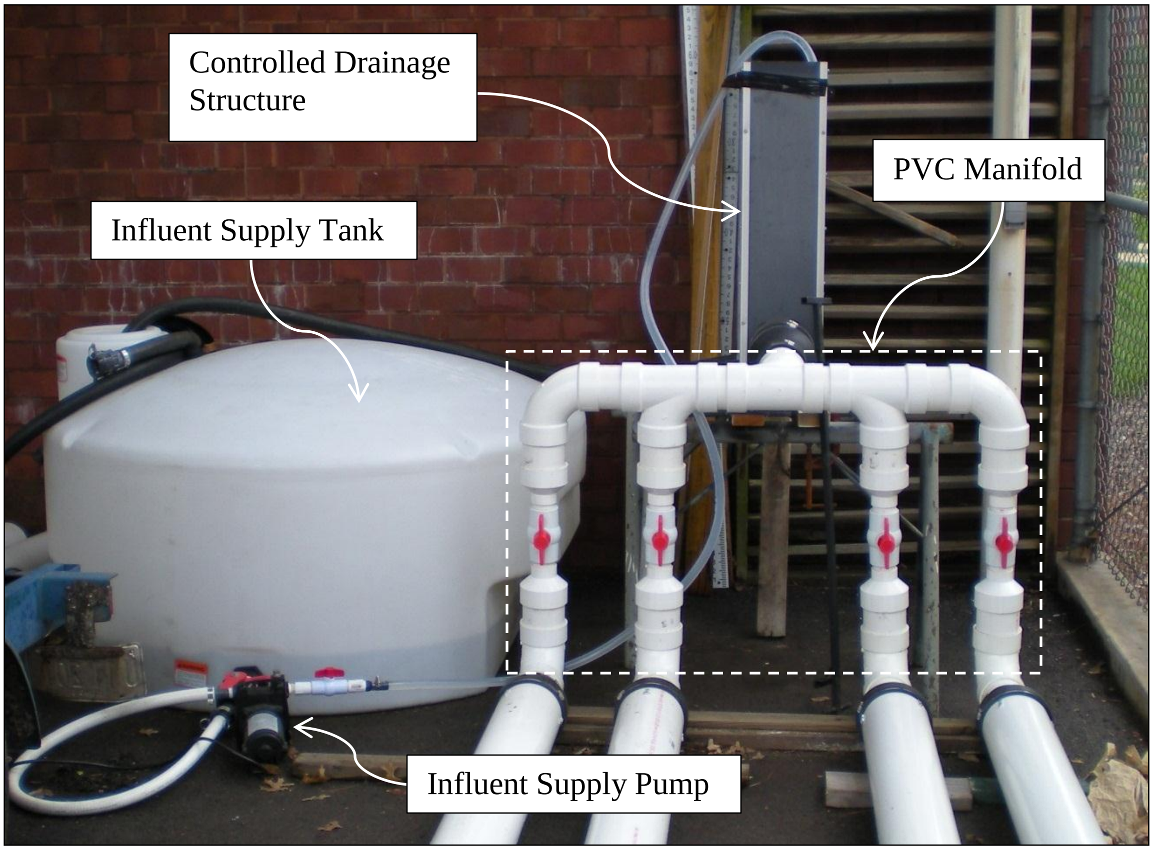

**Figure 5.2 Drainage Control Structure and manifold assembly.**

The outlet of each column consisted of a 5.08 cm (2 in) diameter PVC pipe. The outlet pipe could be rotated to any angle to achieve any head difference from 0 to 152.4 cm (0 to 5 ft) below the inlet water level to induce flow. Figure 5.3 shows an image of the outlet assembly.

**Figure 5.3 Outlet of each column and rotating outlet assembly.**

In order to test the effect of the steel turnings on the nitrate removal efficiency of the woodchips, two columns were positioned with the steel turnings section upstream of the woodchips section and two were placed with the steel turnings section downstream of the woodchips section. Sampling ports for collecting water samples were installed at the intersection of the steel turnings section and the woodchips section in each column. The ports were installed to allow for samples to be collected from the center of the flow profile by extending in to the center of the 0.1016 m (4 in) diameter PVC pipe that was used to adjoin the steel turnings and woodchips sections of each column. Figure 5.4 shows an image of these sampling ports.

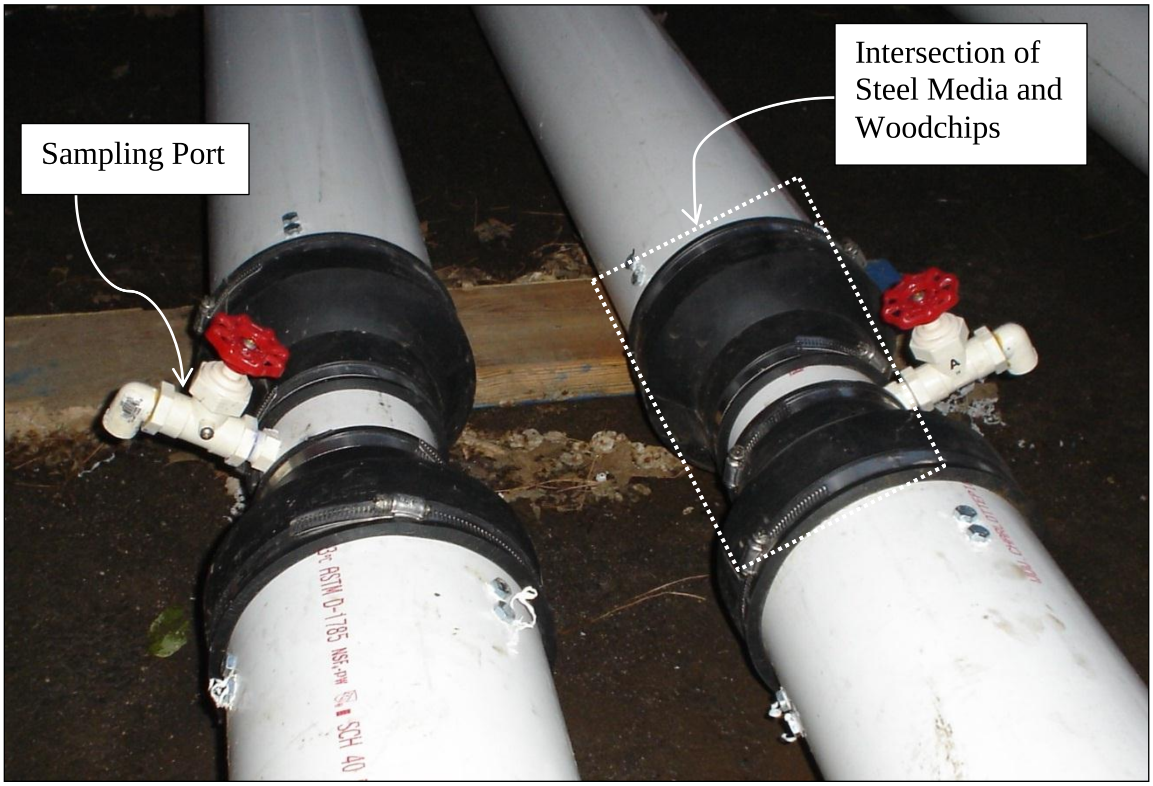

**Figure 5.4 Sampling ports at intersection of woodchip and steel media.**

During each experimental run, two consecutive 30 mL water samples were collected from the inlet, the sampling port at the intersection, and the outlet of each column. One sample was vacuum filtered by a 0.45 micron filter and stored at 4° C and analyzed for ortho-phosphorus according to EPA Method 365.1 and one was treated with concentrated sulfuric acid (0.25 ml) and stored at 4° C and analyzed for nitrate-N according to EPA Method 353.1 (EPA, 2001). Figure 5.5 and Figure 5.6 show an image and an aerial schematic of the reactor at its location at the Agricultural Engineering Sciences Building on the University of Illinois campus in Urbana, IL.

Figure 5.5 Four-Column Reactor used in Column Reactor Experiments.

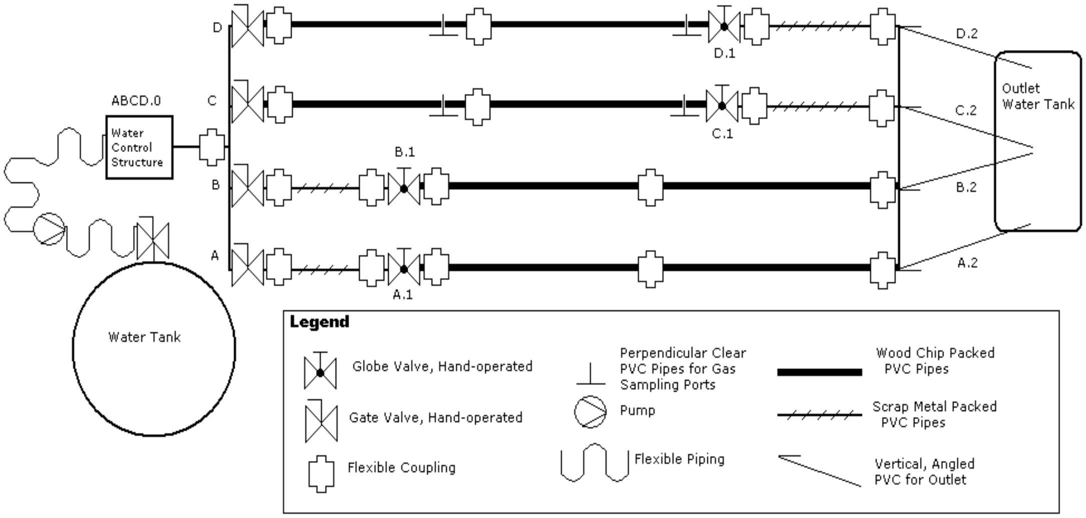

Figure 5.6 Aerial Schematic of Column Reactor.

### 5.1.2 Collection and Preparation of Materials

Woodchips, steel turnings, and creek water were collected from local sources for use in the laboratory-scale column reactor study. The woodchips used in the study were collected from an existing field-scale bioreactor near Decatur, IL. This site was chosen because it has been established for a period of years and has shown a high capacity for nitrate-N reduction in the past. The woodchips in the bioreactor consist of a random mixture from a municipal source in the Decatur, IL area. The woodchips were collected from the surface down to a depth of approximately 0.61 m (2 ft). This depth was assumed to be deep enough to contain woodchips which had been previously inundated allowing for the establishment of denitrifying microorganisms. A picture of the bioreactor and its location near Decatur can be seen in Figure 5.7. The woodchips were collected in plastic bins and transported back to the Agricultural Engineering Sciences Building on the University of Illinois campus where they were packed in to the PVC columns. The columns sections were vertically packed as shown in Figure 5.8, to achieve an approximately uniform density throughout all of the columns.

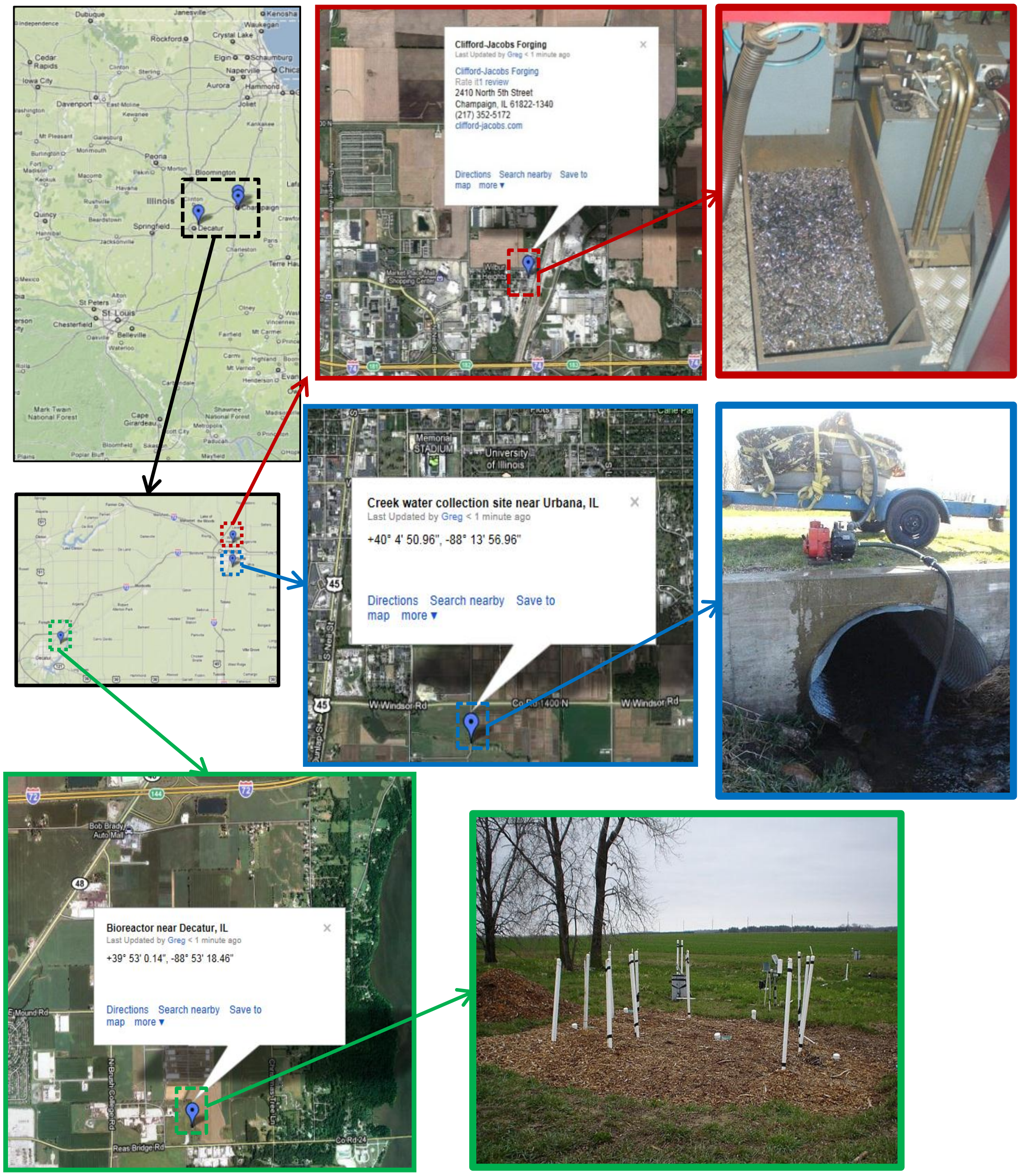

**Figure 5.7. Location and Photo of Field-Scale Bioreactor near Decatur, IL, Clifford-Jacobs Forging Company near Champaign, IL, and the Creek Water Collection Site near Urbana, IL.**

**Figure 5.8. Column mounted vertically during packing procedure.**

The steel turnings material was collected from Clifford-Jacobs Forging Co. in Champaign, IL. The original intent throughout the column experiment portion of the study was to use the steel turnings material from the same source (Kurland Steel) as in the batch trials, however due to a reduction in milling workload, they did not have a sufficient supply to sustain the column study. Therefore, an alternate source (Clifford-Jacobs Forging Co.) was chosen. The new material was also a by-product of computer numerical control (CNC) milling process. The location and a photo of the material are shown in Figure 5.7.

The turnings were lightly coated with lubricating oil from the manufacturing process, so the turnings were washed in order to remove the oil. The process consisted of washing the savings in a solution of degreasing dish detergent and hot water, a rinse with hot water, and a final rinse with de-ionized (DI) water. The washed turnings were vertically packed into each of the columns at approximately the same density.

Creek water was collected and used during the column reactor experiments. It was collected from a stream located south of Windsor road located near the University of Illinois campus in Urbana, IL. This location for collection was the same one used for similar laboratory scale column experiments conducted by Chun (2007). As the result of this study will have implications to subsurface (tile) drainage, the original intent was to use tile water, but due to difficulty of collection and transport, creek water was used. It was determined that the use of stream water would be sufficient for this study based on evidence found by Blowes et al. (1994) concluding that the chemical components of stream water very closely resemble those of tile water. A photo showing the collection technique and location are shown in Figure 5.7.

### 5.1.3 Characterization of Materials

Effective porosity and bulk density (dry basis) measurements were collected in order to better characterize the material used in these experiments. The effective porosity was determined on a mass basis while the materials were compacted to densities representative of the media during the experiments. It was measured by placing the two different materials in containers of known volume and measuring the net increase in mass after enough water was added to the container to fully inundate the material. The volume of water added was then calculated using a density of 1.0 g/cm$^3$ and ratio of this volume to the total volume of the material and water was used to calculate the effective porosity.

Bulk density (dry basis) was also measured for both materials. This was done by packing the materials (to densities approximating those used during the experiments) into containers of known mass and volume, drying the materials in an oven at 140 degrees Celsius for 24 hours, and then weighing the materials. The results of these measurements can be seen in Table 5.1.

**Table 5.1. Bulk Density and Effective Porosity of Steel Turnings and Woodchips.**

| Material Characteristics | | | |
|---|---|---|---|
| | Steel Turnings | Woodchips | *units* |
| **Bulk Density (Dry Basis):** | 0.988 | 0.200 | *g/cm$^3$* |
| **Effective Porosity:** | 89.3 | 54.5 | *%* |

Size distribution of the materials was not physically measured, but can be observed in figure 5.9. The general distribution based on observation ranged from approximately 0.25 cm to 10 cm for the woodchips and 0.5 cm to 3 cm for the steel turnings. The woodchips were of varying thickness and length, while the steel turnings tended to be more uniform and generally shaped like a ribbon.

**Figure 5.9. Size distribution of Steel Shavings and Woodchips.**

### 5.1.4 Calibration of Columns

A calibration of the columns was conducted on April 30, 2009. This consisted of collecting volumetric flow measurements from the outlet of each column and surveying the established inlet and outlet height corresponding to each flow rate measurement taken. Three different flow rates were achieved and each flow measurement was collected in triplicate. The effective hydraulic conductivity ($K_e$) values for each column were solved for according to Darcy's equation (5.1) and are listed in Table 5.1:

$$K_e = \frac{Q}{A} \cdot \frac{L}{\Delta H} \qquad (5.1)$$

Where:

$K_e$ = effective hydraulic conductivity [L/T]
$Q$ = Flow [$L^3$/T]
A = Area [$L^2$]

$L$ = column length [L]
$\Delta H$ = head difference [L]

The effective hydraulic conductivity ($K_e$) values found during the calibration are listed in Table 5.2. With the exception of Column B, conductivity values were consistent across columns, with average values of 3.101 cm/s, 3.014 cm/s, and 2.573 cm/s for columns A, C, and D respectively. Column B had the lowest average conductivity, 1.149 cm/s, which indicated that the woodchips were packed tighter in this column. However, due to the ability to vary outlet elevation for each column, flow rate for the columns could be independently adjusted to achieve similar retention times between columns.

**Table 5.2. Effective Hydraulic Conductivity values listed per column.**

| | Ke 1 (cm/s) | Ke 2 (cm/s) | Ke 3 (cm/s) | Average Ke (cm/s) |
|---|---|---|---|---|
| Column A: | 3.023 | 3.309 | 2.972 | 3.101 |
| Column B: | 1.505 | 1.120 | 0.823 | 1.149 |
| Column C: | 2.628 | 3.159 | 3.255 | 3.014 |
| Column D: | 2.318 | 2.643 | 2.757 | 2.573 |

### 5.1.5 Column Reactor Experiments

The column reactor pictured in Figure 5.5 was used to conduct experiments testing for the removal of orthophosphate from solution as well as the remediation of nitrate-N. The column reactor was used for a series of three experiments that tested for two specific results. The first was the ability of the steel turnings material to remove orthophosphate from solution in a flowing water scenario. The second was to examine the effect of woodchip and steel turning placement (upstream or downstream with respect to each other) on the soluble N and P concentrations remaining in solution. In addition to the collection of water samples for soluble phosphorus and nitrate nitrogen analysis, water quality parameters including dissolved oxygen, hydrogen ion concentration (pH), and temperature were measured. The parameters were measured using a Hach Quanta multi-parameter water quality probe, which was calibrated according to manufacturer procedures prior to every experiment (Hydrolab: Revision C, 2002). An image of the Quanta being used to measure those parameters during one of the experiments can be seen in Figure 5.10.

Figure 5.10. Hach Quanta multi-parameter water quality probe.

Before the beginning of the experiment, approximately 400 L of stream water was used to flush and initialize the columns. At the start of each experiment, approximately

1600 L of stream water was spiked with the appropriate amount of $KH_2PO_4$ and $KHNO_3$ to produce an approximate 5 mg-P/L and 12 mg-N/L solution. This solution was then pumped by an electric pump into the controlled drainage structure that served as a constant head device and the inlet for the manifold connected each of the four column reactors. The overflow from the constant head device was allowed to spill back into the holding tank, continuously mixing the solution. After the start of the experiment, an initial water sample and water quality parameters were collected from the holding tank. Once the experiment had begun, water samples and water quality parameters were then collected every four hours for the duration of the experiment. Volumetric flow measurements were also taken on every four hour interval. The outlet elevations for each column were then adjusted as needed to maintain an approximately constant flow throughout the experiment.

## 5.2. Results and Discussion

### 5.2.1 Column Experiment 1

Experiment 1 was conducted on May 27, 2009 and samples were collected every four hours for a span of 28 hours. Since columns A and B were replicates of each other and had the same media configuration (steel turnings upstream and woodchips downstream) and columns C and D were also replicates of each other and had the same media configuration (woodchips upstream and steel turnings downstream), the results from columns A and B and the results from columns C and D were averaged. These results are located in Appendix A.1. Figure 5.11 represents the average changes in orthophosphate and nitrate concentration leaving each treatment section for the media arrangement with steel turnings upstream of woodchips and Figure 5.12 represents the average changes in orthophosphate and nitrate concentrations for the media arrangement with woodchips upstream of steel turnings observed for experiment 1. The 4-hour time from start sample was omitted from all averages due to insufficient time for the nutrients to reach the outlet give the calculated retention times.

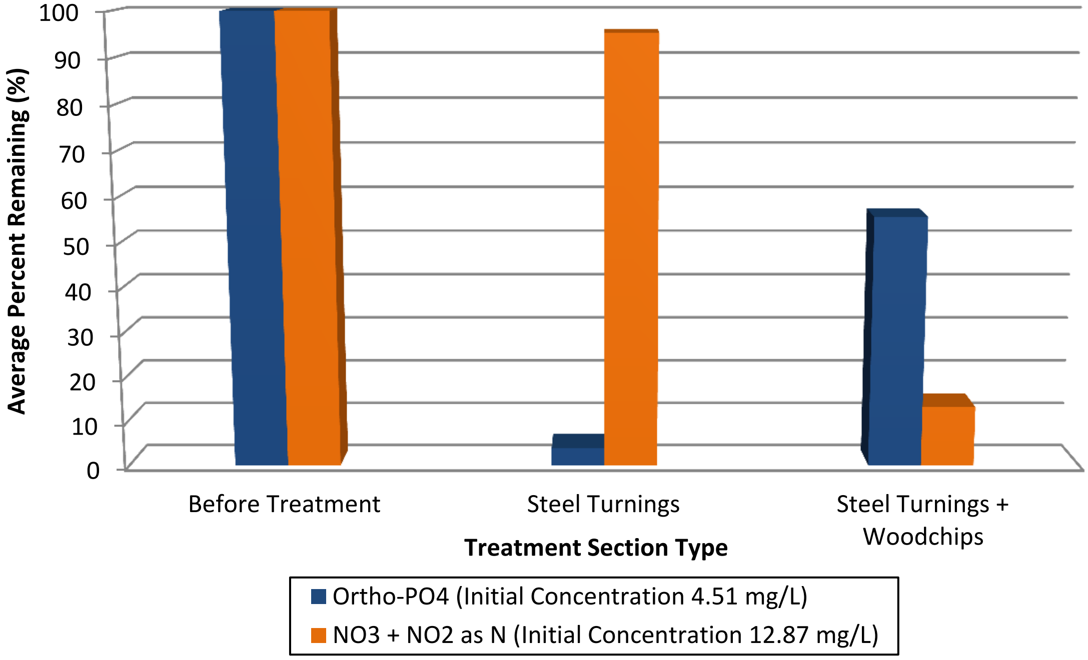

Figure 5.11. Overall orthophosphate and nitrate-N reduction for steel turnings upstream of woodchips (average of two columns) for experiment 1.

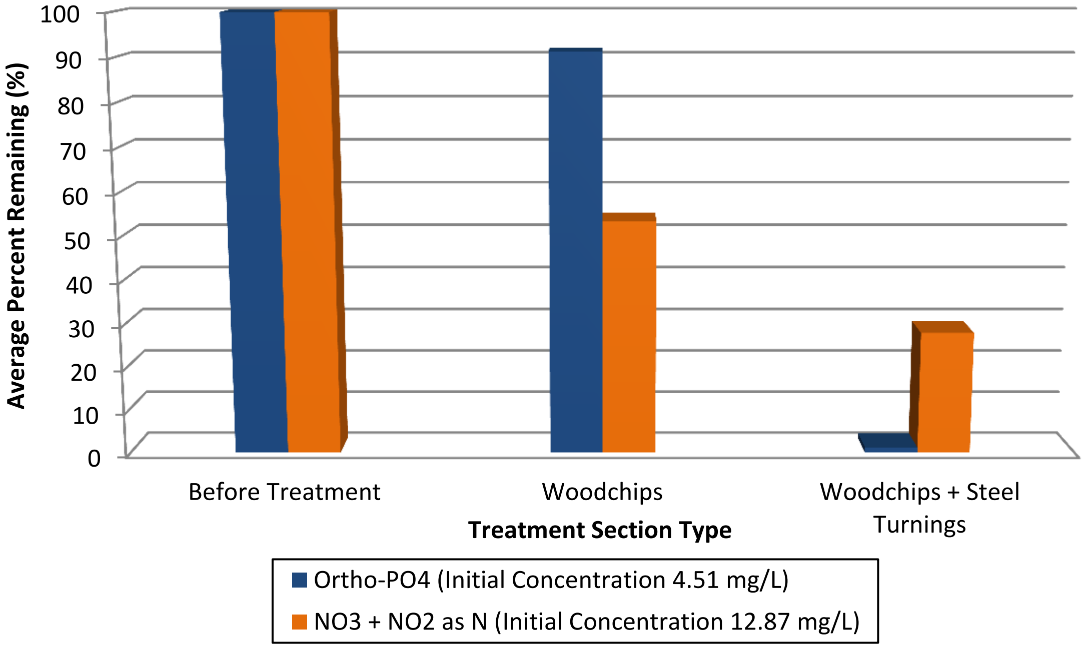

Figure 5.12. Overall orthophosphate and nitrate-N reduction for woodchips upstream of steel turnings (average of two columns) for experiment 1.

#### *5.2.1.1 Orthophosphate Results*

Significant changes in the orthophosphate concentrations were observed as a result of passing the nutrient spiked influent through the woodchip and steel turnings sections of the column reactors. In Figure 5.11, it can be seen that there was an average reduction of 96.1% (from 4.51 mg/L-PO4 to 0.17 mg/L-PO4) in orthophosphate concentration after water was passed through the steel turnings section of the column reactor throughout the duration of the experiment. However, subsequent passage of the water through the woodchip section of the reactor resulted in a significant increase (to over 50% of the initial influent concentration in some cases) in orthophosphate concentration, giving a mean concentration at the outlet of the two sections of 2.51 mg/L-PO4.

The results from the alternate media arrangement (woodchips upstream and steel turnings downstream) can be seen in Figure 5.12 and were somewhat different than those occurring from media arrangement in columns A and B. The woodchips sections in these columns seemed to have little effect on the orthophosphate concentration, while the steel turnings section again greatly reduced orthophosphate remaining in solution by an average of 98.9% (average reduction from 4.51 mg/L PO4 to 0.05 mg/L PO4).

The orthophosphate concentrations remaining in solution after passage of the influent through the steel turnings sections of the column reactors were somewhat expected based on the conclusions drawn from the steel media trials in the beaker experiments. However, the increase in orthophosphate concentration resulting from water passage through woodchips following passage through steel turnings was unanticipated.

### *5.2.1.2 Nitrate Results*

Significant changes in nitrate concentration were also observed in the influent water as a result of passage through the woodchip and steel turnings sections of the column reactor for both media arrangements. In Figure 5.11 it can be observed that the steel turnings section upstream of woodchips had essentially no effect on the concentration of nitrate remaining in solution, but nitrate concentration leaving the woodchip section was reduced by an average of 86.8% (from 12.87 mg/L NO3 to 1.70 mg/L NO3) over the course of the experiment. Nitrate concentrations in water leaving the woodchip sections of columns with woodchips upstream of steels turnings, however, only resulted in an average reduction of 46.4% (from 12.87 mg/L NO3 to 6.89 mg/L NO3). Also, nitrate concentrations leaving steel turnings sections following woodchip sections showed further reduction for a total overall reduction of 72.0% (from 12.9 mg/L NO3 to 3.60 mg/L NO3) for this media arrangement.

### *5.2.1.3 Flow and Retention Times*

A summary of the volumetric flow rates and the associated retention times for experiment 1 can be seen in Table5.3.

**Table 5.3. Flow Rates and Retention Times for Experiment 1.**

| Time from Start (hr) | Column A | | | Column B | | |
|---|---|---|---|---|---|---|
| | Flow Rate (mL/s) | Retention Time (hr) | | Flow Rate (mL/s) | Retention Time (hr) | |
| | | Woodchips | Steel Turnings | | Woodchips | Steel Turnings |
| 4 | 5.21 | 3.02 | 1.15 | 2.92 | 5.39 | 2.05 |
| 8 | 2.72 | 4.39 | 1.67 | 1.63 | 7.52 | 2.86 |
| 12 | 2.01 | 6.79 | 2.58 | 1.19 | 11.41 | 4.34 |
| 16 | 1.61 | 8.78 | 3.34 | 2.39 | 9.87 | 3.75 |
| 20 | 2.22 | 8.40 | 3.19 | 1.87 | 7.49 | 2.85 |
| 24 | 2.07 | 7.34 | 2.79 | 1.55 | 9.27 | 3.52 |
| 28 | 1.83 | 8.09 | 3.07 | 1.37 | 10.79 | 4.10 |
| *Mean:* | *2.52* | *6.69* | *2.54* | *1.85* | *8.82* | *3.35* |
| *Std. Deviation:* | *1.23* | *2.18* | *0.83* | *0.61* | *2.13* | *0.81* |
| **Time from Start (hr)** | **Column C** | | | **Column D** | | |
| | **Flow Rate (mL/s)** | **Retention Time (hr)** | | **Flow Rate (mL/s)** | **Retention Time (hr)** | |
| | | **Woodchips** | **Steel Turnings** | | **Woodchips** | **Steel Turnings** |
| 4 | 4.33 | 3.63 | 1.38 | 3.33 | 4.71 | 1.79 |
| 8 | 3.79 | 3.89 | 1.48 | 3.01 | 4.96 | 1.89 |
| 12 | 3.60 | 4.26 | 1.62 | 2.94 | 5.28 | 2.01 |
| 16 | 2.82 | 4.96 | 1.89 | 2.79 | 5.48 | 2.08 |
| 20 | 3.13 | 5.29 | 2.01 | 2.76 | 5.65 | 2.15 |
| 24 | 3.47 | 4.78 | 1.81 | 2.96 | 5.50 | 2.09 |
| 28 | 3.76 | 4.35 | 1.65 | 3.10 | 5.19 | 1.97 |
| *Mean:* | *3.56* | *4.45* | *1.69* | *2.99* | *5.25* | *2.00* |
| *Std. Deviation:* | *0.49* | *0.59* | *0.23* | *0.19* | *0.33* | *0.13* |

Flow rates and associated retention times for this experiment were comparable for columns that had the same media arrangement (A comparable to B and C comparable to D), but some variation was observed in columns with different media arrangements (A compared to C or D, or B compared to C or D). The average flow rates for columns A and B (steel turnings upstream of woodchips) throughout the experiment were 2.52 mL/s and 1.85 mL/s with associated average retention times of 6.69 hours and 8.82 hours for woodchip sections and 2.54 hours and 3.35 hours for steel turning sections, respectively.

These values were significantly higher than those observed for columns C and D, which had average flow rates of 3.56 mL/s and 2.99 mL/s and associated average retention times of 4.45 hours and 5.25 hours for woodchip sections and 1.69 hours and 2.00 hours for steel turning sections, respectively.

From examining the measured flow rate data, it can be determined that because there were differences in parameters in both columns for each media arrangement that placing the steel turnings section upstream of the woodchip section significantly slowed flow rate, therefore increasing associated retention times.  However, the explanation behind this effect cannot be explicitly determined.  Although these differences in flow rate between columns with different media arrangements did not have a noticeable effect on the orthophosphate data, it can be interpreted that the retardations in flow rate likely reflect some of the variations observed in the nitrate data due to longer associated retention times in columns A and B.

#### *5.2.1.4 Temperature, Dissolved Oxygen, and pH Results*

Plots of the temperature, dissolved oxygen, and pH data collected during experiment 1 can be seen are featured in Appendix A.1.  As in the orthophosphate and nitrate results, values for these parameters are plotted as averages between columns with like media arrangements (columns A and B averaged and columns C and D averaged). No change in water temperature was observed between woodchips sections and steel turnings sections across either media arrangement.  Inlet temperatures tended to be higher throughout the experiment, but this is likely do to heat exchange with the supply pump as water was circulated before entering the columns.  Dissolved oxygen values displayed the general trend of decreasing significantly (from 11.75 % DO to 2.25% DO on average) after passage through the first treatment section, regardless of media type (woodchips or steel turnings), and then slightly increasing (from 2.25% DO to 3.89% DO on average) after passage through the second treatment section, again irrespective of media type. The pH results generally showed that pH is only affected by the woodchips sections. For both media arrangements, the pH became more acidic after passage through the woodchip section and essentially remained unchanged by the steel turnings. This decline in pH was generally slightly greater than one. A slight increase in pH was also observed throughout the course of the experiment (approximately 0.5) and was observed at all locations sampled, irrespective of treatment or media arrangement.

### 5.2.2 Column Experiment 2

Experiment two was conducted on June 4, 2009. Experiment 2 was simply a replicate of Experiment 1, so all sample collection procedures during this experiment were performed exactly as those in Experiment 1. Table 5.4 contains the measured volume per time flow rates collected for each column as well as the retention time associated with each flow rate for each material. Figure 5.13 represents the changes in orthophosphate and nitrate concentration leaving each treatment section for the media arrangement with steel turnings upstream of woodchips and Figure 5.14 represents changes in orthophosphate and nitrate concentrations for the media arrangement with woodchips upstream of steel turnings observed for experiment 2. The 4-hour and 8-hour time from start samples were omitted from all averages due to insufficient time for the nutrients to reach the outlet given the calculated retention times.

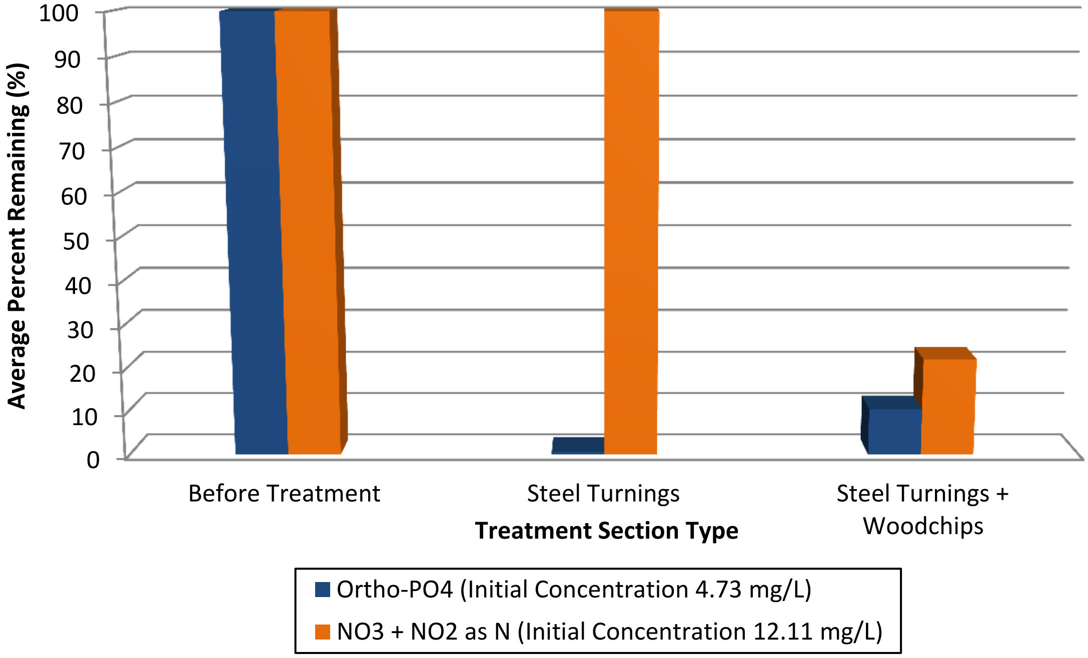

**Figure 5.13. Overall orthophosphate and nitrate-N reduction for steel turnings upstream of woodchips (average of two columns) for experiment 2.**

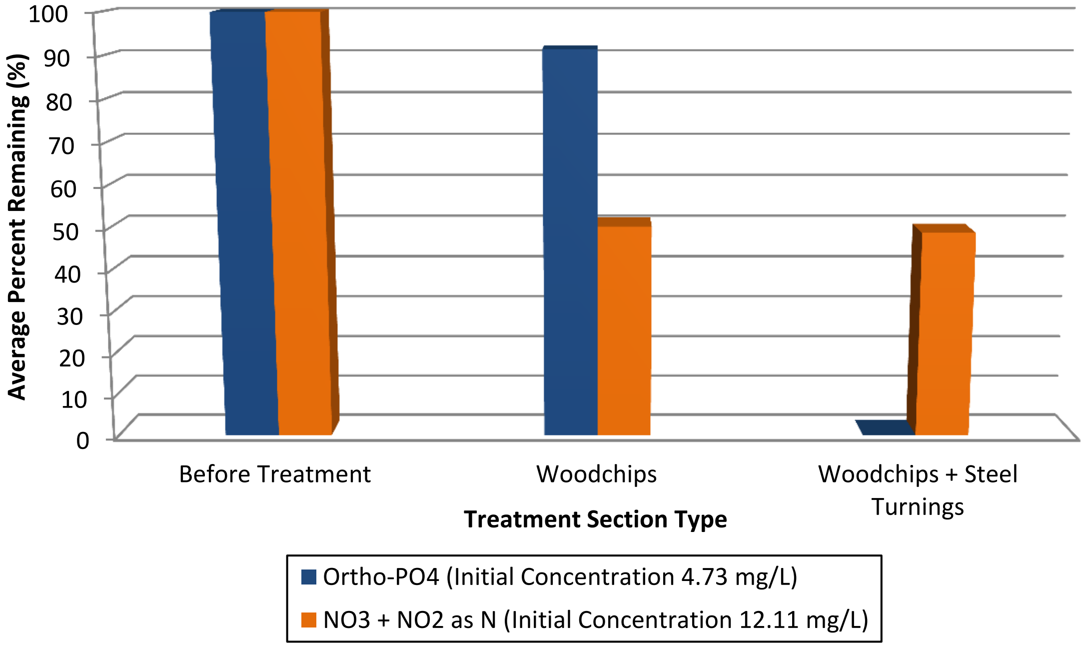

**Figure 5.14. Overall orthophosphate and nitrate-N reduction for woodchips upstream of steel turnings (average of two columns) for experiment 2.**

#### *5.2.2.1 Orthophosphate Results*

The orthophosphate results from experiment two were very similar to those observed in experiment one among both media arrangements. For the media arrangement where steel turnings were upstream of woodchips, the average reduction in orthophosphate concentration after passage through steel turnings was 99.4% (from 4.73 mg/L PO4 to 0.03 mg/L PO4), with an increase back to 10.6% (from 0.03 mg/L PO4 to 0.50 mg/L PO4) of original observed after subsequent passage through the woodchips. This result was very similar to the result for this media arrangement on orthophosphate concentration in solution from experiment one, except for the increase in orthophosphate concentration observed after treatment with woodchips. Experiment one yielded an increase back to 55.7% (from 0.17 mg/L PO4 to 2.51 mg/L PO4) of original, whereas an increase back to only 10.6% of the initial concentration (from 0.03 mg/L PO4 to 0.50 mg/L PO4) was observed for experiment two.

The results from the alternate media arrangement of woodchips upstream of steel turnings on orthophosphate concentration very closely mimicked the results of experiment one. In this experiment, orthophosphate was reduced by 8.5% (from 4.73 mg/L PO4 to 4.33 mg/L PO4) of original after passage through woodchips with 100% (from 4.33 mg/L PO4 to 0.00 mg/L PO4) being removed after subsequent passage through steel turnings.

#### *5.2.2.2 Nitrate Results*

The nitrate results for experiment two also very closely resembled the results observed during experiment one. For the media arrangement where steel turnings were upstream of woodchips, the nitrate concentration after passage through steel turnings was essentially unchanged. However, after subsequent passage through woodchips, the nitrate concentration was reduced by 77.8% (from 12.11 mg/L NO2+NO3 as N to 2.69 mg/L NO2+NO3 as N). The alternate media arrangement also yielded nearly the same results as experiment one, with the exception of the reduction in nitrate from steel turnings. Woodchips upstream of steel turnings resulted in a reduction in nitrate concentration of 49.6% (from 12.11 mg/L NO2+NO3 as N to 6.10 mg/L NO2+NO3 as N) of original concentration after passage through the woodchips, yet only an additional reduction of 1.6% (from 6.10 mg/L NO2+NO3 as N to 5.91 mg/L NO2+NO3 as N) after passage through steel turnings.

#### *5.2.2.3 Flow and Retention Times*

Flow and associated retention times were similar to those in experiment one, but outlet adjustments were made more regularly during this experiment in an attempt to produce an approximately steady state condition. However, in general, the flow rates and associated retention times for each media showed the same trends as observed in experiment one. Columns with media arrangements where steel turnings were placed upstream of woodchips (columns A and B) tended to have retarded flow rates, which in turn caused longer associated retention times for the media. However, this was less pronounced during experiment two than experiment one due to the more consistent adjustment of outlet elevation to produce similar flow rates among columns during experiment two. The values for flow rate and the associated retention times can be seen in Table 5.4.

**Table 5.4. Flow Rates and Retention Times for Experiment 2.**

| Time from Start (hr) | Column A | | | Column B | | |
|---|---|---|---|---|---|---|
| | Flow Rate (mL/s) | Retention Time (hrs) | | Flow Rate (mL/s) | Retention Time (hrs) | |
| | | Woodchips | Steel Turnings | | Woodchips | Steel Turnings |
| 4 | 4.67 | 3.64 | 1.39 | 2.65 | 4.90 | 1.86 |
| 8 | 3.31 | 4.48 | 1.70 | 2.59 | 5.07 | 1.93 |
| 12 | 2.24 | 5.87 | 2.23 | 2.50 | 5.42 | 2.06 |
| 16 | 2.36 | 5.92 | 2.25 | 2.86 | 5.12 | 1.95 |
| 20 | 2.84 | 6.09 | 2.32 | 2.31 | 6.14 | 2.33 |
| 24 | 3.29 | 5.15 | 1.96 | 2.17 | 7.01 | 2.66 |
| 28 | 3.13 | 4.90 | 1.86 | 1.93 | 7.68 | 2.92 |
| *Mean:* | *3.12* | *5.15* | *1.96* | *2.43* | *5.91* | *2.24* |
| *Std. Deviation:* | *0.81* | *0.89* | *0.34* | *0.31* | *1.08* | *0.41* |
| **Time from Start (hr)** | **Column C** | | | **Column D** | | |
| | **Flow Rate (mL/s)** | **Retention Time (hrs)** | | **Flow Rate (mL/s)** | **Retention Time (hrs)** | |
| | | **Woodchips** | **Steel Turnings** | | **Woodchips** | **Steel Turnings** |
| 4 | 4.42 | 4.02 | 1.53 | 4.20 | 3.91 | 1.49 |
| 8 | 3.73 | 4.21 | 1.60 | 3.31 | 4.57 | 1.74 |
| 12 | 2.96 | 4.76 | 1.81 | 2.76 | 5.22 | 1.98 |
| 16 | 3.60 | 4.46 | 1.70 | 3.62 | 4.45 | 1.69 |
| 20 | 3.27 | 4.59 | 1.74 | 3.42 | 4.46 | 1.70 |
| 24 | 4.00 | 4.37 | 1.66 | 4.26 | 4.14 | 1.57 |
| 28 | 4.55 | 3.69 | 1.40 | 4.67 | 3.53 | 1.34 |
| *Mean:* | *3.79* | *4.30* | *1.63* | *3.75* | *4.32* | *1.64* |
| *Std. Deviation.:* | *0.58* | *0.36* | *0.14* | *0.66* | *0.54* | *0.20* |

### *5.2.2.4 Temperature, Dissolved Oxygen, and pH Results*

As for experiment two, plots of the temperature, dissolved oxygen, and pH results can be seen in Appendix A.2. Similar to experiment one, the temperature data collected throughout experiment two did not illustrate any significant changes among data collected after treatment by the varying media sections. The only significant observation was that the inlet temperature remained warmer throughout most of the experiment, which can be attributed to the heat exchange between the water and pump at the inlet prior to the water entering the treatment sections.

The dissolved oxygen data collected during experiment two again displayed the same trends observed during experiment one. There was a significant decrease in DO (from 12.39 % DO to 2.85 % DO on average) after water was passed through the first treatment section (regardless of material) and a subsequent increase (from 2.85 % DO to 4.58% DO on average) after passage through the second treatment section (also regardless of treatment material).

The pH data collected during experiment two also displayed the same trends observed during experiment one. In general, pH values were lowered by nearly one (from pH of 7.98 to 7.04 on average) by woodchip sections and slightly increased by steel turnings sections (by 0.14 on average). Just as in experiment one, an overall increase (of approximately 0.5) was observed in pH at all locations sampled over the course of the experiment.

### 5.2.3 Column Experiment 3

A different experimental setup and procedure was implemented for Experiment 3. For Experiment 3, the steel turnings sections from columns A and B were moved to the upstream ends of columns C and D to provide steel turnings on both the upstream and downstream ends of the woodchip column. For this experimental trial, only columns C and D were tested. During this trial, water samples and additional water quality parameters were collected at the inlet to the columns, both intersections of the sections where media changed, and at the outlet of both of the columns. Table 5.5 lists the flow rates collected and associated retention times for each column during Experiment 3. Due to the extra steel turnings material placed at the outlets of columns C and D, the flow rates were increased by approximately 20 to 33 percent above the flow rates observed in

Experiments 1 and 2. Figure 5.15 shows the average changes in nitrate and orthophosphate concentrations observed throughout the course of the experiment. The 4-hour time from start sample was omitted from all averages due to insufficient time for the nutrients to reach the outlet give the calculated retention times.

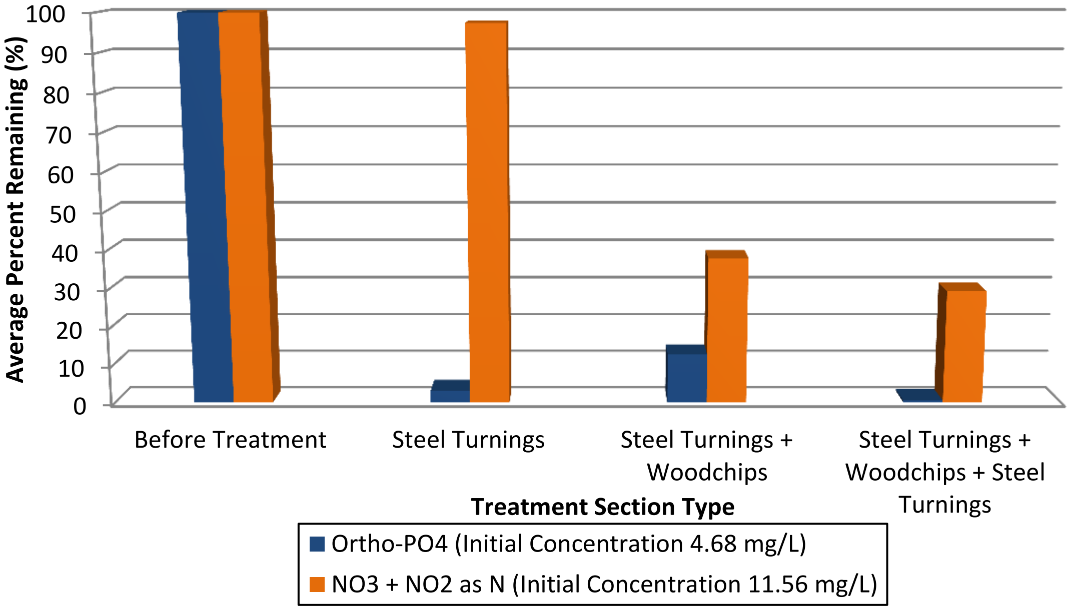

**Figure 5.15. Overall orthophosphate and nitrate-N reduction for steel turnings upstream of woodchips upstream of steel turnings (average of two columns) for experiment 3.**

### *5.2.3.1 Orthophosphate Results*

The orthophosphate results from experiment three displayed the same trends observed in both experiments one and two. Flow through the steel turnings treatment section upstream of woodchips again yielded a large reduction (from 4.68 mg/L PO4 to 0.14 mg/L PO4) in the orthophosphate concentration. This was also, again, followed by a subsequent increase in the orthophosphate concentration back to a concentration of 0.59 mg/L PO4 after water passed through the woodchip treatment section. Different from experiments one and two, however, the second steel turnings treatment section downstream of the woodchip treatment section was able to again remove the orthophosphate from solution producing an average outlet concentration of only 0.02 mg/L PO4.

### *5.2.3.2 Nitrate Results*

The nitrate data collected during experiment three again displayed the same overall trends observed during the first two experiments. The nitrate concentration was nearly unaltered by the upstream most steel turnings section. However, samples collected that were subsequently passed through the woodchips treatment section displayed a reduction of nearly 59.4% (from 11.56 mg/L NO2+NO3 as N to 4.39 mg/L NO2+NO3 as N) in nitrate concentration. Although differing from the first two experiments due to steel turnings section placement upstream and downstream of woodchips, nitrate concentrations exiting the final steel turnings section downstream of woodchips behaved similarly to experiments one and two for that scenario. The nitrate concentration leaving the final steel turnings section downstream of the woodchip section was reduced by an additional 8.6% (from 4.39 mg/L NO2+NO3 as N to 3.39 mg/L NO2+NO3 as N).

### *5.2.3.3 Flow Rate and Retention Times*

The flow rates and associated retention times for each material for experiment three are located in Table 5.5. In general, the flow rates were maintained slightly higher than in experiments one and two, implying shorter retention times for the treatment sections. However, since a second steel turnings section was added during these experiments, the retention times for steel turnings were doubled. Throughout the course of the experiment flow rates were also adjusted more consistently to achieve approximately steady state conditions.

**Table 5.5. Flow Rates and Retention Times for Experiment 3.**

| Time from Start (hr) | Column C | | | Column D | | |
|---|---|---|---|---|---|---|
| | Flow Rate (mL/s) | Retention Time (hrs) | | Flow Rate (mL/s) | Retention Time (hrs) | |
| | | Woodchips | Steel Turnings | | Woodchips | Steel Turnings |
| 4 | 4.13 | 3.80 | 3.14 | 4.24 | 3.71 | 3.22 |
| 8 | 3.77 | 3.79 | 2.73 | 4.12 | 3.58 | 2.84 |
| 12 | 4.12 | 3.48 | 2.76 | 4.48 | 3.40 | 2.96 |
| 16 | 4.27 | 3.31 | 2.74 | 4.22 | 3.56 | 2.89 |
| 20 | 3.83 | 3.72 | 2.73 | 4.85 | 3.10 | 2.97 |
| *Mean:* | *4.03* | *3.62* | *2.82* | *4.38* | *3.47* | *2.98* |
| *Std. Deviation.:* | *0.21* | *0.22* | *0.18* | *0.30* | *0.23* | *0.15* |

#### *5.2.3.4 Temperature, Dissolved Oxygen, and pH Results*

The temperature data throughout experiment three exhibited a similar trend to the temperature data collected during the first two experiments and is located in Appendix A.3. In general, the inlet temperature was higher, again likely due to heat exchange between the water and pump, and there was little difference observed between the other locations throughout time. An overall decrease in temperature occurred, but was likely a result of the ambient air temperature. The dissolved oxygen values throughout this experiment displayed trends that closely followed the results from first two experiments. After water was passed through the first treatment section, the dissolved oxygen concentration was lowered significantly regardless of treatment. A slight increase was observed in some samples collected at the outlet, but this trend was not consistent throughout time. The trend observed for pH also closely resembled the results from the previous two experiments. However, in this experiment, pH was not increased by upstream most steel turnings section as it had been in previous experiments. Conversely, woodchips did have the same effect on the pH, consistently lowering it by approximately one and the downstream steel turnings displayed no effect, as in previous experiments.

### 5.2.4 Synergistic Effects

#### *5.2.4.1 Differences in Nitrate Reduction*

The plot of Nitrate reduction as a function of retention time is shown in Figure 5.16. Although there is high variability among the data in this plot, in general it can be observed that longer retention times tend to be associated with greater reduction. This observation is consistent with results presented by Chun (2007) from a similar woodchip column experiment where he used similar initial concentrations. However, from the results of Chun (2007) it can be determined that a retention time of approximately 12 hours was needed to completely reduce nitrate-N at these initial starting concentrations. It can also be observed in Figure 5.16 that very high reductions were achieved in far less time for the media arrangement of woodchips downstream of iron in these experiments. While this plot depicts all samples taken from the outlet of woodchip sections across all experiments, there is a distinct difference in the distributions of samples collected from woodchip sections downstream of steel turnings as compared to upstream. When examining samples collected from woodchip sections upstream of steel turnings sections, the range of retention times and amount of reduction was much less variable. Although this is not true in all cases, these samples also tended to result in lower reductions when compared with samples having similar retention times collected from woodchip sections downstream of steel turnings sections. From this evidence, it can be speculated that iron may play an important role in the denitrification process within the woodchip sections. However, it remains unclear as to the dynamics behind the observation of this effect.

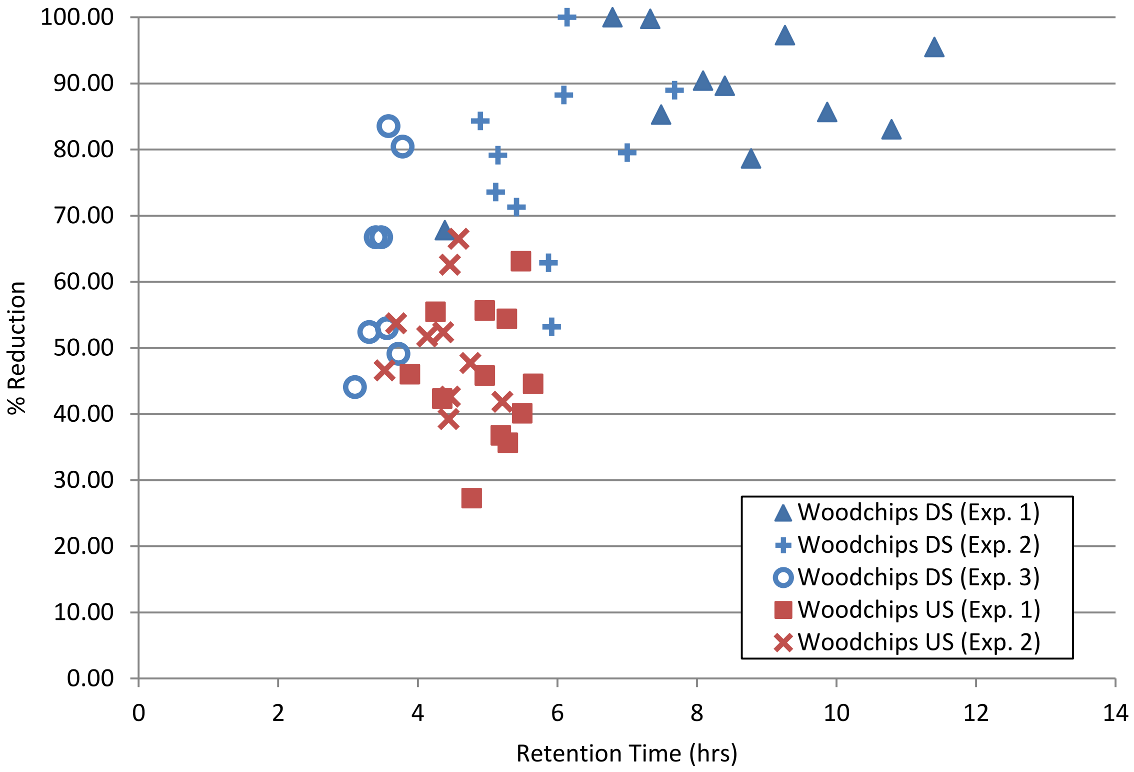

**Figure 5.16. Nitrate Reduction vs. Retention time for all samples analyzed for $NO_3$ + $NO_2$ as N collected from the outlet of woodchip sections for both media arrangements tested (Upstream and downstream denoted US and DS, respectively, in the figure legend).**

Although the specific processes at work behind this observation could not be determined, differences in the data populations were compared. Normalizing the percent reduction results of the two experimental conditions (woodchips upstream or downstream of steel turnings) by the retention time allowed for the comparison of the means of these two conditions (Figure 5.17) without consideration of the factor of retention time using a student's t-Test (assuming unequal variance). This resulted in the rejection of the null hypothesis of the two sample means being equal at the 99% confidence interval (p = 0.0008) indicating a significant difference among sample means.

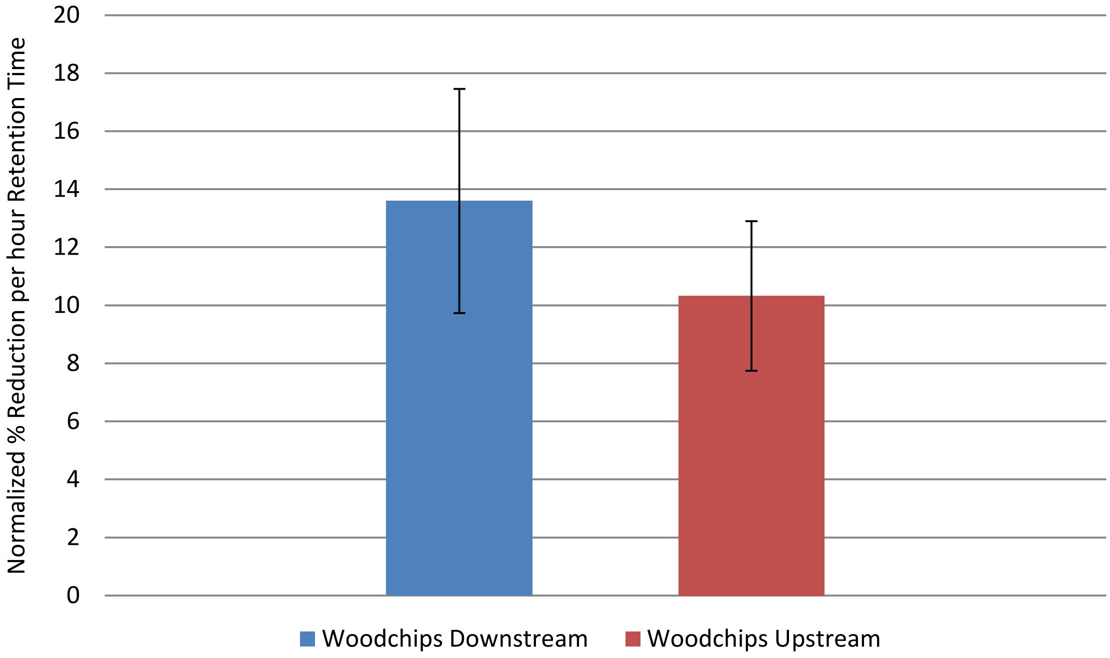

**Figure 5.17. Mean normalized percent reduction of nitrate for both woodchips upstream and downstream of steel turnings (Error bars representing standard deviations of the two populations).**

### *5.2.4.2 Orthophosphate reduction by iron*

No appreciable effects of retention time or media arrangement could be associated with the ability of the steel turnings to remove soluble phosphorus from solution. This was due to very low concentrations of orthophosphate remaining in solution after passing through the steel turnings. This result is likely due to the limited number of retention times tested, which did not capture the range associated with the iron-phosphate sorption process. Although all associated retention times tested in the column experiments were less than retention times associated with the same orthophosphate reductions in the beaker trials, the reason was likely pre-rusting of the turnings in the column experiments from the wash process and calibration runs. This likely initiated the oxidation of the steel turnings prior to the start of the experiments, allowing iron-oxide to react with the orthophosphate more readily than in the beaker trials. This is supported by the findings of Boujelben et al. (2008) during beaker trials with iron oxide coated sorbents, where they observed equilibrium to be reached after time periods of just 15 to 60 minutes of contact time.

### *5.2.4.3 Release of orthophosphate*

Although the reductions in orthophosphate concentrations leaving steel turnings sections were very high for all experimental runs, the subsequent passage of water through woodchip sections resulted in the re-appearance of elevated orthophosphate concentrations. This effect was observed to a varying degree among experiments resulting in the release of approximately 52%, 10%, and 10% on average of previously bound orthophosphate in experiments one, two, and three, respectively. It can be noticed that greater retention times also tended to result in a greater release of orthophosphate (Figure 5.18). While the specific reason behind the release cannot be determined from these experiments, a possible explanation is offered by the observation of orthophosphate release from iron oxides under prolonged anaerobic conditions in inundated paddy rice fields. Under these conditions, it was found that iron in these complexes can be reduced from $Fe^{3+}$ to $Fe^{2+}$, making the iron-phosphate complex more soluble, causing the release of phosphorus into solution (Brady and Weil, 2002). This is said to happen as a result of siderophores, whose purpose is to solubilize $Fe^{3+}$, making it available for uptake by the organism (Sylvia et al., 2005). Sylvia et al., 2005, also notes that the chelation of $Fe^{3+}$ by siderophores from iron phosphate minerals can result in the liberation of orthophosphate. Although there are obvious differences in the experimental conditions in this research as compared to that presented in the literature, the two most critical elements being the state of prolonged anaerobic conditions and mechanisms by which the orthophosphate was previously bound are similar.

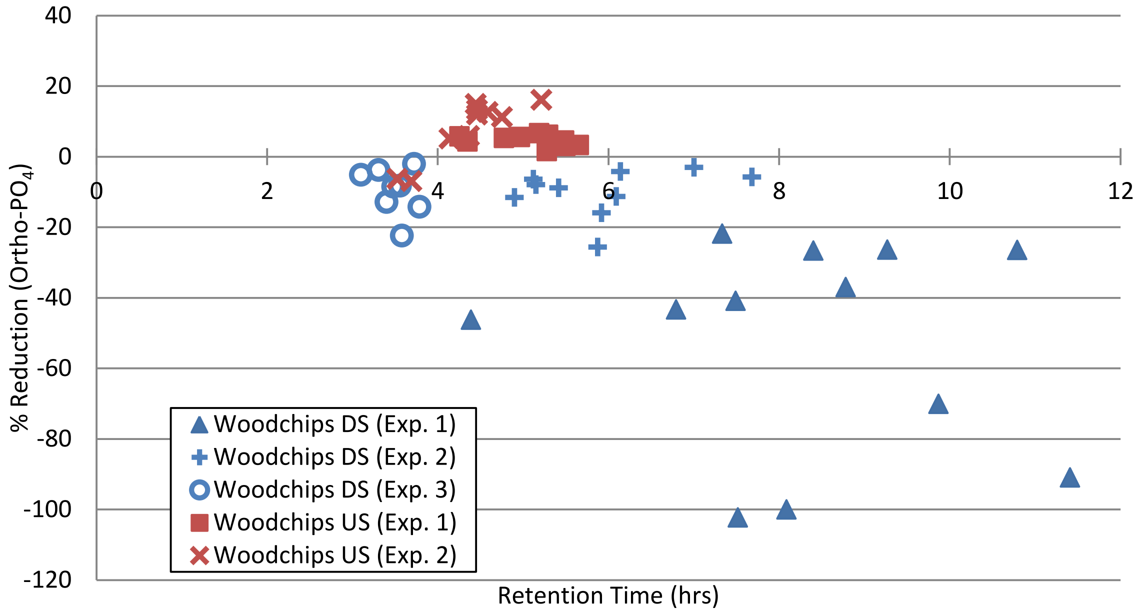

**Figure 5.18. Orthophosphate Reduction vs. Retention time for all samples analyzed for Ortho-PO4 collected from the outlet of woodchip sections for both media arrangements tested (Upstream and downstream denoted US and DS, respectively, in the figure legend and negative percent reductions indicate a net increase in orthophosphate concentration).**

The release of orthophosphate leaving woodchip sections also gives insight into the dynamics of how orthophosphate reacts with iron-oxide. It can be inferred that because concentrations reappear downstream of woodchip sections, that orthophosphate ions are being bound to iron-oxide particles and remaining in solution rather than simply being bound to iron-oxides residing on the surface of the elemental iron or forming iron-phosphate precipitates that settle out of solution. It can be determined that the iron-phosphates formed under these experimental conditions (i.e. subsequent reactor sections tested at these flow rates) tend to remain in solution and are transported into woodchip sections where the orthophosphate is unbound from the iron oxide, releasing orthophosphate back into solution.

It can also be observed in Figure 5.18 that in most cases, the arrangement of woodchips upstream of steel turnings yielded a reduction in the orthophosphate concentration. This reduction tended to generally be in the range of 5% to 15%, and was consistently greater in experiment two as opposed to experiment one. The reasoning behind this cannot be explained as experiments one and two were nearly identical replicates of each other, with the exception of flow rates being maintained more consistently in experiment two. In general, the observation of these reductions occurring in woodchip sections cannot be explicitly determined from these experiments. However, it can be speculated that this occurs as a result of immobilization of the inorganic orthophosphate to the organic form due to the high carbon to phosphorus (C:P) ratio in the woodchip sections of the columns. It is suggested by Brady and Weil (2002) that immobilization of orthophosphate can occur in soils when C:P ratios become greater than 300:1. The C:P ratio in these experiments was found to be much greater, due to the vastly greater C:P ratio within wood as opposed to most soils (Romero et al., 2005). Even considering that this ratio is dampened because of the relatively low surface area to mass ratio of the woodchips as compared to soils, an availability of only 2% of carbon content in the woodchips surpasses this ratio given these experimental conditions. It should be noted, however, that Romero et al. (2005) did observe a release of total phosphorus in the first few months of wood decay, but this was followed by a gross uptake of total phosphorus between years 1 and 2 of their study. This further supports the findings of this research, given that the source of wood for this experiment was an existing bio-reactor, established for a period greater than 1 year.

### *5.2.4.4 Reduction of Nitrate by Steel Turnings*

Although the primary focus of using iron media in this research was to identify its potential to bind orthophosphate, the design of these experiments simultaneously allowed the testing of the effect on nitrate concentration. When examining this effect, the steel turnings were found to reduce nitrate concentrations from approximately -14% to nearly 39% (negative percentages representing higher nitrate-N concentrations leaving than entering that section) (Figure 5.19). Greater reductions tended to be more prevalent in iron sections that were downstream of woodchip sections, with the exception of some negative values observed during experiment two. The observed reductions were also somewhat variable and reduction did not appear to be directly linked to retention time.

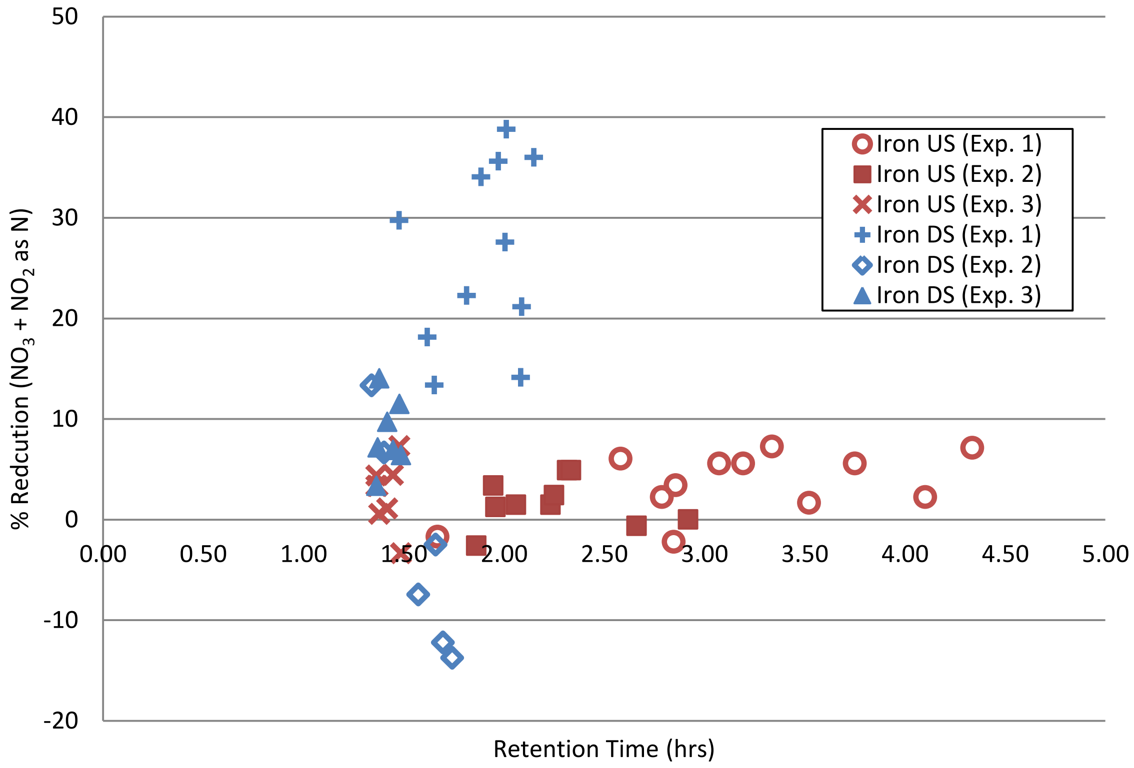

**Figure 5.19. Nitrate Reduction vs. Retention time for all samples analyzed for $NO_3 + NO_2$ as N collected from the outlet of steel turnings sections for both media arrangements tested (Upstream and downstream denoted US and DS, respectively, in the figure legend and negative percent reductions indicate a net increase in nitrate-N concentration).**

While these results were unanticipated, the use of iron media to remove nitrate from wastewater is a well-documented process. A study using a similar iron containing material, Scrap Iron Filings (SIF), was conducted by Hao et al. (2005) where they examined the ability of the SIF to remove nitrate from solution in a batch study. They found that up to 80% nitrate removal (initial concentration of 10.2 mg/L $NO_3$-N), by conversion to ammonium, could be achieved under conditions of low initial pH (2.5) and SIF dosage of 100 g/L in a period of 4 hours. It was also found that initial pH was inversely proportional to nitrate reduction. While Hao et al. (2005) found less than 10% reduction to occur at an initial pH of 4.0, pH tended to drastically increase shortly after the start of the experiment (up to 6.2 at initial pH of 2.5). He also noted that Cheng et al., (1997) found that this reaction nearly stopped at a pH of 8.8. Although the conditions in these experiments are not considered optimal for this reaction to occur, the ranges of pH (approximately 6.75 to 8.5) and relatively low DO (approximately 2% to 6%) do fall within the ranges known to promote this reaction and iron dosage was nearly 10 times greater (988 g/L) in this experiment. These non-optimal conditions can also account for the wide variability in ranges of nitrate-N reduction observed.

It is also unknown why there was presence of negative reductions (i.e. net increases in $NO_3$ + $NO_2$ as N concentrations) for some of the samples collected. It can only be speculated that this is due to limitation within the analytical methods as well as general error with experimental methods.

## 5.3 Summary and Conclusions

Three laboratory-scale column experiments were conducted to examine changes in orthophosphate and nitrate concentrations as a result of interaction with woodchip and iron media. The synergistic effects on nutrient removal ability of each media were also tested by alternating media arrangements among columns during each experiment. This allowed for the observation of previously untested interaction scenarios using this type of remediation media. The similarity of experimental column design to Chun (2007) also allowed for the comparison of nitrate-N reduction in woodchips as a baseline to qualitatively assess synergism. Water quality parameters including temperature, pH, and dissolved oxygen were also collected and used as indicators of the biological and chemical processes responsible for observed changes in soluble nutrient concentrations.

As a result of these experiments, the following net changes (presented as average reduction percentage of initial concentration across all three experiments) in orthophosphate and nitrate-N concentrations were observed:

- Interaction of iron media and orthophosphate resulted in overall reductions in orthophosphate concentrations of 97.5% when upstream of woodchips and 90.9% (99.4% of remaining concentration) when downstream of woodchips.
- Interaction of woodchip media and nitrate-N resulted in overall reductions in nitrate-N concentrations of 48.0% when upstream of iron media and 73.2% (74.9% of remaining concentration) when downstream of iron media.
- Interaction of woodchip media and orthophosphate resulted in overall reductions in orthophosphate concentrations of 8.54% when upstream of iron media and -23.8 (-953.5% of remaining concentration) when downstream of iron media.

- Interaction of iron media and nitrate-N resulted in overall reductions in nitrate-N concentrations of 2.36% when upstream of woodchips and 13.6% (26.1% of remaining concentration) when downstream of woodchips.

The high levels of reductions of orthophosphate achieved as a result of interaction with the chosen iron media confirm results of the beaker trials in this research and validate the choice of this iron material for use in these column trials. It can also be concluded from these findings that there was no appreciable differences observed in orthophosphate reductions from interaction with iron as a result of alternating media configuration. However, higher levels of nitrate-N reduction were found in woodchip sections downstream of iron sections as opposed to upstream. Although a portion of the larger percentage of reduction in woodchip sections downstream of iron can be attributed to longer retention times, this does not explain the elevated reductions observed at relatively low retention times in experiments two and three. Normalizing the means by retention time, however, allowed for the comparison of the means of these two conditions, and showed a significant difference ($p < 0.01$). Thus it can be concluded that placing the iron material upstream of woodchip sections enhanced the ability of the woodchips to reduce nitrate-N concentrations.

The configuration of iron upstream of woodchips, although showing enhanced nitrate-N removal, resulted in relatively large net increases of previously reduced orthophosphate concentrations. This was observed during all experiments and tended to be greater for longer retention times (although occurring to some degree at all retention times observed). Conversely, reductions in orthophosphate concentrations were observed when woodchip sections were placed upstream of iron. This reduction was found to be relatively small (mean of 8.54% on average) in comparison to observed reductions from interaction with iron, but was observed consistently and was not linked to retention time. The media arrangement of woodchips upstream of iron also favored nitrate-N reduction in iron, and was also found to be unrelated to retention time. These results suggest the arrangement of woodchips upstream of iron is favorable for orthophosphate reduction.

Although the synergistic effects of media arrangement suggested opposite arrangements were preferred for the reduction of either orthophosphate or nitrate-N concentrations, but not both, these effects were overcome by placing iron both upstream and downstream of woodchips as tested in experiment three. This arrangement confirmed the findings from experiments one and two, of enhanced nitrate-N removal in woodchips downstream of iron, as well as demonstrating that orthophosphate released by woodchip sections downstream of iron could be removed by the downstream iron section a second time. From these findings it can be concluded that the media arrangement of iron sections both upstream and downstream of woodchips is favorable for the enhanced removal of both orthophosphate and nitrate-N.

# CHAPTER 6: RECOMMENDATIONS FOR FUTURE WORK

Based on the results of this research, the following recommendations are made for future research of this topic:

- A more rigorous batch experiment should be conducted using pre-rusted iron material to identify the optimal retention time needed for orthophosphate sorption to take place. This should include the quantification of maximum sorption capacity by varying the initial concentration of orthophosphate in solution. It should also include desorption tests under a variety of pH and dissolved oxygen ranges. This would help identify whether the desorption occurring from woodchip interaction was a result of combinations of pH and dissolved oxygen or a more complex process as a result of interaction in the woodchip matrix.
- Conduct further column studies with a similar design and include the analysis of other forms of nitrogen and phosphorus in addition to nitrate-N and orthophosphate as information to use a mass balance approach in order to better understand the biological and chemical reactions taking place within the different sections of the reactor.
- Further examine the synergistic effects of media arrangement on orthophosphate and nitrate-N reduction for an array of flow rates, resulting in various retention times to better understand the chemical and biological processes that produced the results found by this study.
- Conduct longer duration column experiments to test the longevity of the iron material used in this study. This could be achieved simply by the collection of the dry mass of the material before and after a longer-duration experiment.

- Based on the findings of these works, the implementation of a field-scale bioreactor utilizing both an iron media and woodchips to assess the effectiveness of the iron media as well as synergism between the two materials in a real-world scenario.

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# APPENDIX

## A.1 Two-Column Averages for Ortho-PO4, $NO_2$+ $NO_3$ as N, Temperature, Dissolved Oxygen, and pH: Experiment 1

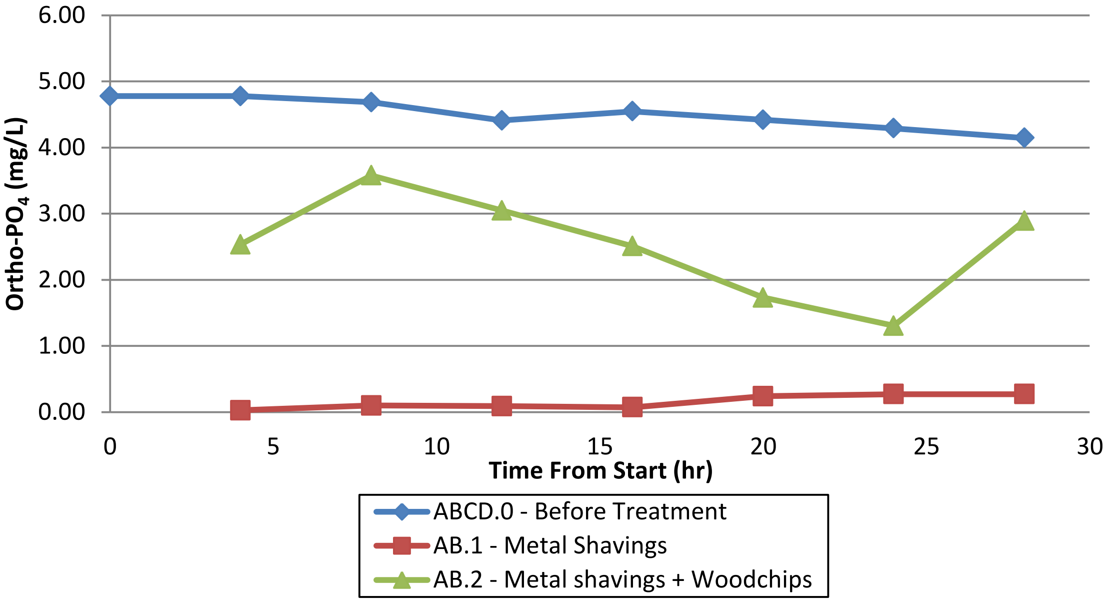

**Figure A.1. Average Ortho-PO4 concentration throughout Experiment 1 for Columns A and B.**

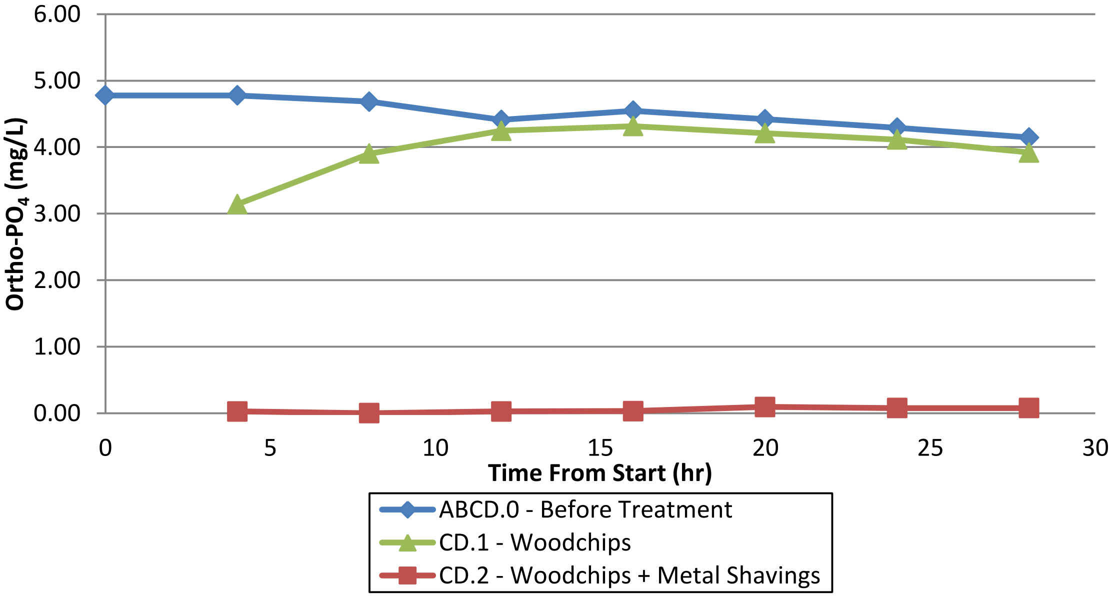

**Figure A.2. Average $PO_4$ concentration throughout Experiment 1 for Columns C and D.**

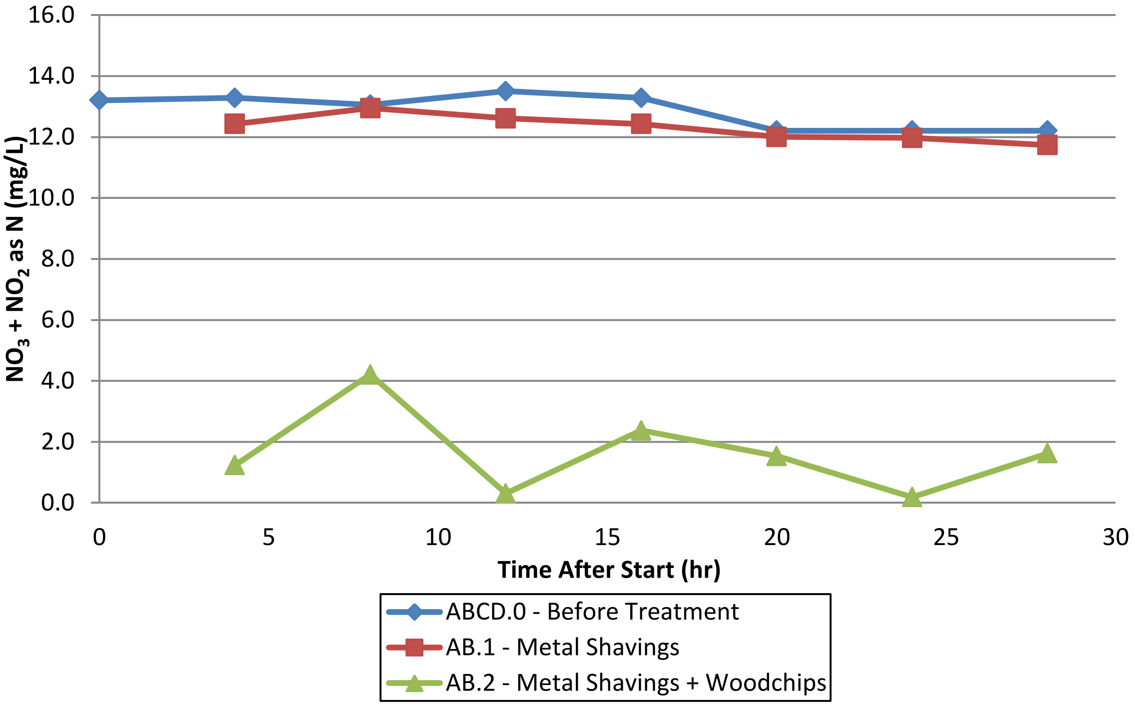

**Figure A.3. Average $NO_2 + NO_3$ as N concentration throughout Experiment 1 for Columns A and B.**

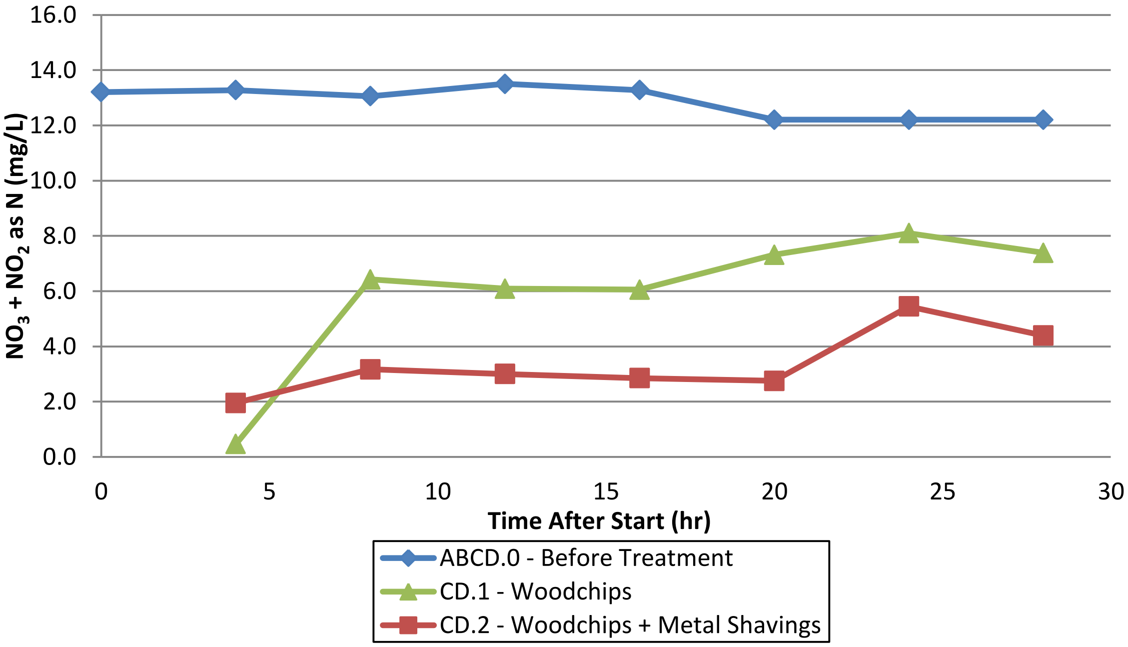

**Figure A.4. Average $NO_2 + NO_3$ as N concentration throughout Experiment 1 for Columns C and D.**

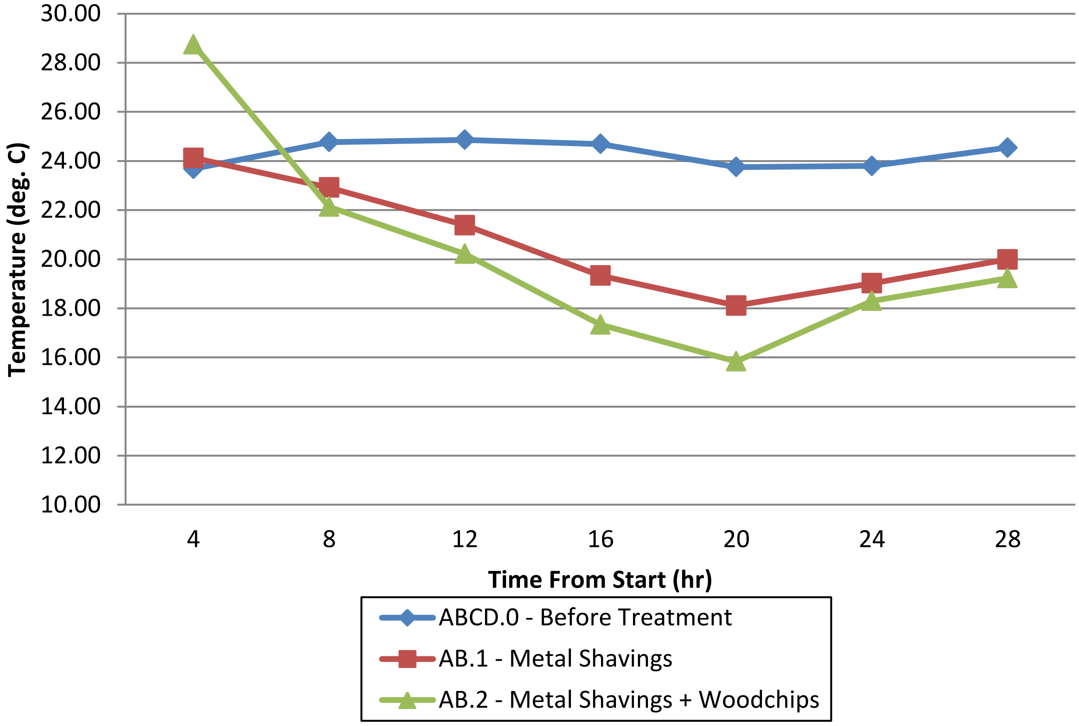

**Figure A.5. Average Temperature throughout Experiment 1 for Columns A and B.**

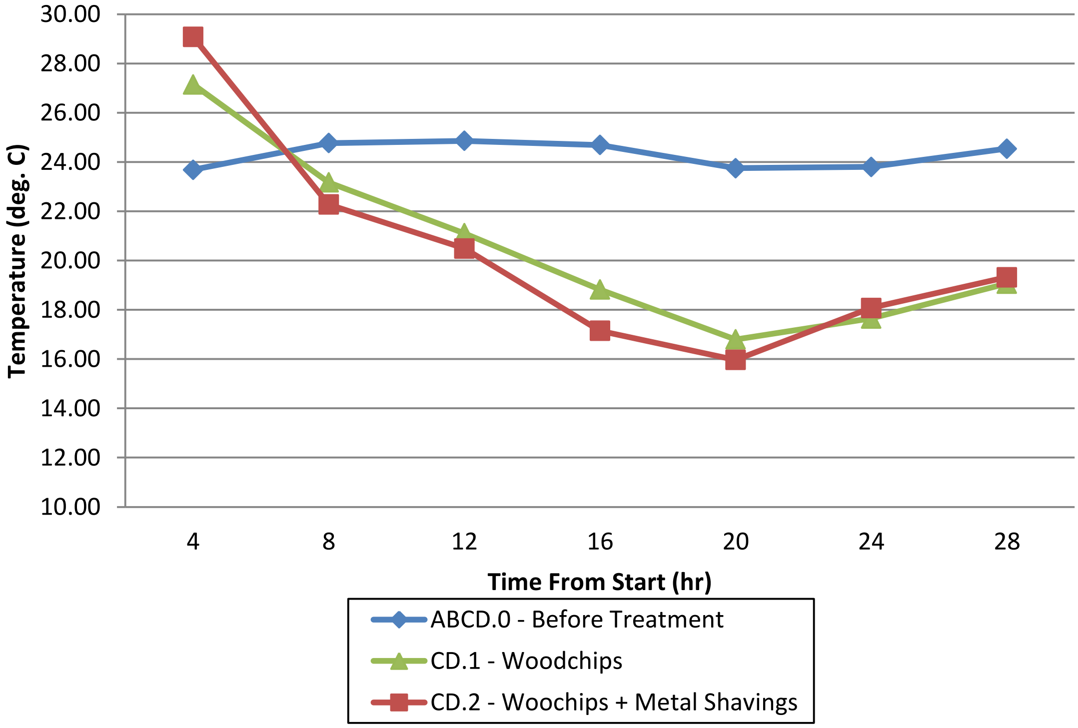

**Figure A.6. Average Temperature throughout Experiment 1 for Columns C and D.**

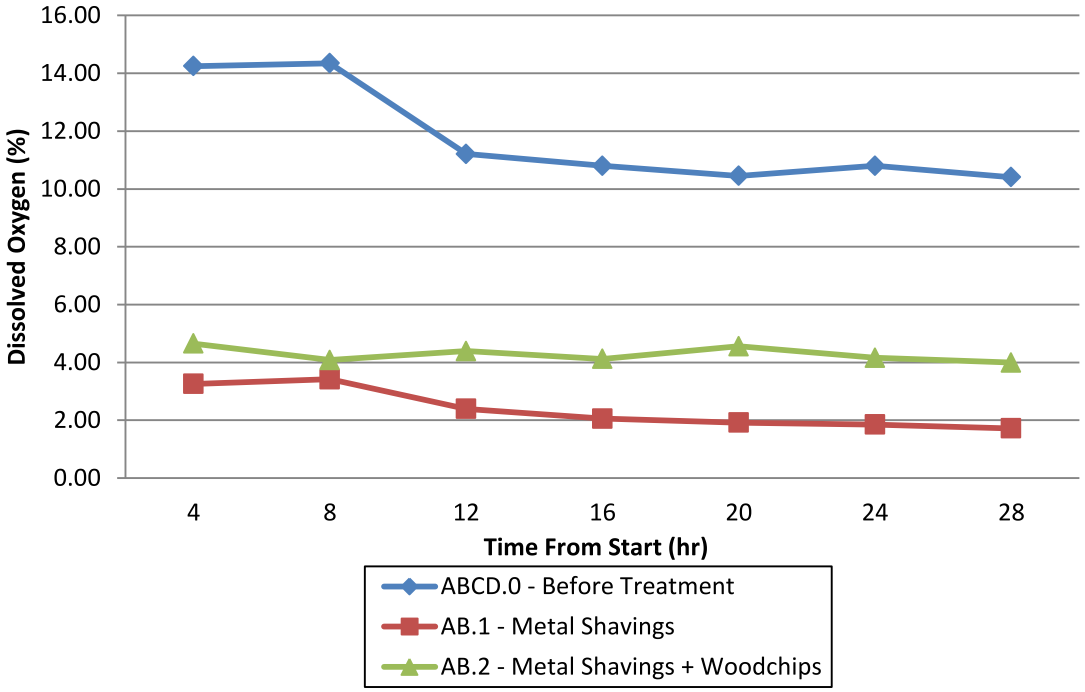

**Figure A.7. Average Dissolved Oxygen throughout Experiment 1 for Columns A and B.**

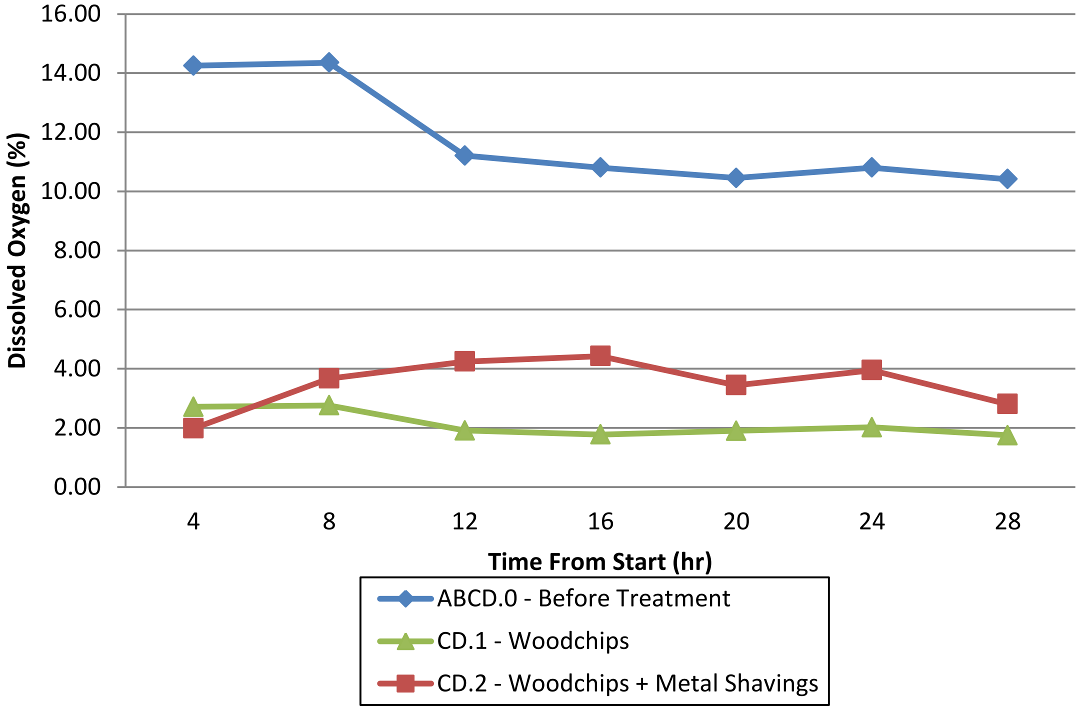

**Figure A.8. Average Dissolved Oxygen throughout Experiment 1 for Columns C and D.**

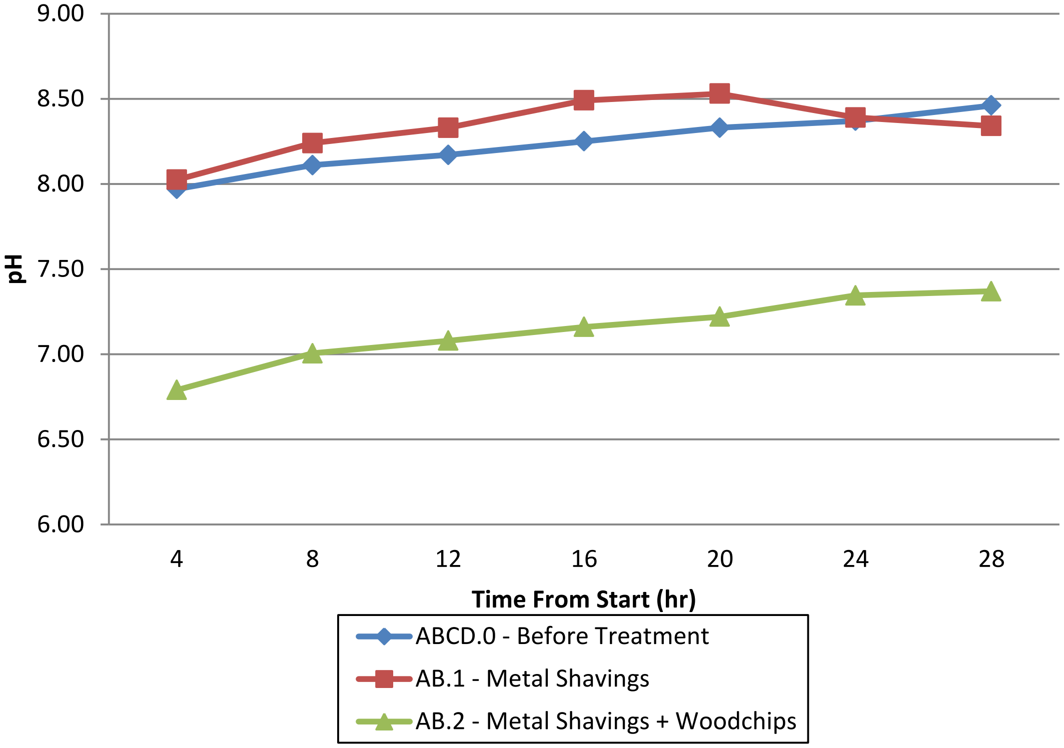

**Figure A.9. Average pH throughout Experiment 1 for Columns A and B.**

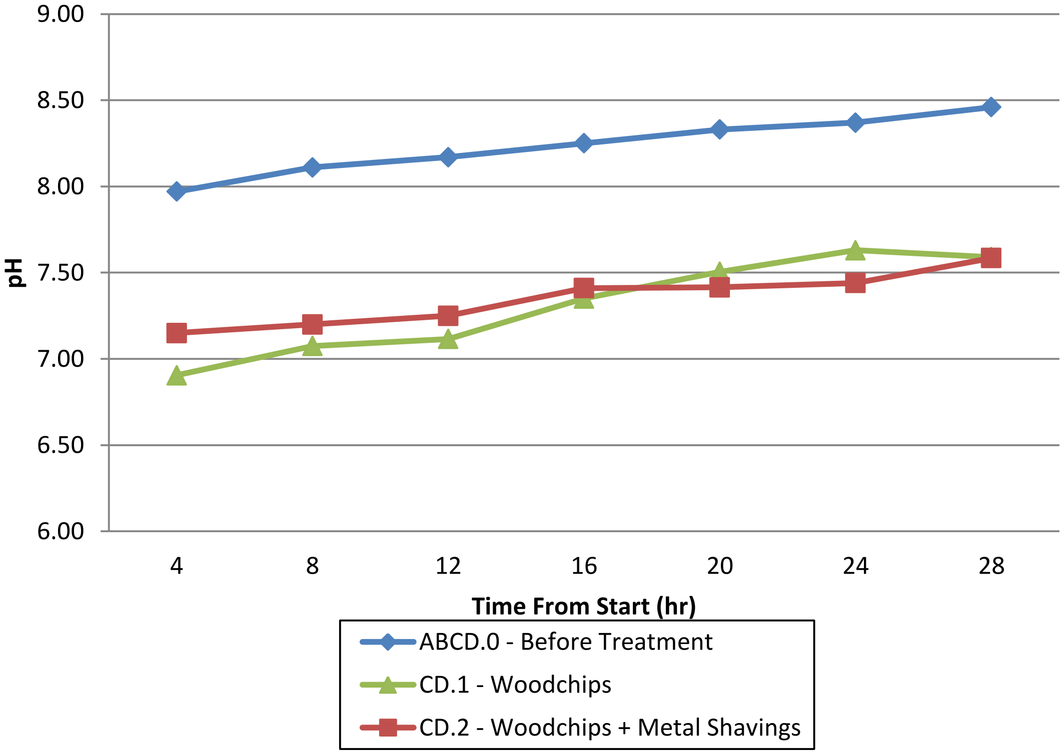

**Figure A.10. Average pH throughout Experiment 1 for Columns C and D.**

## A. 2 Two-Column Averages for Ortho-PO4, $NO_2$+ $NO_3$ as N, Temperature, Dissolved Oxygen, and pH: Experiment 2

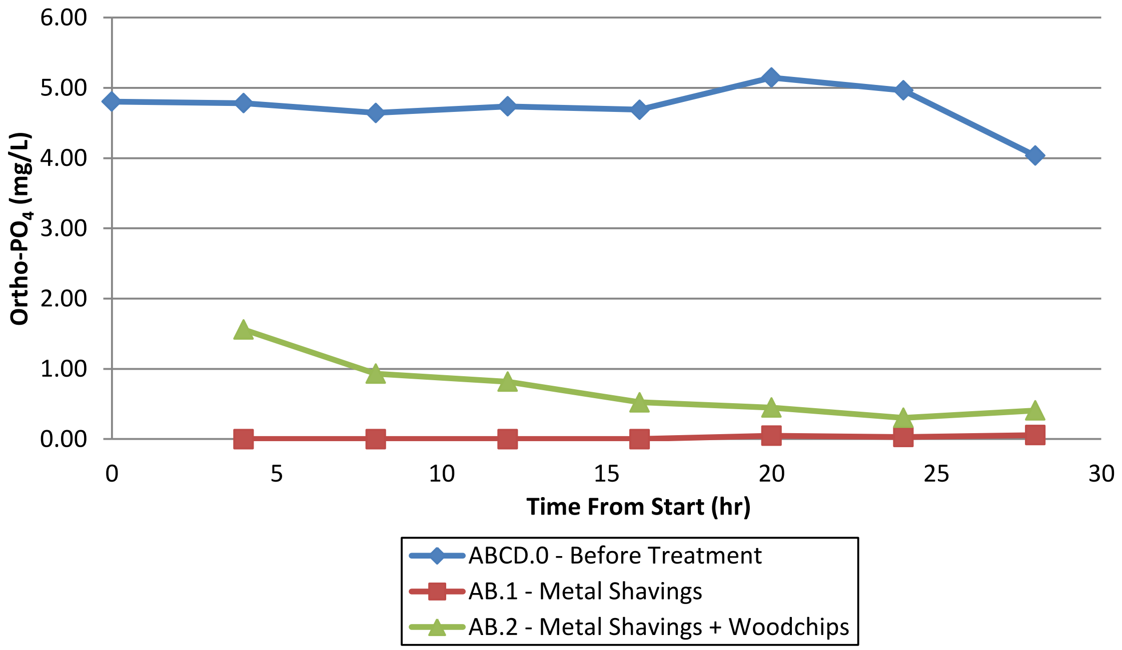

**Figure A.11. Average PO4 concentration throughout Experiment 2 for Columns A and B.**

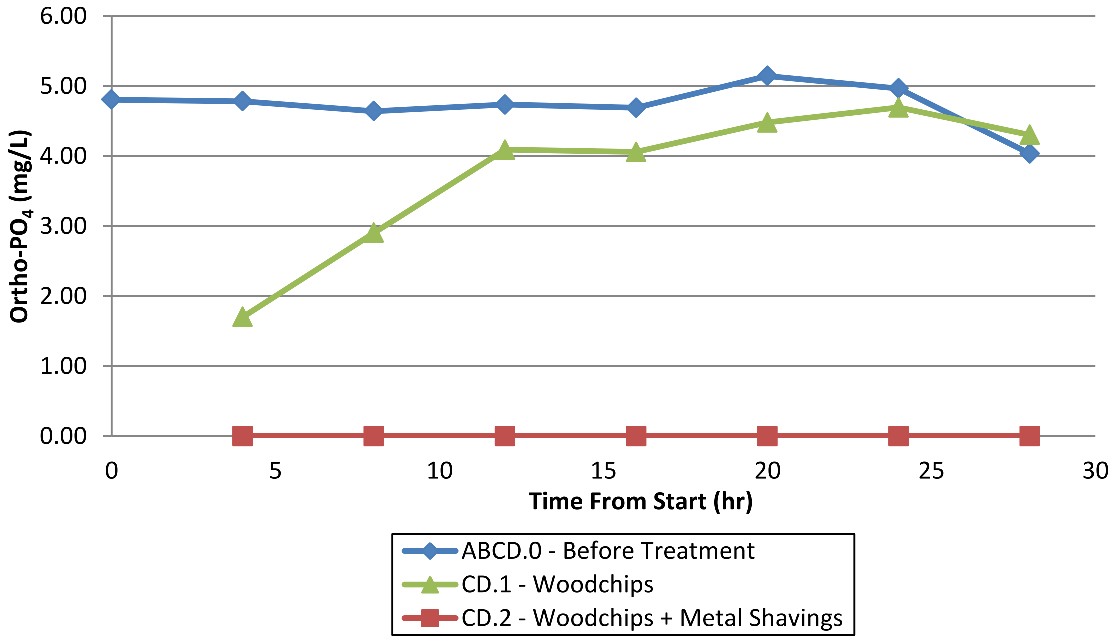

**Figure A.12. Average $PO_4$ concentration throughout Experiment 2 for Columns C and D.**

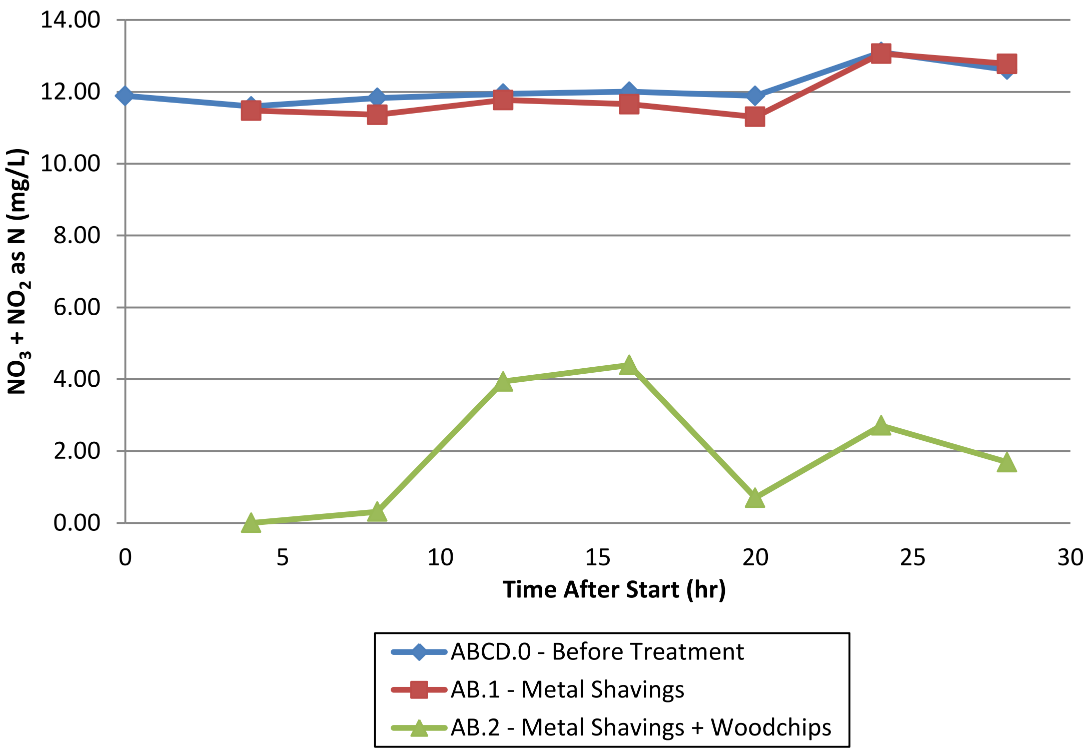

**Figure A.13. Average $NO_{2\,+}NO_3$ as N concentration throughout Experiment 2 for Columns A and B.**

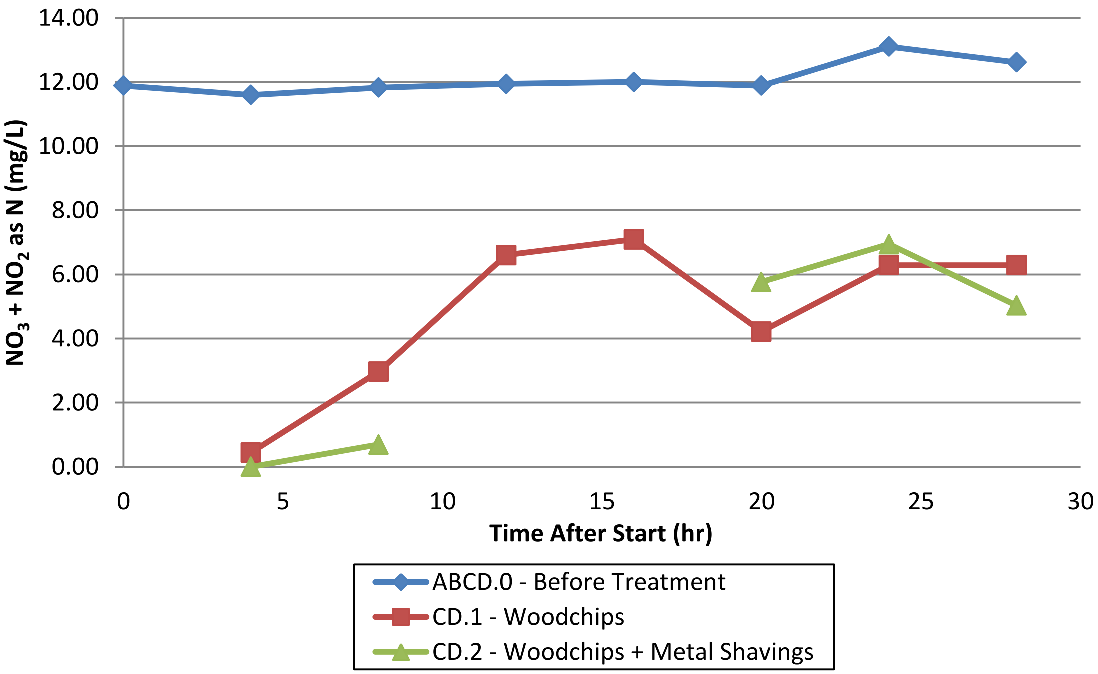

**Figure A.14. Average $NO_{2\,+}NO_3$as N concentration throughout Experiment 1 for Columns C and D.**

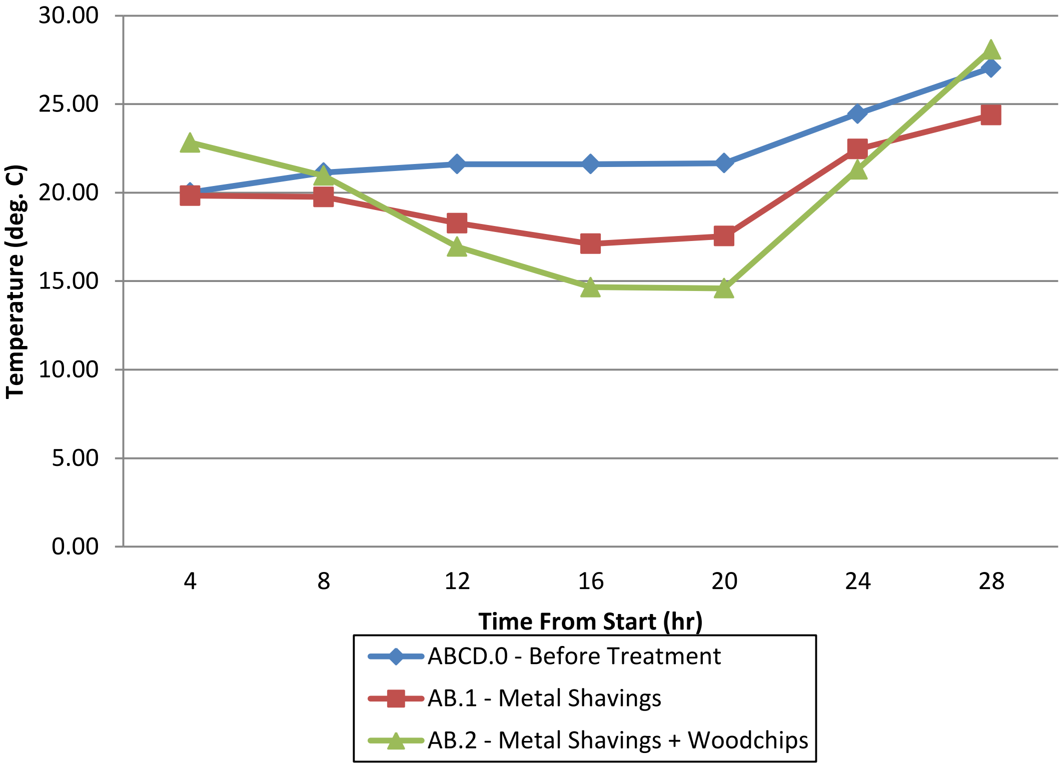

Figure A.15. Average Temperature throughout Experiment 2 for Columns A and B.

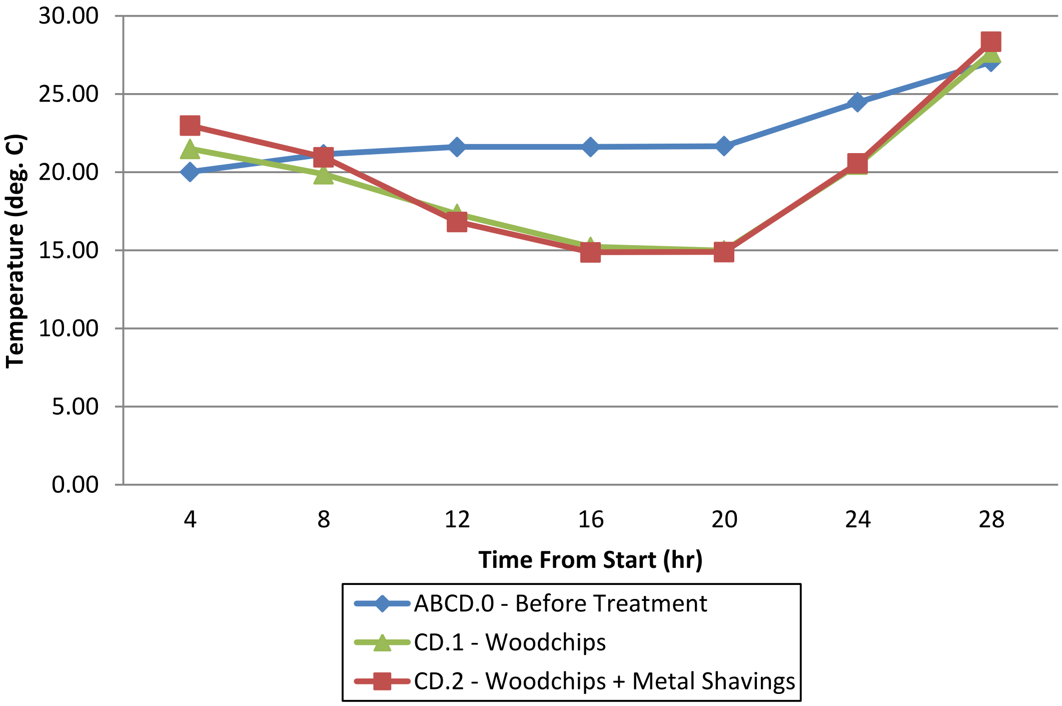

Figure A.16. Average Temperature throughout Experiment 2 for Columns C and D.

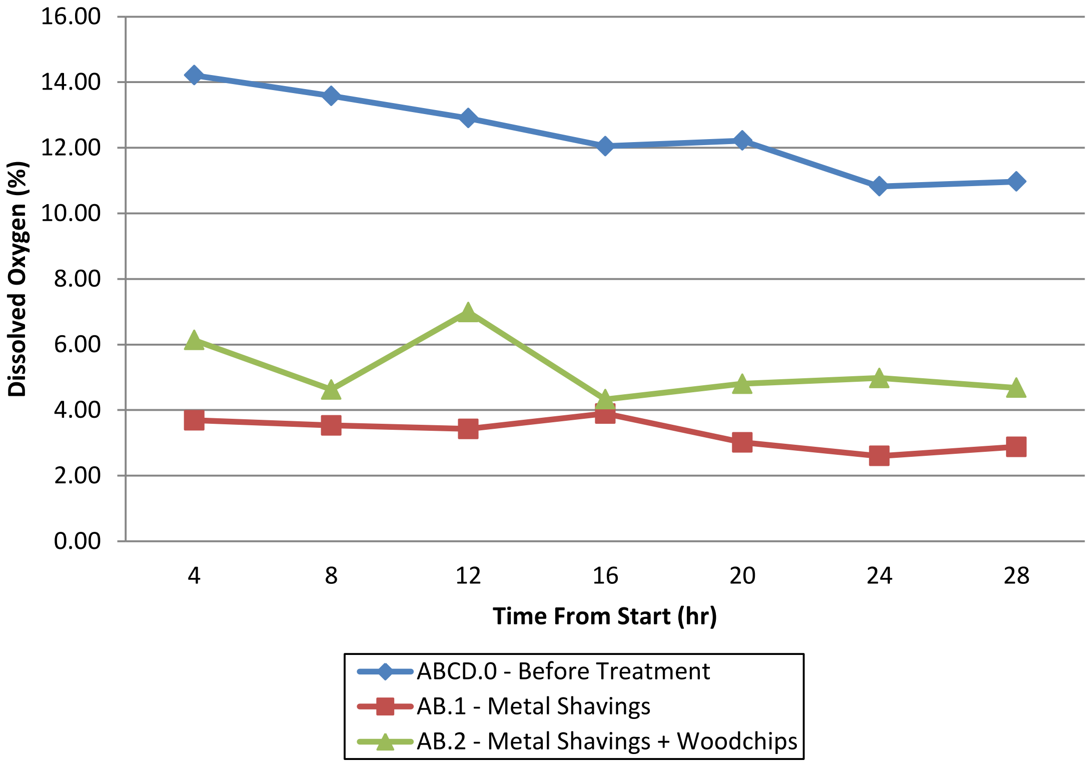

Figure A.17. Average Dissolved Oxygen throughout Experiment 2 for Columns A and B.

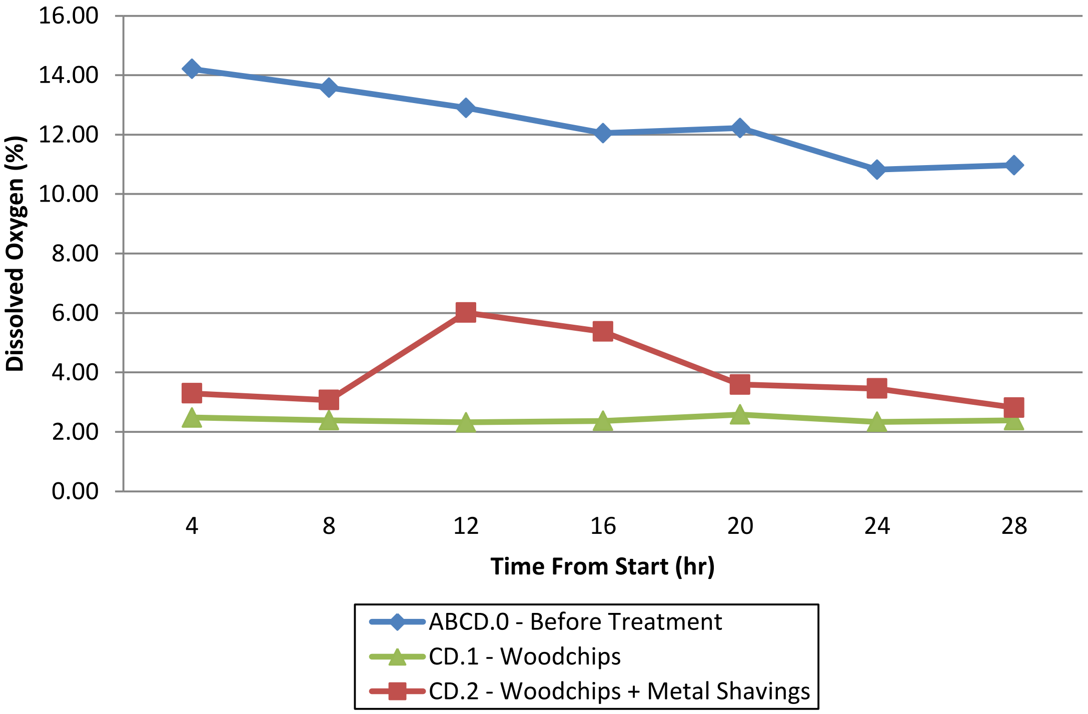

Figure A.18. Average Dissolved Oxygen throughout Experiment 2 for Columns C and D.

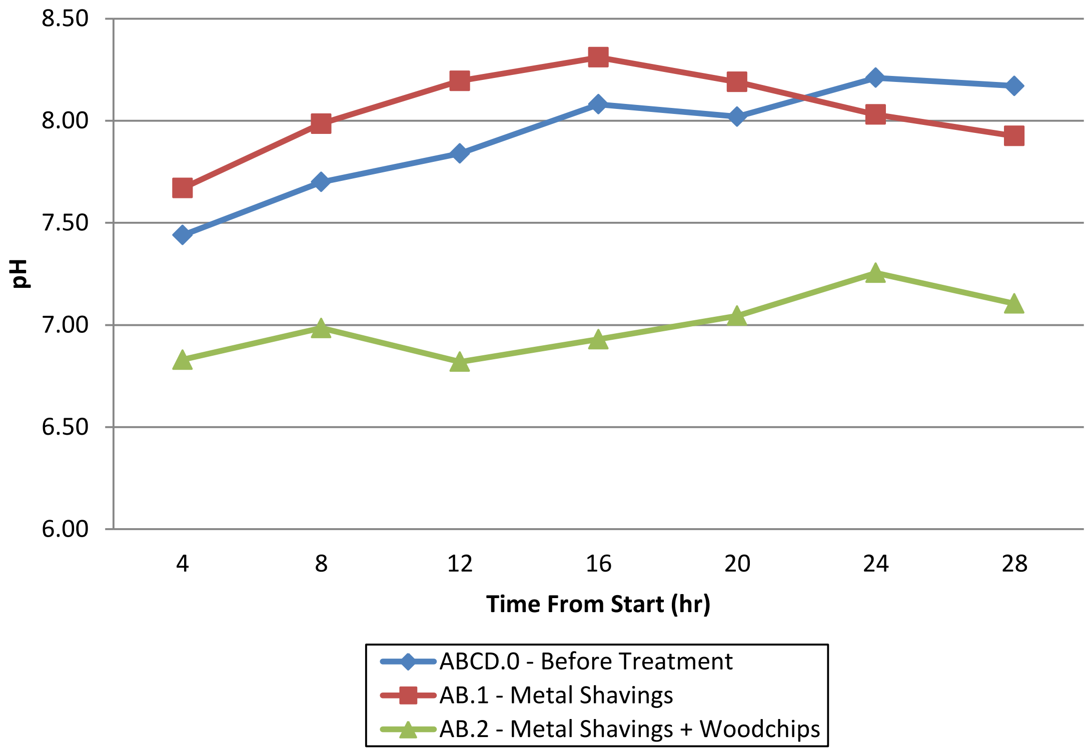

Figure A.19. Average pH throughout Experiment 2 for Columns A and B.

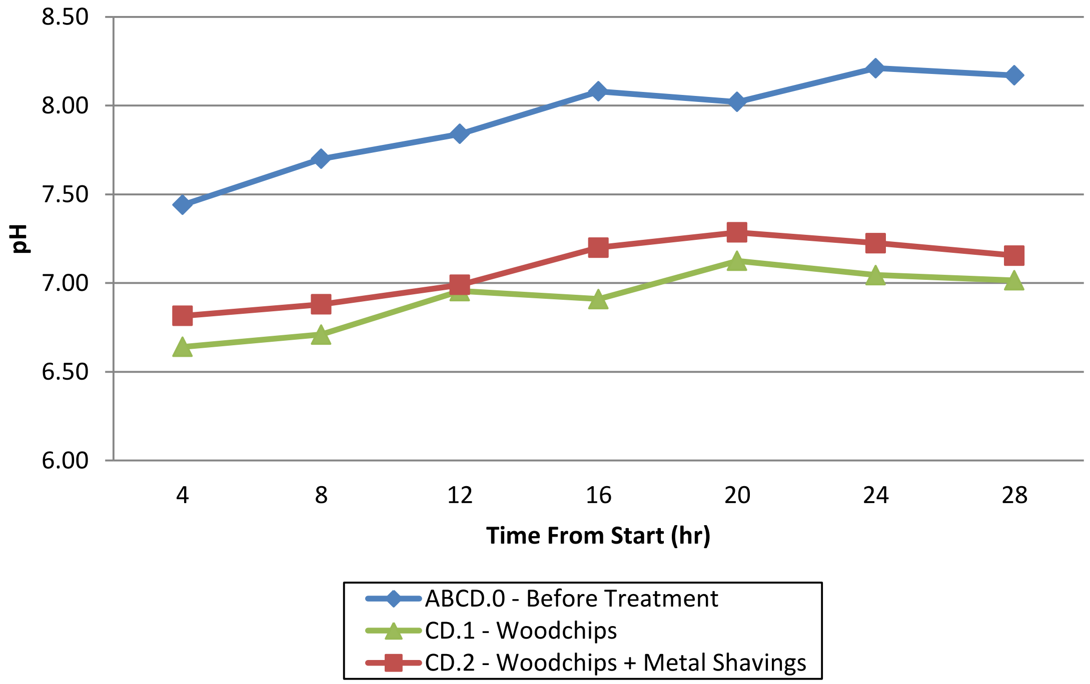

Figure A.20. Average pH throughout Experiment 2 for Columns C and D.

## A.3 Two-Column Averages for Ortho-PO4, $NO_2$+ $NO_3$ as N, Temperature, Dissolved Oxygen, and pH: Experiment 3

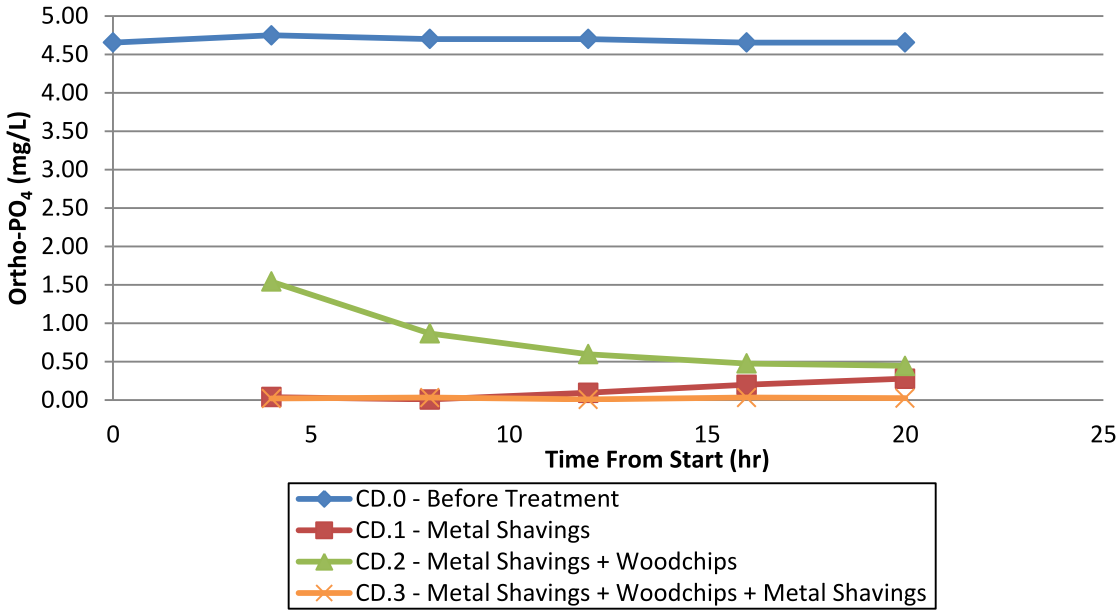

**Figure A.21. Average PO4 concentration throughout Experiment 3 for Columns C and D.**

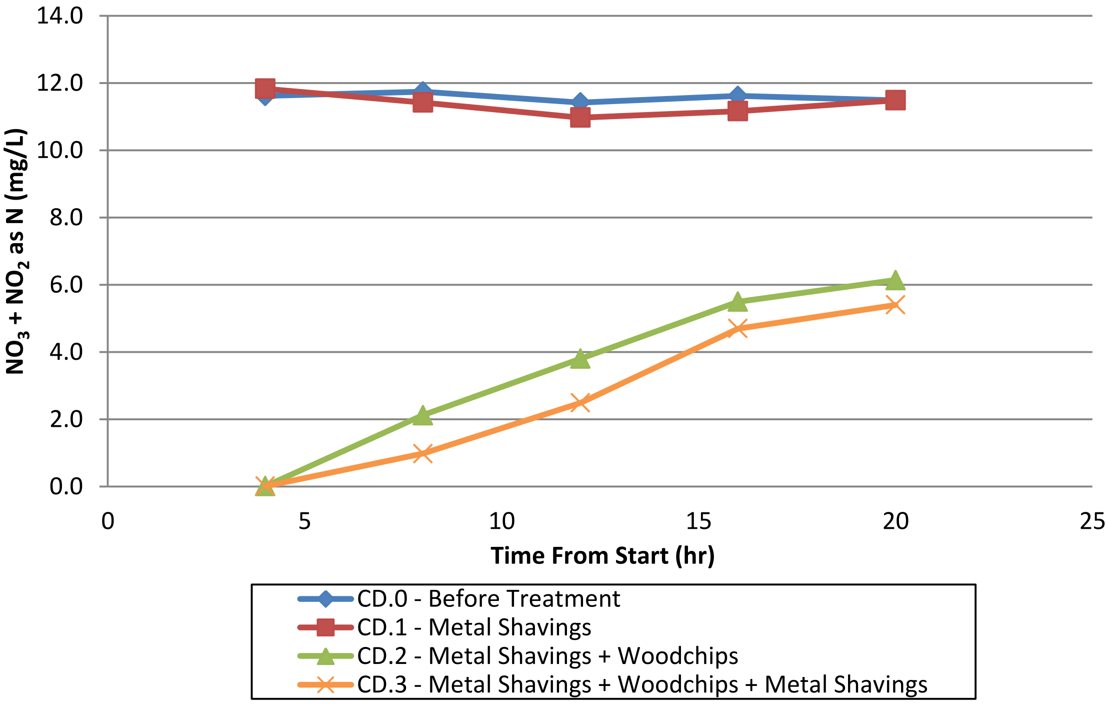

**Figure A.22. Average $NO_2$ + $NO_3$as N concentration throughout Experiment 3 for Columns C and D.**

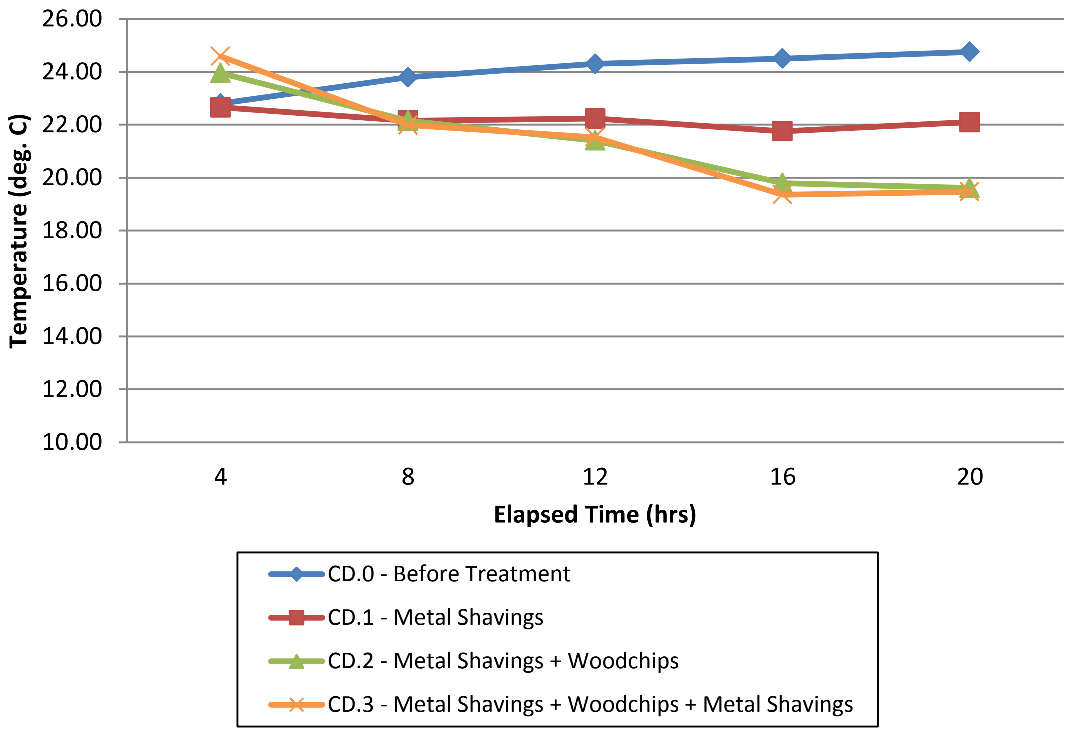

**Figure A.23. Average Temperature throughout Experiment 3 for Columns C and D.**

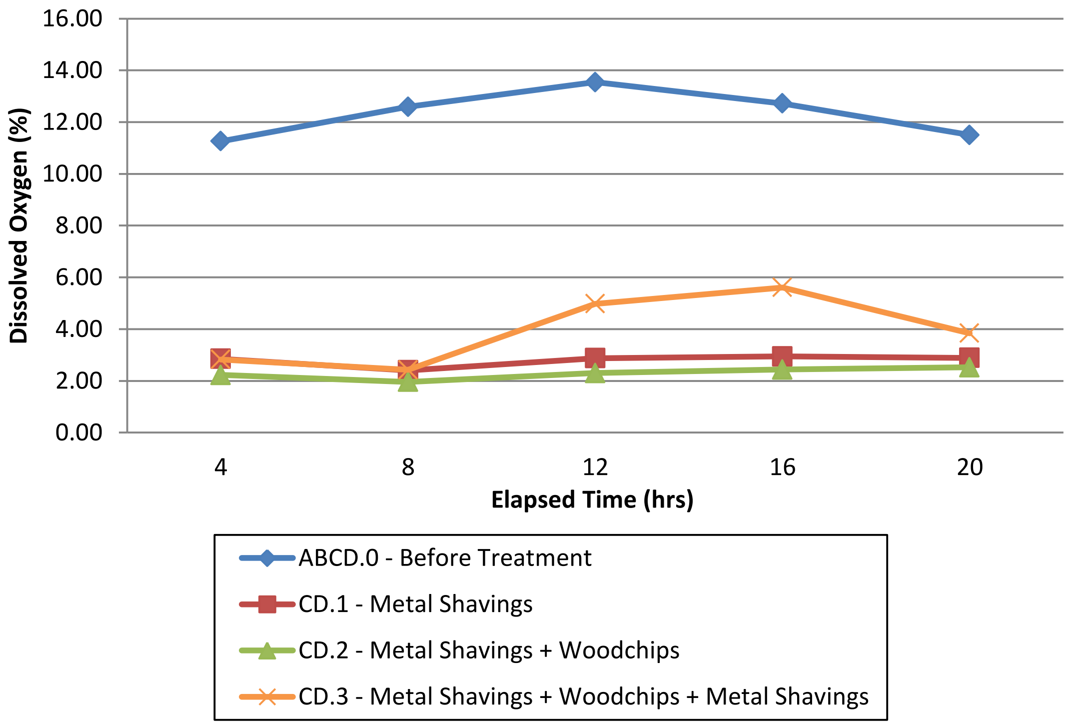

**Figure A.24. Average Dissolved Oxygen throughout Experiment 3 for Columns C and D.**

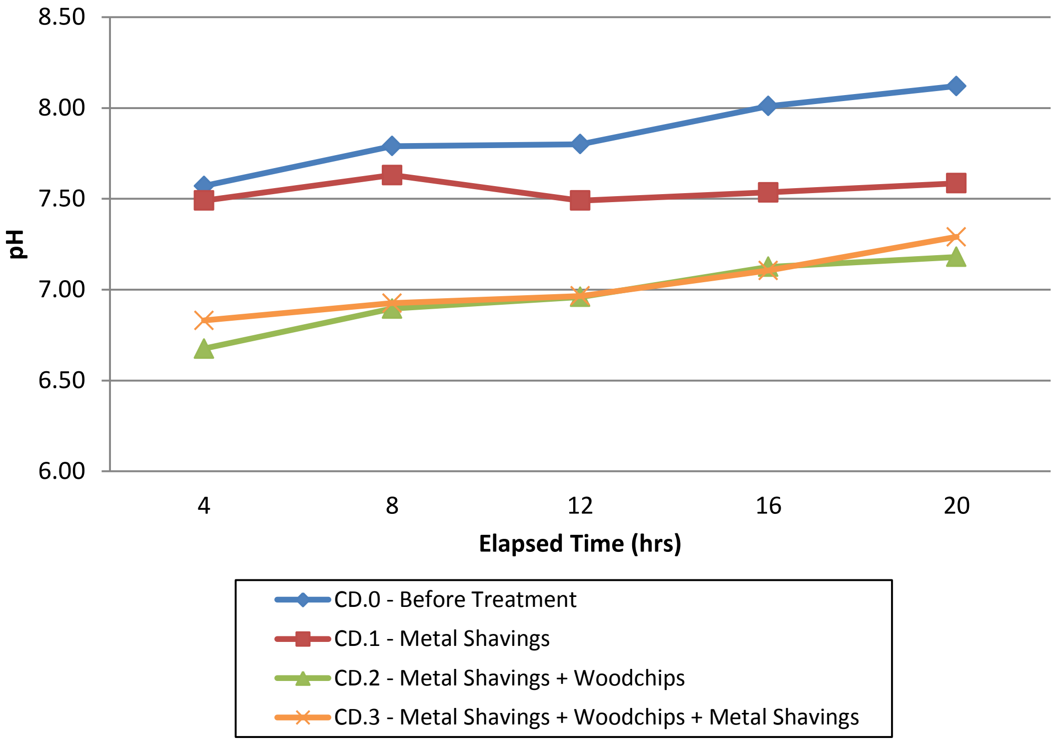

**Figure A.25. Average pH throughout Experiment 3 for Columns C and D.**