ENVIRONMENTAL TRADEOFFS OF DENITRIFYING WOODCHIP BIOREACTORS

BY

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THESIS

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Abstract

The development of row cropped agriculture on hydrologically altered landscapes in the Midwestern United States has led to environmental concerns. Tile drainage in this region acts as a conduit carrying sediment, nutrients, and other environmental pollutants to surface waters. Propelled by these concerns and a desire to meet water quality standards, innovative practices like woodchip tile bioreactors, constructed wetlands, drainage water management systems, and riparian buffer strips for treating agricultural drainage water are continually being developed and implemented across the Midwestern United States.

Like drainage, bioreactors may have the potential to produce additional environmental and health problems. The production of greenhouse gases like carbon dioxide, nitrous oxide and methane are one concern. Unintended increases in these gases in bioreactors would effectively trade one problem for another with equally deleterious effects on the environment.

This study is an examination of the ability of two bioreactors in Central Illinois in 2013, BR1 and BR2, to reduce nitrate-nitrogen (N) loads to surface waters. It is also an exploration of the potential unintended production of nitrous oxide, methane and carbon dioxide fluxes.

The average load reduction for BR1 was 18.5% with average minimum and maximum daily load reductions of 2.1% and 69.8% respectively. The average removal rate was $13\,\mathrm{g\,NO_3\text{-}N\,m^{-3}\,day^{-1}}$. BR1 removed $268\,\mathrm{kg\,N\,m^{-2}}$ and emitted $3.2\,\mathrm{kg\ N_2O\text{-}N\,m^{-2}}$. Therefore, N_2O-N represents 1.2% of the total N removed. Average N_2O-N flux during the study period was $1.0\,\mathrm{mg\,N_2O\text{-}N\,m^{-2}\,hr^{-1}}$. In 2013, $28.7\,\mathrm{kg\,N_2O\text{-}N}$ was emitted from BR1. Average CH_4-C flux from BR1 was $0.02\,\mathrm{mg\,CH_4\text{-}C\,m^{-2}\,hr^{-1}}$. In 2013, $15.4\,\mathrm{kg\,CH_4\text{-}C}$ was emitted from BR1. Average CO_2-C flux from BR1 was $2.9\,\mathrm{g\,CO_2\text{-}C\,m^{-2}\,hr^{-1}}$. In 2013, $2256.4\,\mathrm{kg\,CO_2\text{-}C}$ was emitted from BR1. This represents 7.7% of total C lost from woodchips. At this rate, the carbon in the bioreactor would be depleted in 13 years.

During 2013, BR2 emitted 1.0 kg N_2O-N m^{-2}. Average N_2O-N flux during the study period was 0.5 mg N_2O-N m^{-2} hr^{-1}. In 2013, 9.3 kg N_2O-N was emitted from BR2. Average CH_4-C flux was 0.02 mg CH_4-C m^{-2} hr^{-1}. In 2013, 7.0 kg CH_4-C was emitted from BR2. Average CO_2-C flux from BR2 was 3.1 g CO_2-C m^{-2} hr^{-1}. In 2013, 2578.2 kg CO_2-C was emitted from BR2. This represents 8.8% of total C lost from the woodchips. At this rate, the carbon in the bioreactor would be depleted in 11 years. Gas fluxes were higher during warmer months when nitrate removal was highest. Methane fluxes were in general negligible.

Phosphorus concentrations and loads leaving the bioreactors were greater than those entering them. Phosphorus influent concentrations at BR1 averaged 0.02 mg L^{-1} whereas effluent concentration averaged 0.3 mg L^{-1}. Phosphorus loading was 0.2 g $P0_4$-P m^{-3} day^{-1} at BR1. Phosphorus influent concentrations at BR2 averaged 0.02 mg L^{-1} whereas effluent concentration averaged 0.1 mg L^{-1}.

Data from BR1 was used to update the interactive module for bioreactor design and performance evaluation found on the Illinois Drainage Guide. Routines were added to use inflow and outflow data to derive hydraulic conductivity, and to use inflow data and stop log settings to estimate bypass flow. Hydraulic conductivity was found to lag flow by 6 days suggesting biofilm growth during low flow events and the flushing of biofilms from control structures during peak flow events.

Bypass flow represented 47 % of the flow at BR1 during the study period. The routine accurately predicted 49 % bypass given measured flow data and stop log settings. The visual basic interactive module was found to be a valid tool for predicting bioreactor performance. Therefore, the routine was used to determine board settings for BR1 for future study periods that would optimize bioreactor performance.

The results of this study demonstrate that bioreactors are an effective means to reducing nitrate-N loads from agricultural fields while producing minimal unintended consequences that would have a deleterious effect on the environment. Under flooded conditions, bioreactor performance is not reduced, however adverse effects like methane and hydrogen sulfide gas production and biofilm formation occurred. More long term field studies examining potential adverse effects need to be performed.

To Jeremy

Acknowledgments

It is difficult to imagine that my trek to the Midwestern United States to attend the University of Illinois happened almost two years ago. As my adventure at the U of I reaches its close, I would like to take the opportunity to appreciate those who have helped me better myself academically, professionally and personally.

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Chapter 1

Introduction

During the past 150 years, there have been considerable advances in agriculture. Tile drainage stands as one of the most significant factors in the transformation of the agricultural sector. Drainage has altered the hydrology of the upper Midwestern United States, changing wetlands, unsuitable for agricultural production to some of the most productive farm land in the world. Following drainage, advances in land management, fertilizers, seeds, and tillage consistently continue to improve crop yields in this significant row cropped agricultural expanse. However, this development of agriculture has not come without consequences. Tile drains transport sediment, nutrients, and other environmental pollutants to surface waters.

Nutrients are essential for life and growth. Throughout the Midwestern United States, when soils are deficient, fields are fertilized with nutrients like nitrogen, phosphorus and potassium to promote growth and to increase yields. Nutrients are vital to crop survival but when transported from the soil, they can lead to environmental degradation. Agricultural drainage water can become laden with nutrients present in soil water in agricultural fields. Tile drains act as conduits carrying the nutrients from fields to surface waters. These nutrients can cause eutrophication. Eutrophication threatens and degrades aquatic ecosystems by creating harmful algae blooms and hypoxic zones. Hypoxia occurs when the oxygen concentration falls below the level needed to sustain life ($< 0.2\,\mathrm{mg\,L^{-1}}$). In eutrophic waters, nutrients leads to algae blooms which produce oxygen through photosynthesis in the presence of light. An overabundance of algae blocks light, forcing algae to consume oxygen, rather than produce oxygen. When algae die, the bacteria used to decompose the plant matter further deplete water oxygen levels. Hypoxia is a leading water quality problem in the United States and the world. The coast of the Gulf of Mexico, the outlet of the Mississippi River Basin and the Upper Midwest is a prime example of a hypoxic zone that has resulted

in environmental degradation and economic loss, and where the use of innovative management practices is recommended. Propelled by these environmental concerns and a desire to meet water quality standards, woodchip tile bioreactors, constructed wetlands, drainage water management systems, and riparian buffer strips are continually being developed and implemented across the Midwestern United States.

Woodchip bioreactors are one practice being used to treat drainage water laden with nutrients. Woodchip bioreactors are trenches on the edge of fields filled with woodchips through which tile water flows. Denitrifying bacteria in the bioreactor convert nitrate-N into nitrogen gas by using the carbon in the woodchips as their food source during respiration.

Bioreactors may not be devoid of unintended consequences, and have the potential to produce additional environmental and health problems. The production of greenhouse gases particularly carbon dioxide, nitrous oxide and methane are of concern. Other concerns include methylmercury production, increased phosphorus loading, hydrogen sulfide gas production and biofilm formation. Measured adverse effects would make bioreactor implementation one that effectively trades one problem for another that also has deleterious effects on the environment.

This research is an attempt to determine the effectiveness of bioreactors in reducing nitrate-N losses to surface waters and to characterize any potential greenhouse gas emissions from bioreactors. This study is the examination of nitrate-N loads, and carbon dioxide, nitrous oxide and methane fluxes from two bioreactors in Central Illinois.

Chapter 2

Objectives

This study is one aspect of a larger project. The goal of the latter is to "combine research, education, and extension on using tile-fed constructed wetlands and wood chip tile bioreactors to reduce nitrate losses in the upper Embarras River watershed in east-central Illinois, a dominantly tile-drained, agricultural watershed". This specific study aims to contribute to the overall goal by determining the effectiveness of bioreactors in reducing nitrate-N export from corn and soybean fields and quantify greenhouse gas emissions (N_2O, CH_4, and CO_2) from the bioreactor bed in the Embarras River Watershed in Central Illinois.

The specific objectives of this study are to:

1. Determine the effectiveness of bioreactors in reducing nitrate losses to surface waters
2. Characterize gas fluxes from bioreactors
3. Determine if nitrous oxide concentration is related to bioreactor load reduction or denitrification rates
4. Characterize bioreactor performance under flooded conditions
5. Use measured flow and nitrate-N data to update and validate an existing bioreactor performance model and optimize stop-log settings

Chapter 3

Review of Literature

3.1 Agricultural Development in the Midwestern United States

Nutrient enrichment in streams in the upper Midwestern United States and its outlet in the Gulf of Mexico are a result of intensive agriculture in a modified landscape. Mother Nature and considerable advancements in agriculture have altered the upper Midwestern United States from land unsuitable for agricultural production to some of the most productive farm land in the world. During the past 150 years, tile drainage stands as one of the largest drivers of the transformation of the agricultural sector. Following drainage, advances in land management and fertilizers consistently continue to improve crop yields in this row cropped expanse. The invention of the Haber-Bosch process in particular, which allowed for the synthesis of ammonia for fertilizer, drove large increases in crop productivity and yield. Government subsidies and other incentives continue to facilitate increased crop yields through agricultural intensification.

3.1.1 Glaciers and Tile Drainage

Illinois topography is a result of periods of glaciation that occurred between two million and 10,000 years ago (Illinois State Geological Survey, 2014) as shown in Figure 3.1. During this time, glaciers advanced and melted across the upper Midwestern United States, including 90% of Illinois, carving bedrock, filling valleys and depositing sediment, creating the rich flat land prairies that characterize Illinois (Illinois State Geological Survey, 2014). The soils that developed from the glacial till, outwash and subsequent decomposition of the prairie plants in this region have made for some of the most organic rich and productive soils globally.

Drummer soil, the state soil of Illinois, having 4% to 7% organic matter content is a prime example of the richness of the glacial till soil that developed under prairie vegetation.

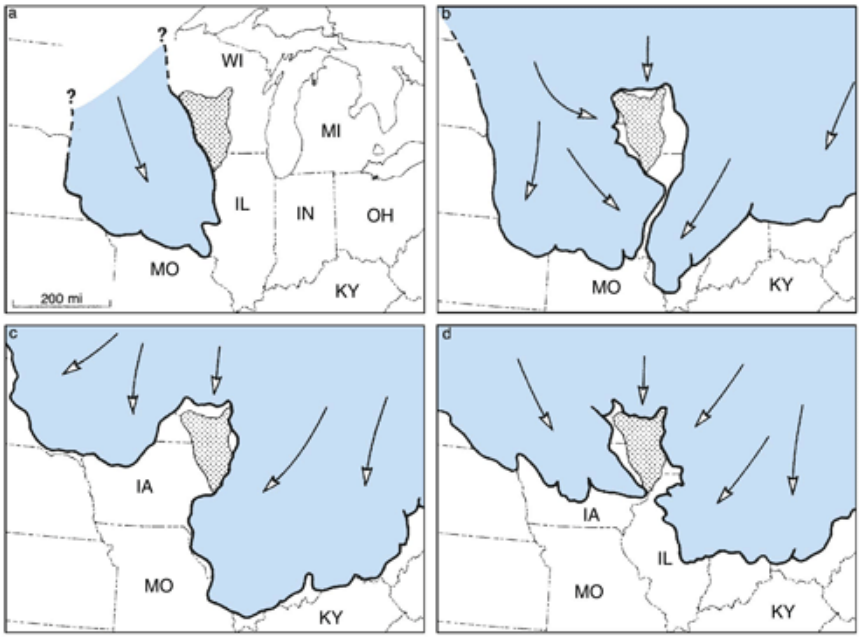

Figure 3.1: Glaciation periods in Illinois from left to right, (a) early Pre-Illinois glacial episode (1,000,000 years ago), (b) late Pre-Illinois glacial episode (600,000 years ago), (c) Illinois Glacial Episode (250,000 years ago), (d) late Wisconsin Glacial Episode (22,000 years ago) (Illinois State Geological Survey, 2014).

The advent of tile drainage in the Midwest during the 19th century altered the hydrology of the prairie making marginal land suitable for agricultural production. Tile drainage is the removal of excess water from land through subsurface pipes. The practice has been utilized globally for thousands of years in places where the surface gradient is limited and soils are poorly drained. Prior to tile drainage, prairie soils across the Midwest were swampland, not suitable for agriculture. The passage of the Federal Swampland Acts of 1849 and 1850, and the transfer of millions of hectares of land propelled the installation of tile drainage in this region (Skaggs & Schilfgaarde, 1999). It has been estimated that in the United States, of the 173 million ha of arable and permanent cropland, 47.5 million ha have been tile drained (International Commission on Irrigation and Drainage, 2011). The highest concentration of tile drainage can be seen in the Upper Midwestern United States as shown in Figure 3.2 (David et al., 2010). The expanse of tile drainage in this region is predominantly corn and

soybean row crops (Dinnes et al., 2002). It is estimated in Illinois, 4 million ha are tile drained, 90% of which are crop land (Kalita et al., 2006).

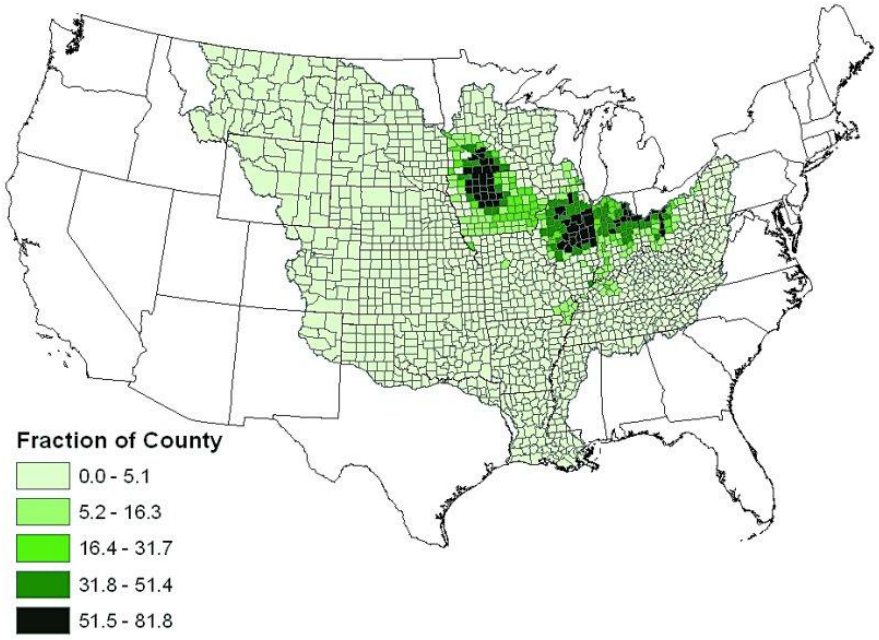

Figure 3.2: Concentration of tile drainage in the Mississippi River Basin, including Upper Midwest, commonly referred to as the corn belt (David et al., 2010).

3.1.2 Nutrients

Following drainage, the invention of fertilizers and a subsequent increase in fertilizer use drove large increases in crop productivity and yield. While nutrients are essential for plant life and growth, they are not always abundant in crop lands or plant available. The three primary nutrients (nitrogen, phosphorus and potassium) therefore are commonly found in fertilizers. Of the three major nutrients, plants require nitrogen in the largest amounts as nitrogen promotes rapid crop growth (Tucker, 1999). Corn and soybeans are among the top three fertilizer-utilizing crops in the United States (The Fertilizer Institute, 2014). Corn and soybeans require on average 19.3 to 25.7 $\mathrm{kg\,m^{-2}}$ and 12.9 to 19.3 $\mathrm{kg\,m^{-2}}$ of fertilizer nutrient respectively (1.5 to 2 lbs per bushel and 1 to 1.5 lbs per bushel of fertilizer nutrient respectively) (The Fertilizer Institute, 2014). In 2013, 116 million cubic meters (3.29 billion bushels) of soybeans and 490 million cubic meters (13.9 billion bushels) of corn were produced

in the U.S. (NASS, 2014). In terms of area, in 2013, 30.9 million hectares (76.5 million acres) of soybeans were planted in the U.S., 30.6 million hectares (75.7 million acres) of which were harvested (NASS, 2014). Correspondingly, in 2013, 38.6 million hectares (95.4 million acres) of corn were planted in the U.S., of which 35.4 million hectares (87.7 million acres) were harvested (NASS, 2014). Illinois represented a large portion of the total for 2013 with 3.8 million hectares (9.42 million acres) of soybeans harvested and 4.8 million hectares (11.8 million acres) of corn harvested (NASS, 2014).

The application of nitrogen on crop lands via fertilizers has allowed for the extensive agricultural productivity of corn and soybeans in the Midwestern United States. However, due to its negative charge and high solubility, nitrate that is not taken up by plants can leach to surface and subsurface water. This has been shown to be true in tile drained crop lands such as the Midwestern United States (Dinnes et al., 2002; Chun & Cooke, 2010). Therefore, despite the benefits of tile drainage in this region allowing for the highest productivities in the world, tile drains can act as conduit, promoting the rapid movement of suspended sediment and nutrients like nitrogen and phosphorus from fields to surface waters (Kalita et al., 2006).

3.2 Nonpoint Source Pollution of Surface Waters with Nutrients

Nonpoint source (NPS) pollution results when runoff carries pollutants from diffuse sources at unidentifiable locations into surface and subsurface waters. According to USEPA, NPS pollution is the leading source of surface water quality impairments in the United States (USEPA, 2012). The majority of NPS pollution is the result of agricultural discharges carrying suspended sediment and nutrients like nitrogen and phosphorus (USEPA, 2012). Notably, 57% of NPS pollution in lakes and 64% of NPS pollution to rivers is a result of agriculture with nutrients and sediment accounting for the bulk of contaminants (Carey, 1991). Data reported by the USEPA shows 94,182 miles of streams impaired as a result of agricultural discharges, and 38,632 miles of streams impaired as a result of nutrient loading (USEPA, 2009).

3.2.1 Environmental Impact of Nutrient Loading

The over-enrichment of water by nutrients leads to eutrophication. Eutrophication has been linked with algae blooms and hypoxic zones (David et al., 2010; Bianchi et al., 2010). Hypoxia is a leading water quality problem in the United States and the world. Hypoxia occurs when the oxygen concentration falls below the level needed to sustain life. In eutrophic waters, the addition of nutrients can lead to algae blooms which produce oxygen through photosynthesis in the presence of light. In eutrophic systems, an overabundance of algae blocks light, forcing algae to consume oxygen, rather than produce oxygen. When algae die, the bacteria used to decompose the plant matter further deplete water oxygen levels. The coast of the Gulf of Mexico as shown in Figure 3.3 is a prime example of a hypoxic zone that has resulted in environmental degradation and economic loss (Bianchi et al., 2010; Petrolia & Gowda, 2006). The hypoxic zone in the Gulf of Mexico is the largest affecting the United States and the second largest worldwide (NCCOS, 2013). The size of this zone is shown in Figure 3.4.

The intensively farmed and extensively tile drained Midwestern United States is acknowledged as the largest contributor of nutrient loads to the Gulf of Mexico (David et al., 2010; USEPA, 2009). Corn and soybean crops are the largest contributor of nitrogen to the Gulf of Mexico and the second largest contributor of phosphorus as shown in Figure 3.5 (Alexander et al., 2008).

The average size of the hypoxic zone in the Gulf of Mexico is 1.5 million metric tons as shown in Figure 3.6. Illinois is the largest supplier of nutrients to the Gulf of Mexico, estimated as contributing $1734.9\,\mathrm{kg\,km^{-2}\,yr^{-1}}$ total nitrogen and $117.4\,\mathrm{kg\,km^{-2}\,yr^{-1}}$ total phosphorus (Alexander et al., 2008). Considering the area of the state is $150{,}000\,\mathrm{km^2}$, the annual nitrate and phosphorus loads from Illinois to the Gulf is roughly 250,000 metric tons and 17,000 metric tons respectively. From a larger perspective, Illinois contributes between 10% and 17% of the nitrogen and phosphorus delivered to the Gulf of Mexico as shown in Figure 3.7 (Alexander et al., 2008).

The Mississippi River Gulf of Mexico Watershed Nutrient Task Force is aiming to reach a 45% reduction in the size of the hypoxic zone by 2015 as shown in Figure 3.4. David

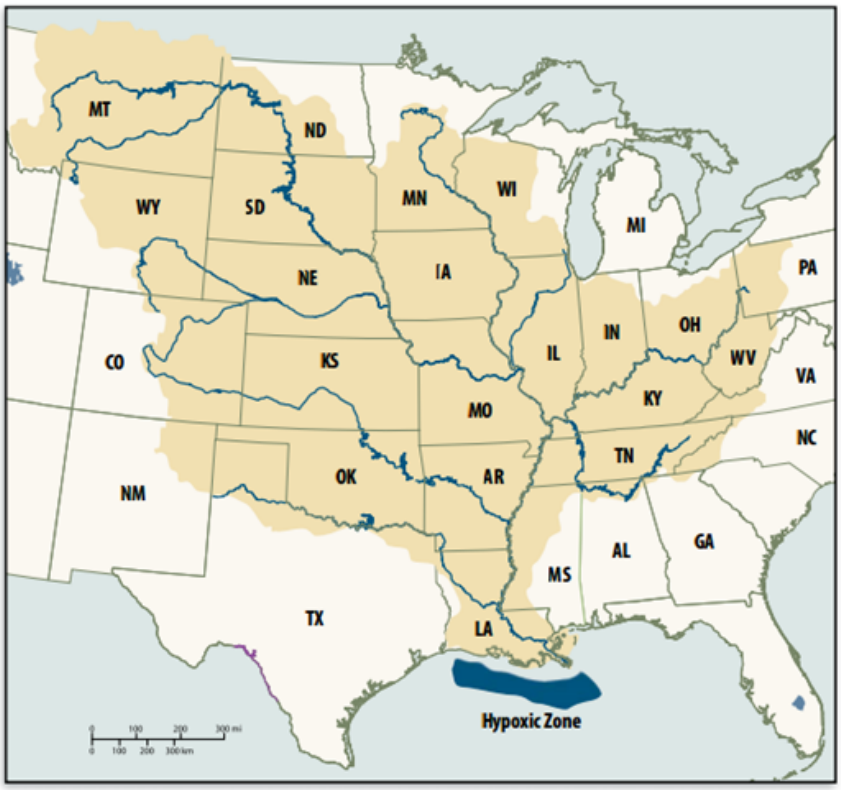

Figure 3.3: The Mississippi River Basin and the hypoxic zone in the Gulf of Mexico at its outlet (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2013).

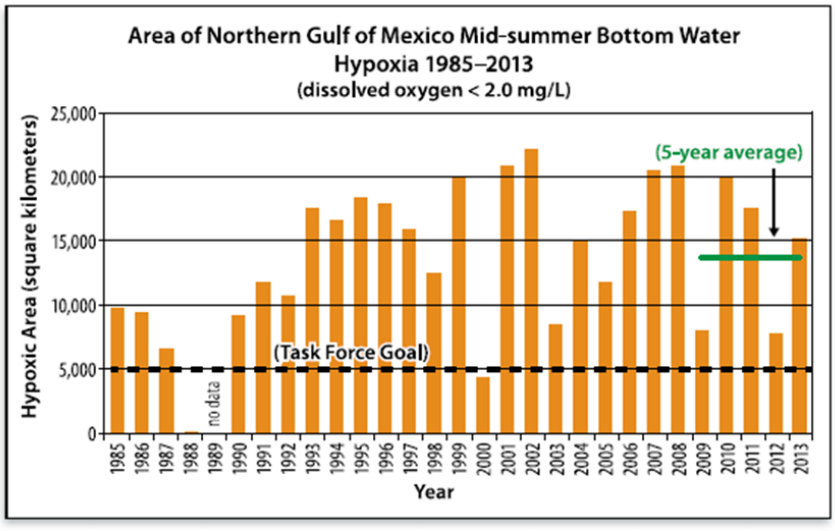

Figure 3.4: Size of the Gulf of Mexico hypoxic zone from 1985 to 2013 (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2013).

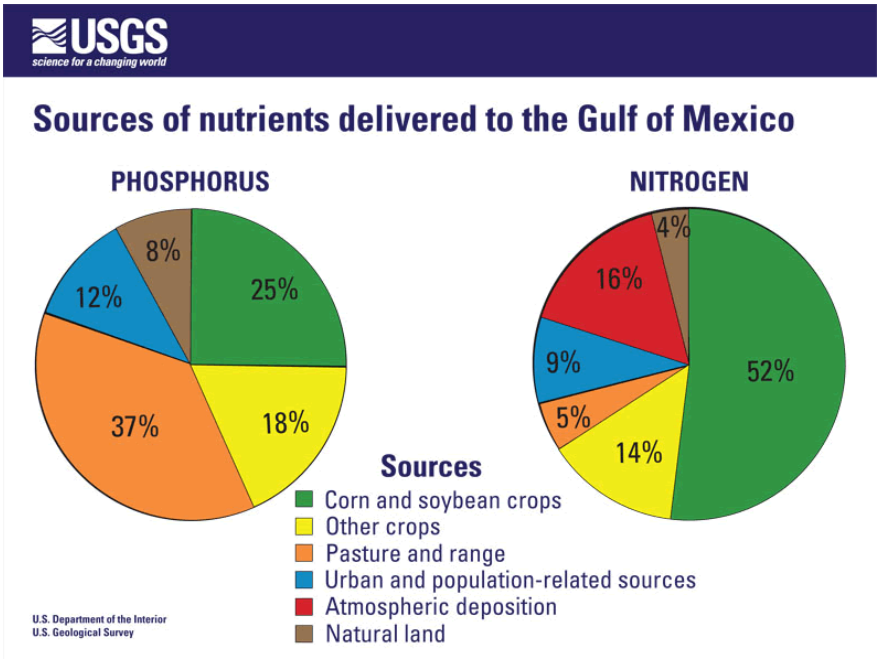

Figure 3.5: Percentages of nitrogen and phosphorus delivered to the Gulf of Mexico (Alexander et al., 2008).

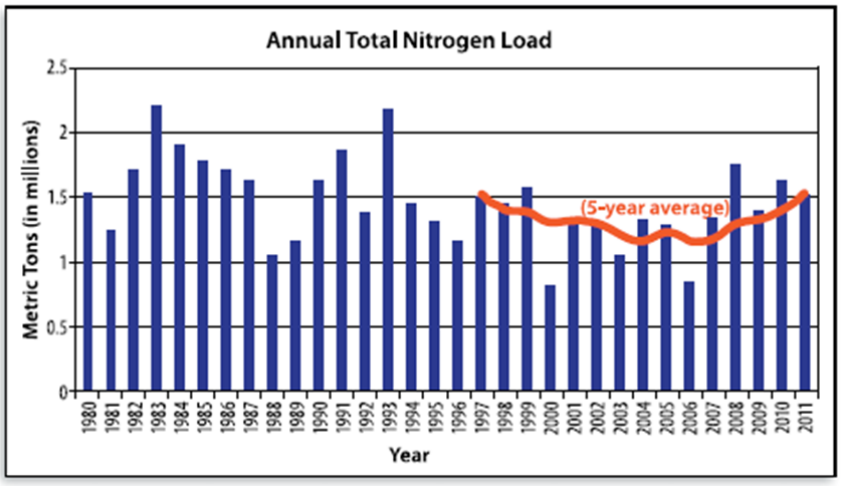

Figure 3.6: Annual Total N load to the Gulf of Mexico (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2013).

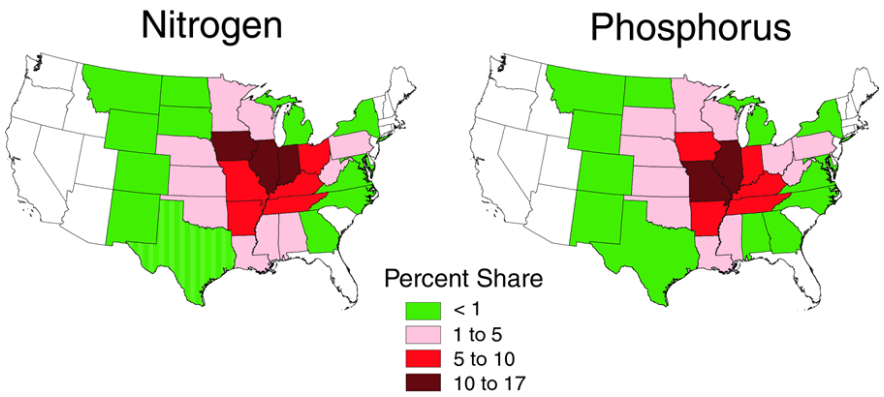

Figure 3.7: Estimated contributions to the Gulf by State (Alexander et al., 2008).

et al. (2013) point out that reaching this goal is a complicated issue. Nitrate losses have remained large even when management practices are implemented. Throughout the Upper Midwest, corn hectares have increased and a subsequent desire for higher yields driven by increase in price due to increased demand for corn ethanol production driven in large part by the United States Farm bill. More frequent, intense precipitation has increased nitrate loading. As David et al. (2013) conclude, this is therefore a complex issue that requires a lot of funding, research and cooperation between researcher and producer. Propelled by these environmental concerns and a desire to meet water quality standards, innovative management practices are continually being developed and implemented across Midwestern United States to treat drainage water.

3.3 Bioreactors for the Treatment of Tile Drainage

One practice that has emerged in this region is denitrification bioreactors or simply bioreactors. Bioreactors are excavated trenches filled with a carbon source such as woodchips through which nitrate laden drainage water is passed. Blowes et al. (1994) published the first study demonstrating that bioreactors filled with tree bark, woodchips or leaf compost could treat nitrate laden drainage effluent. Cooke et al. (2001) were the first to explore bioreactors in an agricultural setting for treatment of tile drainage in the Midwestern United States. Many research studies have found encouraging results using bioreactors to reduce nitrate loading (Cooke & Verma, 2012; Jaynes et al., 2008; Schipper et al., 2010b; Verma

et al., 2010; Woli et al., 2010). Bioreactors are a relatively new best management practice and there are still many questions regarding their nitrate removal efficiency, longevity, maintenance requirements and possible negative effects of their utilization.

3.3.1 Denitrification

Oxidation-reduction reactions or redox reactions play a central role in bioreactors. Bioreactors treat nitrate through denitrification, a reaction that reduces nitrate to atmospheric nitrogen. Microorganisms catalyze this reaction under anaerobic conditions when oxygen is depleted by utilizing nitrate as an alternative electron acceptor (Shah & Coulman, 1978). The bioreactor trenches are filled with a carbon source to facilitate this reaction. Various media are used as a carbon source to aid in denitrification but woodchips are the most widely used due to their low cost and high carbon to nitrogen ratio (Gibert et al., 2012). The reaction is represented by the following equation given by Snoeyink & Jenkins (1982).

$$2NO_3 + 10e + 12H^+ \rightarrow N_2 + 6H_2O \tag{3.1}$$

During this reaction, nitrate is reduce to nitrite, then nitric oxide, nitrous oxide and finally to dinitrogen or unreactive nitrogen gas (Knowles, 1982). Bioreactor use as a best management practice intends that full denitrification occur so nitrate is fully reduced to nitrogen gas.

3.3.2 Nitrate Removal Rates and Efficiency

Various studies have been conducted with bioreactors using different substrates and designs in order to determine their effectiveness in reducing nitrate loading to surface waters. Woodchips and other wood particle media in particular have shown the most sustainable and consistent nitrate removal rates. Current finding in the literature suggest removal rates average between 1 and 20 $\mathrm{g\,N\,m^{-3}\,d^{-1}}$ (Robertson et al., 2000; vanDriel et al., 2005; Warneke et al., 2011b) and efficiencies ranging from 10% to 100% (Blowes et al., 1994; Christianson & Helmers, 2011; Verma et al., 2010).

Blowes et al. (1994) were the first to research using bioreactors to treat agricultural drainage water. Two 200 L bioreactors using tree bark, wood chips and leaf compost were constructed to treat agricultural drainage water with nitrate concentrations of 3 to 6 $\mathrm{mg\,L^{-1}}$. Following an initial acclimation period of two weeks, they found almost complete removal of nitrate with effluent concentrations below 0.02 $\mathrm{mg\,L^{-1}}$. The pilot-scale experiment suggested allowing one day residence time in the bioreactor was sufficient to achieve denitrification of 5 to 10 $\mathrm{mg\,L^{-1}}$ of NO_3-N. This study catalyzed bioreactors for the treatment of redox-sensitive pollutants like nitrate in an agricultural environment.

Studies in other applications like Robertson et al. (2000) who studied woodchip bioreactors to treat groundwater further credited bioreactor use. They reported average nitrate removal rates of 10 $\mathrm{g\,N\,m^{-3}d^{-1}}$ during a long-term study using wood mulch, sawdust and leaf compost as carbon substrates. Woodchip bioreactors were observed having nitrate removal rates between 5 and 30 $\mathrm{mg\,N\,L^{-1}\,d^{-1}}$. Robertson et al. (2000) found that woodchip bioreactors could sustain nitrate treatment for a decade with little to no maintenance.

Cooke et al. (2001) were the first to explore bioreactors for tile effluent treatment in the Midwest. They evaluated bioreactor nitrate reduction performance in a laboratory using reactors filled with gravel and a mix of corncobs or woodchips. The results were used to design field scale systems after finding nitrate removal efficiency was correlated with increased retention time.

Following Cooke et al. (2001), bioreactor research expanded in Illinois and the Midwest. Woli et al. (2010) collected data for three years from two woodchip bioreactors in east-central Illinois receiving drainage effluent from a seed corn-soybean rotation farm and found an overall efficiency of 33% in reducing nitrate loading with periods as high as 100%. The efficiency varied greatly reported as fluctuating between 12% and 99.5%. The nitrate removal rate at this site was 6.4 $\mathrm{g\,N\,m^{-3}\,d^{-1}}$. Verma et al. (2010) also looked at the effectiveness of field scale bioreactors in Illinois. They showed annual load reductions as high as 98%, comparable to Woli et al. (2010). Christianson et al. (2013) found nitrate removal ranged from 7% to 100% mass reduction during a May-August sampling period for a bioreactor implemented nearby in Iowa or 0.38 to 1.06 g N removed per m^3 bioreactor per day. Bell (2013) found average load reductions of 63.1% for three experimental field-scale bioreactors

in Central Illinois, with average minimum and maximum load reductions of 20.1% and 97.5% respectively. Bell (2013) reported average nitrate removal rates of 11.6 g NO_3-N m^{-3} d^{-1}, with minimum and maximum removal rates of 5 and 30 g NO_3-N m^{-3} d^{-1}, respectively.

Robertson (2010) found similar removal rates during controlled laboratory tests on woodchip bioreactors. Woodchip media that had been in use for operation periods between two and seven years were evaluated. Robertson (2010) reported removal rates of 15.4 to 23.0 mg N L^{-1} d^{-1} during the first year of operation, 12.1 mg N L^{-1} d^{-1} after two years and 9.1 mg N L^{-1} d^{-1} after seven years of operation. These results suggest that bioreactors lose 50% of their reactivity during the first year of operation but then stable removal rates remain. Robertson (2010) points out bioreactors may be maintenance free for decades after installation. Comparable nitrate removal rates were found by van Driel et al. (2006) during a 26 month field study on a corn field and 20 month study on a golf course. They found nitrate removal rates between 2 and 3 g N m^{-2} d^{-1}, depending on temperature, in woodchip bioreactors. Comparable longevity estimates were found by van Driel et al. (2006). They found that carbon consumption from denitrification was less than 2% annually and concluded the woodchips could sustain denitrification for many years.

Rodriguez (2010) found effluent nitrate concentrations are dependent on retention time. Removal efficiencies were found to be 39%, 76% and 96% at 4.2, 6.3 and 8.0 hours of retention time, respectively. Based on the results of this experiment, Rodriguez (2010) concluded effluent nitrate concentrations below the EPA's MCL requirements of 10 mg L^{-1} NO_3-N are possible with longer retention times. Christianson et al. (2011) concurs with Rodriguez (2010) as they found denitrification is optimized at constant flow rates and nitrate removal efficiency increased with longer retention times during a study on the impact of flow rate and retention time on six pilot-scale woodchip bioreactors in New Zealand.

Warneke et al. (2011b) found that maize cob and woodchip substrates were the best carbon source for denitrifying bioreactors. Nitrate removal rates for maize cob and woodchips were 6.2 g N m^{-3} d^{-1} and 1.3 g N m^{-3} d^{-1}, respectively. Adverse effects like dissolved nitrous oxide release were found using maize cob while none were observed with woodchips, therefore Warneke et al. (2011b) concluded woodchips are the preferred substrate.

3.4 Conceivable Concerns with Bioreactor Use

Despite the benefits of bioreactors removing nitrate from tile effluent, utilizing bioreactors may result in potential unintended effects, alluding bioreactors could effectively trade one environmental problem of concern for another. Some conceivable concerns include the production of greenhouse gases such as nitrous oxide, methane and carbon dioxide, and hydrogen sulfide and methylmercury. Little research has been conducted on the significance of these concerns. Many questions and much speculation are therefore found in the literature regarding the negative effects bioreactors may have on the environment.

3.4.1 Nitrous Oxide

Under conditions like low pH, low temperature, high dissolved oxygen and low carbon to nitrogen ratio, incomplete denitrification can occur and nitrous oxide, a greenhouse gas, can be the end product rather than nitrogen gas (Seitzinger et al., 2006). The global warming potential of nitrous oxide is 310 times that of CO_2 (USEPA, 2013).

Greenan et al. (2009) evaluated this premise during a laboratory column study of woodchip bioreactors promoting denitrification under varying flow rates. They found that that complete denitrification generally occurred and nitrous oxide production from the columns ranged from 0.003% to 0.028% of the nitrogen denitrified.

Following this laboratory study, Moorman et al. (2010) reported on a woodchip bioreactor operating in the field for 9 years. Pore space gas samples were collected three times between April and May, 2000 and three times during April and May, 2001 for determination of N_2O. They also sampled tile water five times during March-May, 2001 to determine dissolved N_2O concentrations. They found that loses of N_2O due to denitrification in the bioreactor were comparable to those N_2O emissions from tile drainage without the bioreactor. Dissolved N_2O concentrations ranged from 2.6 to 73.2 N_2O-N L^{-1} during the sample period and cumulative N_2O export from the bioreactor averaged 15.1 g N ha^{-1}.

Warneke et al. (2011b) studied both surface emitted and dissolved greenhouse gases from a denitrifying woodchip bioreactor. They studied 12 denitrification beds in New Zealand

for one year. Woodchip, water and gas flux samples were collected every two months. Warneke et al. (2011b) reported an average surface emission of $78.58\,\mu\,\mathrm{g\,m^{-2}\,min^{-1}}$ N_2O-N. They concluded that woodchip bioreactors, although an effective tool for reducing nitrate in effluent, do produce greenhouse gases and suggested this concern needs to be investigated if bioreactors are to be commonly used. Warneke et al. (2011b) detected highest N_2O emissions during warmer months when NO_3 removal was highest.

However, Elgood et al. (2010) and Moorman et al. (2010) reported greater N_2O production in colder months due to slower reaction rates and higher inlet dissolved oxygen concentrations leading to incomplete denitrification.

Woli et al. (2010) collected nitrous oxide samples every two weeks from April to June 2009 from a bioreactor in east-central Illinois receiving effluent from a patterned drained, seed corn-soybean rotation farm. They found little nitrous oxide emissions (0 to $0.14\,\mathrm{mg\,m^{-1}\,h^{-1}}$) and concluded that nitrous oxide is not a problem of concern with bioreactors.

Healy et al. (2012) studied bioreactors in a laboratory setting and found greenhouse gas emissions were dominated by carbon dioxide and methane with little nitrous oxide release regardless of the carbon substrate. They found nitrous oxide emissions of 0.11 to $2.15\,\mathrm{g}$ N_2O-$\mathrm{N\,m^{-1}\,d^{-1}}$ during steady state testing of woodchips. These results were higher than others reported in the literature such as Woli et al. (2010) who found emissions ten times smaller.

Christianson et al. (2013) measured nitrous oxide fluxes from six pilot-scale bioreactors under varying flow rates. They found small fluxes from all treatments ($<1.0\,\mathrm{mg}$ N_2O-$\mathrm{N\,m^{-2}\,hr^{-1}}$) though average fluxes from their soil treatment surface were lower on average than from the woodchip bioreactors (0.05 and $0.4\,\mathrm{mg}$ N_2O-$\mathrm{N\,m^{-2}\,hr^{-1}}$, respectively) suggesting covering bioreactors may reduce N_2O fluxes. The measured N_2O emissions and estimated N_2O lost in effluent represented less than 0.4% of the nitrate removed. These results are much higher than what Greenan et al. (2009) found but still comparable with other published literature as the loss still represents less than one percent. Christianson et al. (2013) concluded that although bioreactors will likely emit N_2O, on-site, these fluxes were predicted lower than those when untreated nitrate was denitrified further downstream.

The differences in nitrous oxide production in bioreactors found in the literature are relatively insignificant considering fertilized corn and soybean plots have been reported to emit

20 to 200 g N_2O-N ha^{-1} day^{-1} (McSwiney & Robertson, 2005). Annual, unfertilized corn reportedly emits 0.3 kg N ha^{-1} yr^{-1} while fertilized corn has been reported to emit on average 24 kg N ha^{-1} yr^{-1} (Dambreville et al., 2008) and 2.2 to 7.7 kg N ha^{-1} yr^{-1} (Smith et al., 2013).

3.4.2 Hydrogen Sulfide and Methylmercury

In general, bacteria can use alternative electron acceptors beyond nitrate as anaerobic conditions become more reducing. Microbes will use electron acceptors according to the order of redox potential with oxygen being the most efficient electron acceptor and carbon dioxide being the least efficient with the lowest redox potential (Snoeyink & Jenkins, 1982). These reactions in order of highest to lowest redox potential are aerobic respiration, denitrification, nitrate reduction, fermentation, sulfate reduction, and lastly methane fermentation (Snoeyink & Jenkins, 1982). Therefore, once the nitrate is removed, the production of hydrogen sulfide and methane may begin. Christianson & Helmers (2011) point out if water remains in reactors for too long, nitrate will be entirely removed and other processes will begin as bacteria seek other sources of electron acceptors.

Sulfate reduction is the transformation of sulfate to hydrogen sulfide gas. Sulfate reducing bacteria use organic compounds as electron acceptors and produce hydrogen sulfide gas, a poisonous, corrosive gas. Its presence can be detected by a rotten egg smell. Robertson (2010) and Elgood et al. (2010) both reported declines of sulfate concentrations and the odor of hydrogen sulfide at the outlet of bioreactors when nitrate concentrations were <1 mg L^{-1}.

Sulfate reducing bacteria are also linked to converting inorganic mercury, whether naturally occurring or deposited from anthropomorphic processes,to methylmercury, a neurotoxin that accumulates in fish that can impair fetal development and affect the central nervous system. Due to its toxicity, pregnant women and children are advised by the Food and Drug Administration and the Environmental Protection Agency to avoid consuming species of fish known to have high concentrations of methylmercury (0.3 to 0.49 ppm). Shih et al. (2011) showed that bioreactors can produce methylmercury when sulfate reducing conditions develop.

Bell (2013) discovered methylation of mercury during the first month of bioreactor operation in Central IL and concluded this was a result of low, nearly zero nitrate-N concentrations. Bell (2013) found no methylation when influent nitrate concentrations were above $10\,\mathrm{mg\,L^{-1}}$. Christianson & Helmers (2011) suggest minimizing hydrogen sulfide and methylmercury concerns by monitoring bioreactors during low flow periods for the rotten egg smell of hydrogen sulfide and lowering the outflow control structure to allow higher flows through the bioreactor.

3.4.3 Methane

Further reducing conditions, following sulfate reduction allow for the use of carbon dioxide as an electron acceptor and for methane fermentation to occur. Microbes called methanogens may begin to use CO_2 as an electron acceptor and produce methane, another greenhouse gas of concern (Snoeyink & Jenkins, 1982). The global warming potential of methane is 21 times that of CO_2 (USEPA, 2013). The reaction that describes this process is provided below by (Snoeyink & Jenkins, 1982).

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \tag{3.2}$$

Methanogenesis has been reported in bioreactors throughout the literature. Elgood et al. (2010) found that CH_4 production in a stream-bed bioreactor in Ontario, Canada, during summer months was higher than some rivers and reservoirs but lower than wastewater treatment facilities. Elgood et al. (2010) calculated CH_4 emissions of $297\,\mathrm{mg\,C\,m^{-1}\,d^{-1}}$ respectively from a stream bed denitrifying bioreactor containing woodchips by taking the difference between inflow and effluent concentrations. Comparable CH_4 emissions for woodchip bioreactors were found in a laboratory experiment conducted by Healy et al. (2012). Warneke et al. (2011a) reported average CH_4 surface emissions of $0.238\,\mu\mathrm{g\,m^{-1}\,min^{-1}}$. They reported that dissolved CH_4 concentrations showed no trends along the length of the bed.

Methane emission rates from unfertilized and fertilized corn fields range from 0.74 to $5.61\,\mathrm{g\,C\,kg^{-1}\,soil\,h^{-1}}$ (Fernandez-Luqueo et al., 2010). Since methane is produced under low redox potential conditions, higher emissions will be found in inundated sources like rice

paddies, wetlands, landfills and animal waste treated land (Fernandez-Luqueo et al., 2010). Therefore based on the literature, emissions from bioreactors may be comparable to fertilized corn and soybean plots during low flow periods and higher during periods of inundation when redox potential becomes low but neither will in general be large sources of methane.

3.4.4 Carbon Dioxide

Carbon dioxide is an end product of denitrification. As carbon is consumed by bacteria during respiration, some of the carbon is given off as carbon dioxide, another greenhouse gas of concern.

Woli et al. (2010) measured CO_2 flux from one bioreactor beds in east-central Illinois receiving effluent from a seed corn-soybean rotation farm three times during June 2009 in order to assess the decomposition rate of the wood chips in the bioreactor. They found fluxes ranged from 4.4 to as high as 7.5 $\mathrm{g\,C\,m^{-2}\,h^{-1}}$. Their results indicated that decomposition of the wood was occurring, causing the anaerobic conditions and reduction of nitrate-N since the transformation of nitrate to nitrogen gas is associated with the release of carbon dioxide.

Warneke et al. (2011a) reported an average bioreactor bed surface emission rate of 12.6 $\mathrm{mg\,m^{-2}\,min^{-1}}$ CO_2. Using comparable units to Woli et al. (2010), these emission rates are much smaller than those reported by Woli et al. (2010) averaging 0.756 $\mathrm{g\,C\,m^{-2}\,hr^{-1}}$.

The lifetime of a bioreactor can be estimated from surface CO_2 emission rates. Warneke et al. (2011a) calculated longevity based on CO_2 surface emissions rates and release of dissolved carbon and found denitrification could be supported for 39 years. Prior to Warneke et al. (2011a), Robertson et al. (2000) had reported that woodchip bioreactors could support denitrification for a decade or more without replenishing the carbon source. Other studies report similar ranges like Schipper et al. (2010b) who reported bioreactors could remove nitrate-N for up to 15 years without maintenance.

3.4.5 Hydraulic Conductivity, Biofilms and Periods of Inundation

Other conceivable concerns include biofilm production in bioreactors during periods of inundation. Chun (2007) documented biofilms at bioreactor sites. These bacteria may interrupt hydraulics in control structures and drainage tiles. Chun (2007) concluded effective hydraulic conductivity decreased during the experiment period because of biofilm formation. These results agreed with Taylor et al. (1990) who suggested biofilm formation leads to reduced hydraulic conductivity during a study of porous medium column bioreactors. Taylor et al. (1990) suggested biofilm forms during low flow periods and is washed away during high flow events. Flow and transport parameters are helpful in understanding bioreactor performance. During a laboratory experiment, Chun & Cooke (2010) estimated the effective porosity of woodchip bioreactors to be 0.79 and an average hydraulic conductivity of woodchip bioreactors to be $3.9\,\mathrm{cm\,sec^{-1}}$. Simiarly, Christianson et al. (2010) reported hydraulic conductivity rates of woodchip bioreactors ranged between 7.33 and $11.11\,\mathrm{cm\,s^{-1}}$. They found porosity varied from 66% to 78%. van Driel et al. (2006) estimated effective hydraulic conductivity of wood-based bioreactors for a lateral flow reactor were between 0.7 and $11.2\,\mathrm{cm\,s^{-1}}$. Little has been documented on bioreactor performance under flooded conditions in general.

3.5 Modeling Bioreactor Flow and Transport Parameters and Performance

A Visual Basic routine was developed for the Natural Resources and Conservation Services (NCRS) as part of a Conservation Innovation grant titled "The Development of Performance Curves for Bioreactors in Illinois". Developing the routine was led by Richard Cooke. The routine is available on the Illinois Drainage Guide website found at http://www.wq.uiuc.edu/dg/. The routine allows users to analyze bioreactor performance and cost as well as transport parameters. The routine is the only program that allows for these analyses in a user friendly interface. One particular model in the routine, developed by Cooke & Bell (2014) can be used for sizing bioreactor systems. The interactive routine allows users to calculate flow rate and residence time for a bioreactor for a specificed return period given historic tile flow

data and user provided stop log height settings. The current routine is very helpful for someone considering installing a new bioreactor. The routine could be improved so users could enter data from an existing bioreactor, assess its performance and potentially improve performance. If such an addition was implemented into the routine, the existing data could be compared to the model output in order to validate the model.

Chapter 4

Methodology

4.1 Site Description

Two bioreactors, BR1 and BR2 were installed in the Embarrass River Watershed in Central Illinois for this study. BR1, a $6\,\mathrm{x}\,15\,\mathrm{x}\,1.3\,\mathrm{m}^3$ woodchip bioreactor was constructed in March 2012 at the outlet of a 30.5 cm diameter tile draining a 20 ha field in rotation of seed corn/corn/soybean. Corn was planted in 2012 and 2013. The field is near the intersection of County Road 1500 E and County Road 300 N in Champaign County, Illinois as shown in Figure 4.1. The primary soil types are Drummer silty clay loam, Clare silt loam and Brenton silt loam. A nearby 20 ha field in rotation of corn and soybean was selected as the second study site and in December 2012, BR2, a $6\,\mathrm{x}\,15\,\mathrm{x}\,1.3\,\mathrm{m}^3$ woodchip bioreactor was installed at the outlet of a 25.4 cm tile. The study site is located near the intersection of County Road 1550 E and County Road 1550 N in Douglas County, Illinois as shown in Figure 4.2. The primary soil types at this field are Drummer silty clay loam, Sawmill silty clay loam, Flanagan silt loam, Russell silt loam and Xenia silt loam. Corn and soybean were both planted at this site in 2013.

Figure 4.1: BR1 site location

Figure 4.2: BR2 site location

4.2 Tile Flow

Determination of drainage flow rates was essential to this study as flow rates were necessary to estimate pollutant loads through the bioreactors. Tile flow through each bioreactor was monitored continuously during the study period by using AgriDrain water level control structures equipped with v-notch weirs, pressure transducers and dataloggers. AgriDrain water level control structures diverted flow from the field through the bioreactors and were used to control flow rates. Boards could be added to the water level control structure to adjust hydraulic head. Dataloggers attached to pressure transducers at the inlets and outlets of the bioreactors were used to record inlet and outlet depth at 30 minute intervals for the entire study period. Depth of flow was measured manually during sampling times using a meter stick and recorded in centimeters of flow depth above or below the crest of the v-notch weir at the sampling time rounded to the nearest 30 minute interval. A calibration equation was created that related depth of flow to the data logger readings and was used to find the depth of flow for times when a physical flow measurement was absent but a data logger reading was available. Flow rates were then calculated using weir equations developed by Chun & Cooke (2010) for crest flow and for v-notch flow. The measured data were linearly interpolated to obtain daily values during the study period.

4.3 Water Sampling

Water samples were collected biweekly or more frequently during storm events from the inlets and outlets of the bioreactors when the tiles were flowing. Samples were collected in 500 mL NALGENE bottles. The bottles and bottle caps were rinsed with sample water at least once before samples were collected. The samples were kept in a cooler for transport from the field to the lab and then in a refrigerator kept at 4 °C until analysis.

4.4 Water Chemistry Analysis

Water samples were taken to the Biogeochemistry Laboratory at the University of Illinois for the following species: choride, sulfate, nitrate-N, ammonium-N, Total Kieldahl-N (TKN), dissolved organic carbon (DOC), dissolved reactive phosphorus (DRP) and total phosphorus (TP). Water samples were filtered through 0.45 micrometer membrane filters prior to analysis to remove any debris. Samples were analyzed for nitrate-N concentrations using ion chromatography-mass spectrometry using EPA Method 353.1, a colorimetric automated hydrazine reduction method. The measured concentrations were linearly interpolated to obtain daily concentrations during the study period so that nitrate-N loads could be calculated for the entire study period.

4.5 Nitrate Analysis

Nitrate loads were calculated by multiplying flow by nitrate-N concentration. Percent load reduction was calculated as the difference between influent and effluent NO_3-N loads divided by influent. Removal rate was calculated as the difference in concentration between influent and effluent NO_3-N multiplied by flow rate and divided by flow volume.

4.6 Gas Sampling

N_2O and CH_4 gas fluxes were measure by static chambers following the USDA-ARS GRACEnet chamber-based trace gas flux measurement protocol. The protocol uses methodology which is sensitive, unbiased, has low associated variance, and allows accurate interpolation over time and space.

Measuring N_2O and CH_4 fluxes requires static chambers made of a permanent anchor and chamber cap. Both the anchors and caps were fabricated by the Mark David water quality lab at the University of Illinois. Three PVC flux chamber anchors were permanently installed at each bioreactor one week prior to the first flux measurements. The chambers were labeled as A, B, and C with chamber A located farthest from the bioreactor inlet flow. Chamber

caps were brought to each bioreactor during sampling times. The total area of each chamber was 0.0310 m^2. Flux chamber caps included a sampling port with butyl rubber septa for gas extraction.

Gas samples were taken at regular intervals as resources allowed. Samples were taken at least monthly for one year and more frequently during assumed high flux months. BR1 was sampled 21 times from 7 February 2013 to 18 December 2013. BR2 was sampled 15 times from 22 May 2013 to 18 December 2013. Samples were collected mid-morning when possible to minimize biases associated with diurnal variations of gas fluxes.

Sampling was done by inserting a syringe into the chamber septa and removing a 15ml sample of chamber headspace every 10 minutes for 30 minutes, beginning at time zero and transferring the sample into an evacuated glass vial sealed with a butyl rubber septum. The syringe was flushed with air between each sample. The samples were stored for later analysis by gas chromatography.

CO_2 fluxes were measured using a LI-8100 Automated Soil CO_2 Flux System. The LI-8100 Analyzer Control Unit was connected to the three flux chamber anchors at each bioreactor. The height of each anchor above the bioreactor bed was measured and recorded in the LI-8100 software application before the LI-8100 was used to sample.

In addition to obtaining gas samples, a thermometer was used to measure the bioreactor bed temperature each sampling day. The temperature was recorded at each sampling ring three times per sampling day to obtain an average bioreactor bed temperature. Average, maximum and minimum air temperatures were also recorded for each sampling day.

4.7 Gas Analysis

N_2O and CH_4 gas samples were analyzed by gas chromatography (GC). The USDA-ARS GRACEnet chamber-based trace gas flux measurement protocol recommends samples are run as soon as possible after collection. For this reason, samples were run within one week of the sampling date. Standards were prepared for each GC sampling run. Standard curves were prepared by plotting the peak heights of the processed standards against the known concentrations. The curves were used to convert the GC output of the samples into units of

ppm by comparing processed sample peak heights with the standard curve. Carbon dioxide equivalent (CDE) which describe for a given amount of greenhouse gas, the amount of carbon dioxide that would have the same GWP (global warming potential) were calculated by multiplying the mass of nitrous oxide gases and methane gases by their respective GWP.

4.8 Hydraulic Conductivity

Maintenance of adequate hydraulic conductivity can affect the longevity of bioreactors (Schipper et al., 2010a). Hydraulic conductivity of the woodchips was calculated on a daily basis using Darcy's Law:

$$Q = Ak\frac{dH}{dL} \tag{4.1}$$

where Q is the volumetric flow rate, A is the flow area perpendicular to L, k is the hydraulic conductivity, L is the flow path length, H is the hydraulic head, and $\frac{dH}{dL}$ denotes the change in H over the path L.

4.9 Hydraulic Retention Time

Hydraulic Retention Time (HRT) can affect bioreactor performance. Longer contact time has been shown to yield a higher percent nitrate load reduction (Schipper et al., 2010a). HRT was calculated on a daily basis by dividing the total water volume (volume of bioreactor multiplied by porosity) by influent flow rate. Porosity was assumed to be 0.7 based on studies reported by Chun & Cooke (2010) and van Driel et al. (2006).

4.10 Modeling

A bioreactor performance model developed in Visual Basic by Cooke & Bell (2014) can be used for sizing bioreactor systems. The routine is available on the Illinois Drainage Guide website. The interactive routine allows users to calculate flow rate and residence time for

a bioreactor given historic tile flow data and user provided stop log height settings. This performance model was validated by comparing existing flow data to the flow generated by the model. The performance model was then improved by adding a routine that would allow users to calculate hydraulic conductivity from measured flow data. The routine was altered so the user could read in flow data and upstream and downstream hydraulic head. The routine was programed to read the data into an array and calculate hydraulic conductivity for each time step. The values were averaged for the entire data set. The model was then used to optimize the stop log height settings for BR1 to increase annual nitrate-N load reduction. A routine was written that would reduce bypass flow by changing the stop log height settings while holding residence time within a reasonable range (two to eight hours) thereby allowing the greatest percentage of tile water to be treated and the highest annual nitrate-N load reduction. Bioreactor performance depends on this balance.

Chapter 5

Results

5.1 Nitrate Removal

Following a drought in 2012, the spring of 2013 received unusually high amounts of precipitation, shown in Figure 5.1. The statewide average precipitation for 2013 in Illinois was 111.2 cm (43.77 in), 9.1 cm (3.58 in) above the 1981-2010 average (Illinois State Climatologist, 2014). The precipitation for the first six months of 2013 totaled 73.6 cm (28.96 in) and was 23.2 cm (9.13 in) above average and the wettest January-June on record (Illinois State Climatologist, 2014). As a result, tiles at both BR1 and BR2 were flowing continuously. The precipitation for the last six months of 2013 (July to December) totaled 37.6 cm (14.81 in) and was 14.1 cm (5.56 in) below average and was recorded as the 19th driest July-December on record (Illinois State Climatologist, 2014). As a result, tiles at both BR1 and BR2 stopped flowing in early July and remained dry for the rest of the year.

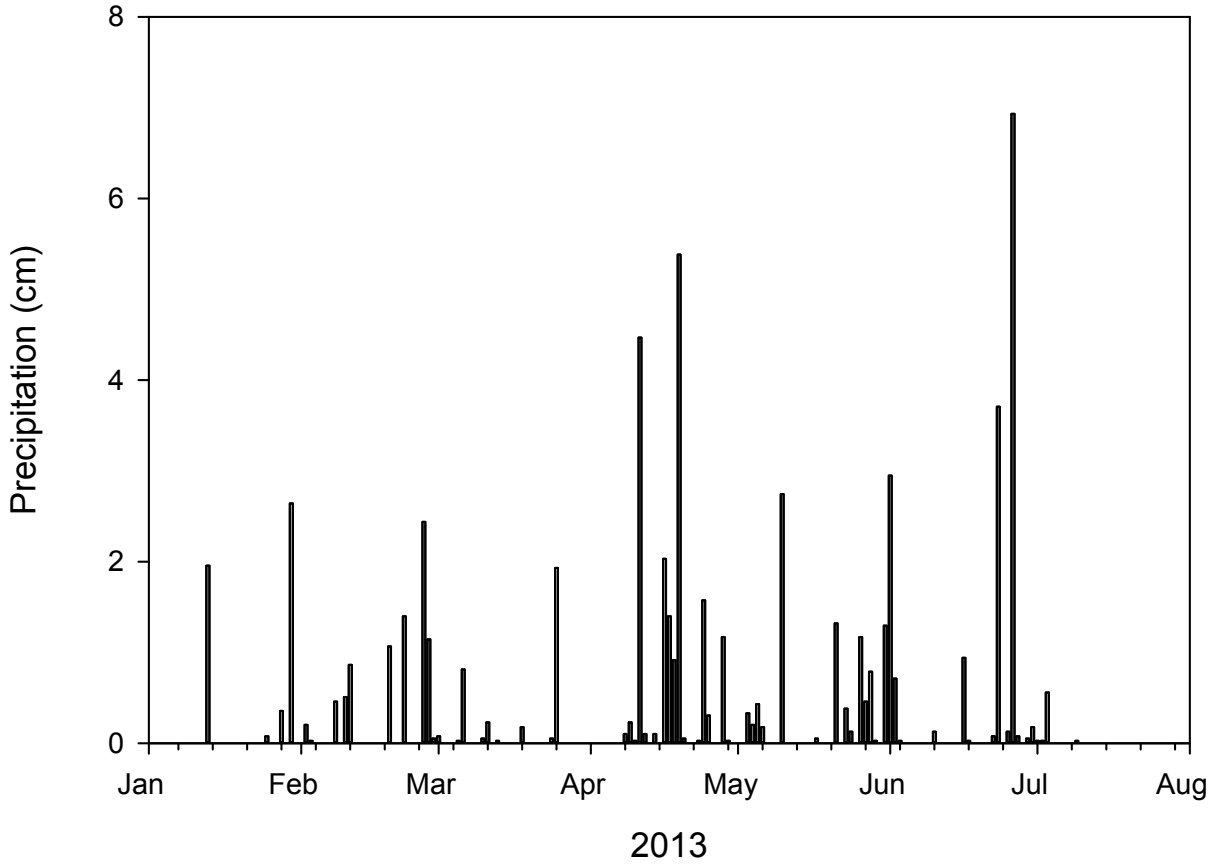

Figure 5.1: Precipitation at BR1 and BR2 during 2013 when drainage tiles were flowing

Although denitrification was not directly measured, conventional heterotrophic denitrification was hypothesized to be the dominant mechanism of nitrate removal rather than immobilisation into organic matter or dissimilatory nitrate reduction to ammonium or Anammox. Mean effluent concentrations of ammonium support this hypothesis as concentrations remained low throughout the study period. Effluent ammonium concentrations averaged 0.1 and $0.1\,\mathrm{mg\,NH_4\text{-}N\,L^{-1}}$ for BR1 and BR2 respectively. At times, the effluent ammonium concentration was higher than the influent ammonium concentration as shown in Figure 5.2 and Figure 5.3. The difference was found to be significant for BR1 but not for BR2.

Due to large amounts of residual nitrate on fields following a drought, nitrate loads into BR1 and BR2 were high in 2013. The nitrate load into BR1 was 2126 kg. Nitrate concentrations into BR1 were also high, on average 30 to $35\,\mathrm{mg\,L^{-1}}$ as shown in Figure 5.4. BR1

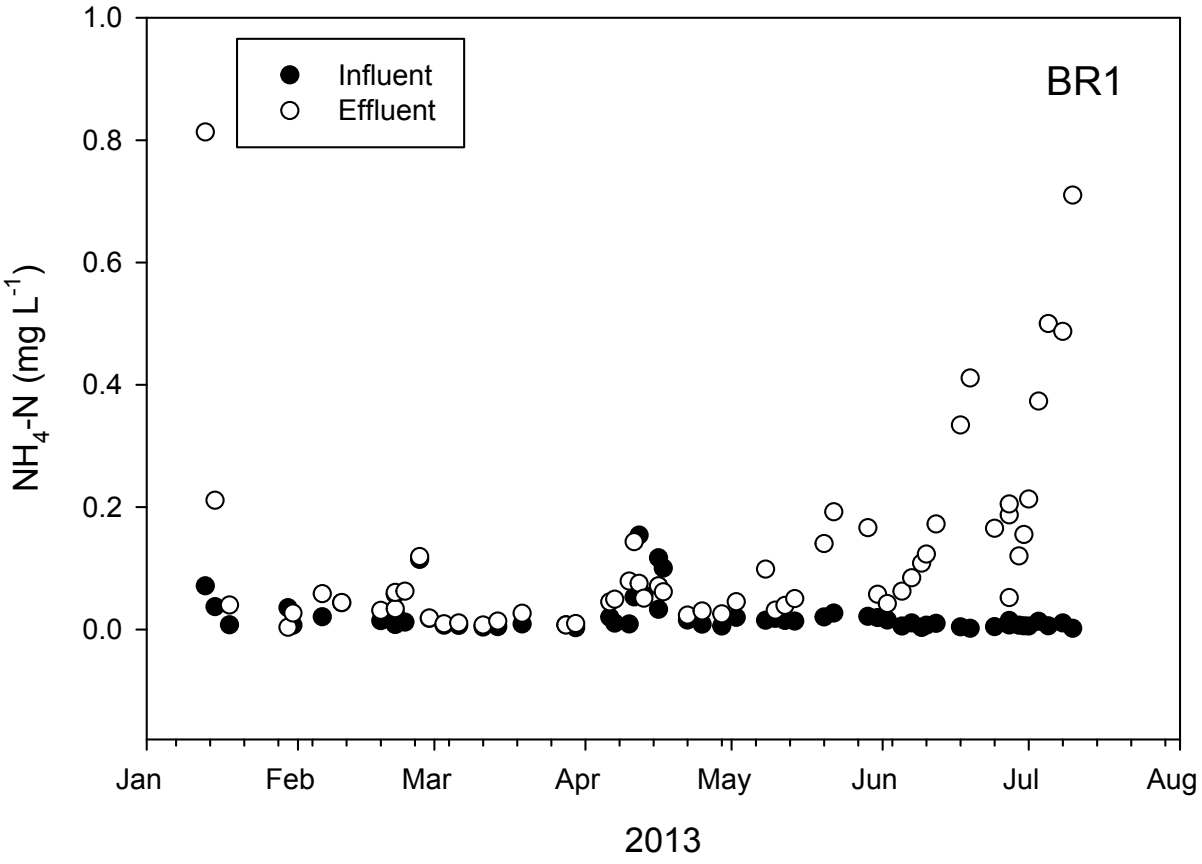

Figure 5.2: Influent and effluent ammonium concentrations during the study period at BR1

only removed 13% of the total tile nitrate meaning 87% of the nitrate load was bypassed. 47% of the flow bypassed and 8% is thought to be leaching from the bioreactor. Given that only 45% of the flow was treated, the nitrate removal rate for 117 m^3 of bioreactor was still found to be high, 13 g NO_3-N m^{-3} day^{-1}. Current finding in the literature suggest removal rates average between 1 and 20 g N m^{-3} d^{-1} (Robertson et al., 2000; vanDriel et al., 2005; Warneke et al., 2011b). Woli et al. (2010) reported an average removal rate at a bioreactor in east-central Illinois of 6.4 g N m^{-3} d^{-1}. Bell (2013) reported average nitrate removal rates of 11.6 g NO_3-N m^{-3} d^{-1}, with minimum and maximum removal rates of 5 and 30 g NO_3-N m^{-3} d^{-1}, respectively.

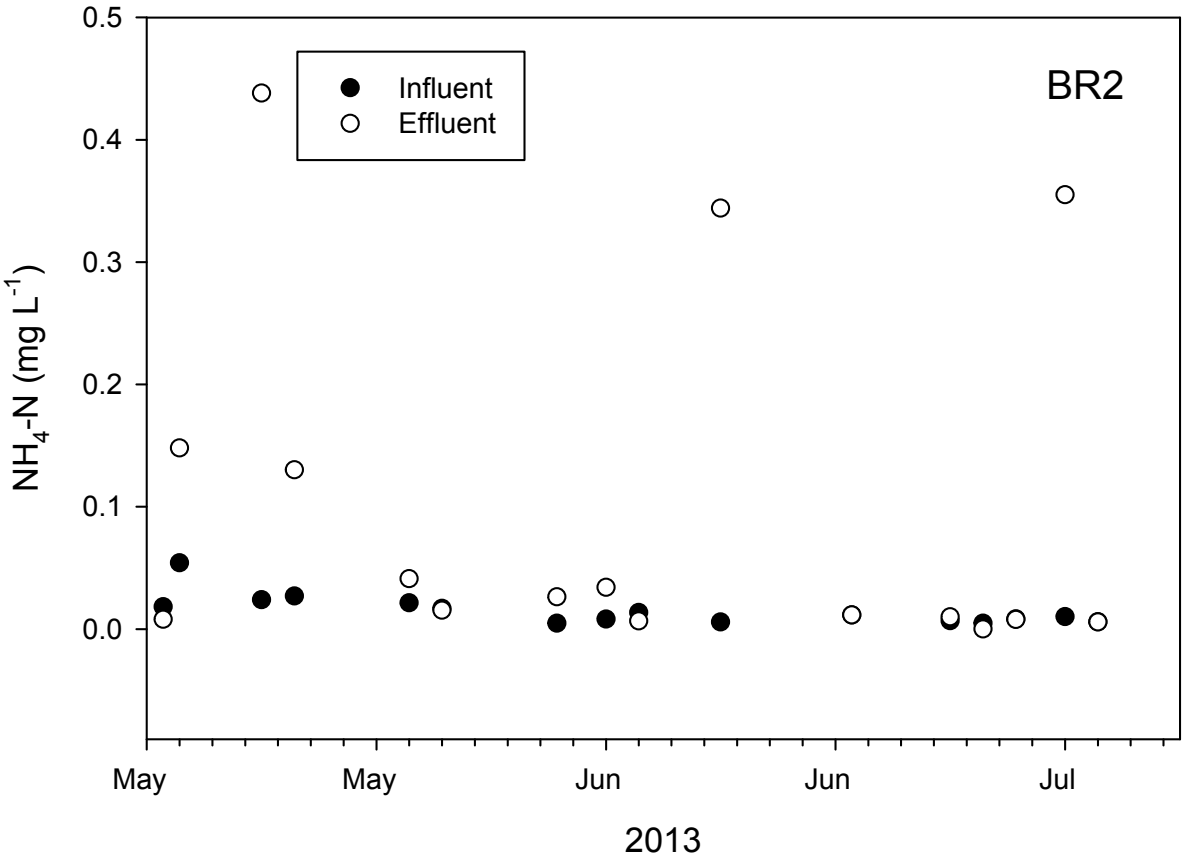

Figure 5.3: Influent and effluent ammonium concentrations during the study period at BR2

Percent load reduction was higher on average during warmer months when influent temperatures were warmer. BR1 had an overall efficiency of 18.5% in reducing nitrate loading. The maximum percent load reduction at BR1 was 69.8%, observed in June. The minimum percent load reduction at BR1 was 2.1% as shown in Figure 5.5. These results are similar to those found in the literature. Woli et al. (2010) collected data from two woodchip bioreactors in east-central Illinois receiving drainage effluent from a seed corn-soybean rotation farm and found an overall efficiency of 33% in reducing nitrate loading with periods as high as 100%. The efficiency varied greatly throughout the year. Verma et al. (2010) showed annual load reductions as high as 98%. Christianson et al. (2013) found nitrate removal ranged from 7% to 100% mass reduction during a May-August sampling period for a bioreactor in nearby Iowa. Bell (2013) found average load reductions of 63.1% for three experimental field-scale bioreactors in Central Illinois, with average minimum and maximum load reductions of 20.1% and 97.5% respectively.

Large and small nitrate removal rates were observed regardless of influent nitrate concentration as shown in Figure 5.6. Large and small nitrate removal rates were observed at both long and short hydraulic retention times as shown in Figure 5.7. It was anticipated that nitrate removal rates would be higher with increasing retention times although this trend was not observed as being significant. Removal rates were consistently in a range of 0 to $20\,\mathrm{g\,NO_3\text{-}N\,m^{-3}\,day^{-1}}$ when retention times were between two and ten hours. When a least squares regression analyses was applied to BR1 for the independent variable hydraulic retention time, a linear model only explained 44% of the variance in the data. Rodriguez (2010) found effluent nitrate concentrations are dependent on retention time. Removal efficiencies were found to be of 39%, 76% and 96% at 4.2, 6.3 and 8.0 hours of retention time, respectively. Based on the results of this experiment, Rodriguez (2010) concluded effluent nitrate concentrations below the EPA's MCL requirements of $10\,\mathrm{mg\,L^{-1}\,NO_3\text{-}N}$ are possible with longer retention times. Christianson et al. (2011) concurs with Rodriguez (2010) as they found denitrification is optimized at constant flow rates and nitrate removal efficiency increased with longer retention times during a study on the impact of flow rate and retention time on six pilot-scale woodchip bioreactors in New Zealand.

At BR1, the highest removal rates were observed in June at BR1 during warm temperatures and long retention times. However, no significant trend in retention time and removal rate or percent load reduction was found.

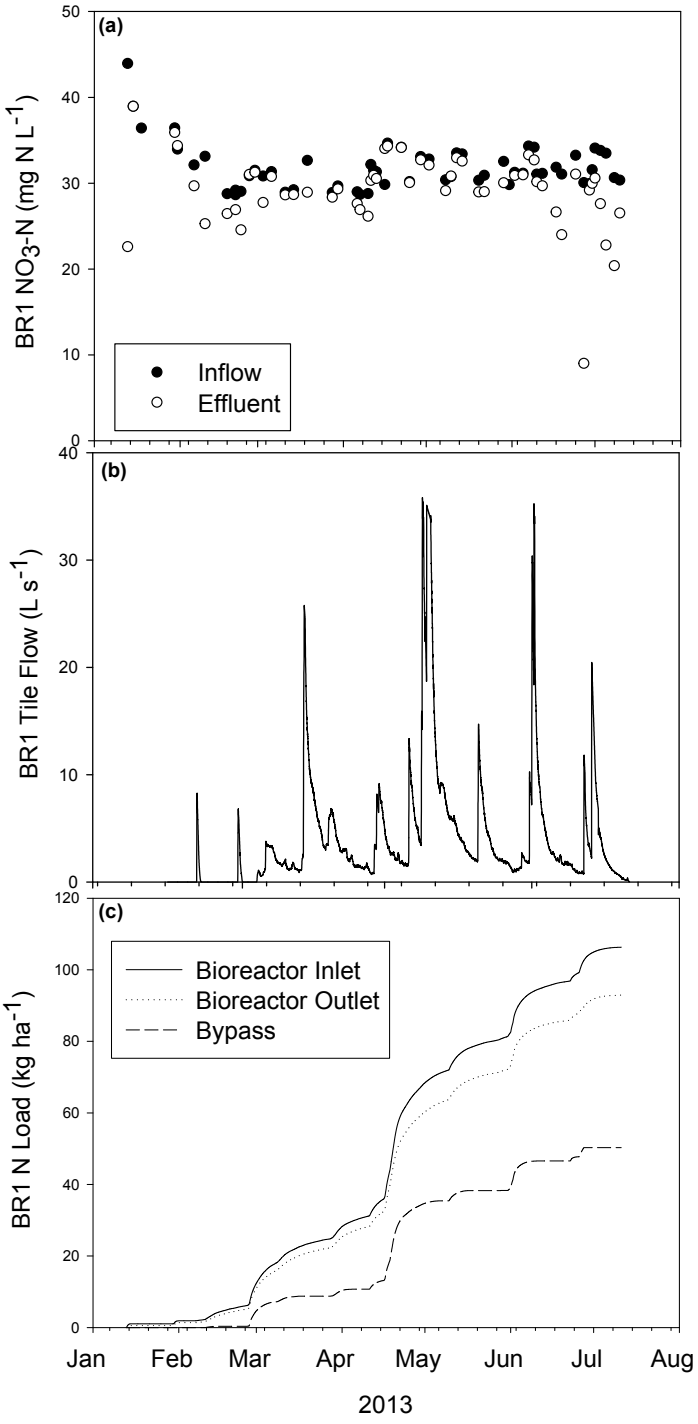

Figure 5.4: BR1 (a) Inlet and Outlet Concentrations, (b) Tile Flow and (c) Load

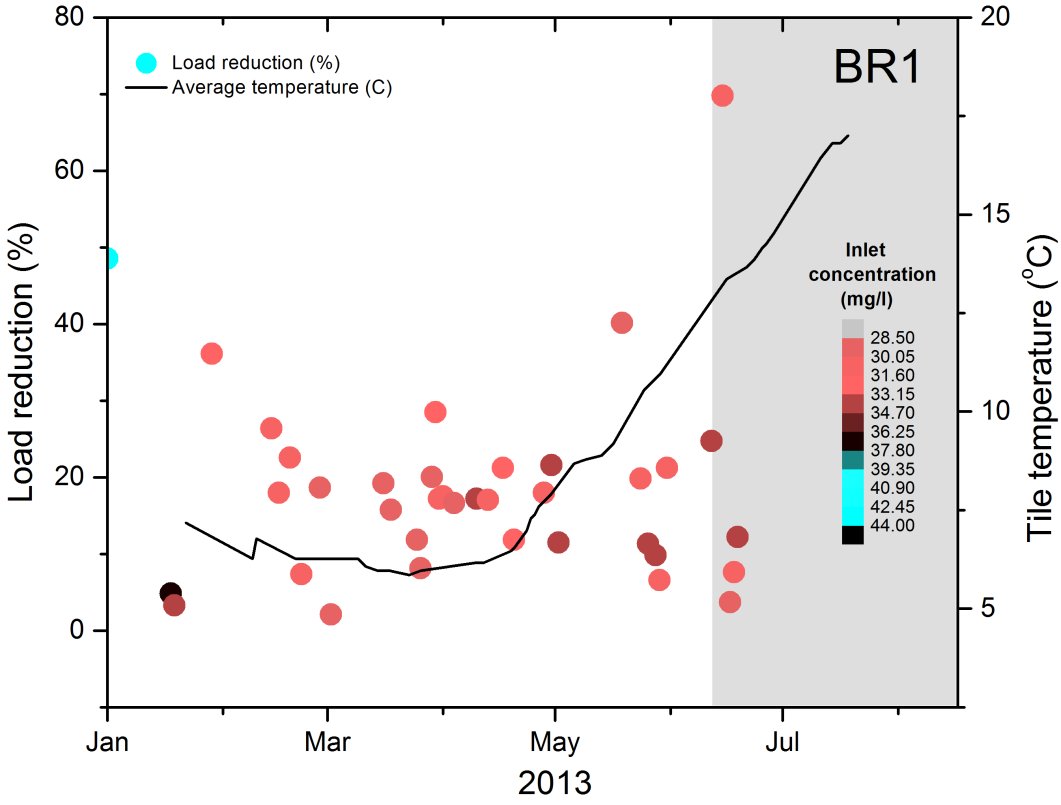

Figure 5.5: BR1 percent load reduction by inlet concentration

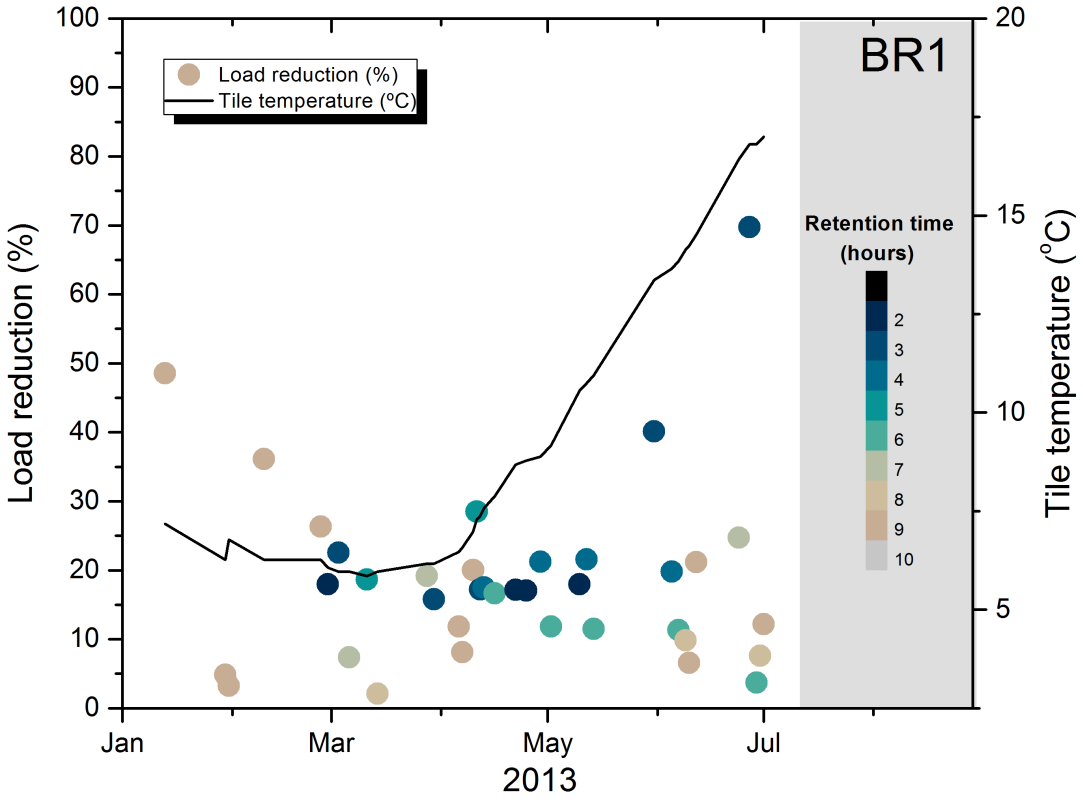

Figure 5.6: BR1 load reduction and tile temperature

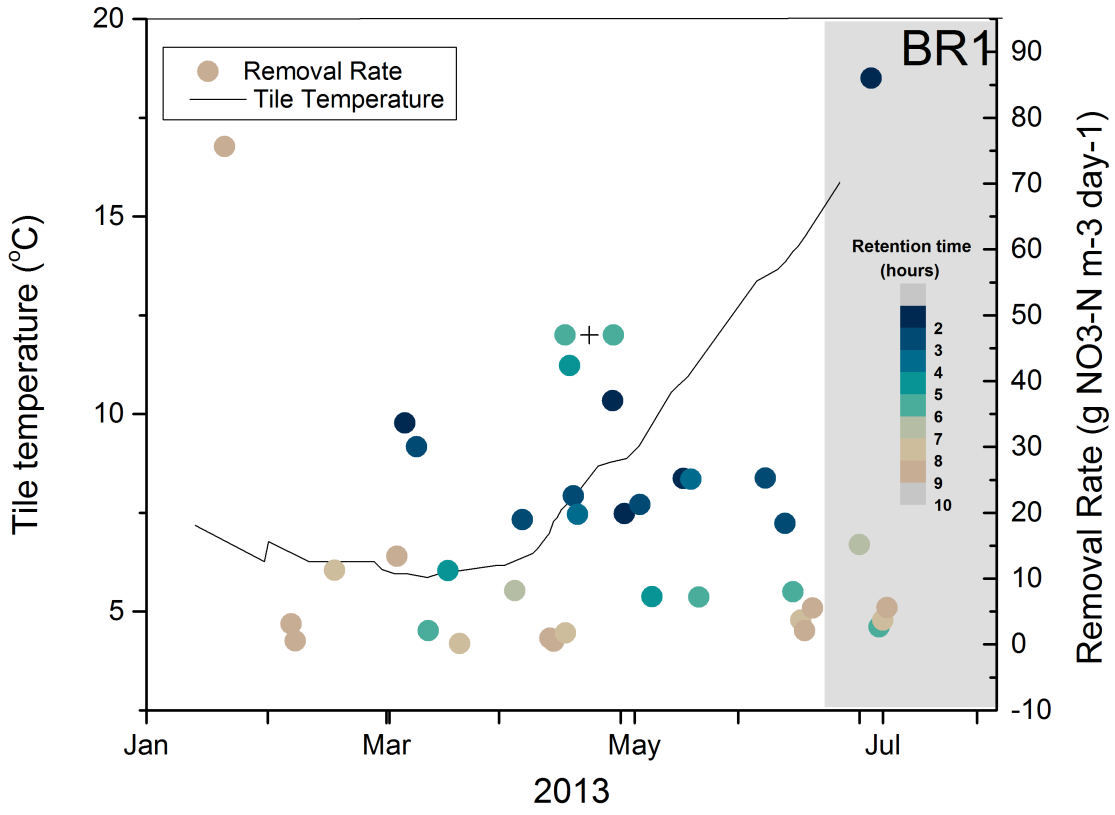

Figure 5.7: BR1 Nitrate-N removal rate

BR2 is located in a field with more than 3 m of fall, in a flood prone riparian buffer strip. Therefore, this site is not ideal for a bioreactor and would have been better suited for a wetland. The bioreactor was installed instead of a wetland as the farmer was not interested in taking land out of production. As a result of this flood prone zone, BR2 was often flooded by the drainage ditch backing into it and was completed inundated on numerous occasions. Consequently, much of the tile flow data for the bypass and outlet is inaccurate. The flow monitoring equipment at this site was also submerged during a major flood event and much of the data was lost. Ultimately, less than a month of tile flow data was usable and nitrate loads could therefore only be calculated accurately during this period. Outflow had to be assumed to be equal to tile inflow as flow backing up from the drainage ditch skewed outflow readings. The result of what was occurring at BR2 serves as a worst case scenario for bioreactor performance under flooded conditions. Calculated loads and load reduction are bias to warm weather and not accurate enough to draw any significant conclusions. Very low outlet concentrations, $< 0.1\,\mathrm{mg\,L^{-1}}$, were consistently measured as shown in Figure 5.8 and residence time was very high leading to the assumption that denitrification was occurring at BR2. Negative effects not observed at BR1 were observed at BR2 likely due to long periods of inundation and high residence time. Given the bias of the flow data set to warmer temperatures months (May to July) and the assumptions needed to analyze the BR2 data, overall results for BR2 can not be compared to BR1.

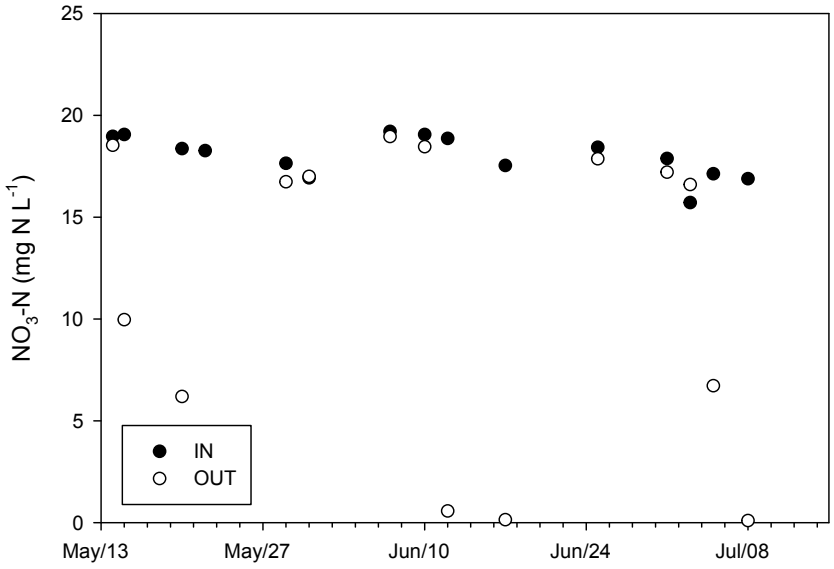

Figure 5.8: Influent and effluent concentrations at BR2 between May and July when the tiles were flowing

5.2 Greenhouse Gas Fluxes

5.2.1 Nitrous Oxide

Average N_2O-N flux at BR1 during the study period was $1.0\,mg\,N_2O\text{-}N\,m^{-2}\,hr^{-1}$, similar to emission rates found in current literature. Nitrous oxide fluxes reported in the literature range from $<1.0\,mg\,N_2O\text{-}N\,m^{-2}\,hr^{-1}$ found by Christianson et al. (2013) to 0.11 to $2.15\,g\,N_2O\text{-}N\,m^{-1}\,d^{-1}$ found by Healy et al. (2012). Woli et al. (2010) is the only other study to collect nitrous oxide samples in east-central Illinois from a bioreactor receiving effluent from a patterned drained, seed corn-soybean rotation farm. They found little nitrous oxide emissions (0 to $0.14\,mg\,m^{-2}\,h^{-1}$) and concluded fluxes were negligible. BR1 removed $268\,kg\,N\,m^{-2}$ during 2013 and emitted $3.2\,kg\,N_2O\text{-}N\,m^{-2}$. Therefore, N_2O-N represented 1.2% of the total N removed. In 2013, $28.7\,kg\,N_2O$-N was emitted from BR1 as shown in Figure 5.9. This is equivalent to $8897\,CO_2$-C. Fertilized corn emits 2 to $7\,kg\,N_2O\text{-}N\,ha^{-1}$ annually on average (Smith et al., 2013). The field draining into BR1 is 20 ha, therefore emits 40 to $140\,kg\,N_2O\text{-}N\,ha^{-1}$ annually on average. Therefore, nitrous oxide fluxes from

BR1 are less than fluxes would be if the $90m^2$ surface area at BR1 were instead planted with fertilized corn. It is also likely that fluxes emitted from bioreactors will be lower than those when untreated nitrate is denitrified further downstream as predicted by Christianson et al. (2013). Nitrous oxide fluxes were higher during warmer months was nitrate removal was highest. Warneke et al. (2011b) also detected highest N_2O emissions during warmer months when NO_3 removal was highest. Monthly nitrate removal rates, nitrous oxide rates and the fraction of nitrous oxide of nitrate removed are shown in Figure 5.10. Cumulative nitrous oxide flux during the 2013 study period are shown in Figure 5.11. When monthly nitrate removal (hypothesized to be due to denitrifcation) rates were observed to be high at BR1, nitrous oxide emissions were observed to be low. Conversely, when denitrification rates were observed to be low at BR1, nitrous oxide fluxes were higher.

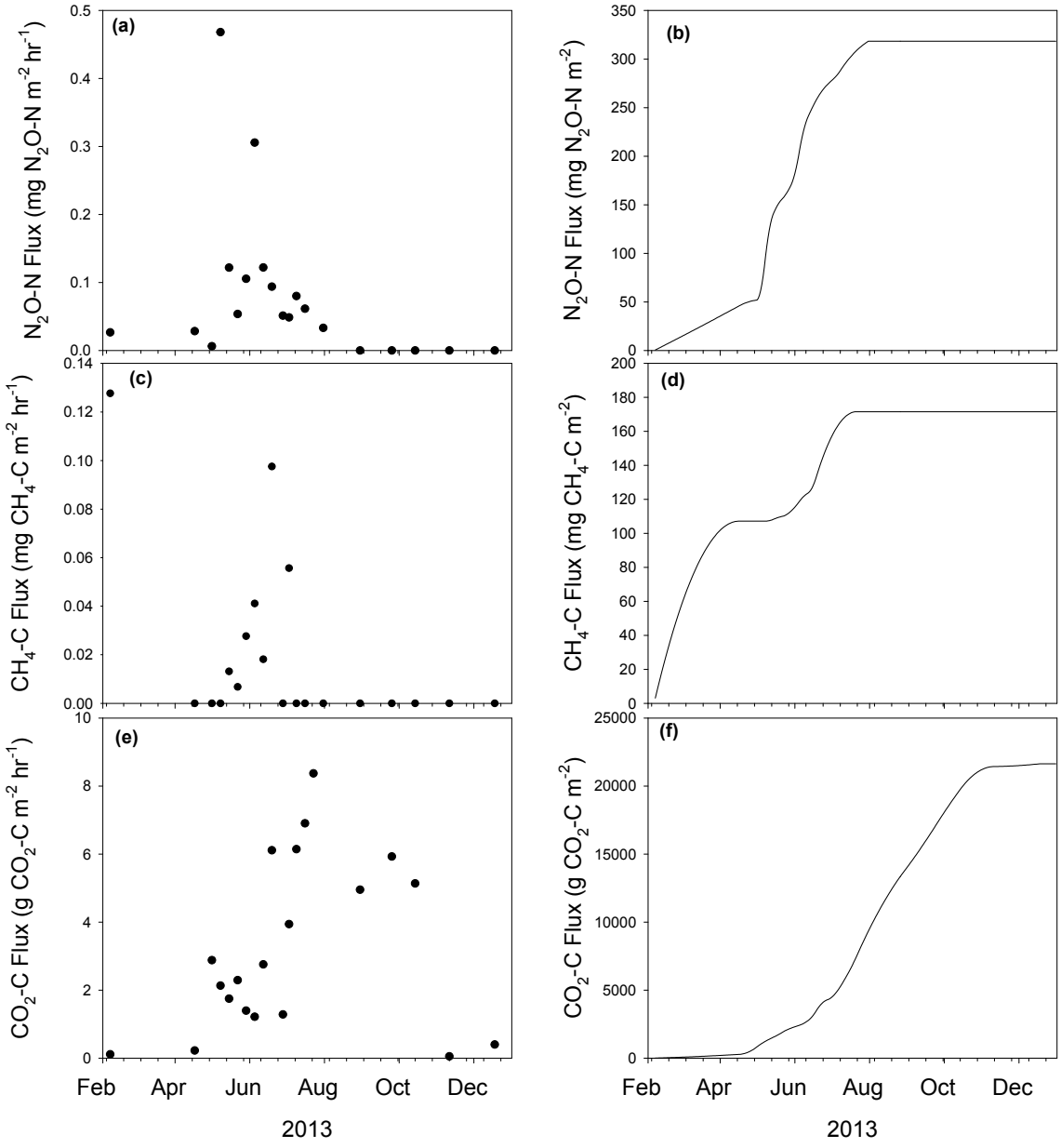

Figure 5.9: (a) BR1 measured N_2O-N Fluxes,(b) BR1 cumulative N_2O-N Flux, (c) BR1 measured CH_4-C Fluxes, (d) BR1 cumulative CH_4-C Flux, (e) BR1 measured CO_2-C Fluxes, (f) BR1 Cumulative CO_2-C Flux.

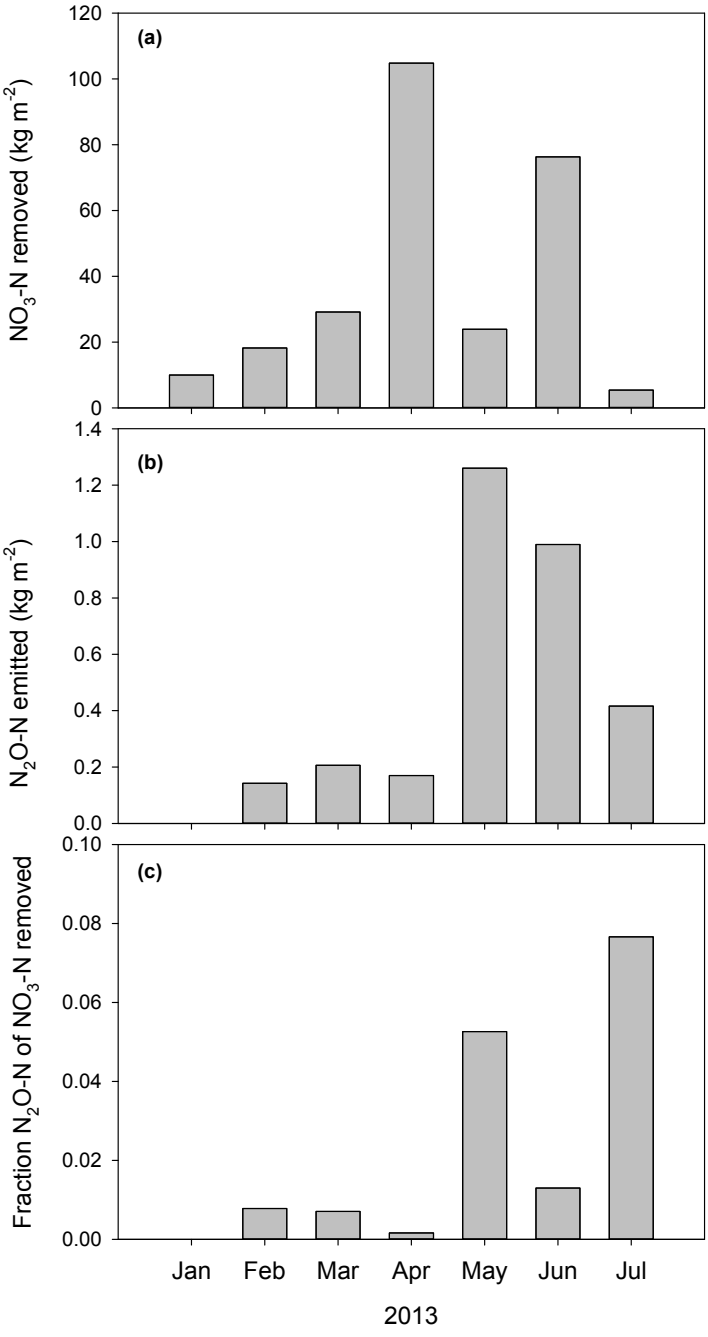

Figure 5.10: (a) Monthly nitrate removed, (b) nitrous oxide emitted and (c) fraction nitrous oxide emitted of the nitrate removed at BR1

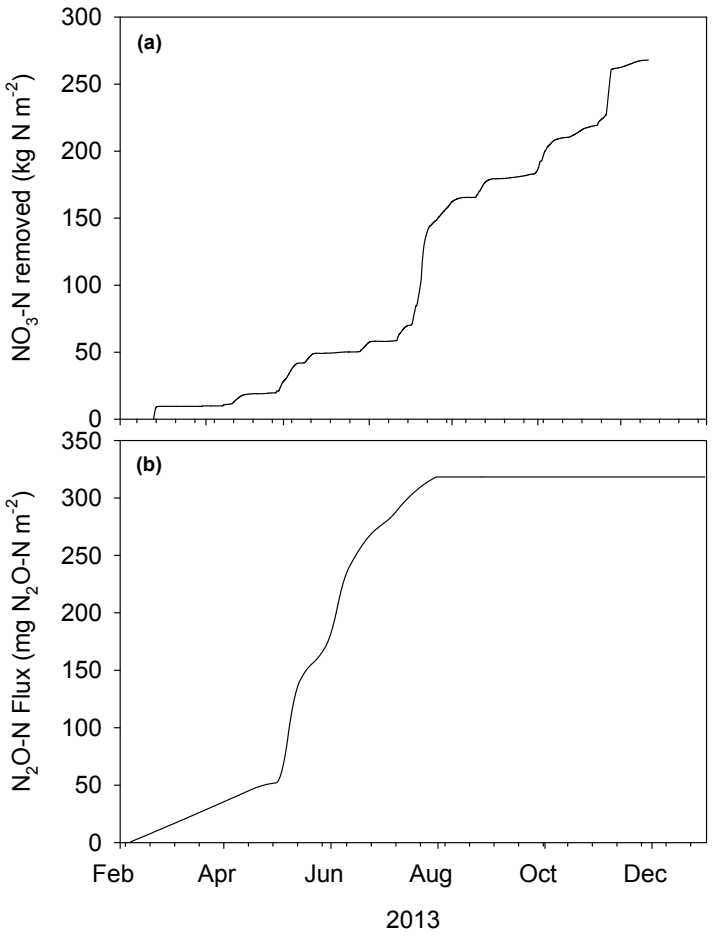

Figure 5.11: Cumulative (a) nitrate removed and (b) nitrous oxide at BR1

Average N_2O-N flux at BR2 during the study period was $0.5\,mg\,N_2O\text{-}N\,m^{-2}\,hr^{-1}$. During the study period, BR2 emitted $1.0\,kg\,N_2O\text{-}N\,m^{-2}$. Therefore, $9.3\,kg\,N_2O$-N was emitted from BR2 in 2013 as shown in Figure 5.12. This is equivalent to $2883\,kg\,CO_2$-C. Therefore, average fluxes at BR2, although smaller on average than fluxes at BR1 were not significantly different from those measured at BR1. Similar to BR1, nitrous oxide fluxes were higher during warmer months.

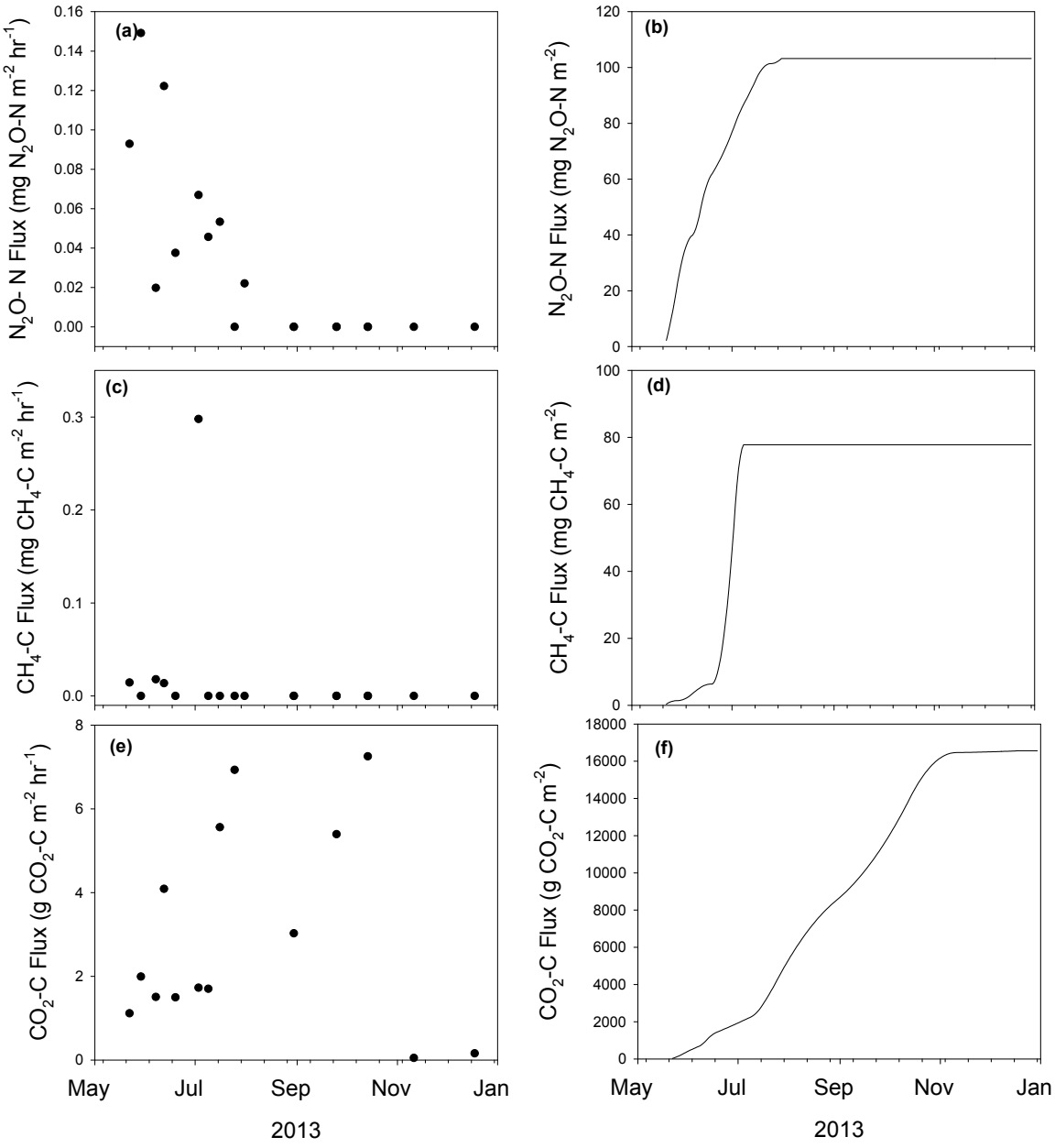

Figure 5.12: (a) BR2 measured N_2O-N Fluxes, (b) BR2 cumulative N_2O-N Flux, (c) BR2 measured CH_4-C Fluxes,(d) BR2 cumulative CH_4-C Flux, (e) BR2 measured CO_2-C Fluxes, (f) BR2 Cumulative CO_2-C Flux.

5.2.2 Methane

Methanogenesis has been reported in bioreactors throughout the literature. Elgood et al. (2010) found that CH_4 production in a stream-bed bioreactor in Ontario, Canada, during summer months was higher than some rivers and reservoirs. Average CH_4-C flux from BR1 was $0.02\,\mathrm{mg\,CH_4\text{-}C\,m^{-2}\,hr^{-1}}$. In 2013, $15.4\,\mathrm{kg\,CH_4}$-C was emitted from BR1. This is equivalent to 323 $\mathrm{kg\,CO_2}$-C. Average CH_4-C flux from BR2 was $0.02\,\mathrm{mg\,CH_4\text{-}C\,m^{-2}\,hr^{-1}}$. These results are shown in Figure 5.9. In 2013, $7.0\,\mathrm{kg\,CH_4}$-C was emitted from BR2. This is equivalent to 147 $\mathrm{kg\,CO_2}$-C. Methane fluxes were higher during periods of inundation in BR1 when all the nitrate was removed and redox potential became low. Neither low or high flow periods produced large methane fluxes in BR1 or BR2. Methane fluxes were negligible throughout the study period for BR2. These results are shown in Figure 5.12. Since methane is produced under low redox potential conditions, it was anticipated that higher emissions would be found at BR2 during periods of inundation, however this trend was not found. Methane emission rates from unfertilized and fertilized corn fields range from 0.7 to $5.6\,\mathrm{g\,CH_4\text{-}C\,kg^{-1}\,soil\,h^{-1}}$ (Fernandez-Luqueo et al., 2010) so emissions that were observed at BR1 and BR2 were likely higher than those from the fields they were draining during periods of inundation.

5.2.3 Carbon Dioxide

Average CO_2-C flux from BR1 was $2.9\,\mathrm{g\,CO_2\text{-}C\,m^{-2}\,hr^{-1}}$. In 2013, $2256.4\,\mathrm{kg\,CO_2}$-C was emitted from BR1. This represents 7.7% of total C lost from woodchips meaning this bioreactor could support denitrification for 13 years. These results are shown in Figure 5.9. Average CO_2-C flux from BR2 was $3.1\,\mathrm{g\,CO_2\text{-}C\,m^{-2}\,hr^{-1}}$. In 2013, $2578.2\,\mathrm{kg\,CO_2}$-C was emitted from BR2. This represents 8.8% of total C lost from the woodchips meaning this bioreactor could support denitrification for 11 years. These results are shown in Figure 5.12. These results indicate the decomposition of the wood and transformation of nitrate to nitrogen gas as it is associated with the release of carbon dioxide. Woli et al. (2010) measured similar CO_2 fluxes from a bioreactor bed in east-central Illinois receiving effluent from a seed corn-soybean rotation farm, with fluxes ranging from 4.4 to $7.5\,\mathrm{g\,C\,m^{-2}\,hr^{-1}}$. Warneke et al.

(2011a) reported an average bioreactor bed surface emission rate of $0.756\,\mathrm{g\,C\,m^{-2}\,hr^{-1}}$, much smaller than those measured in this study and reported by Woli et al. (2010). van Driel et al. (2006) found that carbon consumption from denitrification was less than 2% annually and concluded the woodchips could sustain denitrification for a many years. Robertson (2010) suggested bioreactors may be maintenance free for decades after installation. Warneke et al. (2011a) calculated longevity based on CO_2 surface emissions rates and release of dissolved carbon and found denitrification could be supported for 39 years. Robertson et al. (2000) had reported that woodchip bioreactors could support denitrification for a decade or more without replenishing the carbon source. Schipper et al. (2010b) reported bioreactors could remove nitrate-N for up to 15 years without maintenance. Longevity results from this study fall in the average range of 10 to 15 years reported throughout the literature.

5.3 Other Concerns

5.3.1 Phosphorus

Total phosphorus and dissolved reactive phosphorus (DRP) concentrations were found to be higher in the effluent than in the tile influent at BR1 as shown in Figures 5.13 and 5.14. Phosphorus loading was calculated as $0.2\,\mathrm{g\,P04\text{-}P\,m^{-3}\,day^{-1}}$ in BR1. 13 January 2013 and 27 June 2013 exhibited the largest difference with influent concentrations $< 0.1\,\mathrm{mg\,L^{-1}}$ and effluent concentrations of 3.1 and $3.9\,\mathrm{mg\,L^{-1}}$ respectively. Phosphorus concentrations at BR2 were also found to be higher in the effluent than in the tile influent on average as shown in Figures 5.15 and 5.16. Four samples had effluent concentrations $> 0.1\,\mathrm{mg\,L^{-1}}$. The increase of phosphorus in effluent concentrations was most likely due to sorption of phosphorus to soil particles that were washed out of the bioreactor. The continued increase in effluent concentrations could be due to other biological processes at work. This phenomenon has been observed at the University of Illinois by Goodwin (2012) and Bell (2013). The negative environmental impact of increased phosphorus in bioreactors is small considering influent and effluent concentrations on average are not significantly different and the benefits of nitrate reduction outweigh this cost.

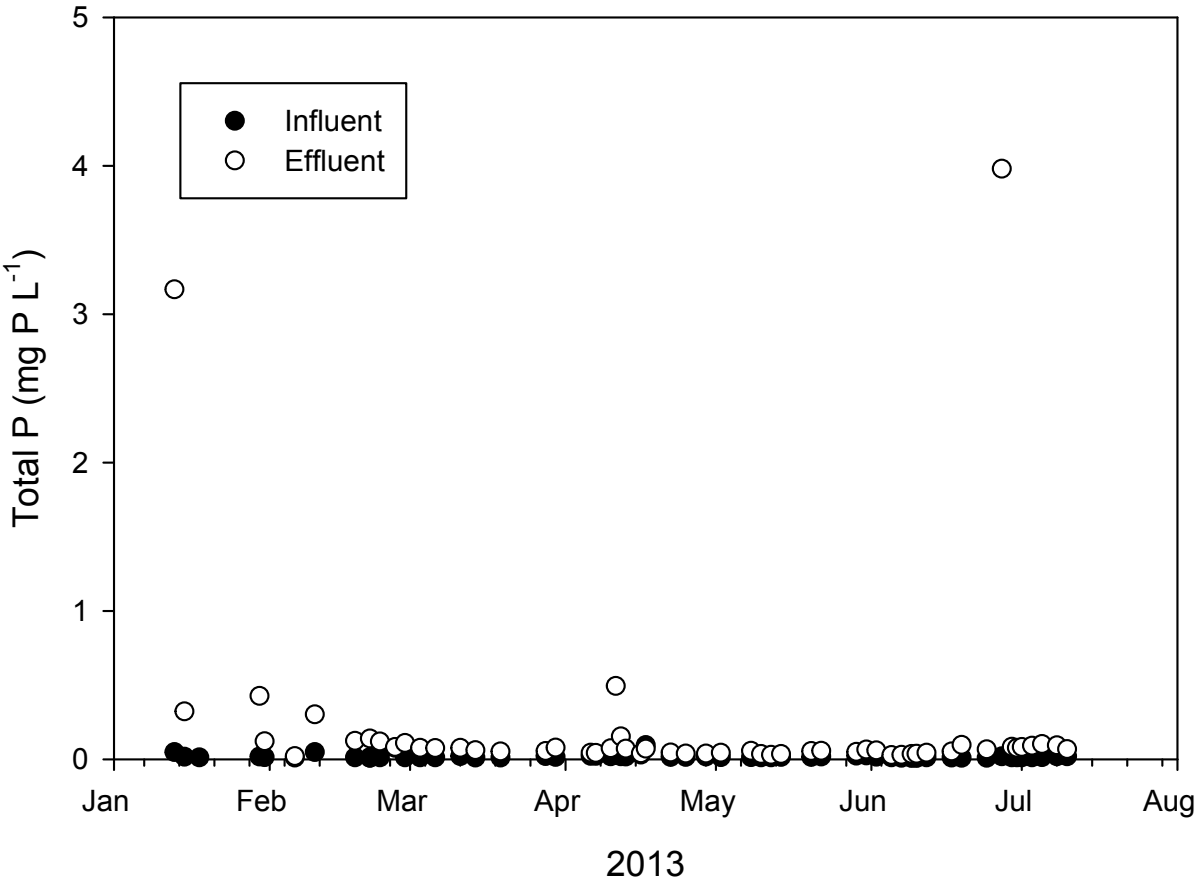

Figure 5.13: Phosphorus concentrations were consistently higher in the effluent than the influent in BR1.

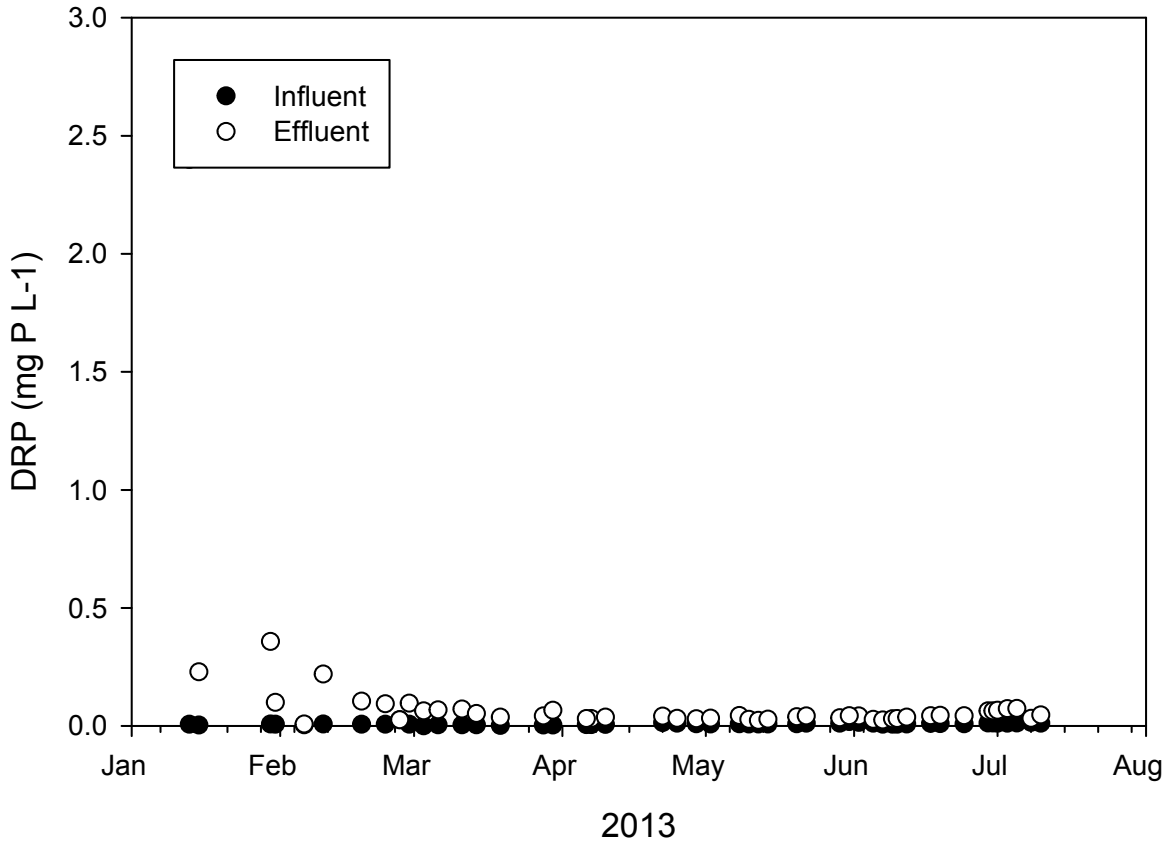

Figure 5.14: Influent and effluent dissolved reactive phosphorus concentrations observed at BR1.

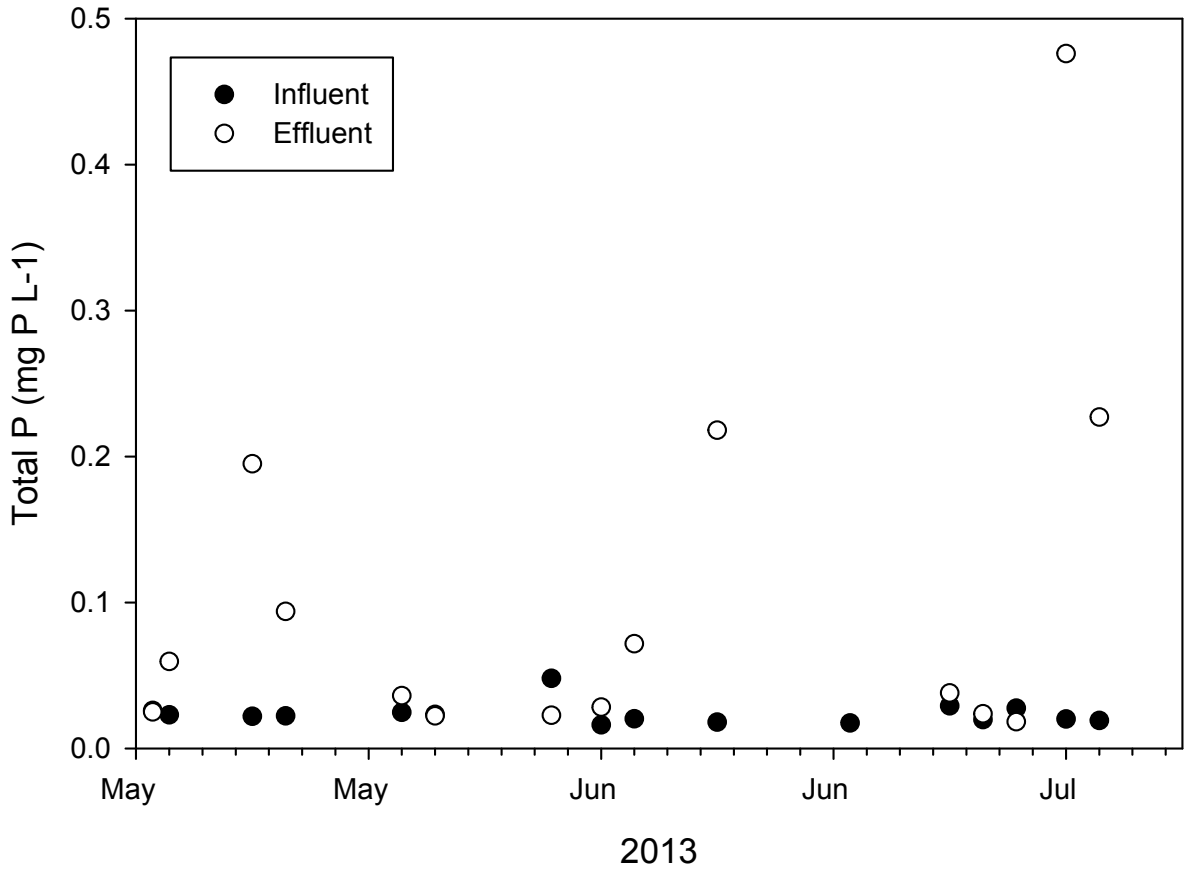

Figure 5.15: Phosphorus concentrations were consistently higher in the effluent than the influent in BR2.

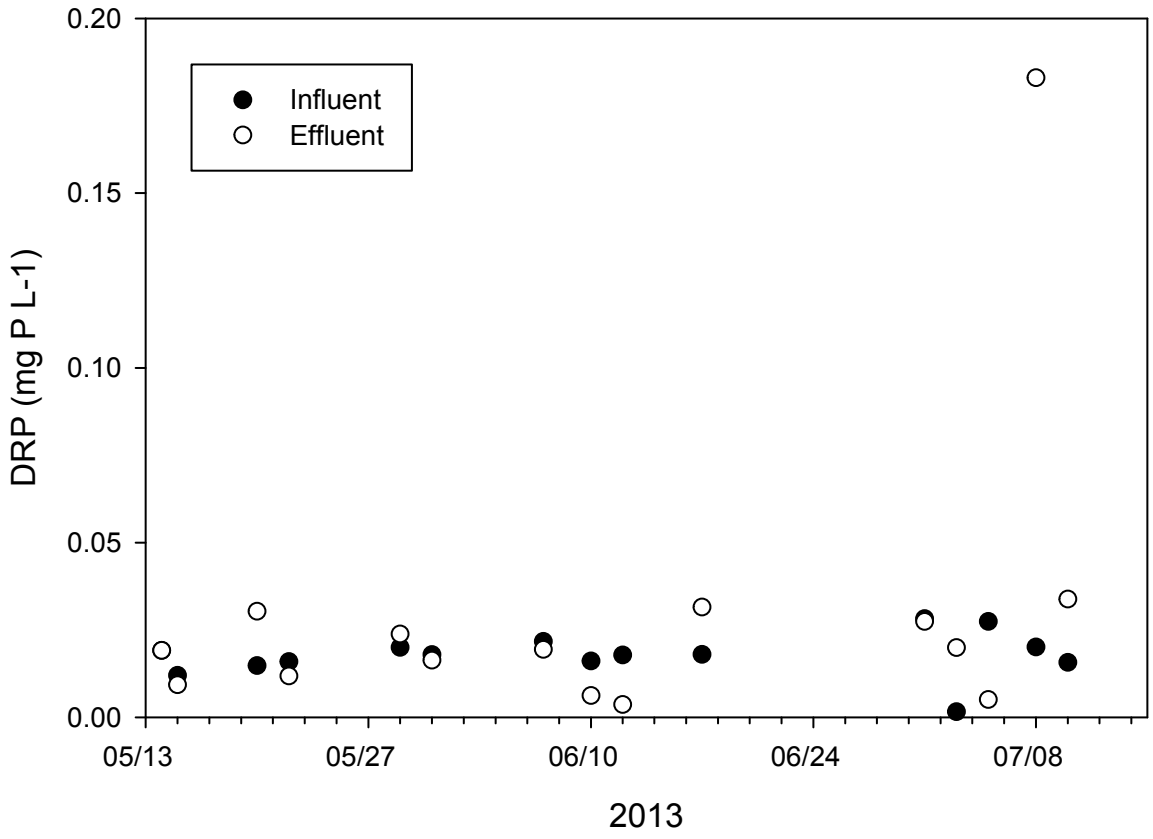

Figure 5.16: Influent and effluent dissolved reactive phosphorus concentrations observed at BR2

5.3.2 Hydrogen Sulfide Gas

During periods of inundation, a rotten egg smell was detected at BR2 and is thought to be the result of the production of hydrogen sulfide gas. This phenomenon was not observed at BR1. A decrease in sulfate concentrations in BR2 as seen in Figure 5.17 support this conjecture.

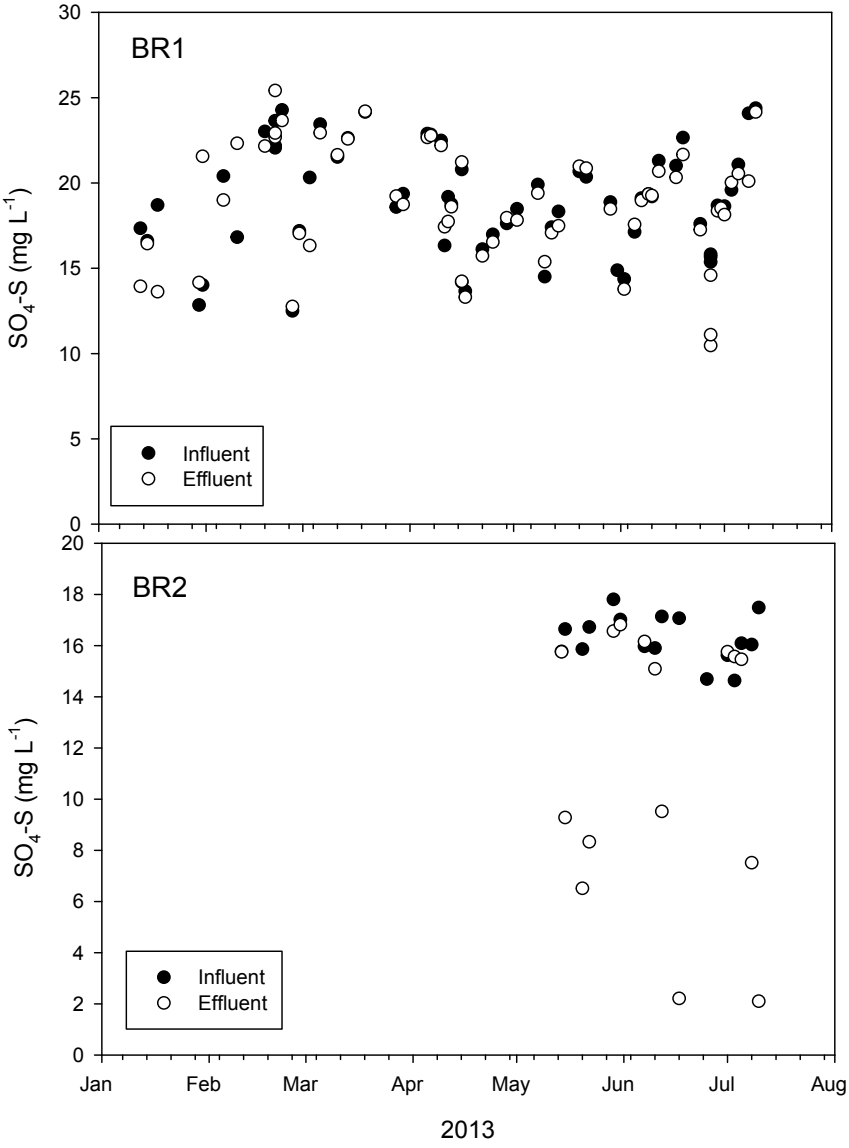

Figure 5.17: Inlet and effluent sulfate concentrations at BR1 and BR2

5.3.3 Biofilm, DOC, pH

A biofilm was also documented following periods of inundation when the drainage ditch had backed up into the bioreactor and water in the bioreactor was stagnant. The biofilm is thought to have impacted the hydraulic conductivity of the bioreactor. Chun et al. (2009) concluded effective hydraulic conductivity decreased because of biofilm formation in woodchip bioreactors. Taylor et al. (1990) also suggested biofilm formation leads to reduced hydraulic conductivity during a study of porous medium column bioreactors. Christianson et al. (2012) suggests biofilms can clog water level control structures and tiles. Water level control structures were observed as being stagnant and clogged during periods when biofilms were documented supporting this conjecture.

Effluent DOC was significantly higher than inlet DOC 4 times at BR1 and on 8 sampling occasions at BR2 as shown in Figure 5.18. The highest effluent DOC at BR1 was observed after the tiles initially started flowing on 13 January 2013. This is thought to be due to labile carbon being initially flushed from the bioreactor. An increase in DOC in the effluent at BR2 throughout the study period may also be to labile carbon being flushed as BR2 is in its first year of operation. Bell (2013) found similar results during a controlled field study at the University of Illinois. The effluent pH at BR1 was lower than influent pH in 47 samples and higher only 3 times as shown in Figure 5.19. The difference was not significant in any case. The average effluent pH of 6.9 falls with the USEPA water quality criteria range of 6.5 to 9 set for the protection of aquatic life (USEPA, 2014). The lowest effluent pH was 6.3 and did fall outside of the USEPA water quality criteria range, however short term exposure to a pH not significantly outside of the range should not have any negative effects on aquatic life. Effluent pH was also in general higher than influent pH at BR2. Effluent pH was higher in 11 samples and lower in four samples. The difference however was not significant. The average effluent pH of 6.6 at BR2 also falls within the USEPA water quality criteria range. A minimum pH of 5.8 was observed on one occasion. Again, short term exposure of aquatic life to a pH of 5.8 is not thought to induce any harm.

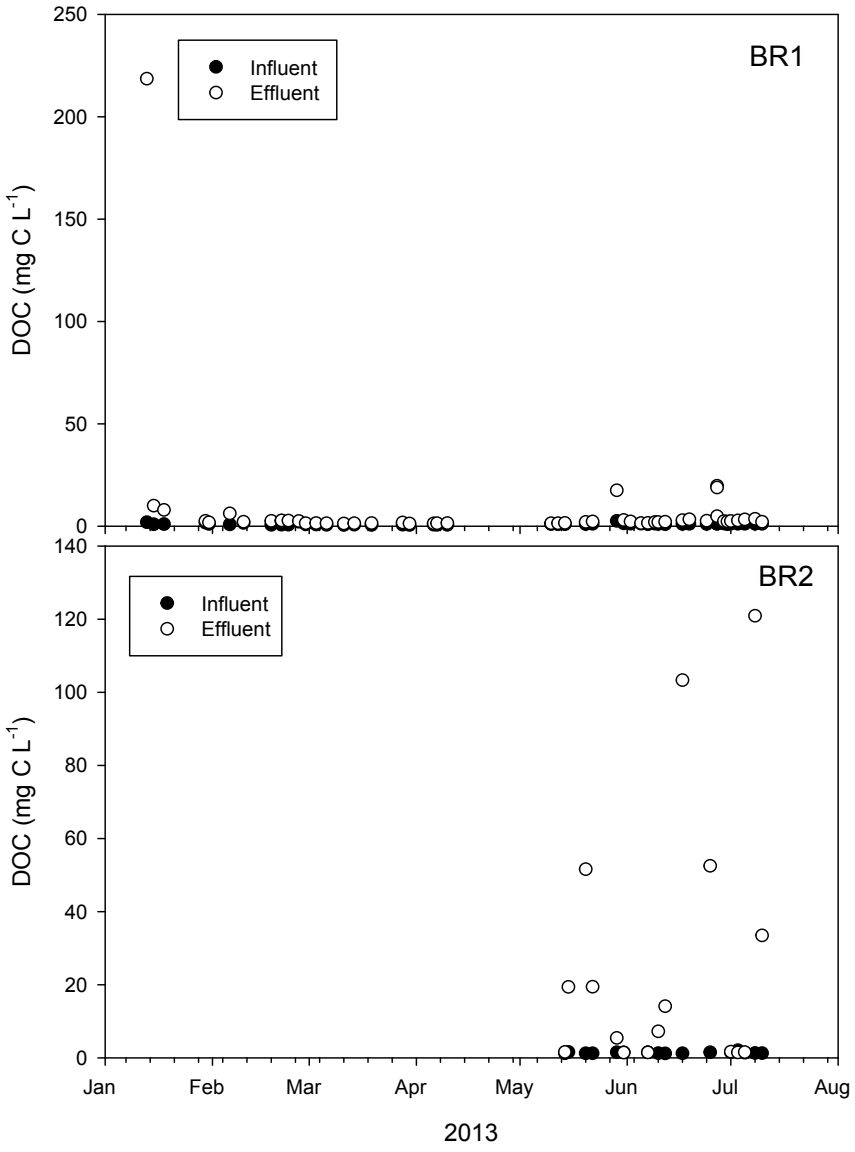

Figure 5.18: Influent and Effluent dissolved Organic Carbon during the study period at BR1 and BR2

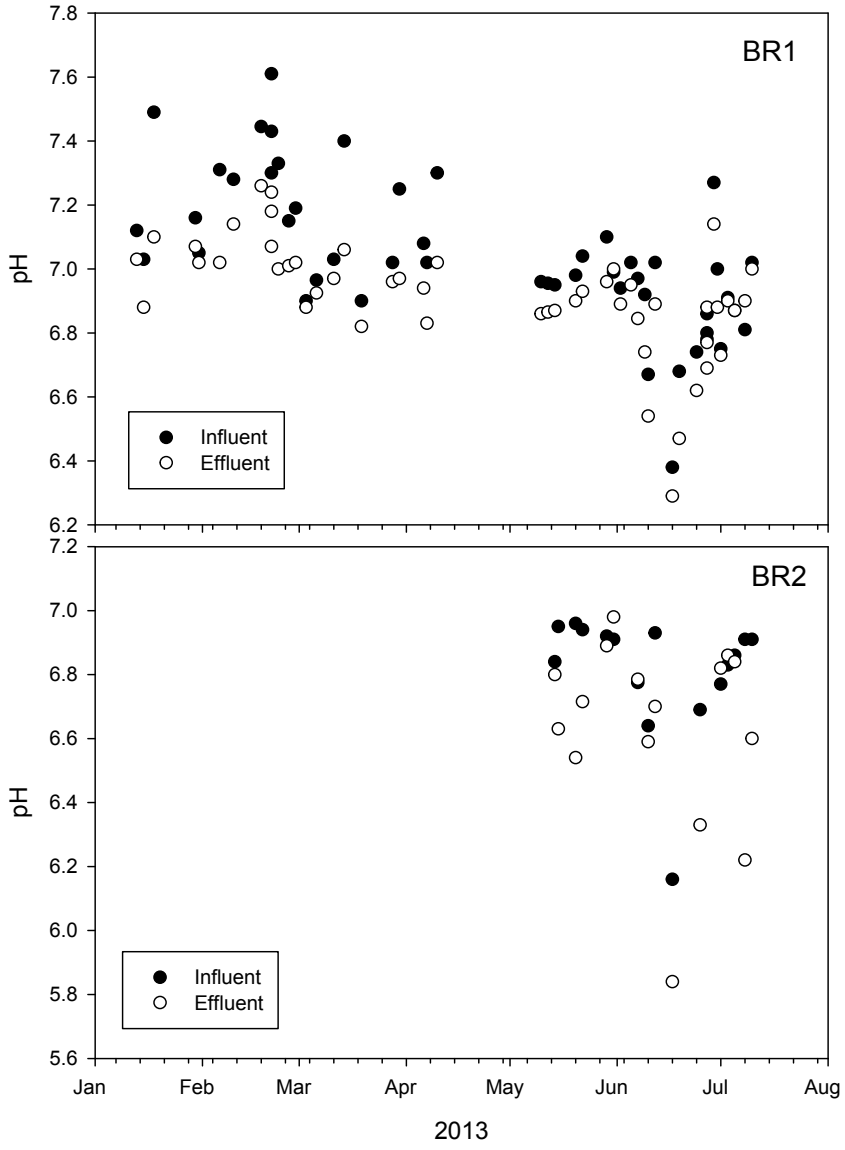

Figure 5.19: Influent and Effluent pH during the study period at BR1 and BR2

5.4 Hydraulic Conductivity

Transport parameters like hydraulic conductivity are helpful in understanding bioreactor performance. A visual basic routine was developed that allows users to calculate hydraulic conductivity for a given bioreactor from actual flow data. The user must input the length and width of the bioreactor, hydraulic head at the inlet and outlet, and influent flow rate. The program calculates hydraulic conductivity using Darcy's Law for each time step provided in the data file. Hydraulic conductivity is averaged over the time period and reported back to the user in units of $\mathrm{ft\,s^{-1}}$. This routine was used to calculated hydraulic conductivity for BR1 and BR2. For BR1, average hydraulic conductivity was found to be $0.2\,\mathrm{ft\,s^{-1}}$ or 5.5 $\mathrm{cm\,s^{-1}}$ as shown in Figure 5.20. For BR2, average hydraulic conductivity was found to be $0.5\,\mathrm{ft\,s^{-1}}$ or 14.9 $\mathrm{cm\,s^{-1}}$. Similar hydraulic conductivities for bioreactors have been reported in the literature ($3.9\,\mathrm{cm\,sec^{-1}}$ by Chun & Cooke (2010), 7.3 to $11.1\,\mathrm{cm\,s^{-1}}$ by Christianson et al. (2010) and 0.7 to $1.2 + 10\,\mathrm{cm\,s^{-1}}$ by van Driel et al. (2006)). The routine is shown in Figure 5.21. Hydraulic conductivities generally decreased as volumetric flow rate decreased during the study period for both BR1 and BR2. Hydraulic conductivity for BR2 was greater than for BR1, agreeing with this conjecture as volumetric flow rate was greater on average through BR2. Hydraulic conductivity peaks appeared to lag flow peaks at BR1. This relationship would represent the flushing of biofilms during high flow events and the buildup of biofilms that were inhibiting hydraulic conductivity during low flow events. A serial cross correlation between flow and hydraulic conductivity was performed in order to assess this relationship. The cross correlation function (CCF) is shown on the cross-correlogram plot in Figure 5.22. The plot shows autocorrelation coefficients versus time lags in days. Provided the data is given as (x,y) pairs, autocorrelations coefficients are defined as:

$$\rho = \frac{S_{xy}}{\sqrt{S_{xx} S_{yy}}} \tag{5.1}$$

where Sxx is given by:

$$S_{xx} = \sum_{i=1}^{N} (x - \bar{x})^2 \tag{5.2}$$

and Syy is given by:

$$S_{yy} = \sum_{i=1}^{N} (y - \bar{y})^2 \tag{5.3}$$

and Sxy is given by:

$$S_{xy} = \sum_{i=1}^{N} (x - \bar{x})^2 (y - \bar{y})^2 \tag{5.4}$$

where N is the number of sample points. The autocorrelation coefficient at each lag, k was calculated using the EXCEL built-in CORREL function. Autocorrelations ranges between -1 and +1, representing negative and positive correlations respectively. Stronger correlations are closer to ± 1. Lags that are significant lie outside of the confidence interval of the cross-correlogram. The confidence interval was given by:

$$\pm \frac{z_{1-\frac{\alpha}{2}}}{\sqrt{N}} \tag{5.5}$$

The cross-correlogram revealed hydraulic conductivity does in fact lag flow as shown in Figure 5.22. Hydraulic conductivity lags flow by 6 days. This suggests biofilm formation is decreasing hydraulic conductivity in bioreactors but the issue is fixed when high flow events flush biofilms from the control structures.

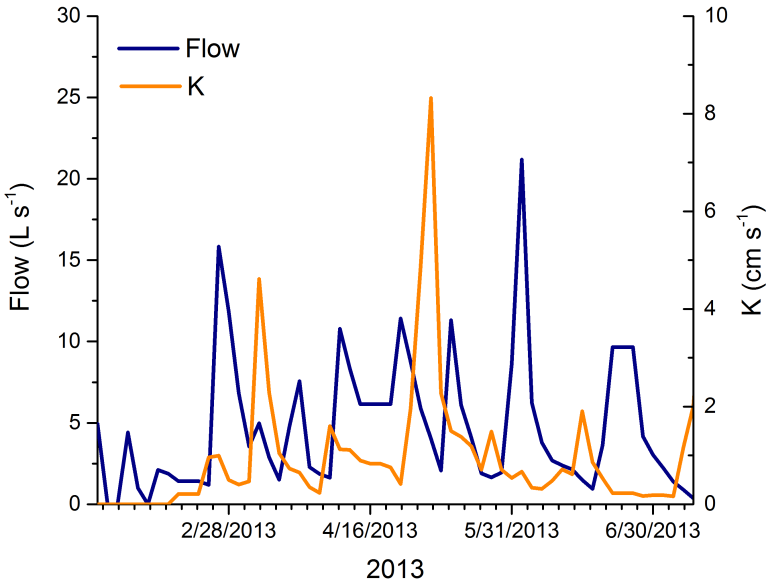

Figure 5.20: Hydraulic conductivity at BR1 during the study period

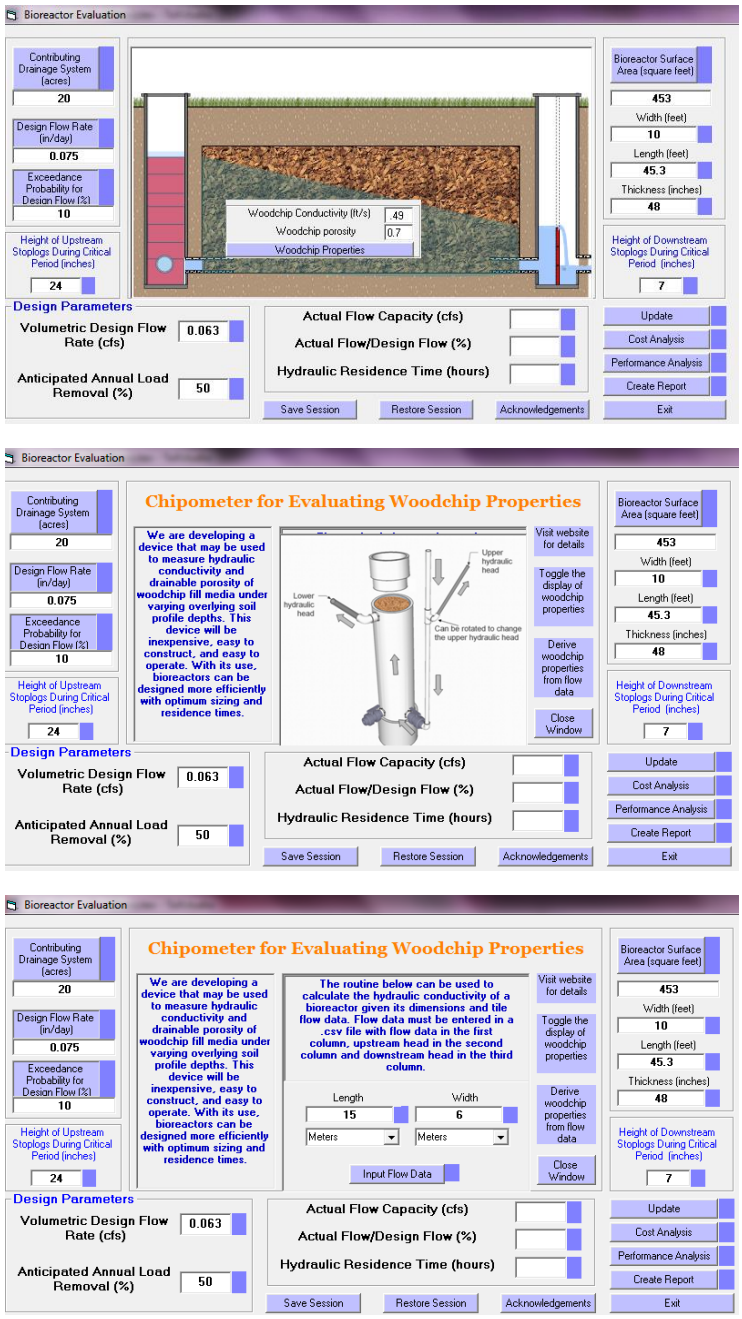

Figure 5.21: Visual basic routine for calculating hydraulic conductivity for a given bioreactor using actual flow data

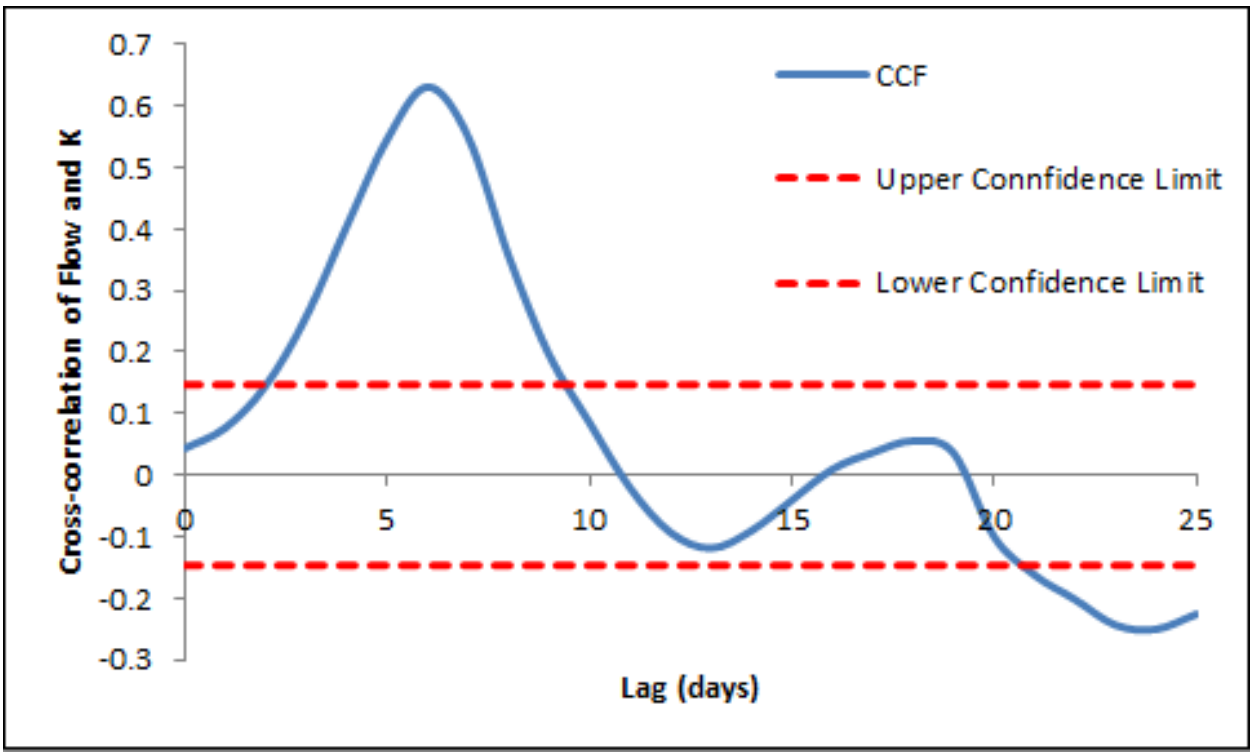

Figure 5.22: Cross-Correlogram of Flow and Hydraulic Conductivity at BR1

5.5 Optimization Routine

An existing Visual Basic routine found on the Illinois drainage guide that examines bioreactor performance was altered so a user could read in measured flow data and water level control structures heights to examine performance of an existing bioreactor. After the user inputted the measured flow data file and manually entered water level control structure board settings, the routine was used to calculate the amount of bypass flow. The program was run using flow data and board settings at BR1. It was found that 49% bypass flow occurred at BR1 during the 2013 study period as shown in Figure 5.23. The black line represents measured flow into the control structure. The red line represents flow through the bioreactor. Any flow above the red line bypasses the bioreactor. The difference between the predicted 49% bypass flow and measured 47% bypass flow was determined to be not significant.

Therefore, given this confidence in the validity of the model, this routine was then used to maximize performance at BR1 for the upcoming 2014 tile flow season. 47 % of bypass flow occurred at BR1 during the 2013 tile flow season, causing 87 % of the nitrate load to bypass the bioreactor. Ostensibly, if the amount of bypass was reduced, more of the nitrate load could be treated and a higher nitrate removal rate and/or percent load reduction could be achieved.

Thirty years of historic climate data for Illinois were used to simulate bioreactor performance in order to find settings that could achieve increased performance. Board configurations were entered into the program as if the inlet and outlet had been raised or lowered by one board or 12.7 and 17.8 cm (5 and 7 in) of head at increasing intervals. With only options of adding or removing 12.7 and 17.8 cm boards, limited hydraulic head depths are possible in the control structures. The model was run under the assumption that the person maintaining the bioreactor would only want to set the boards once per year. Bioreactor performance may be further improved if the boards were set at different heights for wet and dry months. Changing the boards settings during different seasons may be unrealistic for farmers interesting in best management practices with little to no maintenance, therefore this scenario was not explored when executing the model. As anticipated, it was found that bypass flow could be reduced at BR1 by changing the board configurations. The optimal

setting options were determined to be that which reduced bypass flow while maintaining residence time within a range of two to eight hours. Residence time is the amount of time that any one particle spends in the bioreactor. In the residence time graph displayed in the model, critical residence time is shown in red and residence time based on board settings is shown in blue. Both the critical residence time and the predicted are horizontal since only annual values were specified rather than season specific. In the graph of flow rate, the 10 year-24 hour flow rates are shown in red and the actual flow rates based on board settings are shown in black. The amount of flow above the red line indicates bypass flow. It was found that setting the inlet board height at 76.2 cm and the outlet board height at 12.7 cm would reduce bypass flow to 3.4 % while maintaining an average residence time of 2.6 hours. Ideally, this setting should provide an operator with optimal performance. If an operator wanted to maintain a residence time higher than 2.6 hours to ensure full denitrification, other settings on the chart provide options with longer residence times while maintaining bypass flow much less than the 2013 study period. One setting example is using 78.7 cm of upstream head and 35.6 cm of downstream head which provides a residence time of 4.1 hours and only 12% bypass flow. Currently, BR1 is set with an upstream head of 78.7 cm and a downstream head of 53.3 cm for the 2014 study period. These settings are predicted to result in 39.9 % bypass flow and a residence time of 6.5 hours as shown in Figure 5.24. To achieve a 6.5 hour residence time with less bypass flow, the operator could use an upstream head of 78.7 cm and a downstream head of 50.8 cm, which only allows for 24% bypass. When the 2014 study is complete, the measured data should be compared with the predicted data to further validate this model. Finding optimal board settings without any guide is difficult. If residence time is too long, all the nitrate will be removed from the tile water and then other redox processes will occur. If the residence time is too short, contact time of the nitrate laden water with denitrifying bacteria is not long enough for nitrate to be removed. Bioreactor performance depends on this delicate balance of residence time and bypass flow. Many board settings will provide bioreactor operation that will allow for complete denitrification and lessen bypass flow and unintended consequences. A chart of options obtained from the routine, sorted in ascending order of percent bypass flow are shown in Appendix A. The options are shown in the routine interface in Appendix A. A box plot showing percent bypass flow color mapped

by retention time at varying inlet and outlet hydraulic heads is shown in Figure 5.25. A contour plot showing percent bypass flow color mapped by retention time at varying inlet and outlet hydraulic heads is shown in Figure 5.26. Most of the data predicted residence times < 10 hours. These options provide an operator with a much needed guide.

A flat contour map of bypass flow for varying upstream and downstream stop-log settings is shown in Figure 5.27. The contour plot does not show one minimum, rather bypass flow tends to decrease as upstream head increases and downstream head decreases. Residence time is smallest when the difference between upstream head and downstream head is largest. Operators will have to choose how important reducing bypass flow is in conjunction with maintaining adequate residence time. There is not one optimal residence time for bioreactors in the literature. However, increasing retention times has been shown to decrease effluent concentrations. Rodriguez (2010) found effluent nitrate concentrations are dependent on retention time. Removal efficiencies were found to be of 39%, 76% and 96% at 4.2, 6.3 and 8 hours of retention time, respectively. Too long of retention times may result in production of adverse effects like methane emissions, hydrogen sulfide gas production, sulfate reduction and methylation of mercury. Christianson & Helmers (2011) point out if water remains in reactors for too long, nitrate will be entirely removed and other processes will begin as bacteria seek other sources of electron acceptors. So bioreactors should be monitored by operators and if any effects are noticed, other inlet and outlet hydraulic heads should be explored. This routine is an effective tool for finding balances that can maximize bioreactor performance. Farmers could presumably use this routine to model a specific bioreactor to determine how to operate it more effectively.

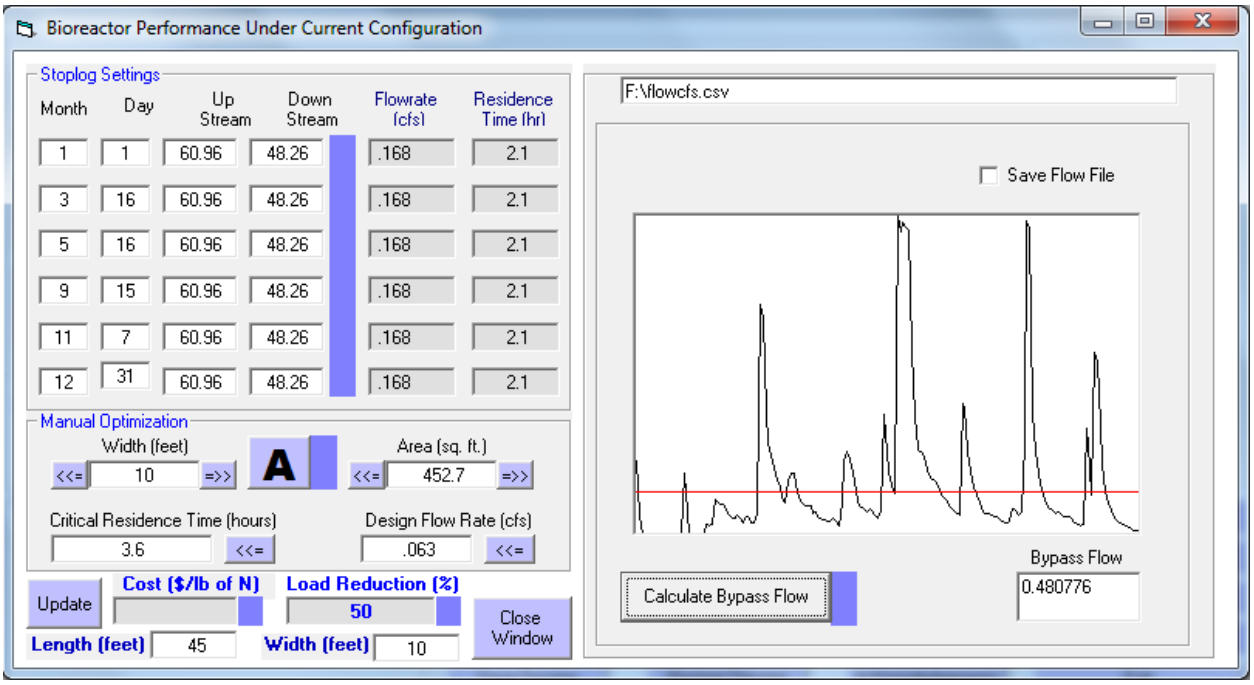

Figure 5.23: Bypass flow at BR1 calculated using Visual Basic Routine during 2013 study period

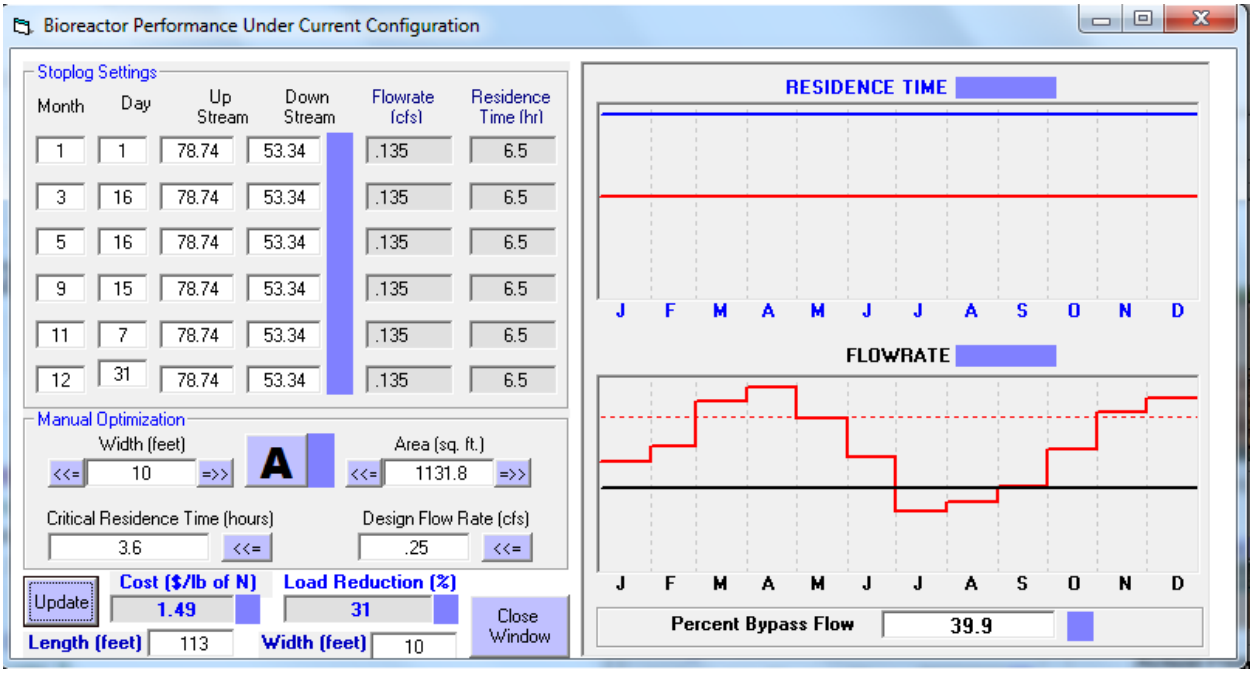

Figure 5.24: Predicted bypass flow, flow rate and residence time at BR1 given measured board settings currently in place for 2014 study period

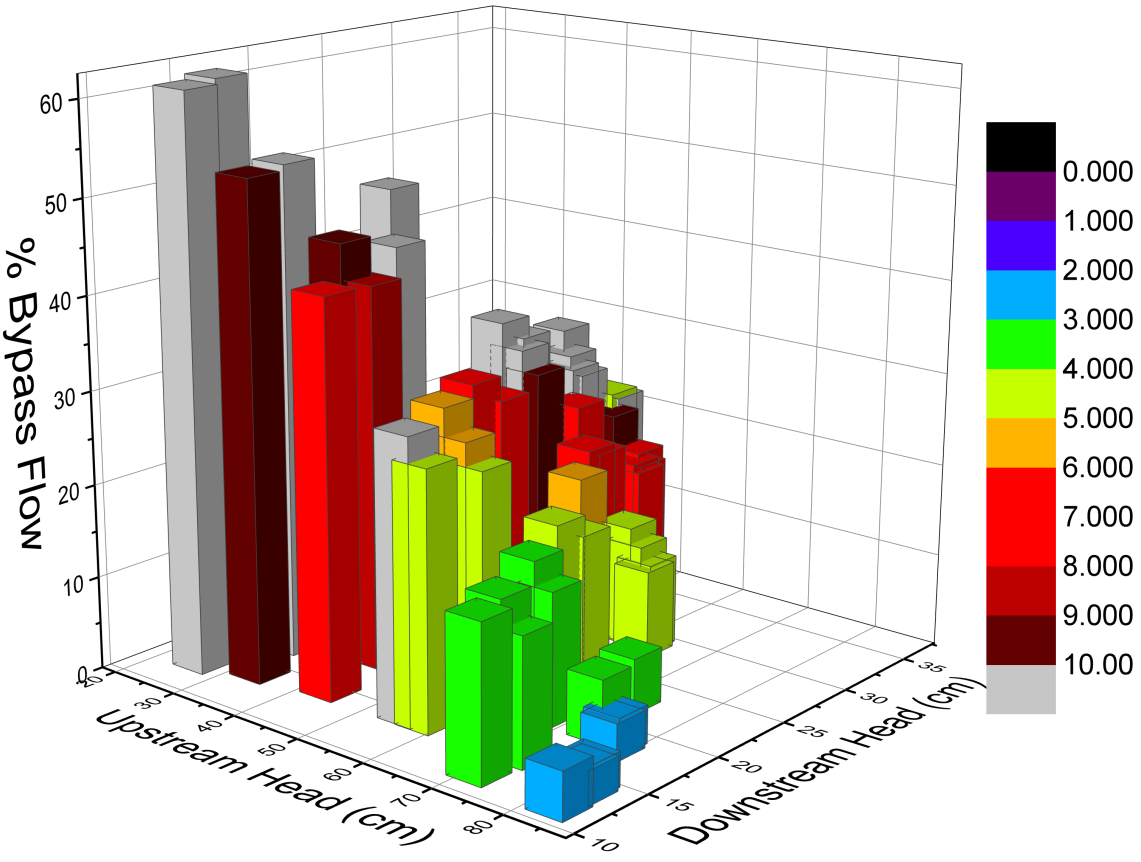

Figure 5.25: Box plot of predicted bypass flow color mapped by residence time for upstream and downstream head board settings at BR1

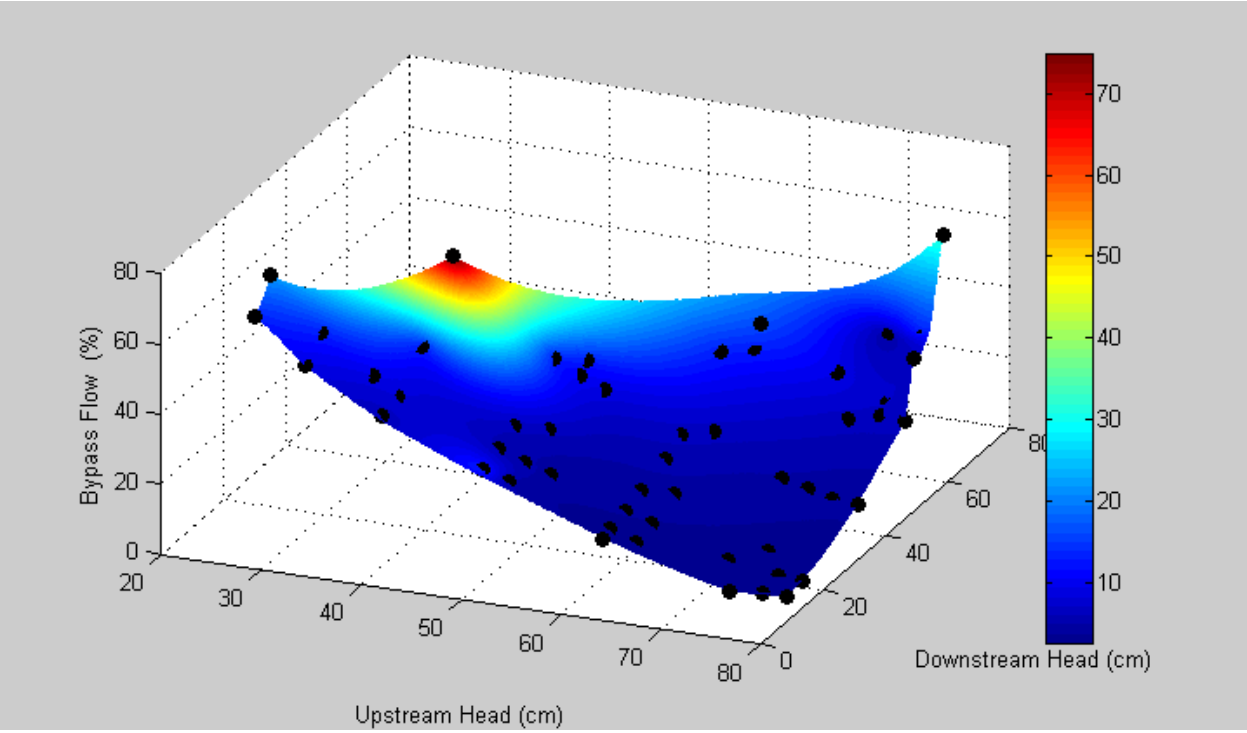

Figure 5.26: Contour plot showing predicted percent bypass flow on the z-axis for varying upstream (x-axis) and downstream head (y-axis) settings at BR1 color mapped by residence time

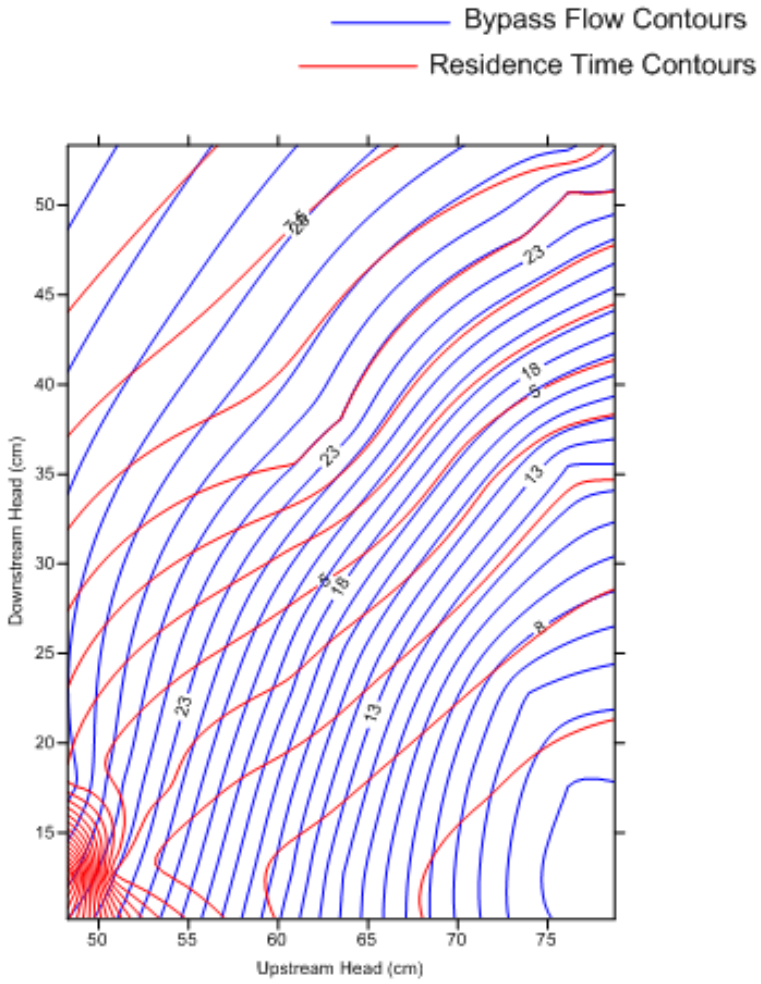

Figure 5.27: Contour plot of predicted percent bypass flow and residence time at BR1

Chapter 6

Conclusion

During 2013, two bioreactors in Central Illinois in the Embarras River Watershed were monitored and evaluated for performance efficiency in reducing nitrate-N loads to surface waters and production of nitrous oxide, methane and carbon dioxide emissions. Water samples were collected biweekly or more frequently during storm events from the inlets and outlets of the bioreactors when the tiles were flowing. Gas samples were collected from each bioreactor at least monthly and more frequently during warmer months. The results of this study revealed bioreactors are an effective means to reducing nitrate-N loads from agricultural fields while producing minimal unintended consequences that would have a deleterious effect on the environment. Since this management practice was not found to be completely devoid of environmental tradeoffs, bioreactors should continue to be monitored for performance efficiency and potential production of greenhouse gas emissions, hydrogen sulfide gas production, biofilm formation and increased phosphorus loading.

N_2O-N represented 1.2% of the total N removed at BR1. Methane fluxes were found to be negligible at BR1 and BR2. Annually, CO_2-C fluxes from BR1 represented 7.7% of total C lost from woodchips meaning this bioreactor could support denitrification for 13 years. Annually, CO_2-C fluxes represented 8.8% of total C lost from the woodchips at BR2 meaning this bioreactor could support denitrification for 11 years.

Phosphorus influent concentrations were consistently higher than effluent concentrations at BR1 and BR2. Solutions to addressing increased phosphorus loading should continue to be studied. Goodwin (2012) explored adding a iron filings chamber to bioreactors to address P loading but more research is needed to determine if such an addition is necessary and if the results would be beneficial.

Bioreactor performance and reduction of potential adverse effects depends on optimal

operation. A balance between residence time and bypass flow is needed to increase nitrate reduction and decrease environmental tradeoffs. Engineers, farmers and scientists should be aware of this balancing act when implementing bioreactors as a management practice and utilize tools like the visual basic tool developed during this study to enhance bioreactor performance. The visual basic interactive module found on the Illinois drainage guide was validated and improved during this study and is now an effective tool for predicting and optimizing bioreactor performance.

This study served as one of few that explored both bioreactor efficacy and greenhouse gas emissions from field scale bioreactors. It is also one of few studies that has documented sulfate reduction and biofilm formation in bioreactors. This study has addressed important concerns regarding potential widespread implementation of bioreactors. Even so, more long-term field studies should be carried out in order to ensure bioreactors are not solving one environmental issue while creating others. Future studies should explore ways to treat operate bioreactors more efficiently to reduce concerns of environmental tradeoffs. Bioreactors are just one management practice that should be utilized in conjunction with others like land and fertilizer management and cover crops to solve pressing environmental concerns.

Chapter 7

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Appendix A

Optimization Analysis Results

Table A.1: Predicted bypass flow and residence time at varying upstream and downstream head settings at BR1

Upstream Head	Downstream Head	Bypass Flow	Residence Time
76.2	12.7	3.4	2.6
78.74	12.7	3.4	2.6
76.2	17.78	4	2.8
78.74	17.78	4	2.8
73.66	10.16	4.5	2.6
73.66	22.86	6.1	3.3
71.12	17.78	6.6	3.1
76.2	35.56	12	4.1
78.74	35.56	12	4.1
63.5	12.7	12.1	3.3
63.5	17.78	13.5	3.6
73.66	35.56	13.9	4.4
60.96	10.16	14.2	3.3
60.96	12.7	14.8	3.4
71.12	35.56	15.9	4.7
60.96	17.78	16	3.8
63.5	25.4	16.2	4.4
60.96	22.86	17.8	4.4
60.96	30.48	21.1	5.4
53.34	17.78	23.2	4.7
60.96	35.56	24	6.5
63.5	38.1	24	6.5
73.66	48.26	24	6.5
76.2	50.8	24	6.5
78.74	50.8	24	6.5
50.8	12.7	24.1	4.4
50.8	17.78	25.5	5
76.2	53.34	26.2	7.3
48.26	12.7	26.4	13.1
48.26	17.78	28.6	5.4

Table A.2: Continued predicted bypass flow and residence time at varying upstream and downstream head settings at BR1

Upstream Head	Downstream Head	Bypass Flow	Residence Time
50.8	25.4	29.3	6.5
50.8	25.4	29.3	6.5
48.26	22.86	30.8	6.5
71.12	53.34	32.3	9.3
53.34	35.56	33.7	9.3
50.8	35.56	36.8	10.9
38.1	12.7	37.3	6.5
60.96	48.26	38.1	13.1
60.96	48.26	38.1	13.1
63.5	50.8	38.1	13.1
73.66	60.96	38.1	4.7
76.2	63.5	38.1	13.1
38.1	17.78	39	8.2
50.8	38.1	39.2	13.1
50.8	38.1	39.2	13.1
78.74	53.34	39.9	6.5
48.26	35.56	40.7	13.1
63.5	53.34	43	16.3
35.56	17.78	44	9.3
38.1	25.4	47.3	13.1
30.48	12.7	48.7	9.3
30.48	17.78	53.9	13.1
25.4	12.7	60.1	13.1
76.2	71.12	60.1	32.7
38.1	35.56	65.4	75.2
25.4	17.78	68.1	21.8

Appendix B

Visual Basic Simulation Results

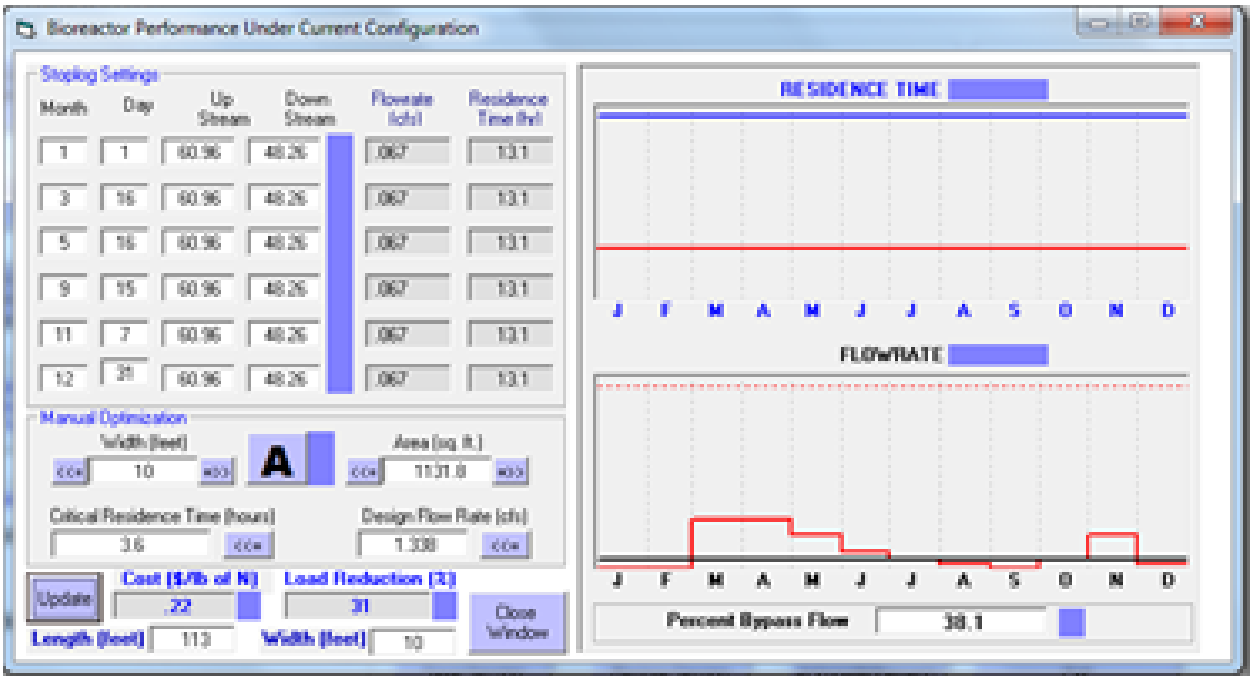

Figure B.1: Predicted bypass flow, flow rate and residence time at BR1 given 60.96 cm inlet head and 48.26 cm outlet head

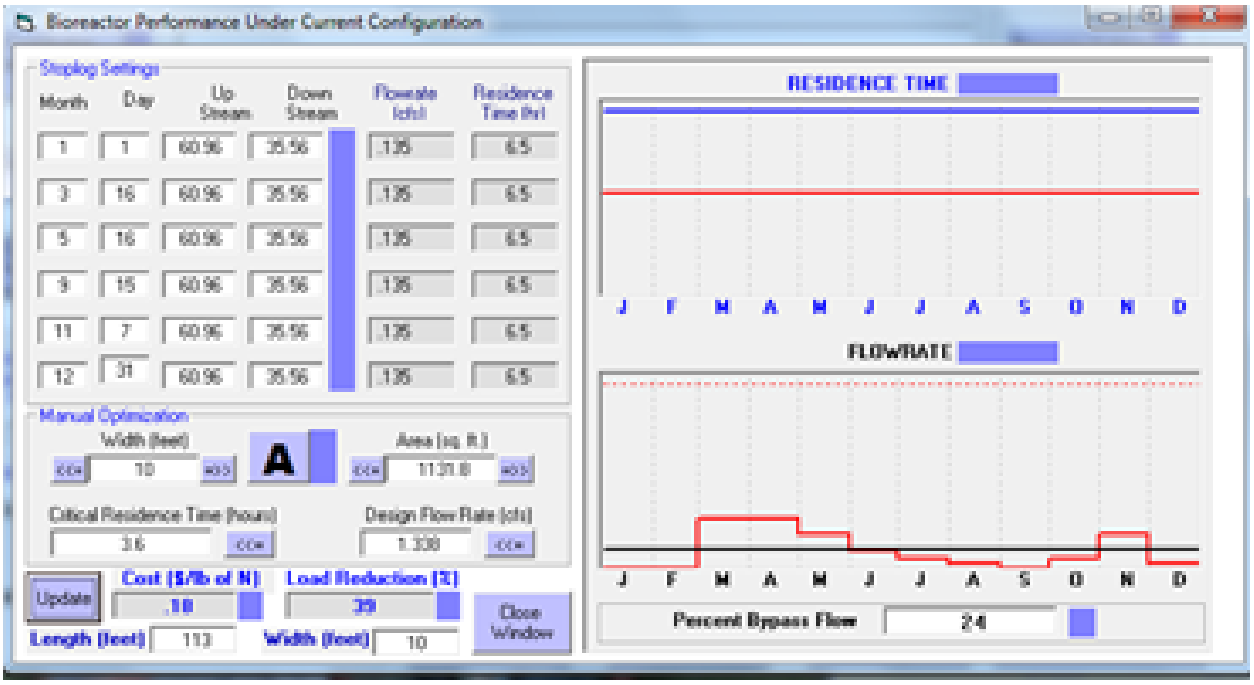

Figure B.2: Predicted bypass flow, flow rate and residence time at BR1 given 60.96 cm inlet head and 35.56 cm outlet head

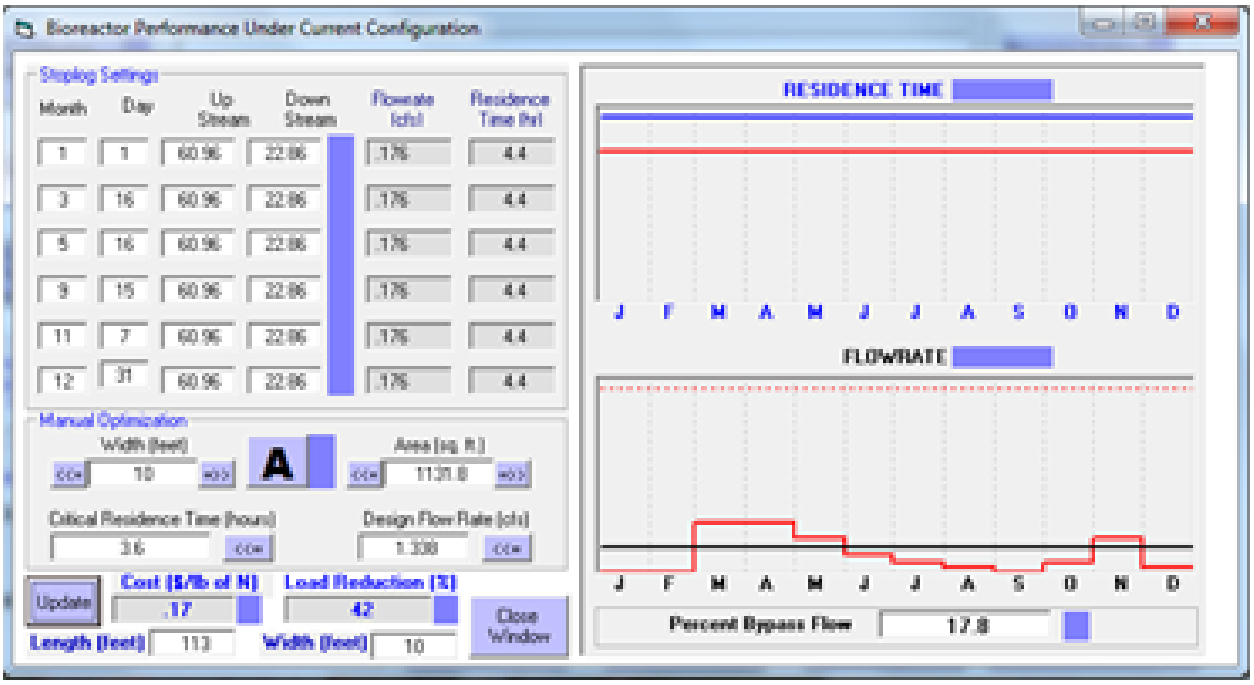

Figure B.3: Predicted bypass flow, flow rate and residence time at BR1 given 60.96 cm inlet head and 22.86 cm outlet head

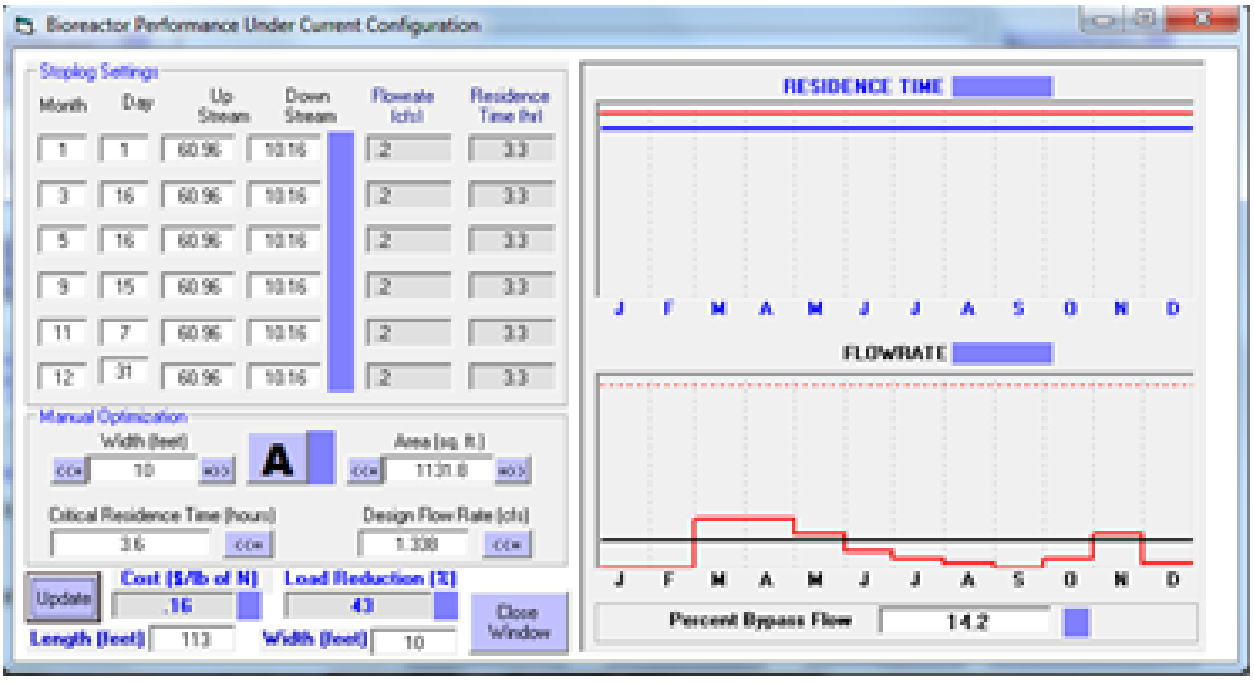

Figure B.4: Predicted bypass flow, flow rate and residence time at BR1 given 60.96 cm inlet head and 10.16 cm outlet head

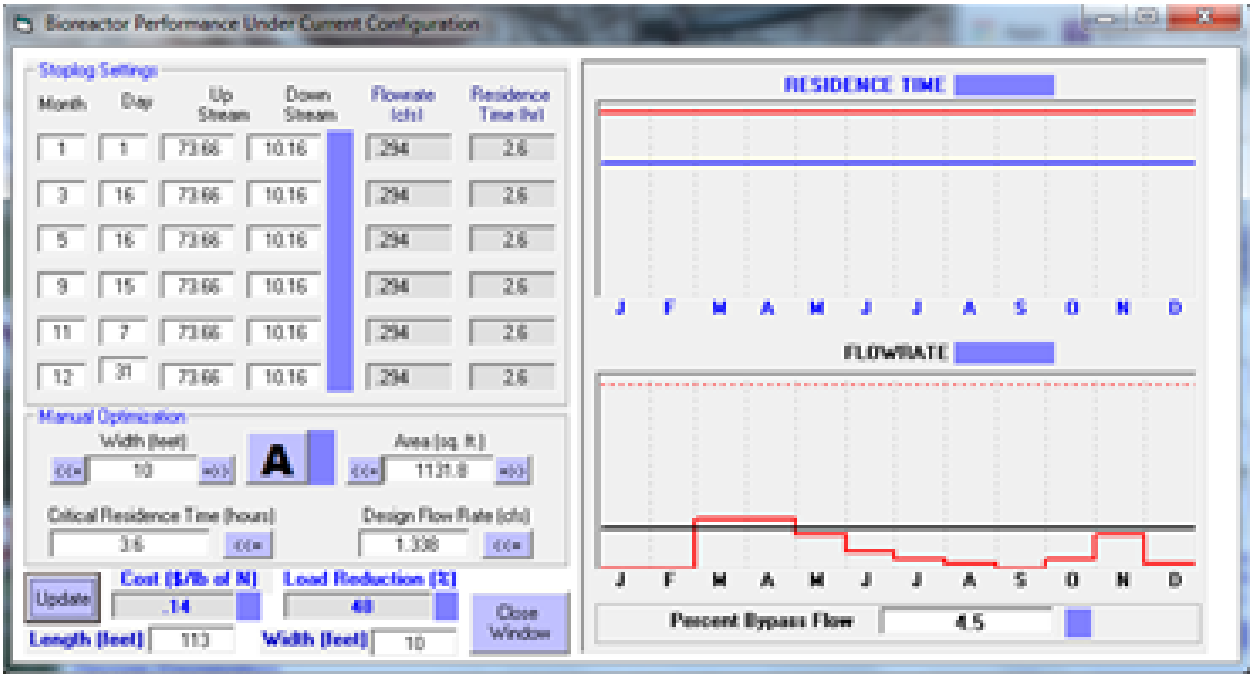

Figure B.5: Predicted bypass flow, flow rate and residence time at BR1 given 73.66 cm inlet head and 10.16 cm outlet head

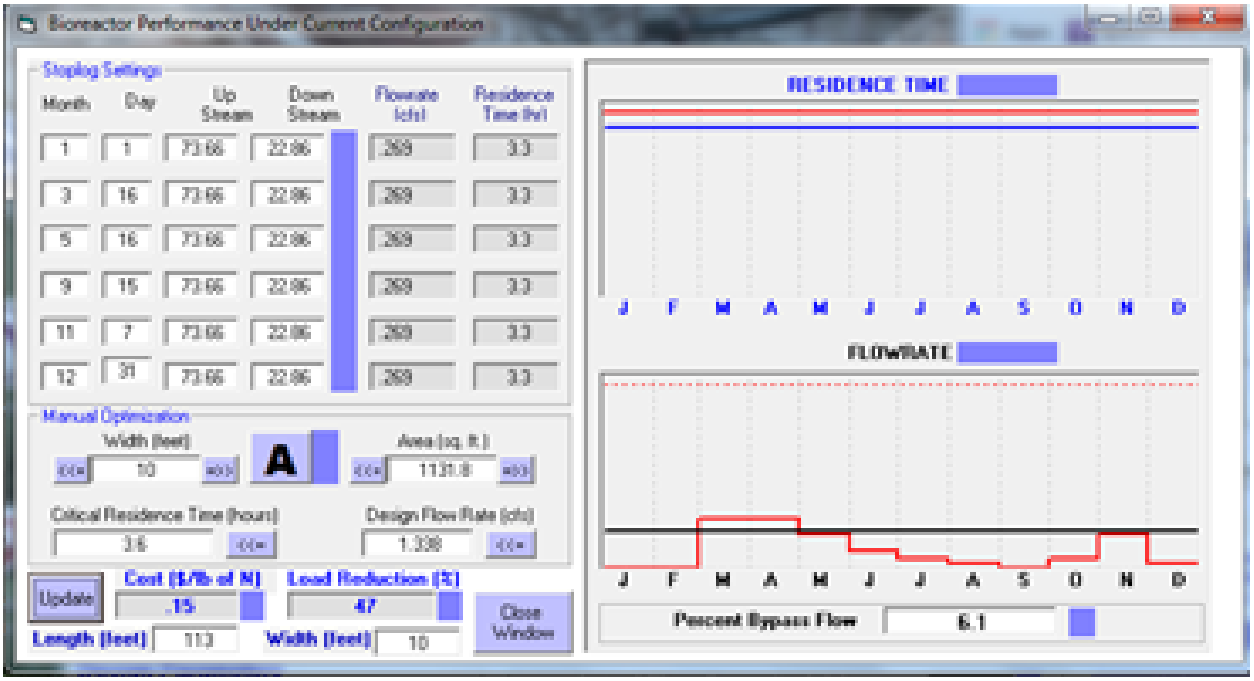

Figure B.6: Predicted bypass flow, flow rate and residence time at BR1 given 73.66 cm inlet head and 22.86 cm outlet head

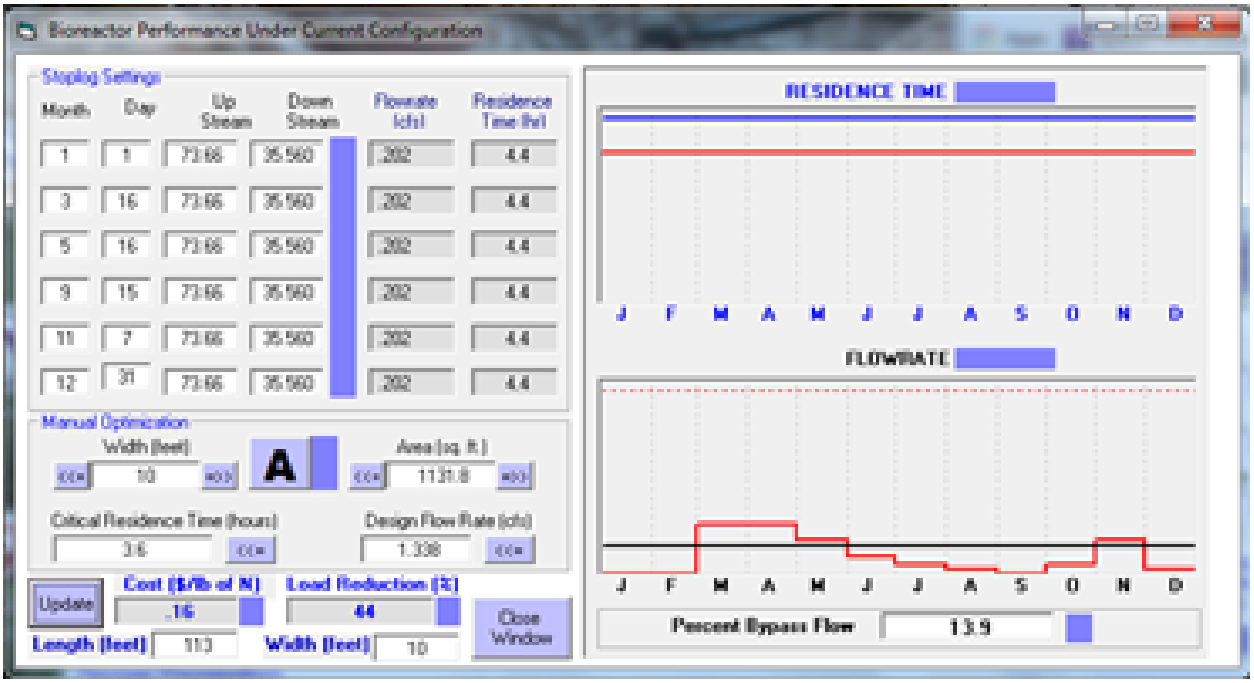

Figure B.7: Predicted bypass flow, flow rate and residence time at BR1 given 73.66 cm inlet head and 35.56 cm outlet head

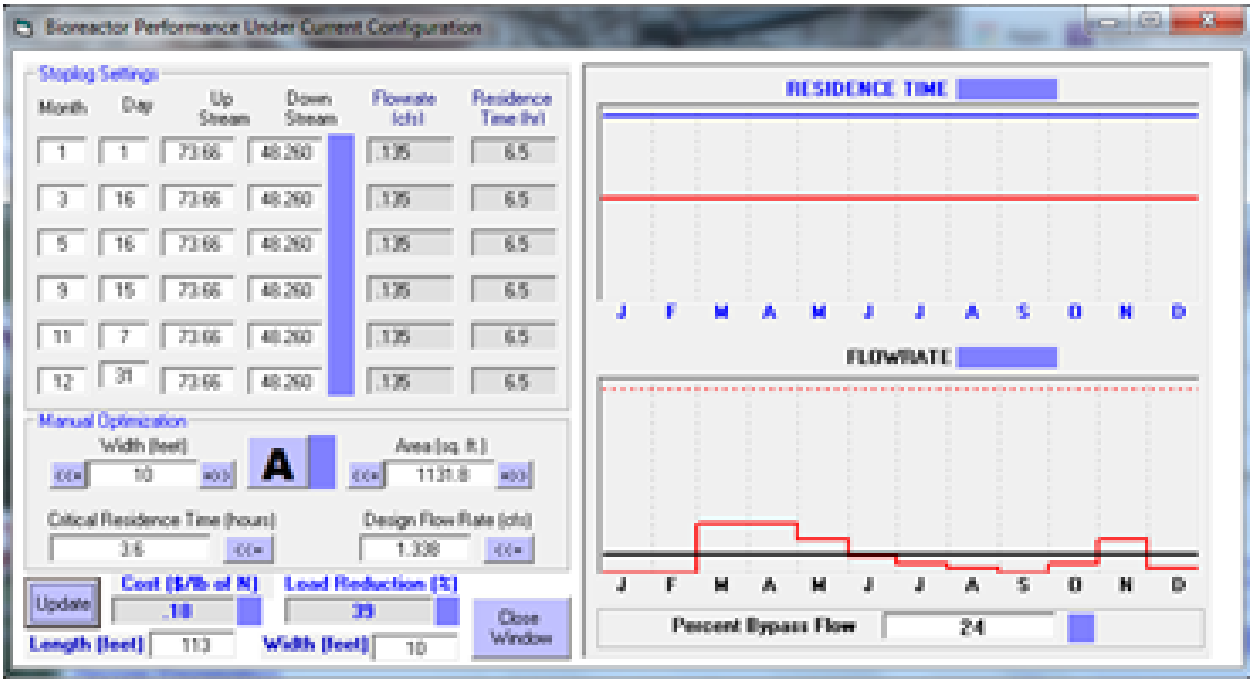

Figure B.8: Predicted bypass flow, flow rate and residence time at BR1 given 73.66 cm inlet head and 48.26 cm outlet head

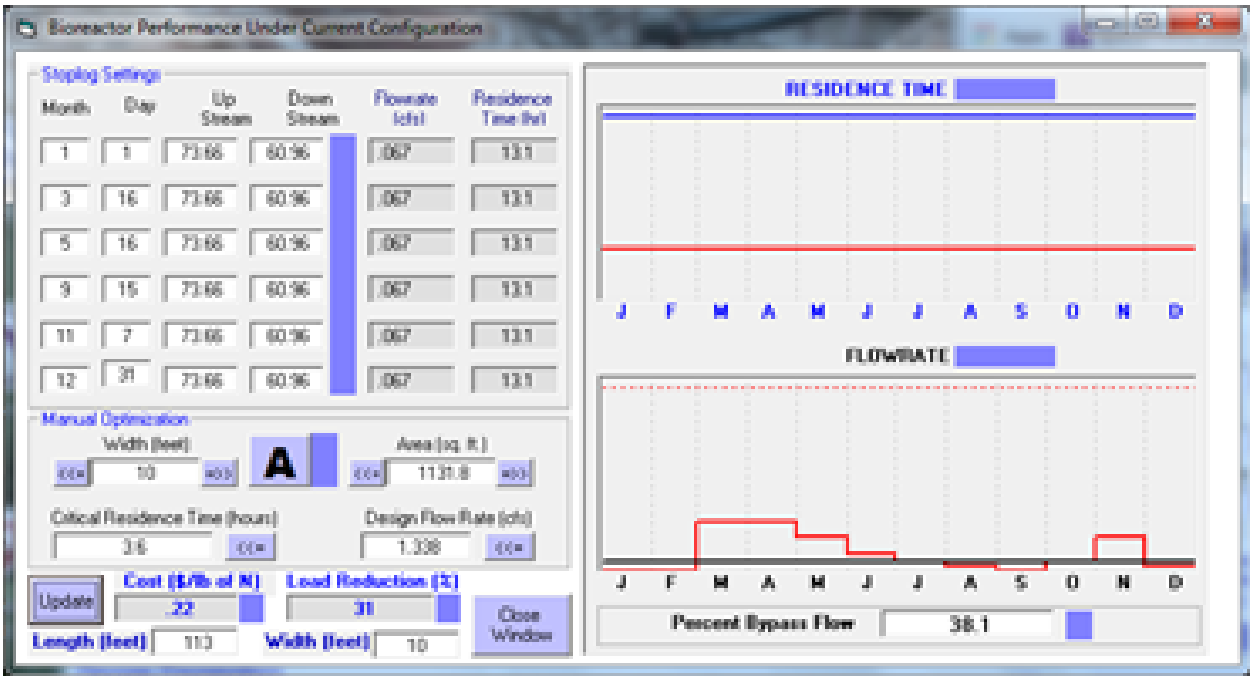

Figure B.9: Predicted bypass flow, flow rate and residence time at BR1 given 73.66 cm inlet head and 60.96 cm outlet head

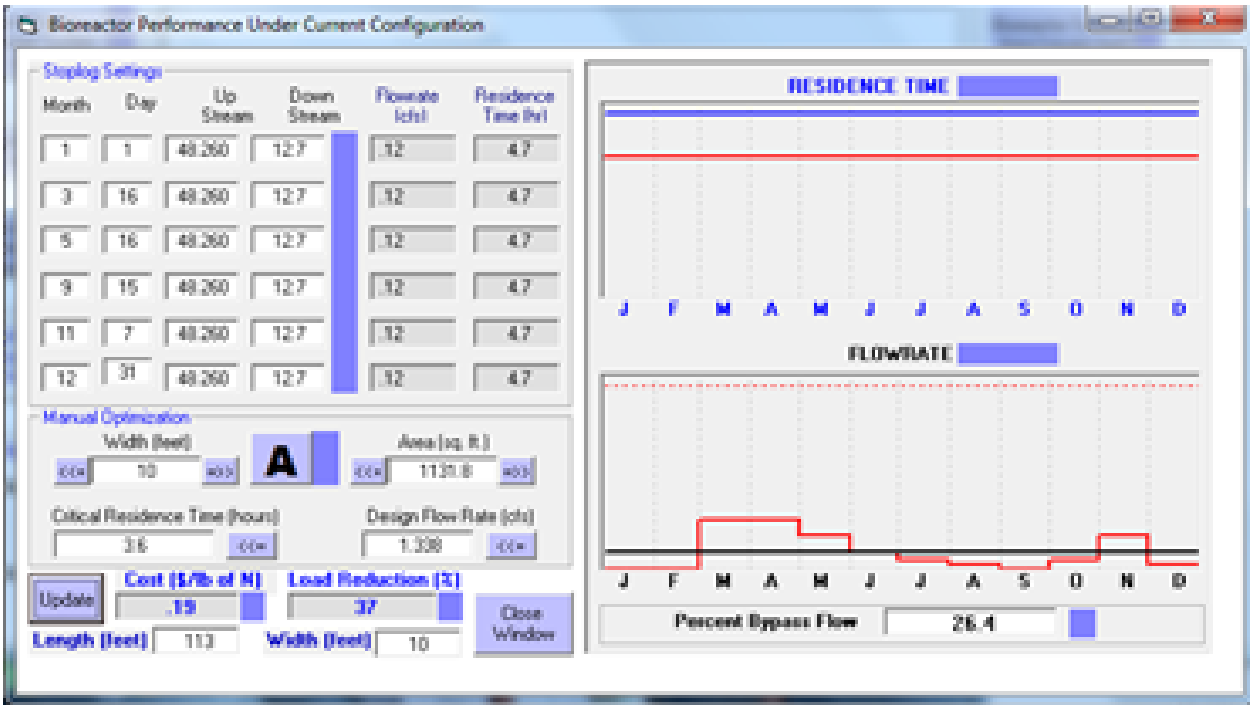

Figure B.10: Predicted bypass flow, flow rate and residence time at BR1 given 48.26 cm inlet head and 12.7 cm outlet head

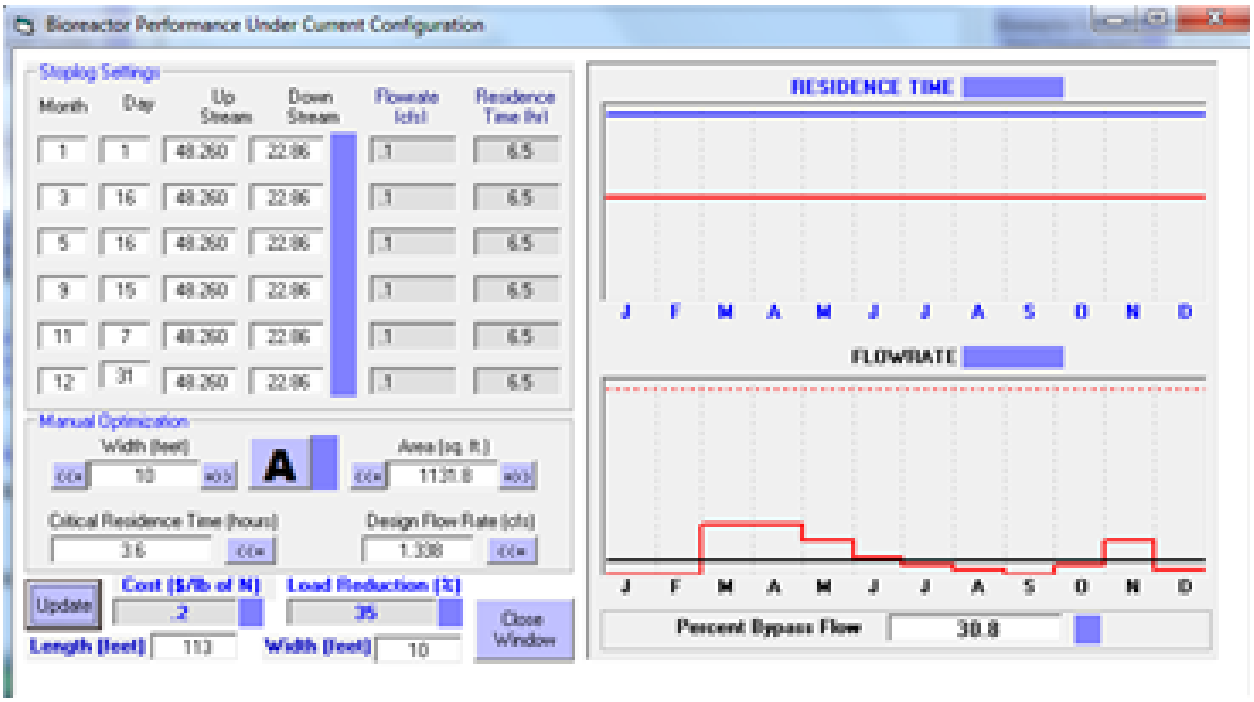

Figure B.11: Predicted bypass flow, flow rate and residence time at BR1 given 48.26 cm inlet head and 22.86 cm outlet head

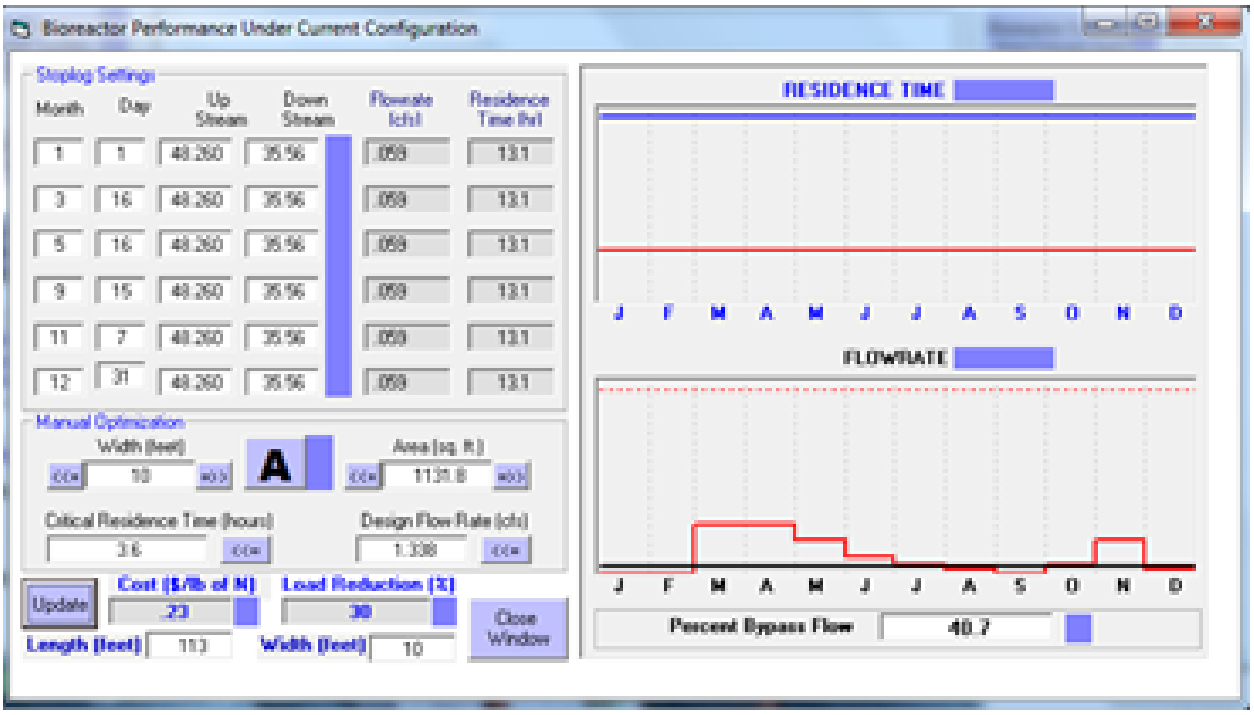

Figure B.12: Predicted bypass flow, flow rate and residence time at BR1 given 48.26 cm inlet head and 35.56 cm outlet head

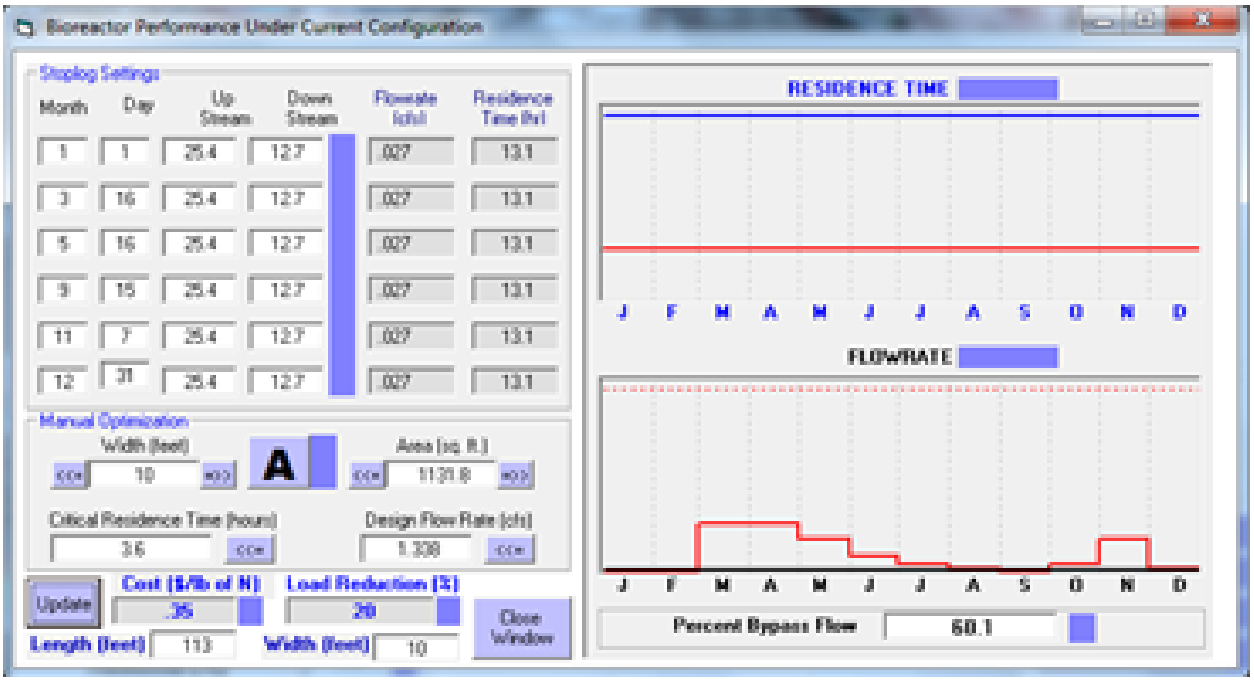

Figure B.13: Predicted bypass flow, flow rate and residence time at BR1 given 25.4 cm inlet head and 12.7 cm outlet head

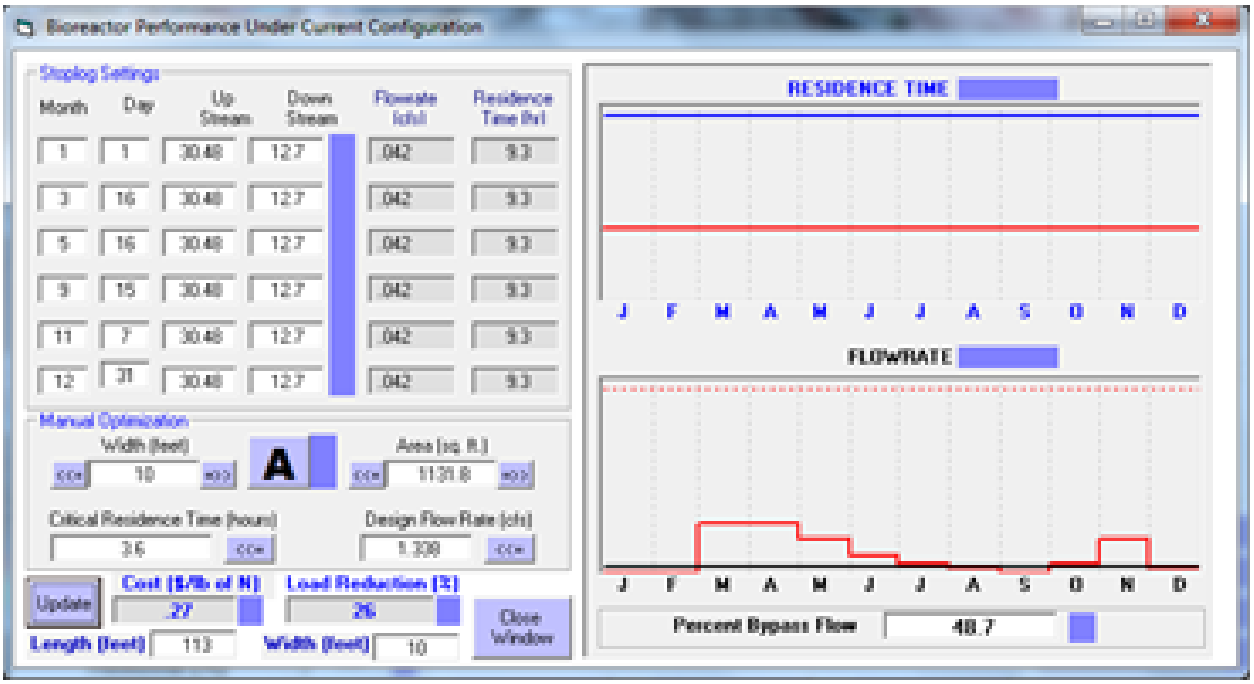

Figure B.14: Predicted bypass flow, flow rate and residence time at BR1 given 30.48 cm inlet head and 12.7 cm outlet head

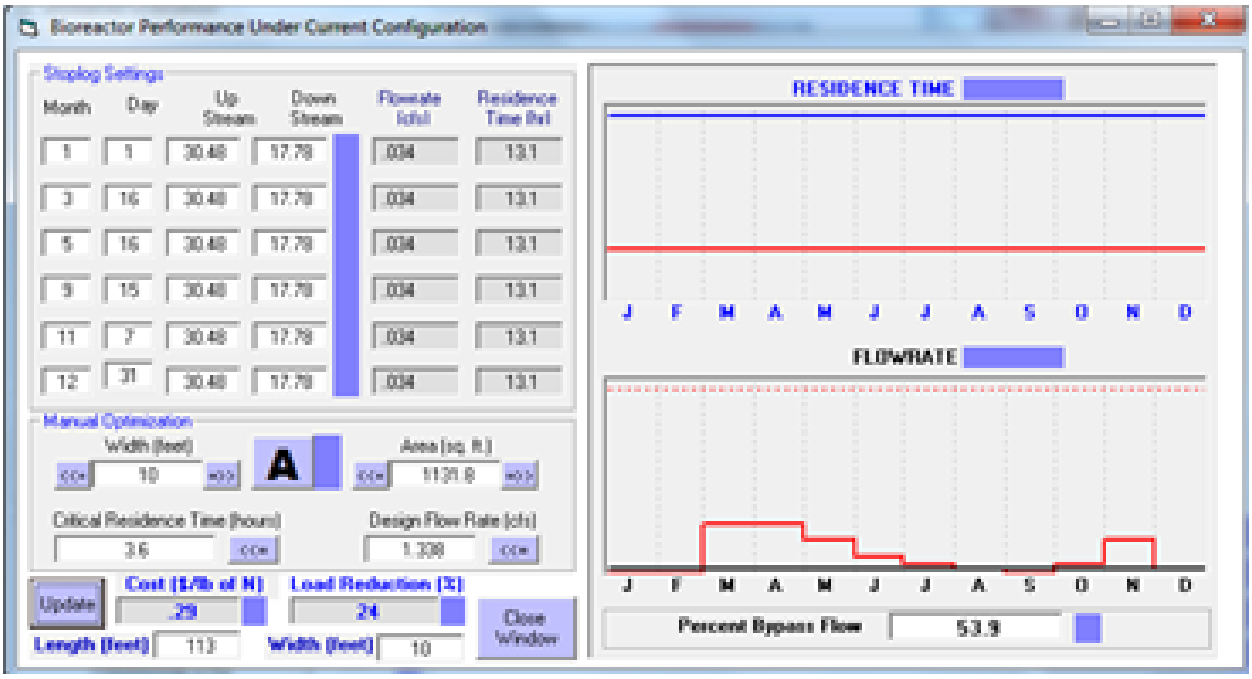

Figure B.15: Predicted bypass flow, flow rate and residence time at BR1 given 30.48 cm inlet head and 17.78 cm outlet head

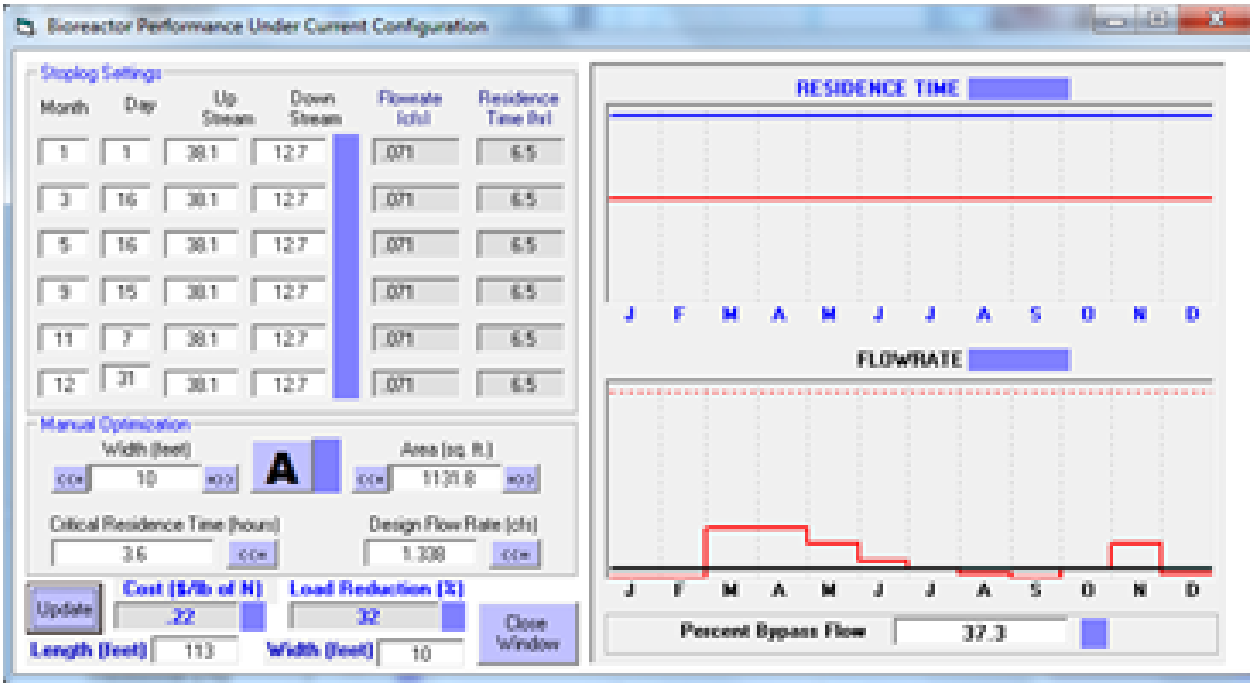

Figure B.16: Predicted bypass flow, flow rate and residence time at BR1 given 38.1 cm inlet head and 12.7 cm outlet head

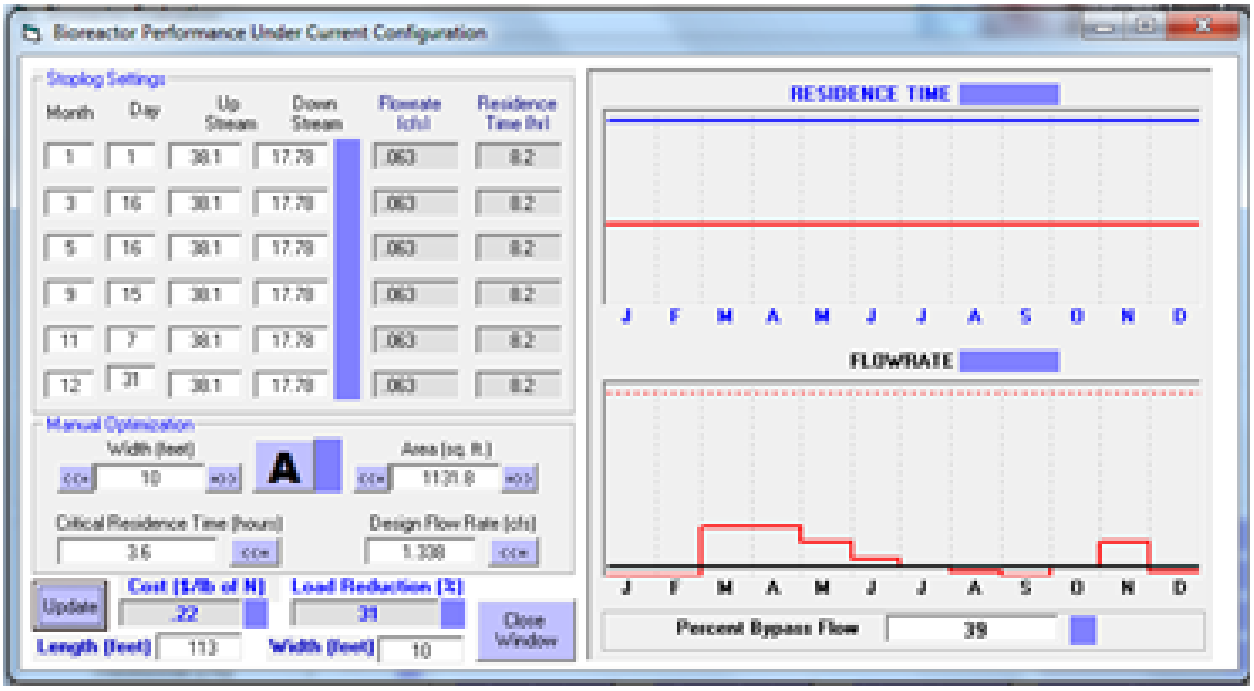

Figure B.17: Predicted bypass flow, flow rate and residence time at BR1 given 38.1 cm inlet head and 17.78 cm outlet head

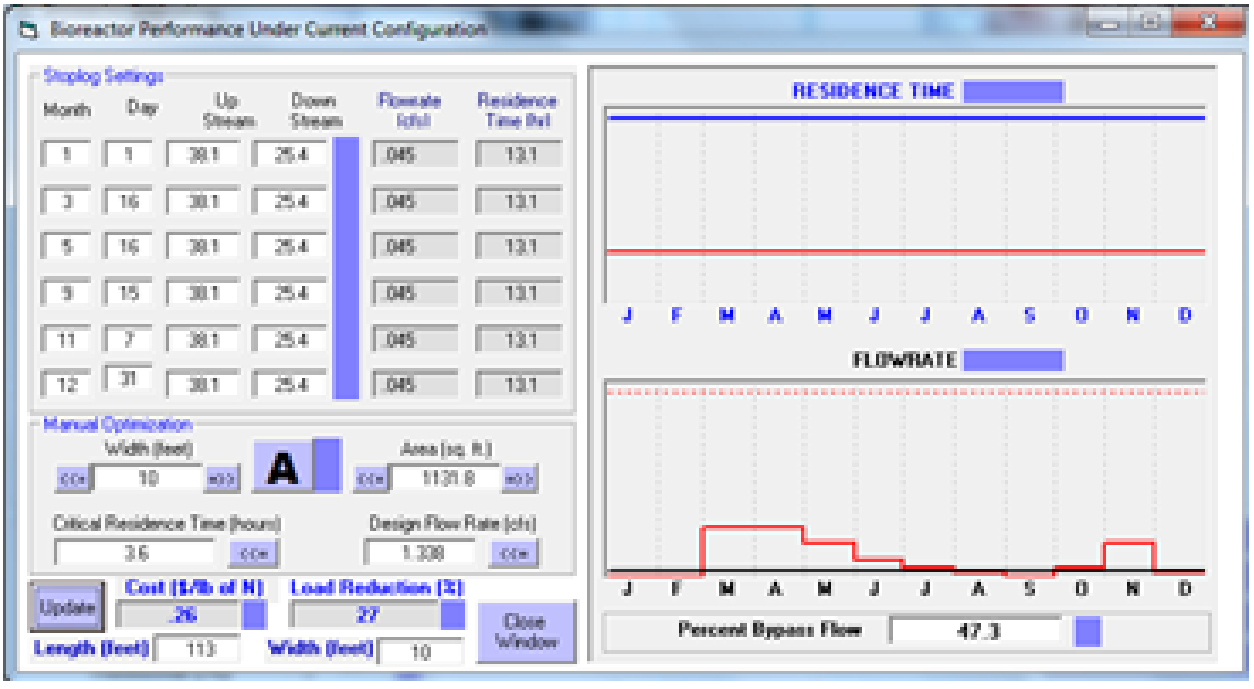

Figure B.18: Predicted bypass flow, flow rate and residence time at BR1 given 38.1 cm inlet head and 25.4 cm outlet head

Appendix C

Statistical Analysis Results

Table C.1: Paired t-test for BR1 Influent and Effluent Ammonium sample means

BR1 Ammonium Inluent and Effluent		
t-Test: Paired Two Sample for Means		
	Variable 1	*Variable 2*
Mean	0.022036721	0.126276721
Variance	0.000915213	0.026645098
Observations	61	61
Pearson Correlation	0.013342005	
Hypothesized Mean Difference	0	
df	60	
t Stat	-4.915842679	
P(T<=t) one-tail	3.59371E-06	
t Critical one-tail	1.670648865	
P(T<=t) two-tail	7.18742E-06	
t Critical two-tail	2.000297822	

Table C.2: Paired t-test for BR2 Influent and Effluent Ammonium sample means

BR2 Ammonium Inluent and Effluent		
t-Test: Paired Two Sample for Means		
	Variable 1	*Variable 2*
Mean	0.015212	0.104594
Variance	0.000169	0.022496915
Observations	15	15
Pearson Correlation	0.200190541	
Hypothesized Mean Difference	0	
df	14	
t Stat	-2.340023314	
P(T<=t) one-tail	0.017307558	
t Critical one-tail	1.761310136	
P(T<=t) two-tail	0.034615117	
t Critical two-tail	2.144786688	

Table C.3: BR1 Regression of Removal Rate and Retention Time

SUMMARY OUTPUT					
Regression Statistics					
Multiple R	0.112694041				
R Square	0.012699947				
Adjusted R Square	-0.014725055				
Standard Error	13.12490445				
Observations	38				
ANOVA					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	79.77146066	79.77146	0.463079167	0.500541916
Residual	36	6201.472201	172.2631		
Total	37	6281.243662			

Table C.4: BR2 Regression of Removal Rate and Retention Time

SUMMARY OUTPUT					
Regression Statistics					
Multiple R	0.104119474				
R Square	0.010840865				
Adjusted R Square	-0.071589063				
Standard Error	40.69589647				
Observations	14				
ANOVA					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	217.8112	217.8112	0.131516	0.723172172
Residual	12	19873.87	1656.156		
Total	13	20091.68			

Table C.5: Two-Sample F-Test for Nitrate Load Reduction between BR1 and BR2

Nitrate Load Reduction BR1 and BR2		
F-Test Two-Sample for Variances		
	Variable 1	*Variable 2*
Mean	18.65852053	42.49432
Variance	401.5844984	2169.099
Observations	38	14
df	37	13
F	0.185138843	
P(F<=f) one-tail	2.50402E-05	
F Critical one-tail	0.501197649	