6-2008

Bioretention Systems for Control of Non-Point Sources of Nitrogen

Ryan L. Siegel

University of Massachusetts - Amherst

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BIORETENTION SYSTEMS FOR CONTROL OF NON-POINT SOURCES OF NITROGEN

A Master of Science Project Report

by

Ryan L. Siegel

Department of Civil and Environmental Engineering
University of Massachusetts Amherst
Amherst, MA 01003

MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING

JUNE 2008

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Approved as to style and content by:

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Dr. Sarina J. Ergas, Chair

_____

Dr. Chul Park, Member

_____

Dr. John E. Tobiason
Graduate Program Director, MSEVE
Civil and Environmental Engineering

ACKNOWLEDGMENTS

ABSTRACT

BIORETENTION SYSTEMS FOR CONTROL OF NON-POINT SOURCES OF NITROGEN

JUNE 2008

RYAN L. SIEGEL, B.S., UNIVERSITY OF MASSACHUSETTS, AMHERST

M.S., UNIVERSITY OF MASSACHUSETTS, AMHERST

Directed by: Dr. Sarina J. Ergas

Environmental protection programs have successfully improved water quality over the past few decades through the control of point sources of nitrogen. However, control of non-point sources of nitrogen, such as atmospheric deposition, leaking septic systems, runoff and agricultural runoff, has lagged. There is unanimous agreement that arresting nitrogen influxes into aquatic ecosystems is essential to control eutrophication. Protecting drinking water sources from elevated levels of nitrate and nitrite nitrogen from non-point sources is also necessary to protect public health. Elevated levels of nitrate and nitrite in drinking water are known to cause methemoglobinemia (blue-baby syndrome) in infants.

The overall objective of this research project was to develop a robust and efficient bioretention system to control non-point sources of nitrogen. Two pilot-scale denitrifying bioretention systems were investigated, one was configured for autotrophic denitrification (S:OS unit) and the other was configured for heterotrophic denitrification (Denyte unit). The experimental program tested the performance of the bioretention

units under both laboratory and field conditions. A synthetic stormwater, intended to mimic nitrogen levels in runoff from agricultural croplands, was utilized as the influent during laboratory testing. Water from a waste treatment lagoon located at a dairy farm in Northeastern CT was used as the influent during field testing.

Laboratory testing resulted in an average of 63% (S:OS) and 93% (Denyte) TP removal, 92% and 88% TN removal, 80% and 88% NH_4^+ removal and >95% (S:OS and Denyte) NO_3^- removal. Typical field results showed an average of 68% (S:OS) and 62% (Denyte) TP removal, 55% and 42% TN removal, , 88% and 73% TSS removal, 89% and 75% VSS removal, 43% and 35% COD removal, and 65% and 34% BOD_5 removal. Breakdown of particulate organic N and ammonification appeared to limit the extent to which TN removal could be achieved during the field testing of the bioretention units.

The results of this research project demonstrate that bioretention units can be used to achieve nitrogen removal from stormwater runoff. However, the characteristics of the stormwater runoff will dictate the performance of the bioretention units. Laboratory results showed that bioretention units can achieve excellent TN removal from runoff that is characteristic of agricultural croplands. Field results showed that the treatment of high strength runoff from dairy farm waste treatment lagoons was challenging for the bioretention units. Comparison of results revealed that the Denyte unit performed better than the S:OS unit.

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CHAPTER 1:   INTRODUCTION

Environmental protection programs have successfully improved water quality over the past few decades through point source pollution control. However, aquatic ecosystems remain impaired, primarily due to the complex pollution problems caused by non-point sources of pollution (USEPA, July 2003). Non-point source pollution, unlike point sources of pollution such as industrial and sewage treatment plants, comes from many diffuse sources (USEPA, March 2005) including atmospheric deposition, leaking septic systems, urban runoff and agricultural runoff.

In 1998, approximately 32% of U.S. surface waters were assessed for water quality (USEPA, 2000). Of the waters assessed, approximately 40% of U.S. streams, lakes and estuaries were not clean enough to support uses such as fishing and swimming. Non-point sources of pollution were the most prevalent cause for impairment of the evaluated waters. Sediment, bacteria, nutrients and metals were found to be the leading pollutants, while runoff from agricultural lands and urban areas were the primary sources of these pollutants. Runoff from agricultural land occurs when water from precipitation and/or snowmelt travels across the land and/or building surfaces and is conveyed to nearby surface waters. Runoff can also be incorporated into groundwater through the process of infiltration. Pollutants are often integrated into agricultural runoff, which becomes a non-point source of pollution.

Nutrients, animal wastes, sediment, salts and pesticides are the primary pollutants associated with agricultural runoff (USEPA, January 1993). Nitrogen and phosphorus

are the two major nutrients often transported with agricultural runoff. Sources of nitrogen and phosphorus in agricultural runoff include commercial fertilizers, animal wastes, crop residues and atmospheric deposition. The term animal waste includes manure, urine, process waters, feed and bedding materials. Agricultural runoff can be polluted by coming into contact with one or more of the animal waste components. Sediment is incorporated into agricultural runoff due to the process of erosion. The presence of salts in agricultural runoff is due to the natural weathering process of soil and geologic material. Agricultural runoff can also transport pesticides (and their by-products), which are widely used to control plant pests and improve plant production (USEPA, 1993).

The focus of this project is the control of nitrogen in agricultural runoff, which is a concern due to its contributions to eutrophication. Nitrogen can also be a public health concern if incorporated into a drinking water supply. Elevated levels of nitrogen in the form of nitrate and/or nitrite in drinking waters are known to cause methemoglobinemia in infants (USEPA, July 2003). Eutrophication occurs when nutrients are introduced at higher than background levels into an aquatic environment, resulting in a dramatic increase in aquatic plant growth. Eutrophication degrades water quality due to excessive plant growth and depletes aquatic life. The adverse effects that agricultural runoff can have are difficult to minimize through treatment of the runoff due to its non-point source characteristics. However, proper management along with stormwater runoff control and treatment technologies can help diminish the extent of non-point source pollution from agricultural sources.

Reducing the load of a certain pollutant at its source is one method of proper

management that can reduce the effects of non-point source pollution. For example, a

farmer can create a nutrient management plan that specifies the proper amount of

fertilizer to apply to a crop to meet the nutrient needs of that crop. This can reduce the

nutrient load in runoff that occurs from excess fertilization of cropland. Management by

itself can not completely address the problems of agricultural runoff. Control of

stormwater runoff along with treatment technologies, often called best management

practices (BMPs), is sometimes necessary when management alone cannot reduce the

non-point source pollution to an acceptable level. BMPs are often site specific

technologies, meaning that one BMP might work well at one site but might not be the

best option at a different site. The following are some BMPs that can be used by

agricultural operations to diminish their contributions to non-point source pollution:

- Sedimentation Basins;

- Treatment Lagoons and Storage Ponds;

- Constructed Wetlands;

- Vegetative Filter Strips; and

- Bioretention Systems (proposed in this research).

Selection of the proper BMP for a certain site can depend on many factors such as

treatment goals, land availability, cost and cost effectiveness of the BMP. In order to

reduce non-point source pollution, appropriate BMPs need to be available to treat a wide

variety of pollutants under a wide variety of conditions. BMPs have proven to be

effective at treating a wide variety of stormwater pollutants. However, little information is available on the performance and optimization of stormwater BMPs for the control of nitrogen.

1.1 Research Objectives

The overall objective of this research project was to develop a robust and efficient bioretention system to control non-point sources of nitrogen. Specific objectives include:

- Design and construction of bioretention systems to achieve total nitrogen removal;

- Acclimate system for optimal performance; and

- Evaluate the bioretention systems operation and performance under both controlled laboratory and field conditions.

1.2 Scope of Work

Two pilot-scale denitrifying bioretention systems were designed to include; a ponding region, a mulch region, a top soil region, a nitrification region and a denitrification region, as shown in Figure 1.1. The only difference between the two bioretention systems was their denitrification region. One was used to carry out autotrophic denitrification by supplying the denitrification region with an inorganic electron donor while the other was used to carry out heterotrophic denitrification by supplying the denitrification region with an organic electron donor. The evaluation of the operation and performance of the two bioretention systems was carried out in a three phase experimental program. The objective of Phase I was to design, construct and acclimate

the two bioretention systems. In Phase II, the bioretention systems were set-up in the

laboratory and evaluated under controlled conditions using a synthetic stormwater as the

influent, intended to mimic nitrogen levels contained in runoff from agricultural

croplands. The objective of Phase III was to investigate the performance of the

bioretention systems under field conditions. Water from a waste treatment lagoon at a

dairy farm in Northeastern CT was used as the influent during Phase III.
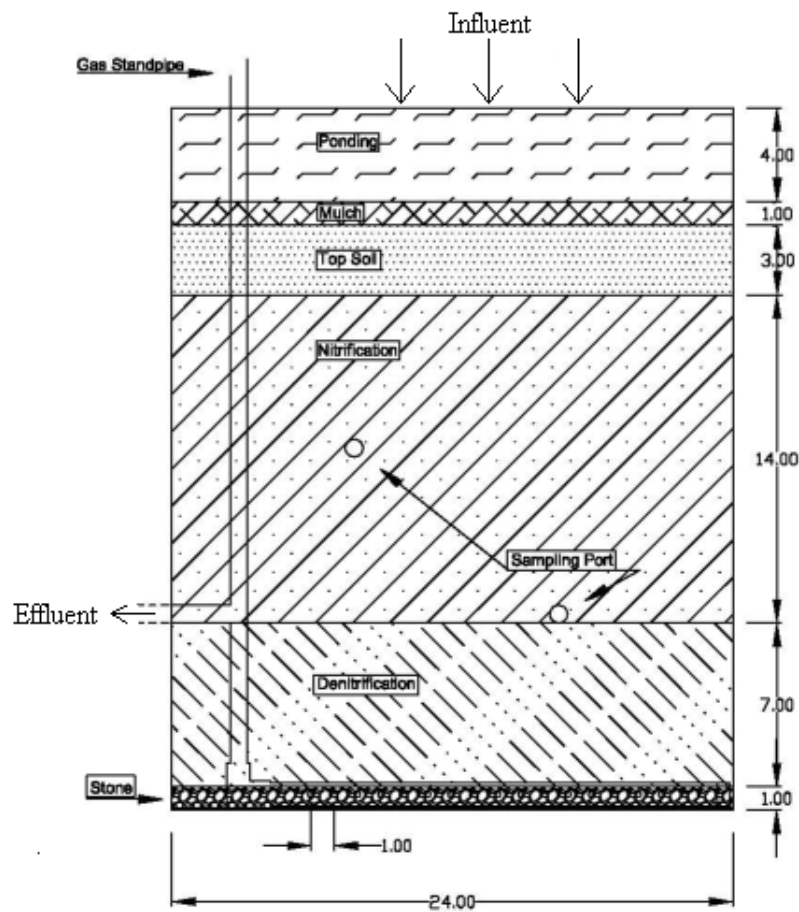
Figure 1.1: Bioretention System Schematic
(dimensions in inches)

Throughout this research project, the evaluation of the two bioretention units was

conducted through laboratory analysis of influent and effluent samples. The performance

of the two bioretention units was based on their ability to treat various pollutants

including nutrients (N & P), organic matter, sediment and metals. However, the major

pollutant of concern was nitrogen since the overall goal of the bioretention units was

nitrogen removal.

CHAPTER 2:   LITERATURE REVIEW

This literature review begins with an overview of the health and environmental impacts of excess nitrogen inputs into aquatic environments. The components of the nitrogen cycle related to this research project are discussed in detail. The sources and concerns of the primary pollutants associated with agricultural runoff are discussed. Agricultural runoff treatment technologies that are deployed to reduce the non-point source pollution from agricultural runoff are presented.

2.1   Health and Environmental Impacts of Excess Nitrogen

Although nitrogen is an essential element for plants, animals and microorganisms it can have detrimental affects on human health. Elevated levels of nitrogen in the form of nitrate (NO_3^-) and/or nitrite (NO_2^-) in drinking waters are known to cause methemoglobinemia (also known as blue baby syndrome) in infants. When NO_3^- is consumed it can be microbially reduced to NO_2^- within the human body which in turn can transform the oxygen binding hemoglobin into non-oxygen binding methemoglobin (Fewtrell, 2004). Elevated levels of methemoglobin lead to insufficient levels of oxygen in the bloodstream. To protect human health, the United States Environmental Protection Agency (USEPA) has set the drinking water maximum contaminant level (MCL) at 10 mg/L and 1mg/L (as nitrogen) for NO_3^- and NO_2^-, respectively.

Along with human health concerns, the influx of various forms of nitrogen can also have detrimental affects on aquatic ecosystems. A decrease in dissolved oxygen (DO) concentrations, fish toxicity and eutrophication are all water quality concerns associated

with nitrogen (Metcalf and Eddy, 2003). When nitrogen in the form of ammonium (NH_4^+) enters aquatic ecosystems, the DO concentration can be depleted due to the oxygen demanded when NH_4^+ is converted to NO_3^- through the process of nitrification. Dissolved NH_4^+ can also be toxic to fish, especially trout, at concentrations above 0.2 mg/L (USEPA, 2003). In aquatic environments, nutrient availability (i.e. nitrogen and phosphorus) usually limits plant growth. When nutrients are introduced into a stream, lake, or estuary at elevated levels, aquatic plant production may increase dramatically. This process is known as eutrophication. Increasing the amount of aquatic plants increases the amount of organic matter in the ecosystem, which eventually dies and decays. This decaying organic matter produces unpleasant odors and depletes the oxygen supply required by aquatic life. Besides the affect on aquatic life, excess plant growth can also interfere with recreational activities normally supported prior to the eutrophic conditions of the aquatic ecosystem such as swimming (USEPA, 1993).

An important detail related to eutrophication is that generally phosphorus availability is the limiting factor for plant growth in freshwater ecosystems. The limiting factor for plant growth in marine ecosystems is generally nitrogen (USEPA, 2003). In freshwater ecosystems, nitrogen fixing blue-green algae have the ability to obtain their required nitrogen by fixing nitrogen gas dissolved in water (WEF, 1998). This implies that fixed forms of nitrogen available in freshwater systems do not limit the growth of these bacteria. Therefore, any excess phosphorus that enters the freshwater ecosystem can cause an increase in plant and algae growth and lead to eutrophic conditions. Nitrogen is the limiting nutrient in marine ecosystems because phosphate is generally present in

abundance and blue-green algae do not grow in saline environments (WEF, 1998). Therefore, plant growth is generally limited by the available nitrogen in marine ecosystems.

Many authorities believe that controlling phosphorus inputs into freshwater aquatic ecosystems alone can control the problem of eutrophication. However, some studies have shown that during the summer months algal growth can be limited by inorganic nitrogen levels (ammonia and nitrate) (WEF, 1998). Therefore, nitrogen control in freshwater systems under these circumstances, as well as in estuarine ecosystems, is necessary to avoid eutrophic conditions. The control of both ammonia-nitrogen and nitrate-nitrogen is necessary to reduce eutrophication.

2.2   The Nitrogen Cycle

Nitrogen comes in various forms and is an essential element for the survival of plants, animals and microorganisms. The forms of nitrogen important to aquatic ecosystems include nitrogen gas (N_2), ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-) and organic nitrogen (Org N). The oxidation state of NH_4^+, most Org N, N_2, NO_2^-, and NO_3^- is -3, -3, 0, +3, and +5, respectively (WEF, 1998; Metcalf and Eddy, 2003). N_2 is the most abundant gas in our atmosphere and accounts for 78% (by volume) of the air we breathe (Davis and Masten, 2004). However, nitrogen in the form of N_2 is not available for use by plants, animals and most microorganisms. In order for plants, animals and microorganisms to be able to utilize nitrogen, N_2 must be converted to a more chemically

available form such as NH_4^+, NO_3^- or Org N (Harrison, 2003). Therefore, the cycling of

N_2 is an essential process that is necessary to maintain life. Figure 2.1 shows the

nitrogen cycle and the various transformation pathways that take place between the

different forms of nitrogen.
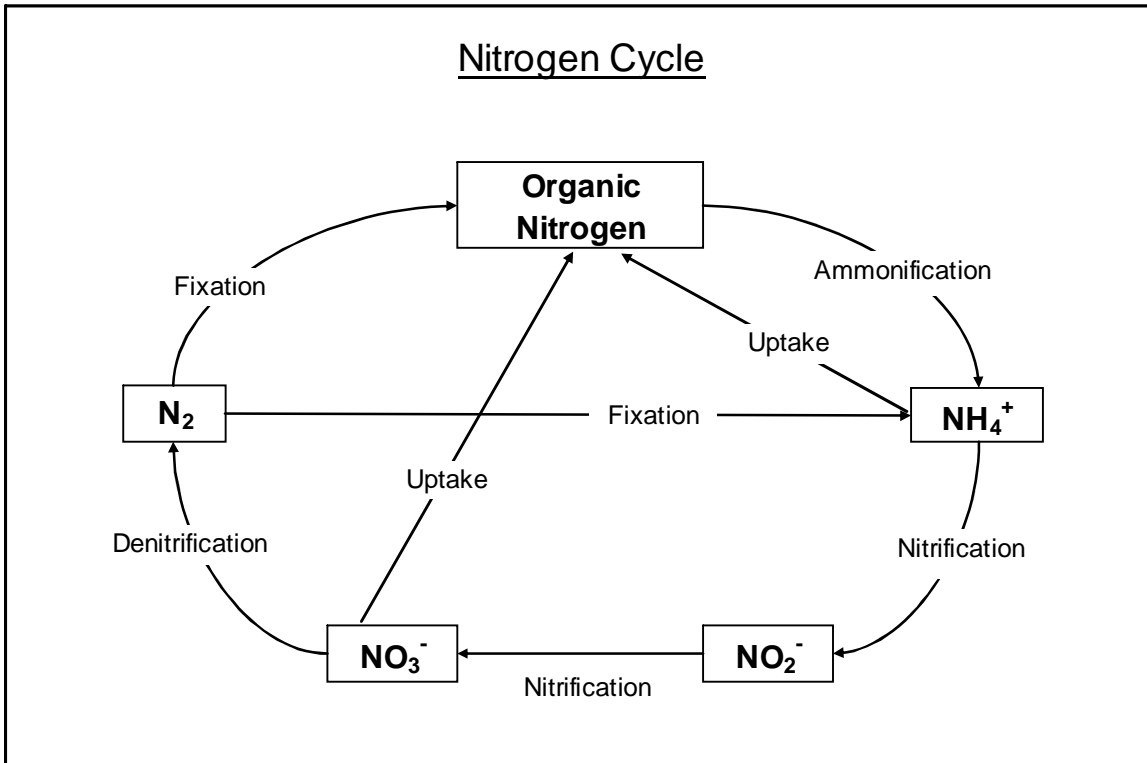
Figure 2.1: The Nitrogen Cycle
(adapted from Madigan et al., 1997; Harrison, 2003; King, 1987; Metcalf and Eddy,

2003)

There are five major transformation pathways in the nitrogen cycle that are responsible

for cycling nitrogen between its various forms: nitrification, denitrification, nitrogen

uptake, nitrogen fixation, and ammonification. Nitrification and denitrification are the

major transformation pathways related to this research and will be discussed in detail in subsequent sections.

Nitrogen uptake, sometimes called nitrogen assimilation, occurs when NO_3^- or NH_4^+ is converted to Org N. Both plants and microorganisms carry out the process of nitrogen uptake in order to obtain the necessary element of nitrogen. The nitrogen obtained through the process of uptake is utilized to form proteins, nucleic acids and other Org N compounds (King, 1987).

Nitrogen fixation occurs when N_2 is reduced to NH_4^+, which in turn is usually directly converted to Org N. Fixation is the only pathway in which N_2 can be utilized directly from the atmosphere and can only be carried out biologically by certain microorganisms. Nitrogen fixation can also occur chemically in the atmosphere during lightning events and during the manufacturing of nitrogen containing fertilizers. However, chemical fixation occurs to a lesser extent than biological fixation (Madigan et al., 1997).

The presence of the nitrogenase enzyme system is required for biological nitrogen fixation (Hubbell and Kiddler, 1992). The nitrogenase enzyme acts as a catalyst in the reduction of N_2 to NH_4^+ and certain Org N compounds. Biological nitrogen fixation can be carried out by free-living microorganisms as well as microorganisms that create symbiotic relationships with host plants. Examples of free-living microorganisms that carry out nitrogen fixation include *Azotobacter and Beijerinckia* (non-photosynthetic aerobic bacteria), *Clostridium* (non-photosynthetic anaerobic bacteria) and *Anabaena*

(photosynthetic cyanobacteria, often called blue-green algae) (Hubbell and Kiddler, 1992). In the legume family of plants (i.e. beans, peas, clover) symbiotic relationships with N_2 fixing microorganisms, frequently in the genus *Rhizobium,* are often established. The microorganisms live within legume root nodules and receive carbohydrates along with a favorable living environment from their host plant, and in return the plant utilizes some of the N_2 fixed by the microorganisms (Harrison, 2003). The NH_4^+ and Org N created through nitrogen fixation can be further transformed into other nitrogen compounds through the process of nitrification, nitrogen uptake or ammonification.

Ammonification, which can also be called nitrogen mineralization, is the transformation of Org N to NH_4^+. Ammonification can occur when animals excrete excess organic nitrogen, in the form of urea ($CO(NH_2)_2$), which is transformed into NH_4^+ through enzymatic hydrolysis (Muck, 1982). The urease enzyme is responsible for the hydrolysis of urea and can be found in feces as well as soils (Muck, 1982; Havlin et al., 1999). A large number of bacteria, fungi and actinomycetes possess the enzyme urease and transform urea into NH_4^+ through the following reaction (Havlin et al., 1999):

$$CO(NH_2)_2 + H^+ + 2H_2O \rightarrow 2NH_4^+ + HCO_3^- \qquad\qquad (2.1)$$

The rate of ammonification of urea can be affected by temperature, pH and soil moisture content. Generally, higher rates occur in warm temperatures, near neutral pH values and at soil moisture contents that are optimal for plant growth (Muck, 1982; Havlin et al., 1999). In soils that exhibit the optimal environmental conditions, most of the urea is

transformed to NH_4^+ within several days after introduction (Havlin et al., 1999). In a typical freestall barn (urea and feces in contact) the majority of urea will be transformed to NH_4^+ within 6 hours at 30ºC and within 24 hours at 10ºC (Muck, 1982).

The hydrolysis of urea is not the only pathway in which ammonification occurs. Ammonification also takes place during the decomposition of organic matter. Heterotrophic microorganisms consume dead organic matter and during this process a significant amount of the nitrogen contained within the organic matter is converted to NH_4^+ (Harrison, 2003). A large number of heterotrophic organisms are capable of decomposing organic matter and can range from aerobic to anaerobic, acid-sensitive to acid-resistant, and spore-forming to non-spore-forming microorganisms (Alexander, 1991). Therefore, the decomposition of organic matter in most instances will be carried out as long as microbial life is viable. However, environmental conditions such as moisture content, pH and temperature can affect the rate of ammonification of organic matter (Alexander, 1991).

Ammonification can be carried out by aerobes and anaerobes at a wide range of moisture contents. However, the optimum rate of ammonification generally occurs when the moisture content is at 50% to 75% of the water holding capacity of a soil. The rate of ammonification generally diminishes at low moisture contents (Alexander, 1991). Generally, ammonification rates are greatest at near neutral pH and are depressed under acidic conditions (Alexander, 1991). Rates can also be affected by the temperature of the environment in which ammonification of organic matter is taking place. In general,

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low temperatures reduce the rate while higher temperatures increase the rate.

Ammonification can be carried out at near freezing temperatures, however, optimum

rates usually are observed when the temperature is between 40ºC and 60ºC (Alexander,

1991). No matter what the rate is of ammonification, the NH_4^+ produced from the

process can be further transformed into other nitrogen species through either the

processes of uptake or nitrification.

2.2.1   Nitrification

Nitrification is a two step process in which NH_4^+ is oxidized to NO_2^- and then NO_2^- is

oxidized to NO_3^-, as shown below. The overall balanced reaction for the complete

oxidation of NH_4^+ to NO_3^- is shown in equation 2.2 (Rittmann and McCarty, 2001):

Step 1: $2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$

Step 2: $2NO_2^- + O_2 \rightarrow 2NO_3^-$

Overall Balanced Reaction:

$$NH_4^+ + 1.815O_2 + 0.1304CO_2 \rightarrow$$

$$0.0261C_5H_7O_2N + 0.973NO_3^- + 1.973H^+ + 0.921H_2O \qquad (2.2)$$
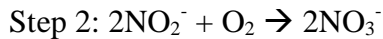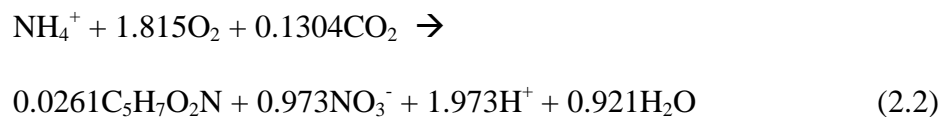
The two step process of nitrification is carried out by bacteria known as nitrifiers. The

most common genus of bacteria that carries out the first step is *Nitrosomonas* while the

Nitrobacter is the most common genus of bacteria responsible for the second step in the

nitrification process (Rittmann and McCarty, 2001). *Nitrosomonas* and *Nitrobacter*

along with other nitrifying bacteria require certain environmental conditions in order to carry out nitrification.

Nitrifying bacteria are classified as autotrophs, chemolithotrophs and obligate aerobes (Rittmann and McCarty, 2001). The autotrophic nature implies that these bacteria utilize inorganic carbon sources such as CO_2. The chemolithotrophic characteristic of these bacteria means that they use reduced inorganic compounds (NH_4^+ and NO_2^-) as electron donors in energy yielding reactions. The characteristic of being obligate aerobes implies that oxygen (O_2) is utilized as an electron acceptor in energy yielding reactions. Therefore, in order for nitrification to take place, nitrifying bacteria normally require environmental conditions in which CO_2, NH_4^+, NO_2^- and O_2 are available. One exception to these requirements is the process referred to as the *anammox reaction*. During this reaction bacteria are able to oxidize ammonia under anoxic conditions (Madigan et al., 1997).

Besides the required environmental conditions, the process of nitrification can be influenced by several other characteristics of the surrounding environment. The hydrogen-ion concentration (pH), alkalinity, temperature, metal concentrations and presence of toxins all can have an affect on the process of nitrification (Metcalf and Eddy, 2003). Nitrification is a pH sensitive process that is usually carried out in wastewater treatment processes in a pH range of 7 to 7.2. Optimal nitrification reaction rates occur when the pH is in the 7.5 to 8.0 range and rates are significantly reduced when the pH falls below 6.8. Alkalinity is consumed in the nitrification process, as

shown in Equation 2.2, which in turn will reduce the pH of the surrounding environment if sufficient alkalinity is not available. Therefore, in some nitrification processes an outside source of alkalinity may be needed if the alkalinity of the water being treated is not sufficient to buffer the acidity produced. Temperature affects the growth rates of the nitrifying bacteria, which in turn affects the rate at which nitrification occurs. Generally, decreasing the temperature will decrease the nitrification rate. The optimum temperature for nitrification has been reported to be between 30ºC and 36ºC, with nitrifier growth observed between 4ºC and 50ºC (WEF, 1998). Between 8ºC and 30ºC, Equation 2.3 can be used to estimate the specific growth rate of the nitrifiers (WEF, 1998).

$$\mu = 0.47 * e^{0.095*(T-15)} \tag{2.3}$$

where:
μ = specific growth rate of nitrifiers (d^{-1})
T = temperature (ºC)

Solvent organic chemicals, amines, proteins, tannins, phenolic compounds, alcohols, cyanates, ethers, carbamates, benzene and heavy metals are known to be toxic to nitrifying bacteria. Therefore, in order to have nitrification occur, both the requirements of the process and the desired environmental conditions must be met.

Nitrification can occur in natural ecosystems, such as soils, if the necessary requirements and desired environmental conditions are available. The process of nitrification can also be carried out in water and wastewater treatment processes. Nitrification is sometimes desired in municipal wastewater treatment due to water quality concerns over (1) the

effect of ammonia on receiving water with respect to dissolved oxygen (DO)

concentrations and/or fish toxicity, (2) the need to provide nitrogen removal to control

eutrophication, and (3) the need to provide nitrogen control for water-reuse applications

including groundwater recharge (Metcalf and Eddy, 2003). With a goal of nitrogen

removal, nitrification is one of the processes carried out in the bioretention systems

utilized in this project. However, when the goal of a treatment process is total nitrogen

removal, the process of nitrification must be followed by denitrification.

2.2.2   Denitrification

Denitrification is the only nitrogen transformation pathway in the nitrogen cycle that has

the ability to remove nitrogen from ecosystems with its end product being N_2 (Harrison,

2003). Therefore, denitrification is required in treatment processes for total nitrogen

removal. Some key examples of denitrification are (1) advanced treatment of

wastewater discharged to watersheds that must be protected against eutrophication, (2)

treatment of wastes with high levels of nitrogen, such as agricultural runoff and

wastewater from feedlots, (3) and treatment of drinking waters that contain elevated

$NO_3^- + NO_2^-$ levels, thereby reducing the human health risk associated with

methemoglobinemia (Rittmann and McCarty, 2001).

The NO_3^- reduction reaction, known as denitrification, includes intermediate steps in

which NO_3^- is transformed to NO_2^-, to nitric oxide (NO), to nitrous oxide (N_2O), and

then to N_2 (Metcalf and Eddy, 2003):

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad\qquad (2.4)$$

The process of denitrification is carried out by bacteria known as denitrifiers. Denitrifiers are widespread among both heterotrophic and autotrophic bacteria (Rittmann and McCarty, 2001). *Halobacterium*, *Methanomonas* and *Pseudomonas* species are a few examples of denitrifiers that are classified as heterotrophic (Metcalf and Eddy, 2003). *Thiobacillus* and *Thiomicrospira* are examples of species of denitrifiers that are classified as autotrophic (Zhang and Lampe, 1998). Both heterotrophic and autotrophic denitrifiers require certain environmental conditions in order to carry out denitrification.

Heterotrophic and autotrophic denitrifiers by nature are facultative aerobes as well as chemotrophs (Rittman and McCarty, 2001). The trait of being a facultative aerobe means that these bacteria shift to NO_3^- or NO_2^- respiration when O_2 becomes limiting. This means that NO_3^- or NO_2^- becomes the terminal electron acceptor in energy yielding reactions when O_2 becomes limited. Environments that are anoxic (low O_2 levels) and contain NO_3^- or NO_2^- will promote the process of denitrification. Along with being facultative aerobes, denitrifiers are chemotrophs that can use either organic or inorganic electron donors. Those that utilize organic electron donors are heterotrophs and those that utilize inorganic electron donors are autotrophs. Heterotrophs have been shown to use a wide array of organic compounds including but not limited to methanol, acetate and biodegradeable organic matter that is present in wastewater. During autotrophic

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denitrification inorganic electron donors such as hydrogen and sulfur are utilized

(Metcalf and Eddy, 2003). Equation 2.5 shows the overall heterotrophic denitrification

reaction when organic matter (CH_2O) is utilized as the electron donor (derived following

the McCarty (1975) procedure). Equation 2.6 represents the overall autotrophic

denitrification reaction when elemental sulfur (S^0) is utilized as the electron donor

(Bachelor and Lawrence, 1978).

$$1.866CH_2O + NO_3^- + 0.97H^+ \rightarrow$$

$$0.104C_5H_7O_2N + 1.343CO_2 + 1.993H_2O + 0.448N_2 \tag{2.5}$$

$$1.1S^0 + 0.4CO_2 + NO_3^- + 0.76H_2O + 0.08NH_4^+ \rightarrow$$

$$0.08C_5H_7O_2N + 1.1SO_4^{-2} + 0.5N_2 + 0.781H^+ \tag{2.6}$$
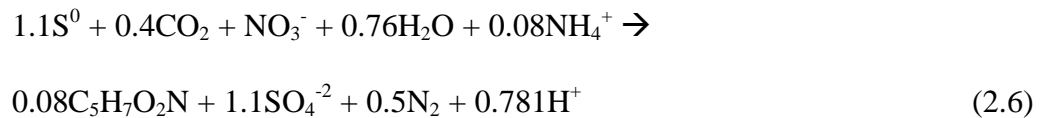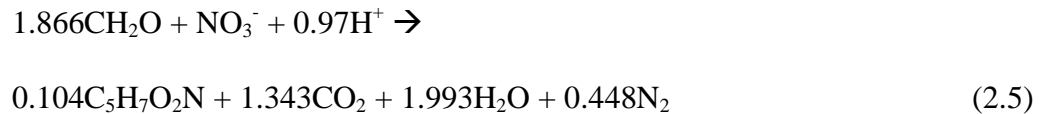
From Equation 2.5, it can be determined that 3.57 grams of alkalinity (as $CaCO_3$) are

produced per gram of NO_3^- reduced during heterotrophic denitrification. From Equation

2.6, it can be determined that 4.5 grams of alkalinity (as $CaCO_3$) are consumed per gram

of NO_3^- reduced during autotrophic denitrification. Typically, when alkalinity is

produced the pH of the surrounding environment is elevated and the opposite occurs

when alkalinity is consumed, the pH will decrease. Generally, the buffering capacity of

the surrounding environment will dictate the extent of the pH change. Unlike the pH

sensitive process of nitrification, there is less of a concern over pH influences on

denitrification rates. No significant effect on the rate of heterotrophic denitrification has

been reported for pH values in the range of 7.0 to 8.0. However, a decrease in the rate

of heterotrophic denitrification has been observed when the pH was decreased to 6.0 (Metcalf and Eddy, 2003). The optimum pH values for autotrophic denitrification using sulfur is between 6 and 8 (Holt et al., 1994). Autotrophic denitrification rates have been shown to be severely inhibited below pH 5.5 (Liu and Koenig, 2002).

2.3   Agricultural Runoff

During the field testing phase of this project the bioretention units utilized runoff from an agricultural (dairy farm) operation. This section of the literature review discusses agriculture, the constituents in agricultural runoff and the impact that runoff from agricultural lands can have on the water quality of the receiving water(s). In view of the fact that runoff from a dairy farming operation was exploited in the field testing of the bioretention units, the main focus of this section will be on the impacts of dairy farming. However, impacts from the agricultural industry as a whole are also included to illustrate the concerns related to non-point source pollution from agricultural practices.

Approximately half of the land area of the United States is used for agricultural purposes including cropland, pastureland and rangeland. The profession of agriculture often has detrimental effects on surface and groundwater resources, soil erosion and the depletion of water quality (Davis and Masten, 2004). Surface and groundwater resources are often depleted due to the high water demands for irrigation purposes, especially in arid regions. Loss of top soil, through the process of erosion, is often a problem if proper grazing and cropping practices are not followed.

Runoff from agricultural land occurs when water from precipitation and/or snowmelt travels across the land and/or building surfaces and is conveyed to nearby surface waters. Runoff can also be incorporated into groundwater through the process of infiltration. A variety of constituents are integrated into agricultural runoff, many of which can lead to the degradation of the receiving water. Animal wastes, nutrients, organic matter, salts, fecal microorganisms, metals, sediments, and pesticides are the primary pollutants associated with agricultural runoff (USEPA, 1993, 2005; NRCS, 1992). The sources and related pollution concerns of the primary pollutants are discussed in the following sections. Unless noted otherwise, the information pertaining to these primary pollutants was adapted from the USEPA's document "National Management Measures for the Control of NonPoint Pollution from Agriculture" (USEPA, 1993).

2.3.1   Animal Wastes

The USEPA defines the term animal waste to include: the fecal and urinary wastes of livestock; process water (such as from a milking parlor); and the feed, bedding, litter, and soil with which they become intermixed (USEPA, 2003). The following pollutants can be transported by runoff if it comes into contact with animal wastes.

- Oxygen-demanding substances;
- Nitrogen, phosphorus, and other major and minor nutrients;
- Organic solids;
- Salts;

- Bacteria, viruses, and other microorganisms (i.e. fecal microorganisms);

- Metals; and

- Sediments.

Due to the wide array of pollutants listed above it is evident that runoff, that has come into contact with animal wastes, can cause various concerns related to the quality of the receiving waters. Oxygen-demanding wastes deplete a water body of O_2, which in turn can be harmful to aquatic species that require O_2 to survive.

Animal wastes can be incorporated into runoff from a dairy farm in various ways and is greatly dependent on the operational procedures of a specific farming operation. For instance, the manner in which cattle are held will affect the extent that animal wastes are incorporated into runoff. Cattle confined under a roofed enclosure will help diminish the direct contact between runoff and animal wastes. However, if cattle are allowed to roam freely in pasturelands, runoff from this land will incorporate the feces and urea excreted on the land surface. Dairy farming operations often utilize manure as a fertilizer source. In between fertilizing events, the method of manure storage can have an impact on the extent to which runoff comes into contact with animal wastes. Runoff will come into contact less with manure that it is contained within a storage tank compared with manure that is collected and stored in an area that is open to the elements.

When land application of the stored manure is carried out, the timing as well as the method used, can impact the water quality of runoff from these lands. The time of year

as well as the time between application and runoff events can both affect the extent to which animal wastes are incorporated into the runoff. Manure applied to frozen ground or snow covered ground can result in higher concentrations of animal wastes during rainfall or snowmelt, especially when runoff events occur shortly after application. Consequently, the application of manure should (ideally) be on land that is not frozen nor covered with snow and at a time when precipitation is not forecasted in the near future. Surface spreading and subsurface incorporation (i.e. injection) of manure are two methods that can be used when fertilizing lands with manure. The practice of surface spreading allows the direct incorporation of animal waste into runoff to a further degree than when manure is injected into the subsurface. Therefore, if it is possible, subsurface incorporation of manure can be beneficial to the water quality of runoff.

2.3.2 Nutrients

In order for dairy farming operations, as well as all agricultural practices, to have successful crop production an adequate supply of nutrients, such as nitrogen (N), phosphorus (P) and potassium (K), as well as a proper soil pH needs to be provided (Davis and Masten, 2004). The primary sources of crop nutrients are commercial (chemical) fertilizers and manure (USEPA, 2003). The most widely used chemical fertilizers contain lime (to maintain a proper soil pH), N, P and K at varying concentrations depending on the crop needs (Davis and Masten, 2004). The source of manure is usually from farm animals; however, the sludge or effluent from municipal and industrial wastewater treatment plants can also be utilized as soil amendments (USEPA,

2003). There are few environmental concerns associated with lime and K but widespread problems are associated with N and P (Davis and Masten, 2004). In addition to fertilizers; atmospheric deposition, irrigation water, wildlife and crop residues also can be sources of N and P (USEPA, 2003).

Dairy farming operations can discharge N and P to the environment in various ways including runoff or seepage from animal holding areas, rupture of manure storage lagoons, failure of liners in manure storage lagoons or the accidental spillage of fertilizers. However, the major source of N and P release to the environment is through runoff or seepage from croplands. N and P are purposely applied to croplands by farmers to promote crop production as well as naturally added through atmospheric deposition and excretions from livestock and wildlife. The extent to which N and P are incorporated into runoff from naturally occurring sources is hard to control. However, through proper farming practices, the extent to which the intentionally added N and P are incorporated into runoff can be diminished (Davis and Masten, 2004). As discussed previously with regards to land application of manure, proper timing, methods and rates of fertilizer applications can help reduce the N and P incorporated into the runoff. The rate at which of N and P are added to the land should be based on the crops needs and the soil N and P levels. When N and P are added to the land at rates that exceed a crops needs, the excess nutrients can be incorporated into runoff and lead to detrimental effects on the quality of the receiving water such as eutrophication.

2.3.3 Organic Matter

Organic matter is usually composed of a combination of carbon, hydrogen, oxygen and sometimes nitrogen (Metcalf and Eddy, 2003). All animal and vegetable originating substances contain carbon compounds creating various sources from which organic matter can be incorporated into agricultural runoff (NRCS, 1992). Organic matter present in runoff is of concern because of various detrimental affects it can have when incorporated into surface waters.

Animal wastes, fertilizers and crop residues are some of the sources from which organic matter can be incorporated into runoff from a dairy farm operation. Manure consists largely of organic matter and therefore, when utilized as a fertilizer can provide a significant source of organic matter that can be incorporated into runoff. Another contributor of organic matter in runoff from dairy farm operations can be crop residues. When crops are harvested, the remaining plant material often is incorporated into the soil. This crop residue can be transported by runoff and become a concern with regards to the quality of the receiving water.

Water quality becomes a concern when organic matter is decomposed by bacteria. Bacteria consume or degrade organic matter to obtain energy for cell maintenance and the synthesis of new cell tissue (Metcalf and Eddy, 2003). When O_2 is present, the degradation process can be carried out by both aerobic bacteria which require the presence of O_2 to survive, and facultative bacteria which can survive with or without the presence of O_2 (NRCS, 1992). If sufficient oxygen and aerobic or facultative bacteria

are present, the aerobic degradation of organic matter will continue until all the biodegradeable waste is consumed. During the degradation process three activities are carried out by the bacteria: oxidation of organic matter, cell synthesis and endogenous respiration. The following generalized equations represent these activities (Metcalf and Eddy, 2003).

Oxidation of Organic Matter:

Organic Matter + O_2 + Bacteria $\rightarrow$

CO_2 + H_2O + NH_3 + Other End Products + Energy $\qquad\qquad$ (2.7)

Cell Synthesis:

Organic Matter + O_2 + Bacteria + Energy $\rightarrow$

New Cell Tissue $\qquad\qquad$ (2.8)

Endogenous Respiration:

Cell Tissue + O_2 $\rightarrow$ CO_2 + NH_3 + H_2O $\qquad\qquad$ (2.9)
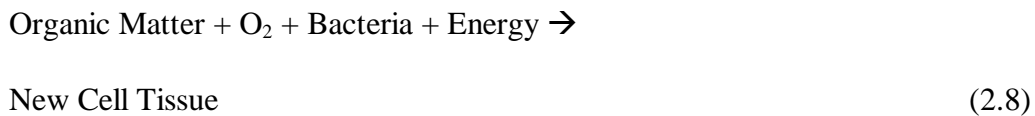
Water quality can be negatively impacted during aerobic degradation due to the depletion of O_2 throughout the process. The addition of organic matter to a water body can lower O_2 levels to such an extent that fish and other aquatic life can die from asphyxiation. The extent to which O_2 levels are depleted primarily depends on the amount of organic matter present, the initial O_2 levels of the waste stream and receiving water, the re-aeration abilities of the receiving water and the temperature of the water. In addition to the concerns over O_2 depletion, the decomposition of organic matter can also create color, taste, odor and disinfection by-product problems associated with public

water supplies. The decomposition of organic compounds containing nitrogen can also lead to issues related to water quality with respect to nitrogen inputs, which were discussed previously.

2.3.4   Salts

Salts are naturally present in all soils as well as fresh waters, coastal waters, estuarine waters and ground waters. The presence of salts is due to the natural weathering process of soil and geologic material. Salts dissolve into water as it percolates through soil and rock formations (Davis and Masten, 2004). The movement and deposition of salts depends on the amount and distribution of rainfall and irrigation, the soil and underlying strata and evapotranspiration rates. In humid regions, salts are naturally leached through the soil and substrata by rainfall. In arid and semi-arid regions salts that have not been removed by natural leaching are concentrated in the soil. The extent of natural leaching will affect the naturally occurring salt concentrations in soils and waters. However, salt concentrations can be significantly influenced by irrigation of agricultural lands.

The water used for irrigation, whether from ground, surface or reclaimed waters, has a background concentration of salts. When water is lost due to plant consumption or by evaporation, the salts remain in the soils and become concentrated. This is referred to as the "concentrating effect." This effect increases the amount of salts that can dissolve into runoff, which can lead to negative impacts related to water quality of the receiving

water body. The salt concentrations in runoff from a dairy farm operation will be directly related to the water used for irrigation as well as the geographical location of the dairy farm. For instance, a dairy farm that uses irrigation water with moderate to high salt concentrations and is located in an arid or semi-arid location will most likely have runoff with elevated salt concentrations.

Runoff with elevated salt concentrations that is introduced into a fresh water ecosystem can have toxic affects to both aquatic plants and fish species. Generally, salt water ecosystems are not influenced by runoff with elevated salt concentrations. However, anadromous fish can be adversely affected. Anadromous fish primarily live in saline waters but rely on freshwater systems near the coast for crucial portions of their life cycles. Therefore, freshwater systems with elevated salt concentrations near the coast can have negative affects on anadromous fish.

2.3.5   Fecal Microorganisms

Warm-blooded animals excrete large quantities of microorganisms including bacteria, viruses, parasites and fungi. Some of these microorganisms are considered pathogens because they can cause diseases in animals and humans (NRCS, 1992). Various diseases that can be transmitted to humans through contact with animal manure are listed in Table 2.1.

Table 2.1: Diseases and Microorganisms Spread By Animal Manure (from NRCS, 1992)

Disease	Responsible organism	Disease	Responsible organism
Bacterial		Viral	
Salmonella	Salmonella sp.	New Castle	Virus
Leptospirosis	Leptospiral pomona	Hog Cholera	Virus
Anthrax	Bacillus anthracis	Foot and Mouth	Virus
Tuberculosis	Mycobacterium tuberculosis	Psittacosis	Virus
	Mycobacterium avium		
Johnes disease	Mycobacterium paratuberculosis	Fungal	
		Coccidioidomycosis	Coccidoides immitus
Brucellosis	Brucella abortus	Histoplasmosis	Histoplasma capsulatum
	Brucella melitensis	Ringworm	Various microsporum and trichophyton
	Brucella suis		
Listerosis	Listeria monocytogenes	Protozoal	
Tetanus	Clostridium tetani	Coccidiosis	Eimeria sp.
Tularemia	Pasturella tularensis	Balantidiasis	Balatidium coli.
Erysipelas	Erysipelothrix rhusiopathiae	Toxoplasmosis	Toxoplasma sp.
Colibacilosis	E. coli (some serotypes)		
Coliform mastitis-metritis	E. coli (some serotypes)	Parasitic	
		Ascariasis	Ascaris lumbricoides
		Sarcocystiasis	Sarcocystis sp.
Rickettsial			
Q fever	Coxiella burneti		

Dairy farm runoff can transport fecal microorganisms after coming into contact with barnyards, pastures, rangelands, feedlots, manure storage areas and areas where land application of manure occurs. The quality of the receiving water body can be negatively impacted due to the various diseases that can result from human contact with fecal microorganisms. Some studies have shown high levels of antibiotic resistance in microorganisms in runoff from livestock operations. This is a concern since antibiotics are often utilized for human treatment. Drinking water contamination (both surface and groundwater), beach closures and shellfish contamination can all be results of fecal microorganism contamination from agricultural runoff (USEPA, 2003).

2.3.6 Metals

All living organisms require various metals at varying concentrations for proper growth, including iron (Fe), chromium (Cr), copper (Cu), zinc (Zn) and cobalt (Co). However, all these metals can be toxic when present at elevated concentrations (Metcalf and Eddy, 2003). Metals can accumulate and disrupt organs, lead to cancer and cause birth defects. Therefore, aquatic ecosystems and human health can be at risk when water resources contain metals at elevated concentrations.

Sources of metals in agricultural runoff include plant residues, animal wastes, fertilizers, specific herbicides and fungicides, and the use of municipal and industrial wastewater effluent or sludge for fertilizer (Csuros and Csaba, 2002). The type of metals incorporated into the runoff is directly related to the operational procedures of a certain farming operation (i.e. types of fertilizers, fungicides, etc. used). For instance, farmers often feed swine a diet high in Cu and Zn to promote growth; however, 80-90% of this Cu and Zn is excreted from the animal (USEPA, May 2004). This animal waste has elevated levels of Cu and Zn and can possibly lead to water quality concerns if they are incorporated into runoff. Copper sulfate foot baths are another operational practice carried out by dairy farmers which can lead to Cu being integrated into agricultural runoff. Copper sulfate foot baths are utilized for hoof health. Often times, spent copper sulfate solution is integrated into liquid manure which is then land applied (Rankin, 2004). The Cu can in turn be transported within runoff from these lands and possibly lead to water quality concerns.

Domestic wastewater effluents, as well as the sludge from the process, can contain

various metals from metabolic waste products, corrosion of distribution/collection

systems and from household products, such as detergents. Some examples of metals that

can be found in domestic wastewaters include Cu, lead (Pb), Zn, cadmium (Cd), Fe,

manganese (Mn), Cr, nickel (Ni), Co, boron (B) and arsenic (As) (Csuros and Csaba,

2002). Agricultural operations that utilize wastewater effluent or sludge as a fertilizer

source are inadvertently applying metals to the land surface. These metals can be

incorporated into runoff and detrimentally affect the quality of the receiving waters.

2.3.7 Sediment

Sediment is the solid material, both mineral and organic, that is incorporated into

agricultural runoff due to the process of erosion. Erosion, caused by runoff, occurs

when soil is removed by flowing water (Davis and Masten, 2004). Dairy farming

practices such as spreading manure as a fertilizer, tilling for crop production as well as

cattle handling can all have an influence on the amount of sediment incorporated into

runoff. A land surface that is fertilized with manure has a certain amount of solids

applied to it, which in turn can lead to an increase of sediment in the runoff from this

land surface. Field management, such as tillage or cultivation, is necessary for dairy

farmers to perform for crop production. When these practices are carried out, the top

soil of the land is loosened and repositioned. When runoff occurs over this loose land

surface the amount of sediment carried by runoff can be elevated. The manner in which

cattle are handled at a dairy farm operation can lead to similar affects that fertilization

with manure and field management have on sediment levels in runoff. For example, cattle fed by grazing in pasturelands, introduce manure to the land surface as well as loosen the land surface due to cattle movement. Runoff from dairy operations that carry out confined handling of cattle can have elevated levels of sediment if runoff comes into contact with these areas. Manure, feed, bedding, litter and soils can all be contributors of sediment to runoff that comes into contact with confined handling areas.

Sediment in runoff is a concern due to the detrimental effects that suspended solids, turbidity and settling of solids can have on the receiving water body. Suspended solids can deplete aquatic plant populations by decreasing the amount of sunlight available for photosynthesis. Suspended solids also affect fish species by covering spawning areas and food supplies, clogging the filtering capacity of filter feeders, and clogging and harming the gills of fish. The turbidity associated with sediment is known to interfere with the feeding habits of certain species of fish. Solids contained in sediment can also settle out of suspension and be deposited into the receiving water body. Deposited sediment can reduce the transport capacity of streams and rivers as well as reduce the storage capacity of rivers and lakes. The reduction in capacities can affect aquatic ecosystems as well as cause more frequent flooding.

In addition to the concerns associated with sediment that have already been discussed, the organic characteristics of sediment can have further detrimental affects on the receiving water body. Section 2.3.3 discusses the concerns related to organic matter.

Sediment can also transport certain chemicals in an absorbed state such as various pesticides, phosphorus and ammonium. These transported chemicals can have their own adverse affects on the water quality of the receiving water bodies. Section 2.3.2 discusses the concerns related to phosphorus and ammonium and Section 2.3.8 discusses the concerns related to pesticides.

2.3.8 Pesticides

The USEPA defines the term *pesticide* as any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest or intended for use as a plant regulator, defoliant, or desiccant (USEPA, July 2003). Insecticides, herbicides, fungicides and miticides are some of the various pesticides utilized in agriculture to control plant pests and improve crop production. The use of pesticides is beneficial for agriculture, but can create negative impacts if they are incorporated into surface or groundwaters. The extent to which pesticides are incorporated into dairy farm runoff depends on factors such as the length of time between pesticide applications and rainfall/irrigation occurrence, intensity and duration of rainfall/irrigation, the amount of pesticide applied as well as the persistence of the pesticide in the environment.

Pesticides can have a high potential for human harm as well as harm to aquatic environments due to their variations in chemical makeup (USEPA, July 2003). However, the effects of pesticides on humans and aquatic life are not yet fully understood (USGS, 1999). Possible human health effects from overexposure to

pesticides include cancer, reproductive or nervous-system disorders, and acute toxicity (Copeland, 2005). Recent studies suggest that some pesticides can disrupt endocrine systems and affect reproduction by interfering with natural hormones of aquatic species (Copeland, 2005). Even though pesticide toxicity is not yet fully understood, the need to manage and monitor pesticide use and distribution within the environment is evident.

2.4 Agricultural Runoff Treatment Technologies

A variety of constituents that can have detrimental effects on the quality of the receiving water(s) when integrated into agricultural runoff. Controlling the extent to which these constituents enter runoff as well as the treatment of polluted runoff can help reduce the non-point source pollution caused by agricultural runoff. This section focuses on some of the methods that can be deployed to reduce the non-point source pollution associated with agricultural runoff.

The direct treatment of runoff from agricultural lands is difficult to accomplish due to its non-point source characteristic. However, proper management along with stormwater runoff control and treatment technologies can help diminish the extent of non-point source pollution. This is often referred to as the implementation of Best Management Practices (BMPs). Non-structural as well as structural BMPs are often utilized in agricultural operations. Unlike structural BMPs, non-structural BMPs do not require any physical construction. BMPs are designed to reduce the quantities of pollutants that

are generated and/or delivered from a source to a receiving water body through the following approaches (USEPA, 2003).

- Minimizing pollutants available (source reduction);

- Retarding the transport and/or delivery of pollutants, either by reducing water transported, and thus the amount of the pollutant transported, or through deposition of the pollutant; or

- Remediating or intercepting the pollutant before or after it is delivered to the water resource through chemical or biological transformation.

Reducing the load of a pollutant at its source is one method of proper management that can reduce the effects of non-point source pollution. For example, a farmer can create a nutrient management plan that specifies the proper amount of fertilizer (manure or chemical) to apply to a crop to just meet the nutrient needs of that crop. This can reduce the nutrient load in runoff that can occur from excess fertilization of cropland. Nutrient management plans are an excellent non-structural BMP that reduces the amount of nutrients available to be transported by runoff. Farmers can also develop additional management plans, in the same manner as nutrient management plans, that are aimed at source reduction of the other major contaminants discussed in Section 2.3. Diet manipulation is another form of management that can help reduce waste products excreted by farm animals. Diet manipulation consists of determining the proper diet requirements (nutrients, protein, etc.) of an animal and adjusting the feed composition to meet the requirements without exceeding them. Studies have shown that the proper selection of a protein source in cattle feed can reduce nitrogen excretion by 15 to 25%

(NRCS, 2003b). The same management plans; however, can not entirely eliminate non-point source pollution from agricultural operations. Structural BMPs aimed at controlling stormwater runoff as well as treating polluted runoff are sometimes necessary when management alone can not reduce the non-point source pollution to an acceptable level. Structural BMPs are often site-specific technologies, meaning that one BMP might work well at one farm but might not be the best option at another farm. Selection of the proper BMP for a certain site can depend on many factors such as treatment goals, land availability, cost and cost effectiveness. The following are some structural BMPs that can be used by agricultural operations to diminish their contributions to non-point source pollution:

- Sedimentation Basins;

- Treatment Lagoons, Storage Ponds and Storage Tanks;

- Constructed Wetlands;

- Vegetative Filter Strips; and

- Bioretention Systems (proposed by this research).

2.4.1 Sedimentation Basins

Sedimentation basins are constructed to collect and store debris or sediment in an attempt to reduce or abate pollution by sediment and debris being transported in runoff (NRCS, 2003a). The main purpose of a sedimentation basin is the removal of sediment and debris from runoff, in order to preserve the capacity of the receiving water (NRCS, 2003a). Sedimentation basins can require runoff control strategies, such as diversion

structures, in order to have the desired runoff enter the basin area. A sedimentation basin may be desirable to treat runoff from barnyards, feedlots and other areas that contribute an elevated amount of sediment and debris to agricultural runoff. Typically, a sedimentation basin will retain 40-65% of the total solids that enter into it (NRCS, 2005). The physical removal of solids retained within a sedimentation basin is occasionally required in order to maintain a properly working basin. Sedimentation basins can also be installed as a pretreatment step to the other structural BMPs, listed above.

2.4.2 Treatment Lagoons and Storage Ponds

Treatment lagoons and waste storage ponds are structural BMPs that are often associated with waste management plans. Figure 2.2 depicts some of the various waste handling options that are available to dairy farmers. The purpose of a treatment lagoon when associated with a waste management plan is to biologically treat waste, such as manure , and thereby reduce pollution potential (NRCS, 2003d). A lagoon treats manure as a liquid after it has been diluted by wash water and/or runoff. For the purpose of this section it will be assumed that lagoons are operated to treat runoff containing high levels of animal wastes (i.e. from barnyards, feedlots, etc.). The purpose of a waste storage pond is to retain manure, bedding and runoff liquid for later use, such as land application for fertilization (NRCS, 1992). Waste storage ponds are not intended to biologically treat the waste but inevitably some biological activity will take place within a storage pond in the same manner as in a treatment lagoon.
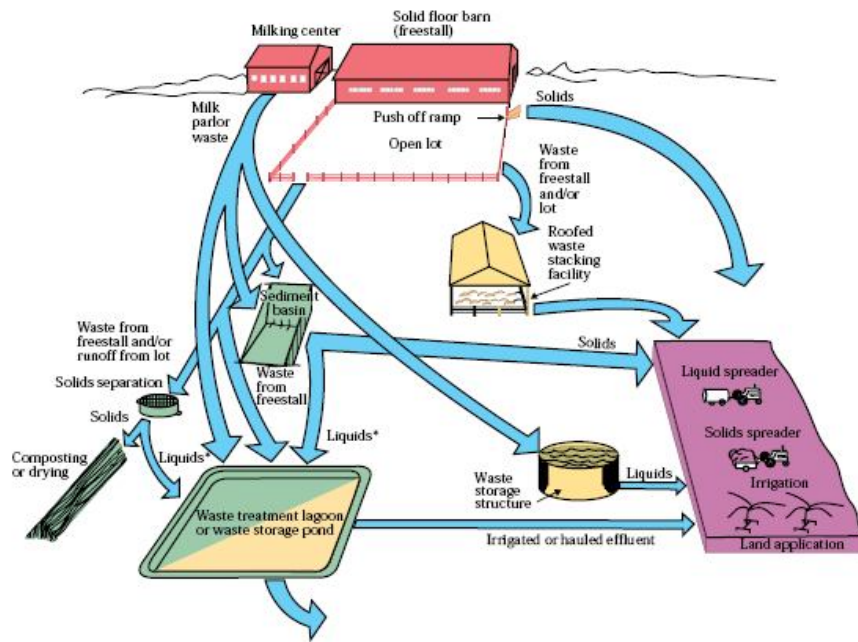
Figure 2.2: Waste Handling Options at a Dairy Farm (NRCS, 1992)

Biological treatment within a lagoon is primarily carried out by aerobic and/or anaerobic bacteria (Barker, 1996). Biological treatment of organic matter as well as the transformation of nitrogen species can be achieved in both aerobic and anaerobic lagoons. Nitrogen transformations that take place in a lagoon depend directly on the environmental conditions of the lagoon, especially the dissolved oxygen concentration, as discussed in Section 2.2.

Under aerobic conditions, treatment lagoons and storage ponds can generate nitrate through the process of nitrification. Leaching of nitrate from lagoons and storage ponds can occur depending on the permeability of the underlying soil. Nitrate leaching is a concern due to the human health risks related to elevated levels of nitrate in drinking

water. To prevent nitrate leaching, lagoons and storage ponds should be constructed in soils with relatively low permeability. In certain instances where native soils are highly permeable, low permeability liners can be constructed out of concrete, geomembranes and/or clay to reduce leaching. If anoxic conditions exist within a lagoon or storage pond the nitrate produced can be converted to nitrogen gas through the process of denitrification. This can result in total nitrogen removal (biologically) within a lagoon or storage pond, which may not be desirable if the liquid is intended for use as fertilizer.

In addition to biological treatment, physical treatment can also occur through the settling of solids that enter a treatment lagoon or waste storage pond. Lagoons and ponds that treat runoff containing animal wastes should always have initial solids settling, separation or removal prior to the waste stream entering the lagoon (Barker, 1996). Pretreatment is essential to avoid excessive solid buildup rates within a lagoon. A sedimentation basin is an example of a pretreatment step that can be utilized to remove a portion of the solids contained in the runoff. However, some solids will inevitably pass through a sedimentation basin and in turn have the ability to settle out of solution and be incorporated into the sediment of the lagoon or storage pond.

As shown in Figure 2.2, the effluent from a treatment lagoon or a waste storage pond can either be used for land application or discharged into the environment. Land application is most commonly carried out and serves as irrigation water as well as a nutrient source for crops (Hamilton et al., 2002). If a treatment lagoon or storage pond is operating properly, the effluent should contain lower levels of pollutants in comparison

to influent levels, which in turn reduces the amount these constituents can be incorporated into runoff and lead to non-point source pollution. Up to 80% of the total nitrogen entering lagoons cannot be accounted for in lagoon effluent and a great portion of the phosphorous contained in manure is retained in the lagoon sediment (Hamilton et al., 2002). Therefore, lagoons are successful at retaining or transforming a large portion of the nutrients, N and P, which could be integrated into agricultural runoff and lead to detrimental effects such as eutrophication. However, the nitrogen loss within a treatment lagoon is mostly due to volatilization of ammonia to the atmosphere (CENR, 2000), which in turn can still contribute to eutrophication when atmospheric deposition of this nitrogen occurs. Table 2.2 gives some typical concentrations of various contaminants within anaerobic and aerobic lagoons operating at a dairy farm (NRCS, 1992). The anaerobic lagoon received a significant loading of manure while the aerobic lagoon was utilized to treat milking parlor wastes only. It can be concluded that the anaerobic lagoon exhibits significantly higher concentrations than does the aerobic lagoon.

Table 2.2: Dairy Farm Anaerobic and Aerobic Lagoon Characteristics (NRCS, 1992)

Contaminant	Anaerobic Lagoon	Aerobic Lagoon
TN	200 mg/L as N	20 mg/L as N
NH_4^+ - N	119.8 mg/L as N	12 mg/L as N
Volatile Solids	1097 mg/LP	200 mg/L
Total Phosphorous	58 mg/L as P	9.6 mg/L as P
BOD_5	350 mg/L	35 mg/L
COD	1498 mg/L as N	150 mg/L

In instances where the effluent is discharged to the environment, further treatment might be desired depending on the effluent characteristics as well as site characteristics. Site

characteristics such as the proximity to water resources will often dictate whether

additional treatment of the effluent is necessary. If desired, further treatment of the

effluent can be achieved through the implementation of additional structural BMPs such

as constructed wetlands or vegetated filter strips.

2.4.3   Constructed Wetlands

According to the Natural Resources Conservation Service, a constructed wetland is a

constructed, shallow, earthen impoundment containing hydrophilic vegetation that can be

designed to treat either point or non-point sources of water pollution (NRCS, 2002).

Constructed wetlands have been utilized in agriculture to treat the effluent from waste

treatment lagoons and waste storage ponds; wastewater from milking parlors; and runoff

from open feedlots and croplands. Figure 2.3 shows how a constructed wetland can be

integrated into a waste management system at a dairy farming operation.
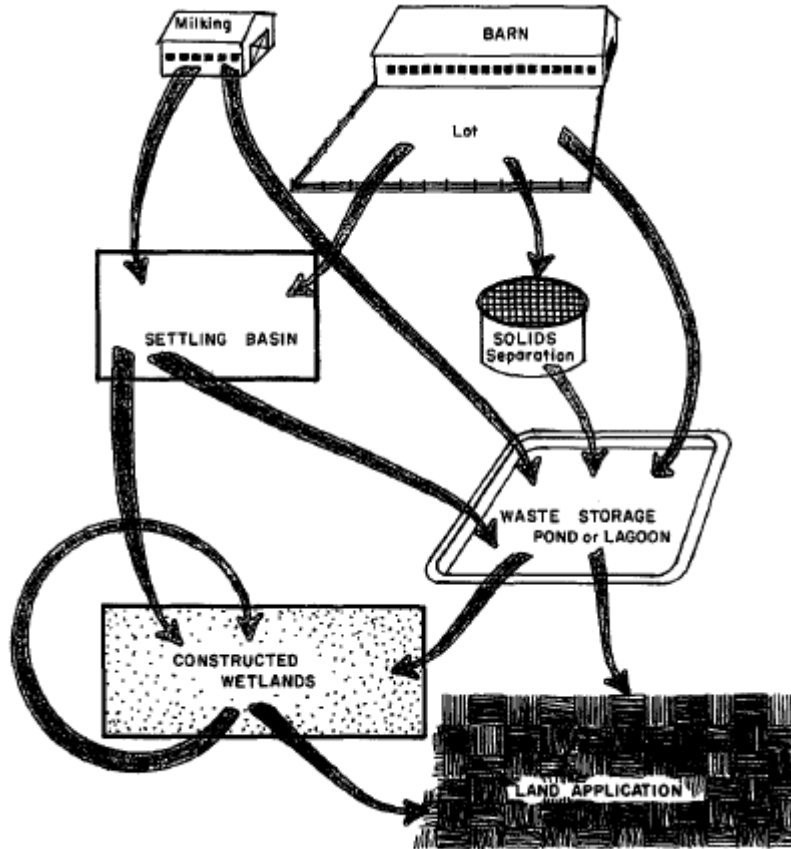
Figure 2.3: Constructed Wetland Integrated into Dairy Farm Waste Management
(Cronk, 1996)

The three principal types of constructed wetlands are known as surface flow wetlands,

subsurface flow wetlands and floating aquatic plant systems (Figure 2.4; NRCS, 2002).

Currently, surface flow wetlands are the preferred method when treating agricultural

wastes and therefore will be the focus of this section.
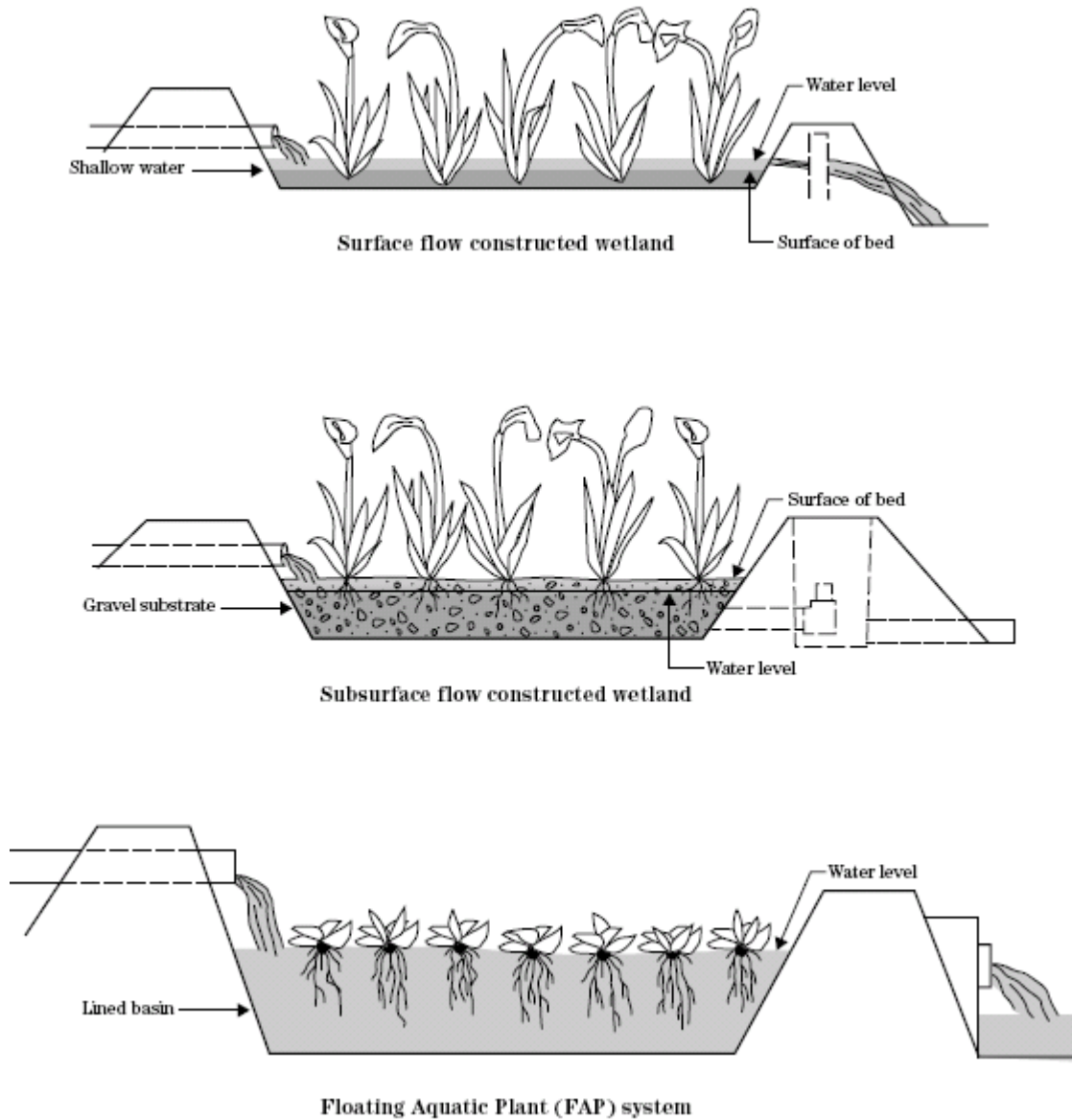
Figure 2.4: Types of Constructed Wetlands (from NRCS, 2002)

Surface flow wetlands are shallow earthen basins planted with rooted, emergent wetland

vegetation (NRCS, 2002). Typical water depths in a surface flow wetland range from 6

to 18 inches. Ideally, bottom slopes are flat from side to side and either flat or slightly

sloped from inlet to outlet. To a large extent the treatment of pollutants entering surface

flow wetlands is the result of microbial activity (i.e. bacteria and fungi). Microorganisms

can be found attached to the submerged plant stems and litter within the wetland, within

the soil/plant root matrix and suspended throughout the entire water column (NRCS, 2002). Microbial activity is not the only method in which treatment of pollutants is achieved in surface flow wetlands. The primary treatment processes that can be achieved through a surface flow wetland system include (Simeral, 1998):

- Uptake and transformation of nutrients by microorganisms and plants;

- Biodegradation and uptake of pollutants by microorganisms and plants;

- Filtration and chemical precipitation through contact with substrate and litter;

- Settling of suspended particulate matter;

- Chemical transformation of pollutants (i.e. ammonification);

- Absorption and ion exchange on the surfaces of plants, sediment, and litter; and

- Predation and natural die-off of pathogens.

Proper design of a surface flow wetland is essential to achieve the desired treatment of contaminants. Removal of settleable solids from the influent and the total water budget are the most important design considerations (Simeral, 1998). If excessive solids enter a wetland system they can destroy the system by essentially filling in the wetland. A water budget takes into account the amount of water going into, flowing out of and remaining in the wetland system. A proper water balance must be maintained in order to sustain plant populations, this is especially important during dry weather periods. Other important design considerations include the physical characteristics (size, shape, slopes, etc.), the soil used for construction, species of vegetation utilized and management of the system after establishment (Simeral, 1998).

Through the aforementioned processes, a properly designed surface flow wetland can be utilized for the treatment of various contaminants associated with agricultural runoff. These contaminants include nutrients (i.e. nitrogen and phosphorous), oxygen demanding substances, sediment, metals and pathogens (fecal microorganisms) (NRCS, 2002; EPA 1996). Table 2.3 summarizes the average contaminant removal from two swine and three dairy facilities surface flow wetlands treating the effluent from waste treatment lagoons.

Table 2.3: Average Contaminant Removal from Surface Flow Wetlands Treating Lagoon Effluent at Swine and Dairy Farm Facilities (Compiled from NRCS, 2002)

Contaminant	Average Removal Efficiency (%)	
	Swine Farm	Dairy Farm
NH_4^+ - N	87.5	69.7
Org N	86.5	54.5
Total Phosphorous	40.0	60.7
PO_4^{3-} - P	70.5	60.0
BOD_5	87.0	77.0
COD	67.5	58.0

From Table 2.3, it can be concluded that properly functioning constructed wetlands can provide significant reductions in nutrients (N and P) as well as oxygen demanding wastes (i.e. organic matter). Discharge techniques of the treated effluent from constructed wetlands include recycling it back through the wetland system (to maintain water budget), utilization for irrigation purposes, release to surface waters or to grass filter strips (Simeral, 1998).

2.4.4 Vegetative Filter Strips

Vegetative filter strips (VFS) are areas of planted or indigenous vegetation that can be used to treat agricultural runoff from various sources such as feedlots, croplands and pasturelands (Lorimor et al., 2002). A properly designed VFS will have the desired runoff flowing evenly throughout the strip, slowing down the runoff velocity and allowing contaminants to settle out (Smith, 2000). In addition to treatment through settling of contaminants (i.e. sediment), a VFS can also treat runoff through other processes such as infiltration, adsorption and aeration (Lorimor et al., 2002). The process of infiltration promotes the filtering of contaminants from runoff and also reduces the volume of runoff leaving a VFS. Soil and plant surfaces within a VFS provide numerous surfaces in which removal of soluble contaminants (i.e. phosphorous) can be achieved through the process of adsorption. Treatment can also occur due to aeration of runoff while it flows through a VFS. Aeration can provide the necessary O_2 that is required for the decomposition of oxygen demanding wastes as well as transformation processes of nitrogen species (i.e. ammonification and nitrification). Overall, a properly designed VFS system has been shown to remove sediment, oxygen demanding wastes, nutrients (nitrogen and phosphorous) as well as fecal microorganisms from agricultural runoff (Lorimor et al., 2002).

The physical characteristics of a VFS system are key design considerations to achieve a properly functioning VFS system. Physical properties of a VFS system include size and shape, land surface slopes, construction material, and the vegetation utilized. The size and shape of a VFS system will depend on land availability as well as the degree of

treatment desired. In general, the degree of treatment increases as the size of a VFS system increases. VFS systems should have flat cross-section with a slight slope ($< 4\%$) in the direction of flow (Lorimor et al., 2002). The construction material utilized (i.e. soils) will directly dictate the infiltration rate of runoff within a VFS. Soils with higher infiltration rates will absorb runoff and its associated dissolved contaminants faster than soils with low infiltration rates (Smith, 2000). VFS systems should consist of permanent herbaceous vegetation consisting of a single species or a mixture of grasses, legumes and/or other species adapted to the soil, climate and the anticipated contaminants being transported by the runoff (NRCS, 2003c).

The hydraulic nature of a VFS system will also dictate how well a VFS system will operate. In order to achieve proper treatment from a VFS system it is important to have even distribution of runoff entering a VFS (Lorimor et al., 2002). This will promote uniform loading across the VFS which will in turn result in slower runoff velocities within the system, encouraging the settling of solids. The uniform depth of runoff across the width of a VFS system should be kept less than 1.5 inches in order to help trap sediment and other constituents (Lorimor et al., 2002).

In addition to the physical and hydraulic design considerations, the characteristics of the runoff to be treated will play an important role in properly designing a VFS system. The concentrations of the constituents of concern (i.e. nutrients, oxygen demanding wastes, etc.) along with the desired degree of treatment from a VFS will be important when sizing the system. Generally, the size of a VFS system will increase as the concentrations

and desired degree of treatment increases. No matter what size a VFS is, heavy

sediment loads can have significant negative impacts on the treatment efficiency. When

runoff carrying a high level of sediment enters a VFS, build up of this sediment occurs

which in turn affects the flow path of the runoff and often can cause short-circuiting

through the system. Short-circuiting greatly decreases the treatment efficiency of VFS

systems. Therefore, VFS systems must be preceded by a properly operating

sedimentation basin when the runoff contains a high level of sediment (Lorimor et al.,

2002). Figure 2.5 illustrates two design variations, Serpentine and Wide, of VFS

systems being utilized to treat runoff from an animal feedlot. In both instances the VFS

system is preceded by a settling basin and even distribution of runoff is promoted. The

Serpentine VFS design utilizes terraces to distribute and dictate the flow of runoff

through the VFS while the Wide VFS design utilizes a gated pipe to evenly distribute the

flow of runoff.
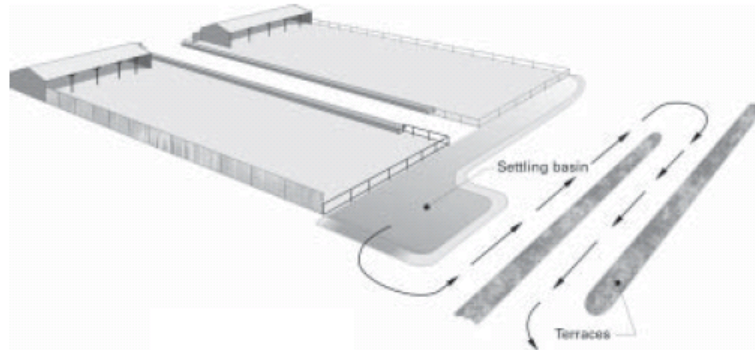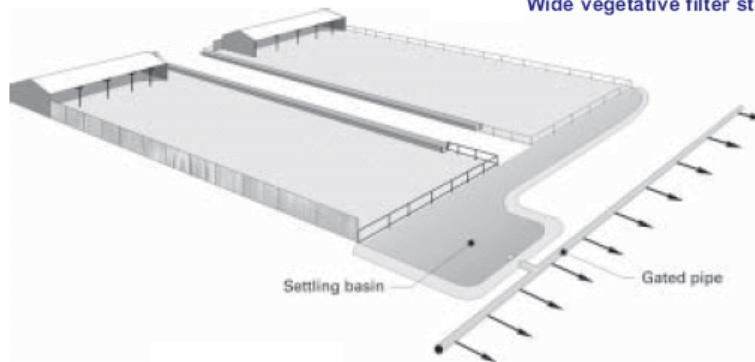
Figure 2.5: Serpentine and Wide VFS Design for Treating Feedlot Runoff (Lorimor et al., 2002)

The depletion of various contaminants from agricultural runoff can be achieved through the proper pretreatment, design and maintenance of a VFS system. Table 2.4 summarizes the removal efficiencies achieved from a properly functioning VFS system treating feedlot runoff contaminants. From these results it can be concluded that a properly functioning VFS system, on an average basis, has been observed to have significant reductions in sediment (total solids), oxygen demanding wastes (COD), nitrogen and fecal microorganisms.

Table 2.4: Summary of VFS Contaminant Removal From Feedlot Runoff (from Lorimor et al., 2002)

Contaminant	Removal Efficiency (%)		
	Average	Maximum	Minimum
Total Solids	64.5	87.0	23.6
COD	74.8	92.1	15.0
Total Nitrogen	71.5	95.3	18.0
NH_4^+ - N	69.4	99.2	18.6
Fecal Coliform	76.6	100.0	31.0

2.4.5 Bioretention Systems

Bioretention systems are a BMP that is conventionally utilized to treat urban stormwater runoff from commercial, residential and industrial areas (USEPA, 1999). However, this research project investigated the possibility of utilizing bioretention systems to treat runoff from agriculture. In a conventional bioretention system, a grass buffer strip and ponding area is used to attenuate peak runoff flows. Water then infiltrates through a vegetated/soil mulch layer and then through a sand layer. Figure 2.6 illustrates the conventional bioretention system layout utilized to treat urban stormwater runoff.
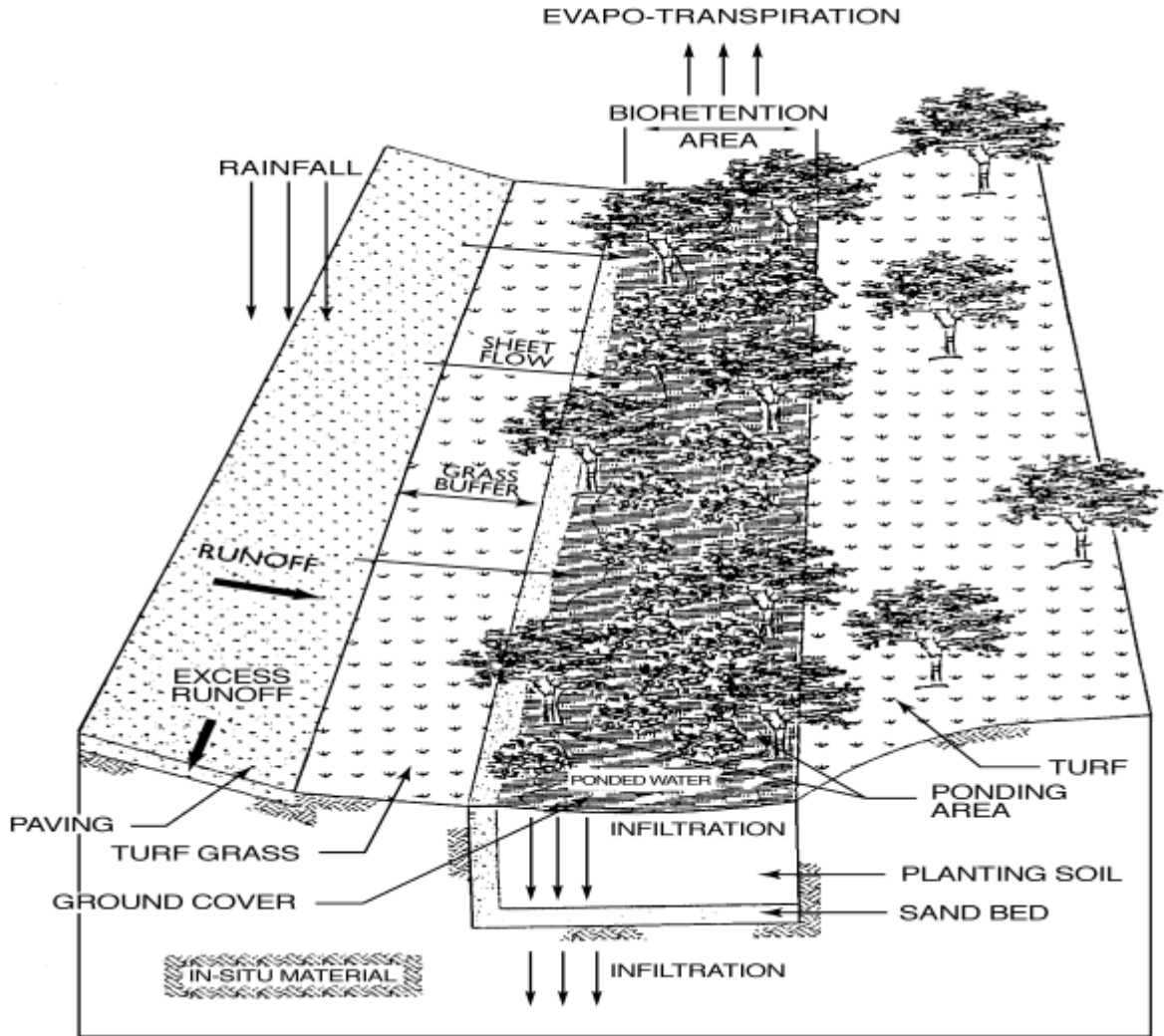
Figure 2.6: Conventional Layout of Urban Bioretention System (from PGDER, 1993)

Treatment of contaminants being transported by the runoff occurs through evapotransporation, plant uptake, biodegradation, filtration and adsorption (USEPA, 1999). Bioretention systems have been reported to remove nutrients (nitrogen and phosphorous), metals, sediment and organic matter through the various treatment mechanisms. Both total suspended solids (sediment) and organic matter have been reported to be reduced by 90% (PGDER, 1993). Davis et al. (2001) reported high reductions in metals (copper, lead, and zinc; >92%) and moderate reductions for

phosphorous (~80%), total Kjeldahl nitrogen (TKN) (NH_4^+ + Org N) (65-75%), and

ammonia (60-80%). However, only low removal rates (< 20%) of nitrate/nitrite nitrogen

have been reported in conventional bioretention systems (Davis et al., 2001; Davis et al.,

2006). Kim et al. (2003), proposed a modification of the bioretention system for

removal of total nitrogen where runoff is conveyed to a ponding area and gradually

infiltrates through a vegetated/mulch area then through a sand media where nitrification

takes place. The nitrified stormwater then travels through a submerged denitrification

region, which is supplied with an electron donor, where nitrate is reduced to nitrogen gas

by anoxic heterotrophic or autotrophic denitrifying bacteria. The outlet from the

bioretention system is configured in a manner so that the denitrification zone remains

submerged to maintain the anoxic conditions required by the denitrifying organisms. A

cross-sectional view of a bioretention system modified for total nitrogen removal is

shown in Figure 2.7.
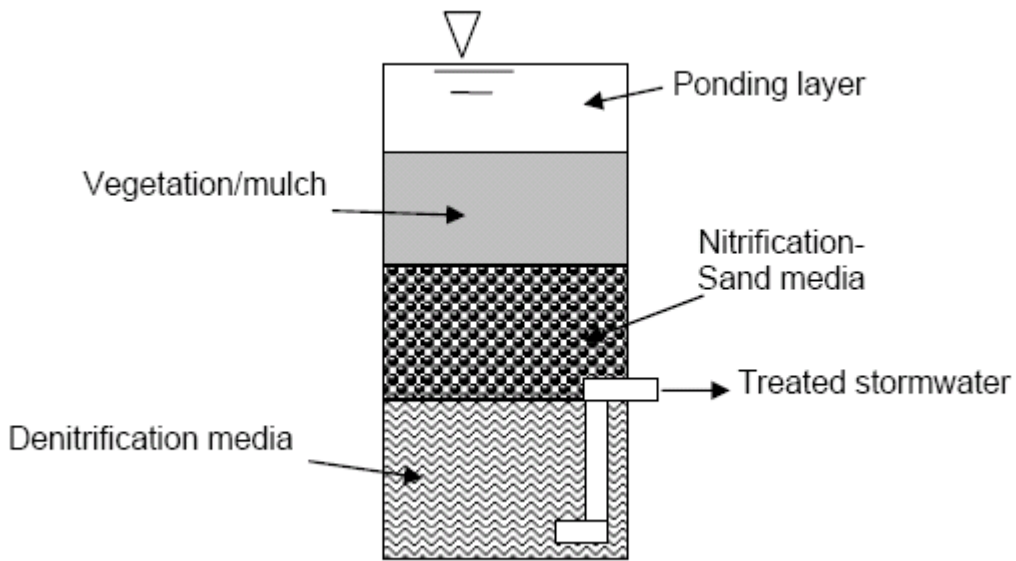
Figure 2.7: Cross-Section of Bioretention System Modified for Total Nitrogen Removal

Kim et al. (2003) investigated the use of one inorganic substrate (sulfur) and six organic substrates (alfalfa, leaf mulch compost, shredded newspaper, sawdust, wheat straw and wood chips) as potential electron donors within the submerged denitrification region. The organic electron donors were mixed with sand at a ratio that provided a sufficient mass of the electron donor for the extent of the column studies. The sulfur was mixed with limestone to provide an alkalinity source to buffer the acidity produced during autotrophic denitrification. Kim et al. (2003) investigated the use of both small (0.6 to 1.18 mm) and large (2 to 2.36 mm) sulfur particles. Through laboratory column studies it was concluded that the newspaper, wood chips and small sulfur/limestone performed the best out of the electron donors studied. During the study, the columns had water applied to them for 35 to 40 days at a flowrate of 2.2 ml/min. The water contained nitrate at a concentration of approximately 2 mg/L as nitrogen. The performance was based on nitrate removal efficiencies and effluent water quality with regards to turbidity and TKN levels. Approximate nitrate removal efficiencies within the shredded newspaper, wood chip and small sulfur/limestone columns were 100%, 95% and 91%, respectively. The mass of sulfur added was the same in the columns containing small and large particles, however, only approximately 30% nitrate removal was achieved in the large sulfur particle column compared with the small sulfur particle column's removal of 91%. Kim et al. (2003) suggests that this is probably due to the increased number of sulfur particles in the small sulfur column, allowing for more surface area for contact with the nitrate-laden water and for attached growth of denitrifyers.

Kim et al. (2003) further investigated the performance of the shredded newspaper, wood chips and small sulfur particles (mixed with limestone) by varying the nitrate loading and flowrate applied to the columns. Of these three electron donors the newspaper column showed the best percentage of nitrogen removal efficiency throughout this study. In particular, the newspaper column out-performed the wood chips and small sulfur columns at higher nitrate loading rates and flowrates.

Further investigation of shredded newspaper was carried out in a pilot-scale bioretention study (Kim et al., 2003). The pilot-scale reactor used was a 30" long by 16" wide by 18" deep plastic box modified to contain an anoxic denitrification region similar to that shown in Figure 2.7. The anoxic denitrification region was 7" in depth and contained the shredded newspaper and sand mixture. Overlying this region was a 7" layer of loamy sand, leaving 4" available for ponding at the top of the pilot-scale bioretention unit. Synthetic runoff containing nitrate at approximately 2 mg/L as N was applied to the bioretention unit at 206 ml/min for 6 hours during laboratory pilot-scale experiments. During the laboratory pilot-scale studies high nitrate removal efficiencies of 70 to 80% were observed.

The modified pilot-scale bioretention unit investigated by Kim et al. (2003) resulted in high denitrification rates and therefore, in theory makes this modified bioretention system a prospective treatment technology for runoff containing high levels of nitrate. However during these pilot-scale studies, nitrate was the only nitrogen species applied to the bioretention units and, therefore, denitrification was the only process carried out within

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the units. Other nitrogen species (i.e. NH_4^+ and Org N) should have been applied to investigate the performance of this modified bioretention system with regard to overall total nitrogen removal through ammonification, nitrification and denitrification.

CHAPTER 3:   METHODS OF INVESTIGATION

Two pilot-scale denitrifying bioretention systems were designed and tested during this research

project. The overall goal of this research was to investigate the efficacy of the systems when

utilized for the treatment of non-point sources of nitrogen such as agricultural runoff. Both units

were constructed and operated identically except that one unit was designed for autotrophic

denitrification while the other unit was designed for heterotrophic denitrification. While nitrogen

removal was the main focus of this project, other constituents were monitored to examine the

overall performance of the two units. The experimental program was carried out in three phases,

shown in Table 3.1.

Table 3.1: Experimental Program Summary

Phase	Description	Dates
Phase I	Design, Construct and Acclimate Bioretention Units	August 2006 to March 2007
Phase II	Laboratory Testing of Bioretention Units	April 2007 to July 2007
Phase III	Field Testing of Bioretention Units	August 2007 to May 2008

A number of water quality parameters were measured throughout the project to gain insight into

the performance of the two units. Table 3.2 presents the various constituents monitored

throughout the project, the analytical methods used and the method detection limits for each

analyte. Ammonium and nitrate were measured using different analytical techniques during

different phases of the project, as noted in Table 3.2. Appendix E contains the quality

assurance/quality control procedures that were followed as close as possible throughout this

project in order to ensure accurate laboratory analysis.

Table 3.2: Analytical Methods Summary

Parameter	Analytical Method	Method Detection Limit
Total Nitrogen (TN)	HACH Test 'N Tube: Persulfate Digestion Method	0.4 mg/L as N
Ammonium (NH_4^+)	APHA et al. (2005) Standard Method 4500-NH_3 D: Ammonia-Selective Electrode Method (used during Phase I and II)	0.06 mg/L as N
Ammonium (NH_4^+)	APHA et al. (2005) Standard Method 4500-NH_3 C: Titrimetric Method (used during Phase III)	5 mg/L
Nitrate (NO_3^-)	HACH Test 'N Tube: Cadmium Reduction Method 8039 (used only for Phase I simulated rain event #1 due to IC problems)	0.3 mg/L as N
Nitrate (NO_3^-)	Dionex Ion Chromatography (IC) System ICS-900 coupled with a Dionex AS40 Autosampler	0.07 mg/L as N
Nitrite (NO_2^-)	Dionex Ion Chromatography (IC) System ICS-900 coupled with a Dionex AS40 Autosampler	0.07 mg/L as N
Phosphate (PO_4^{3-})	Dionex Ion Chromatography (IC) System ICS-900 coupled with a Dionex AS40 Autosampler	0.31 mg/L as P
Total Phosphorous (TP)	HACH Test 'N Tube; Equivalent to APHA et al. (2005) Standard Method 4500-P E: Ascorbic Acid Method	0.02 mg/L as P
Sulfate (SO_4^{2-})	Dionex Ion Chromatography (IC) System ICS-900 coupled with a Dionex AS40 Autosampler	0.45 mg/L
Bromide (Br^-)	Dionex Ion Chromatography (IC) System ICS-900 coupled with a Dionex AS40 Autosampler	0.07 mg/L
5-day Biochemical Oxygen Demand (BOD_5)	APHA et al. (2005) Standard Method 5210B	$DO_i - DO_5 > 2$ mg/L; $DO_5 > 1$ mg/L
Chemical Oxygen Demand (COD)	HACH AcuVac™ Reagent Ampules; APHA et al. (2005) Standard Method 5220C: Closed Reflux Colorimetric Method	3 mg COD/L
Alkalinity	APHA et al. (2005) Standard Method 2320B: Titration Method; End Point pH of 4.5 (Phosphates Present)	20 mg/L as $CaCO_3$
Solids (TSS and VSS)	APHA et al. (2005) Standard Methods 2540D and 2540E	-
Dissolved Oxygen* (DO)	Electrometric Method using a YSI 5000 DO Meter (Yellow Springs, OH)	1 mg/L
pH	Electrometric Method using a Orion EA 940 pH Meter (Beverly, MA)	0-14 pH units
Copper (Cu)	APHA et al. (2005) Standard Method 3111: Flame Atomic Absorption Spectroscopy	1.5 mg/L
Zinc (Zn)	APHA et al. (2005) Standard Method 3111: Flame Atomic Absorption Spectroscopy	1.5 mg/L

*DO measured as part of BOD_5 test. DO MDL is reportable level.

The various parameters that were analyzed during this project were based on a number of objectives. Testing for the various nitrogen species was carried out to evaluate the reactors performance with regards to the goal of total nitrogen removal and understanding the mechanisms of nitrogen removal in the systems. Phosphorous is a constituent often related to non-point source pollution due to its contribution to eutrophication. Sulfate (SO_4^{2-}) was measured because

it is a product of the autotrophic denitrification process carried out in the sulfur/oyster shell bioretention unit. BOD_5 and COD are both common techniques used to measure bulk concentrations of organic matter in aqueous samples (Metcalf and Eddy, 2003). BOD_5 to COD ratios were also used to evaluate the biodegradeability of organic matter contained in the influent and effluent. A ratio of 0.5 or greater generally implies the waste can easily be treated by biological means. Ratios less than 0.3 are often associated with wastes that may contain toxic compounds or require acclimated microorganisms to be treated (Metcalf and Eddy, 2003). Dissolved oxygen (DO) measurements were required as part of the analytical technique used to measure BOD_5. Alkalinity production and consumption occurs during the transformation of nitrogen species that takes place during total nitrogen removal through the processes of nitrification and denitrification. Therefore, alkalinity measurements were conducted as an insight into the processes being carried out within the bioretention units. Total suspended solids (TSS) as well as volatile suspended solids (VSS) were measured in order to gain insight on the bioretention units ability to remove sediment. The measurement of pH gives insight on the aqueous environmental conditions entering and exiting the units. Metals concentrations were measured to evaluate the ability of the bioretention units to remove these constituents and to assess the possibility for toxic effects from the influent to the microbial community within the units.

3.1   Phase I: Design, Construction and Acclimation of Bioretention Units

The first phase of this project included the design, construction and acclimation of the two bioretention units. The reactors were constructed from open top rectangular tanks made of

polyethylene, manufactured by American Tank Company, Inc. Each unit measured 30" tall by 24" wide and 18" deep, resulting in a volume of 7.5 ft^3 or approximately 56 gallons (~212 liters). Figure 3.1 shows the specific regions of the bioretention unit and the corresponding dimensions of each layer. Figure 3.1 also illustrates the general flow through the units; the influent entered the top of the units and flowed by gravity through the various regions and was discharged through an effluent pipe located 8" from the bottom of the unit.
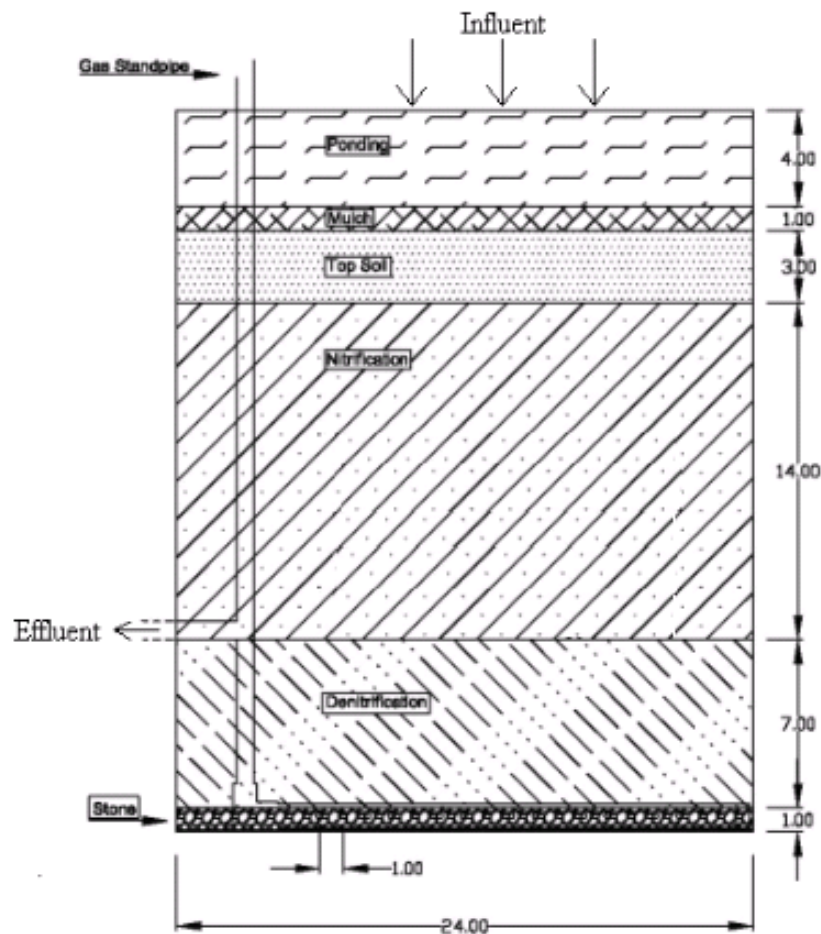
Figure 3.1: Front View of Bioretention Units Illustrating Regions
(Dimensions in inches)

From Figure 3.1, it can be noted that there were six distinct regions that made up the bioretention units. From top to bottom these regions were: ponding, mulch, top soil, nitrification, denitrification and stone. The following gives design specifics for the six regions:

- Ponding Region:
    - Approximately 4 inches in depth
    - Allows for ponding of about 7.5 gallons (28 liters) of stormwater runoff
- Mulch Region:
    - Approximately 1 inch layer of cedar bark mulch that was purchased from the Amherst Farmers Supply store located in Amherst, MA
    - The purpose of the mulch layer is to prevent erosion of the top soil from the influent
- Top Soil Region:
    - Approximately 3 inches of topsoil
    - The topsoil was acquired from a corn field located in Hadley, MA
    - Topsoil was characterized as a silt loam from a soil survey conducted by the USDA (1981) and exhibits moderate permeability
    - The top soil's purpose was to promote ponding and gradual infiltration of stormwater runoff into the underlying nitrification layer

- Nitrification Region:
    - Total depth of approximately 14 inches
    - Unsaturated zone constructed of sand designed to sustain aerobic conditions necessary for of nitrification
    - A blasting sand ("OOS Blasting Sand") was used within this region that was supplied by the Amherst Farmers Supply store located in Amherst, MA
        - Manufactured by Holliston Sand Company, Inc.
        - Grain sizes range from 0.3 to 0.84 mm with approximately 77% by weight between 0.5 to 0.71 mm (from manufacturers specifications)
    - Sand provides surface for attached microbial growth

- Denitrification Region:
    - Total Depth of approximately 7 inches
    - Bioreactor outlet was designed to keep this layer saturated, see Figure 3.2
    - One reactor used a Sulfur/Oyster Shell mixture and the other used a woody material called De-Nyte^{TM} (discussed below)
    - Denitrification media provided a surface for attached microbial growth and electron donor for denitrification

- Stone Layer:
    - Total Depth of approximately 1 inch
    - Angular stone with average size range of 3/8 to 1 inch
    - This stone layer will prevent the denitrification media from clogging the effluent piping

All of the regions except for the denitrification region were identical in both of the bioretention units utilized in this project. The difference between the denitrification regions was the media contained within this region.

The denitrifying media in the unit designed for autotrophic denitrification consisted of a mixture of elemental sulfur pellets and crushed oyster shells at a ratio of 3:1 by volume. This bioretention unit will be referred to as "S:OS." The sulfur was supplied from the Georgia Gulf Sulfur Corporation and is characterized as 4 mm pellets that closely resemble the shape of lentils. Sulfur is a by-product of the oil refinery industry and is inexpensive and readily available. The process of autotrophic denitrification carried out within the S:OS bioretention unit exploited sulfur as the electron donor during the denitrification reaction, as discussed in Section 2.2.2. The crushed oyster shell that was included within this region was manufactured by Core Calcium & Shell Products of Mobile, AL and was purchased from the Amherst Farmers Supply in Amherst, MA. The purpose of the oyster shell was to provide an alkalinity source due to the alkalinity required in the process of autotrophic denitrification, discussed in Section 2.2.2. According to the manufacturing specifications, the crushed oyster shell utilized during this project was >97% $CaCO_3$ making it a prime source of alkalinity within the S:OS bioretention unit. Sengupta et al., (2007) demonstrated that the S:OS mixture provided high denitrification rates from septic system wastewater streams and further investigation of this S:OS mixture for other applications was desired. Therefore, this research project tested the S:OS mixtures ability to remove nitrogen from non-point sources, such as stormwater runoff.

The denitrifying media in the unit that was designed for heterotrophic denitrification consisted of De-Nyte^{TM}, which is manufactured by Presby Environmental, Inc. of Sugar Hill, NH. The De-Nyte^{TM} material was comprised of by volume: 38% maple sawdust, 38% birch sawdust and 25% washed concrete sand. This bioretention unit will be referred to as "Denyte" in this report. During studies carried out by Presby Environmental, Inc. the De-Nyte^{TM} media demonstrated promising nitrate removal rates from septic system effluent (Germano-Presby et al., 2005). Therefore, the decision was made to further investigate this media for other applications such as treatment of stormwater containing elevated levels of nitrogen. Along with the high nitrate removal rates, both sawdust and concrete sand are readily available and relatively inexpensive, making the De-Nyte^{TM} media economically attractive. The process of heterotrophic denitrification carried out in the Denyte bioretention unit exploited the organic matter (sawdust) as the electron donor during the denitrification reaction, as discussed in Section 2.2.2.

The process of denitrification, both heterotrophic and autotrophic, requires an anoxic environment, as discussed in Section 2.2.2. The bioretention units were designed to promote anoxic conditions by keeping the denitrification region submerged. To achieve this the effluent was collected at the bottom of the units using ¾ inch perforated PVC piping located within the stone region and then discharged at the top of the denitrification region, 8" above the bottom of the units.. This configuration of effluent piping required the water being treated travel through the entire depth of the denitrification region prior to being discharged from the reactors but still kept the denitrification region submerged. Figure 3.2 shows the layout of the effluent piping that was used. The ½ inch PVC gas standpipe illustrated in Figure 3.2 provides a vent for the effluent piping and prevents N_2 gas, produced from denitrification, from collecting in the effluent piping.
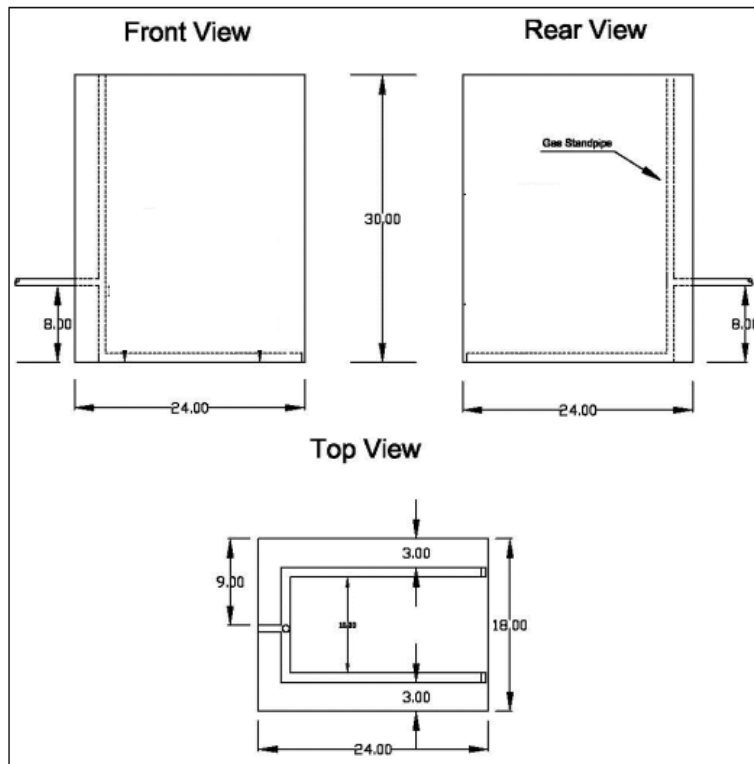
Figure 3.2: Effluent Piping Layout within Bioretention Units

The pilot-scale bioretention units were initially constructed in the Engineering Laboratory II building located on the campus of the University of Massachusetts Amherst. Construction of the units was done from the bottom up (i.e. from stone region up). The acclimation of the units was done simultaneously with the construction of the units in order to establish the necessary microbial communities within the denitrification and nitrification regions. Inoculation started with the denitrification region and proceeded to the nitrification region.

The inoculation procedure was identical for both reactors and was conducted at the same time. The stone and denitrification media was added to both reactors according to the design specifications discussed previously. Mixed liquor from the Belchertown Wastewater Treatment Plant (WWTP) located in Belchertown, MA was collected and allowed to settle in the laboratory.

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Approximately 1.5 liters of supernatant was decanted and mixed with a sodium nitrate ($NaNO_3$) solution with an approximate concentration of 10 mg N/L. Sufficient volume of this mixture was added to both units to recirculate this mixture through the denitrification region. In order to promote anoxic conditions, required for denitrification, the denitrification region was covered with plastic so oxygen transfer from the air was inhibited. The effluent NO_3^- concentration from both units was monitored daily to measure the extent to which denitrification was occurring. Periodically, the region was respiked with NO_3^- when the effluent NO_3^- concentration decreased below 2 mg/L as N. This inoculation procedure was stopped after 23 days, when satisfactory denitrification from both units was observed.

Inoculation of the nitrification regions was carried out in a similar manner as the denitrification procedure. Initially, the nitrification (sand) media was added to both units and mixed liquor was acquired from the Belchertown WWTP. The supernatant from the mixed liquor was added to a stock solution containing $NaNO_3$, glycine (Org N) and ammonium chloride (NH_4Cl) at concentrations of 2 mg N/L, 8 mg N/L and 4 mg N/L, respectively. For approximately one week recirculation was performed in both units. After a week, recirculation was stopped and both units were fed with a solution containing the same compounds at the same concentrations initially used without the supernatant. Approximately 20 liters of this solution was intermittently added to each unit daily. At this point the effluent from both reactors was wasted. Total nitrogen, NH_4^+ and NO_3^- effluent concentrations from both units were monitored in order to gain insight into the extent to which nitrification and denitrification was occurring within the units. Periodically, additional supernatant from the Belchertown WWTP was added to the nitrification region of the reactors to increase the microbial population density. When a satisfactory level of total nitrogen

removal was achieved in both units, through the processes of nitrification and denitrification, construction of the units was completed by adding the top soil and mulch regions. Overall, the inoculation of the nitrification regions took approximately 45 days.

3.2   Phase II: Laboratory Testing of Bioretention Units

Phase II of this project consisted of testing the bioretention units under controlled laboratory conditions. This phase of the project was carried out in the Engineering Laboratory II building located on the campus of the University of Massachusetts Amherst. The experimental program for testing the bioretention units in the laboratory was designed based on similar research projects, characteristics of stormwater runoff from agricultural lands, typical rainfall characteristics for the Western Massachusetts region, and the drainage area the bioretention units was expected to treat. From the research conducted on these topics the testing protocol, and flowrate, duration and chemical make-up of the synthetic stormwater were formulated.

Davis et al. (2001) investigated the use of bioretention systems to treat urban stormwater runoff. The general testing procedure utilized by Davis et al. (2001) was the basis for the protocol that was followed during Phase II of this project. The protocol utilized by Davis et al. (2001) consisted of applying synthetic stormwater that contained various constituents to the bioretention units at a constant flowrate for a specified duration. The synthetic stormwater's various constituents and their concentrations were based on published values corresponding to urban stormwater runoff. The flowrate and duration were based on an average annual precipitation event in the Baltimore, MD-Washington, D.C. area with a duration of six hours. The bioretention

area was set at 5% of the drainage area being treated and a rational method runoff coefficient representative of an urban location was utilized to determine the runoff loading applied to the bioretention system. Effluent samples were collected at selected time intervals throughout the application of the synthetic stormwater.

This project focused on the treatment of agricultural runoff in the Massachusetts region and therefore, some necessary adaptations to the protocol utilized by Davis et al. (2001) were made. The Massachusetts Department of Conservation and Recreation's online precipitation database was utilized for historical precipitation values for Amherst, MA, which were then used to determine the average annual precipitation event. A rational method runoff coefficient representative of agricultural lands was utilized when determining the application rate and duration of synthetic stormwater runoff to the units. The flowrate and the duration at which the synthetic stormwater was applied to the bioretention units along with the basis for these values are as follows (see Appendix C for calculations):

- Flowrate: 240 ml/min (0.063 gpm)

- Application duration: 6 hours

    - Total volume per rain event was approximately 86.4 liters (22.8 gallons)

- The rate and duration were based on the following:

    - Average storm total = 0.6 inches

    - Average. storm duration = 6 hours

    - Bioreactor area is 5% of drainage area (USEPA, September 1999)

    - Runoff coefficient of 0.15, representative of grassed land (WEF, 1992)

Synthetic stormwater nitrogen and phosphorous concentrations were based on the research

carried out by Davis et al. (2001) and literature values of nitrogen levels in agricultural runoff.

Although Davis et al. (2001) studied the treatment of urban stormwater runoff; it was decided not

to significantly change their levels of nitrogen and phosphorous so that the results obtained in this

project could be compared with previously published results. The nitrogen and phosphorous

concentrations utilized in this project and those used by Davis et al. (2001) are shown in Table

3.3. Table 3.3 shows that the addition of NH_4^+ was the only difference between the chemical

make-up of the synthetic stormwater used in Phase II of this project and that used by Davis et al.

(2001). The target total nitrogen concentration of 8 mg/L (as N) was applied to the bioretention

units throughout the laboratory testing of the units.

Table 3.3: Chemical Make-up of Synthetic Stormwaters During Phase II and Davis et al. (2001)

Pollutant	Chemical Used	Phase II Concentration (mg/L)	Davis et al. (2001) Concentration (mg/L)
Nitrate (NO_3^-)	Sodium Nitrate	2 (as N)	2 (as N)
Ammonium (NH_4^+)	Ammonium Chloride	2 (as N)	Not Included
Organic Nitrogen (Org N)	Glycine	4 (as N)	4 (as N)
Phosphate (PO_4^{3-})	Dibasic Sodium Phosphate	0.6 (as P)	0.6 (as P)

Estimated concentrations of nitrogen from various agricultural croplands, with and without

manure applied to the surface, are shown in Table 3.4 (NRCS, 1992). From these values it can be

concluded that the 8 mg/L (as N) contained within the synthetic stormwater is fairly

representative of the nitrogen levels that can be expected in agricultural runoff from croplands.

Therefore, this synthetic stormwater allowed for the investigation on the use of these bioretention

units for the treatment of nitrogen in agricultural runoff and also allowed for the results to be

compared with those of Davis et al. (2001).

Table 3.4: Estimated Nitrogen Concentration in Runoff from Agricultural Croplands With and Without Manure Applied to Surface (NRCS, 1992)

Cropping Conditions	Dissolved Nitrogen Concentration in Runoff (mg/L as N)	
	With Manure Applied	Without Manure Applied
Grass	11.9	3.2
Small Grain	16.0	3.2
Row Crop	7.1	3.0
Rough Plow	13.2	3.0

The experiments carried out in the lab are referred to as "laboratory events." During each event the synthetic stormwater was applied to both units in an identical manner. Between events no synthetic stormwater was applied to the bioretention units. One exception to this was between the first and second laboratory event, where 20 liters of synthetic stormwater was added every three days to both bioretention units. This was done in order to promote the further establishment of the nitrifying and denitrifying microbial communities within the bioretention units.

Two synthetic stormwater storage containers were used during the laboratory events. One contained dechlorinated tap water and the other contained a concentrated solution of the constituents being applied to the units. Based on stoichiometry, the tap water was dechlorinated by adding enough sodium thiosulfate to remove an assumed 1 mg/L residual chlorine concentration. The concentrated solution was mixed with the dechlorinated tap water just prior to being applied to the units at a ratio that gave the synthetic feed the desired composition shown in Table 3.3. The mixing ratio also resulted in the desired flowrate of 4 ml/sec entering the bioretention units. The type of pump and tubing that was used for the concentrated solution were Cole-Parmer Masterflex C/L Model #77120-62 and Cole-Parmer Silicone Tubing (flexible), respectively. The type of pump and tubing that was used for the tap water were Cole-Parmer

Masterflex Model #7553-20 and Cole-Parmer Masterflex Tygon Lab Tubing Model #06409-17, respectively.

The influent synthetic stormwater flowed by gravity throughout the regions of the bioretention units and exited the units through the effluent piping. The effluent synthetic stormwater from the bioretention units was discharged into the sewer. At selected time intervals, influent and effluent synthetic stormwater samples were taken from the S:OS and Denyte units. Samples were taken at the same time from both units in order to keep the testing procedure identical. Laboratory analysis of the samples was conducted in order to gain insight into the overall operation and performance of the two bioretention units. The results of the laboratory events conducted during Phase II of this project are presented in Chapter 4.

In addition to the laboratory events, a hydraulic tracer test was conducted during two of the events in order to gain insight into the hydraulic characteristics of the units. This was done by spiking the influent for one hour with a bromide (Br^-) solution shortly after the start of two laboratory events, 75 minutes for event #2 and 45 minutes for event #3. During the one hour spike, the Br^- solution, which was made by adding potassium bromide (KBr) to the tap water, was added to both units. The Br^- concentration used during the tracer test needed to be high enough to diminish the effects of dilution within the units and was set at approximately 1000 mg/L. Br^- was used for the hydraulic tracer test because it is stable and can also be analyzed using the IC analytical technique, which was already being used for analysis. The effluent samples taken during the laboratory events that had a tracer test conducted were analyzed for Br^- to estimate the

overall mean hydraulic residence time of both bioretention units. The results of the tracer study are presented in Chapter 4.

3.3 Phase III: Field Testing of Bioretention Units

The objective of Phase III was to investigate the performance of the bioretention units under field conditions. The same bioretention units that were utilized during Phase II of this project were used during Phase III. The field site was chosen to test the ability of the bioretention units ability to remove nitrogen contained in agricultural runoff. Other factors that played a role in choosing an appropriate field site were the geographical location, topography, characteristics of the runoff and approval from the landowner. The experimental program carried out during the field testing of the units mimicked the Phase II program as closely as possible to be able to compare the laboratory and field results.

Students from the University of Massachusetts Dartmouth, located in Dartmouth, MA, collaborated with the UMass Amherst research team during the field testing phase of the project. In order to keep travel time and distance to a minimum, an agricultural operation centrally located between the two institutions was desired. Mr. Marc Cohen, Sourcewater Protection Specialist with the Atlantic States Rural Water & Wastewater Association, manages rural watersheds in Connecticut and agreed to give his assistance in finding an appropriate field site location. Mr. Cohen was aware of possible field site locations in Northeastern CT, which is geographically centered between UMass Amherst and UMass Dartmouth.

The desire to have a field site centrally located between UMass Amherst and UMass Dartmouth established the general area in which Phase III of this project would be conducted. The next step was to find an owner of an agricultural operation in this geographical location that approved of the installation and testing of the two bioretention units. In addition to approval, the topography of the land dictated whether the bioretention units could be installed in a manner so control over the flow that entered and exited the units was possible. The need for extensive diversion structures was not desired during the field testing so that the impact these temporary units would have on the agricultural operation was kept to a minimum.

The characteristics of the agricultural runoff also impacted whether or not an agricultural operation would be acceptable for the field testing of the bioretention units. Originally, it was desired to feed the bioretention units runoff from croplands that had manure applied to them, since this was the type of runoff investigated during the laboratory testing of the bioretention units. Therefore, the search for an area that had manure applied to it that met the aforementioned requirements was carried out in collaboration with Mr. Cohen. However, after unsuccessfully searching for a field site that met these requirements and due to time constraints associated with the project, other field testing options were investigated. Mr. Cohen suggested a dairy farming operation located in Putnam, CT that was owned and operated by someone who was very interested in assisting us and willing to allow us to field test our units on his dairy farm. As requested, the exact location and the identity of the owner of the dairy farm will be kept anonymous. While visiting the dairy farm, a waste treatment lagoon located on the property was discussed as an alternative waste stream to apply to the bioretention units. Figures 3.3 and 3.4 show the location of Putnam, CT and an aerial view of the field site, respectively.
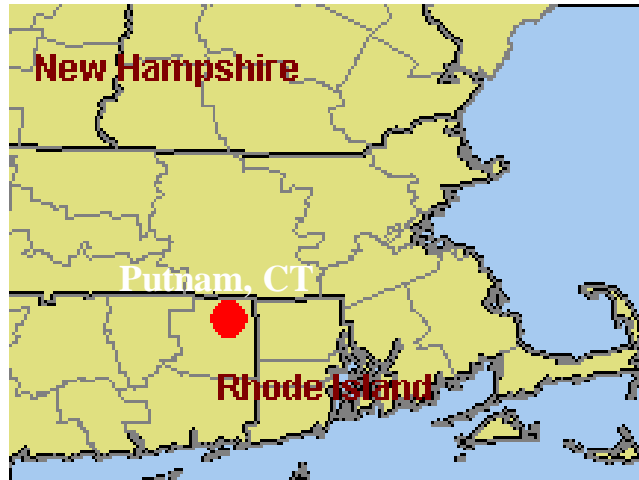
Figure 3.3: Location of Putnam, CT
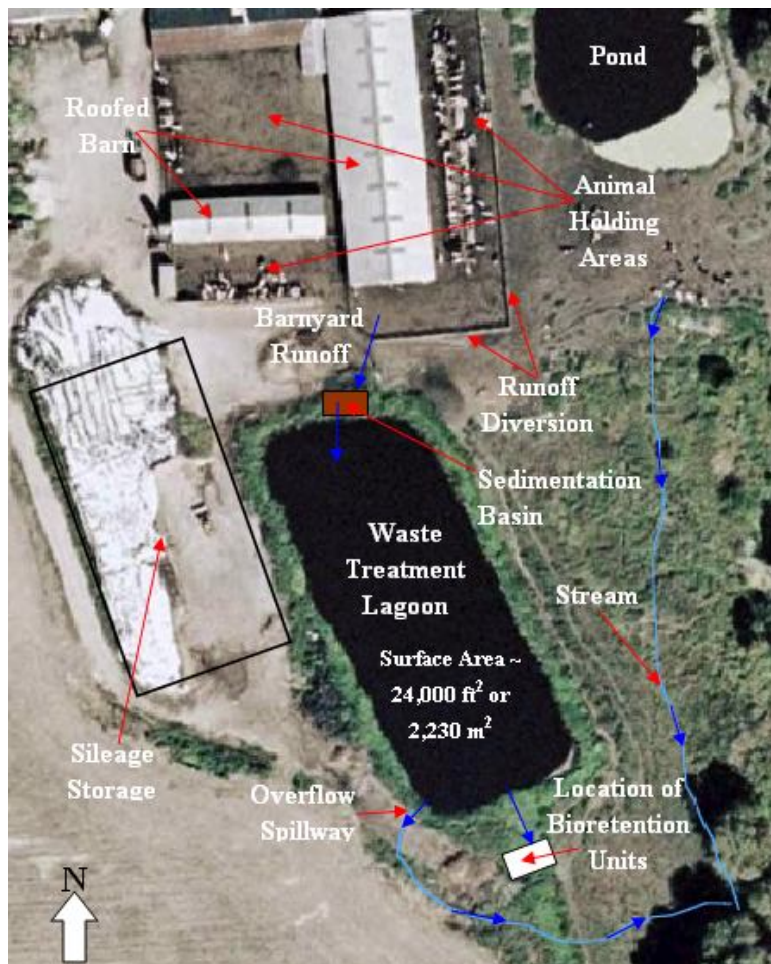
Figure 3.4: Aerial Layout of Field Site (from Google Earth)

Waste treatment lagoons are often associated with agricultural waste management plans, as discussed in Section 2.4.2. As shown in Figure 3.4, runoff from the barn and animal holding areas was diverted into a sedimentation basin where settleable solids are retained. Following the sedimentation basin, the runoff was conveyed into the waste treatment lagoon. The contents of the waste treatment lagoon were not utilized at the dairy farm operation for fertilization purposes. Instead, the contents of the lagoon were released over an overflow spillway when the water level of the lagoon reached the spillway elevation. The overflow from the lagoon then either infiltrated the land surface or flowed into a stream located adjacent to the treatment lagoon. Therefore, this overflow from the lagoon could have environmental impacts both to surface waters and groundwater depending on the infiltration rate and chemical make-up of the overflow water. It was decided to characterize the water contained in the treatment lagoon and investigate the options available for testing the ability of the bioretention units to treat this water. Samples from the waste treatment lagoon were collected on June 1st and June 28th of 2007 to get an initial insight into the characteristics of the water being released from the lagoon. Table 3.5 shows the analytical results of these samples with regards to nutrients (nitrogen and phosphorous) and organic matter (BOD_5 and COD).

Table 3.5: Results of June 1st and June 28th, 2007 Waste Treatment Lagoon Samples

Analyte	June 1st Concentration	June 28th Concentration	Units
NO_3^-	<MDL	<MDL	mg/L as N
NO_2^-	<MDL	<MDL	mg/L as N
NH_4^+	64.4	47.6	mg/L as N
PO_4^{3-}	16.8	19.5	mg/L as P
BOD_5	144	71	mg/L
COD	1,638	1,347	mg/L

Table 3.5 shows that the water contained within the treatment lagoon exhibited relatively high levels of nutrients in the form of NH_4^+ and PO_4^{3-} as well as organic matter. From Table 3.5 it can be seen that the level of NH_4^+ contained within the treatment lagoon was more than 20 times higher than that applied to the units during laboratory testing. The high nitrogen concentration contradicted our original plan of testing the units in the field at similar nutrient concentrations as those applied to the units in the laboratory. However, the high concentration of nitrogen contained within the lagoon was viewed as an opportunity to observe the performance of the bioretention units when used to treat high strength runoff. Therefore, it was decided to utilize the water contained within the waste treatment lagoon as influent to the bioretention units during the field testing phase of this project.

Subsequently, a system to apply the water from the treatment lagoon to the bioretention units needed to be developed. It was decided to design a system that conveyed the waste treatment lagoon water to the bioretention units that did not rely on the overflow spillway. This was chosen since water from the treatment lagoon was not constantly released over the spillway. Therefore, water could be applied to the bioretention units even during times when water was not being released over the spillway. Piping was installed at the southern end of the waste treatment lagoon in order to convey water from the lagoon to the location of the bioretention units (see Figure 3.4). The bioretention units were located at the southern end of the waste treatment lagoon because this area was not utilized by the dairy farmer and therefore, the field testing of the units would not interfere with the dairy farming operation.

The influent piping consisted of 1 ¼" PVC piping and was installed in a manner so that the water

from the waste treatment lagoon flowed by gravity to the bioretention units. At the time of

installation, the influent piping intake was set approximately 2" below the water surface of the

waste treatment lagoon. The photographs of Figure 3.5 depict the influent piping layout from the

waste treatment lagoon to the bioretention units. From Figure 3.5 it can be seen that a single

intake pipe withdrew water from the waste treatment lagoon. Prior to discharging the water into

the bioretention units, the influent piping was divided using a T-connection to convey water to

both of the bioretention units. The water was discharged from the influent piping into the top of

the bioretention units. Valves were installed at the discharge ends of the piping to control the

flowrate at which the waste treatment lagoon water was applied to the bioretention units.

Figure 3.5: Influent Piping Layout during Field Testing of Bioretention Units

The experiments carried out during Phase III of this project are referred to as "field events." In

order to be able to compare results, the experimental program for testing the bioretention units

during Phase III of this project was kept similar to the experimental program followed during

Phase II. The main difference between Phase II and III was the chemical make-up of the water

being applied to the bioretention units. During the field events, the flowrate and duration in which

the waste treatment lagoon water was applied to the bioretention units were 4 ml/sec and 6 hours, respectively (identical to Phase II), except for Field Events #1 and #3 (see Table 3.6). At the start of each field event the influent valves were adjusted so that a flowrate of 4 ml/sec was achieved. Between field events, the influent valves were closed to prevent the waste treatment lagoon water from entering the bioretention units.

Influent and effluent samples were collected from the bioretention units at selected time intervals during each field event. Laboratory analysis of the samples was conducted in order to gain insight into the overall operation and performance of the two bioretention units. The influent was left on for an extended period during Field Event #3 in order to gain insight into the response of the bioretention units to a longer storm event. Table 3.6 presents the dates on which the field events were conducted as well as information pertaining to each of the events.

Table 3.6: Field Event Dates and Comments

Field Event	Date Conducted	Remarks
#1	August 1, 2007	• 3 hour event rather than the usual 6 hour • Full laboratory analysis conducted on samples
#2	August 15, 2007	• 6 hour event • Full laboratory analysis conducted on samples
#3	September 12, 2007	• Extended Event – influent applied for 55 hours • Samples obtained during 1st 6 hours as usual and at 55 hours • No solids, total phosphorous or pH data for samples
#4	November 2, 2007	• 6 hour event • No solids, total phosphorous or pH data for samples
#5	November 28, 2007	• 6 hour event • Full laboratory analysis conducted on samples
#6	April 2, 2008	• 6 hour event • Full laboratory analysis conducted on samples
#7	May 7, 2008	• 6 hour event • Full laboratory analysis conducted on samples

A total of 7 field events were conducted between August 1, 2007 and May 7, 2008. No field events could be conducted between September 12, 2007 and November 2, 2007 due to an extended dry period, which caused the water level of the waste treatment lagoon to drop below the intake pipe for the bioretention units. No field events were conducted between November 28, 2007 and April 2, 2007 due to the freezing of the waste treatment lagoon. The results of the field events conducted during Phase III of this project are presented in Chapter 4.

CHAPTER 4:   RESULTS AND DISCUSSION

The efficacy of two pilot-scale bioretention systems, modified for total nitrogen removal, was investigated through experimental testing of the units in the laboratory (Phase II) and the field (Phase III). During Phase II, the ability of the bioretention units to treat synthetic runoff with nitrogen levels expected in runoff from croplands was investigated. Phase III investigated the ability of the bioretention units to treat water from a waste treatment lagoon at a dairy farm in Northeastern CT. The performance of both units was evaluated through laboratory analysis of influent and effluent samples throughout Phase II and III. Table 3.2 summarizes the various parameters measured to gather insight into the performance of the two bioretention units. Phases II and III were preceded by Phase I, which established the necessary nitrifier and denitrifier microbial communities within the bioretention units. The results obtained during Phase II and III of this research project are presented and discussed in the following sections.

4.1   Phase II Results

A synthetic stormwater, intended to mimic nitrogen levels contained in runoff from agricultural croplands, as discussed in Section 3.2, was used as the influent in Phase II of this project. A total of three laboratory events were performed. Hydraulic characteristics of the bioretention units were also evaluated during Phase II through tracer studies. Full sets of experimental data from Phase II can be found in Appendix A.

Laboratory Event #1 was carried out on April 16, 2007. A total of two influent samples and six effluent samples were collected during this event. Average influent and effluent concentrations

for the various parameters measured are shown in Table 4.1. Standard deviations from the

average values are shown in parentheses.

Table 4.1: Average Results of Laboratory Event #1

Analyte	Average Influent	Average S:OS Effluent	Average Denyte Effluent	Units
pH	6.8 (0.06)	7.7 (0.51)	6.8 (0.16)	
TN	6.5 (0.66)	4.5 (3.45)	4.1 (2.74)	mg/L as N
NO_3^-	2.3 (0.45)	3.7 (2.48)	3.4 (2.84)	mg/L as N
NH_4^+	2.0 (0.19)	1.0 (0.43)	0.6 (0.14)	mg/L as N
TP	0.5 (0.03)	0.2 (0.01)	0.1 (0.01)	mg/L as P
Alkalinity	< MDL	74.0 (19.09)	187.3 (67.53)	mg/L as $CaCO_3$
COD	19.4 (4.42)	30.0 (21.73)	41.3 (37.33)	mg/L
BOD_5	6.2 (1.29)	15.0	57.9	mg/L
TSS	0.4 (0.49)	0.8 (0.57)	9. 3 (3.30)	mg/L
VSS	0.1 (0.14)	0.8 (0.57)	6.5 (1.47)	mg/L

*Standard deviations given in ( ), see Appendix A for # of samples used to determine standard deviations.

Table 4.1 shows that there was an increase in COD, BOD_5, TSS and VSS concentrations in both

of the bioretention units. The generation of organics and solids within the bioretention units was

most likely due to the production of soluble microbial products (SMP) and leaching of organic

material. The higher values observed in effluent samples from the Denyte unit was probably due

to the leaching of organic matter from wood chips in the denitrification zone. Alkalinity

production was observed in both of the bioretention units, with the Denyte effluent exhibiting

higher levels of alkalinity then the S:OS effluent. This can be explained by the production of

alkalinity during the process of heterotrophic denitrification and the consumption of alkalinity

during the process of autotrophic denitrification. Based on the stoichiometry (equations 2.2, 2.5

and 2.6); nitrification results in 7.07 grams of $CaCO_3$ consumed per gram of NH_4^+ oxidized,

heterotrophic denitrification results in 3.57 grams of $CaCO_3$ produced per gram of NO_3^- reduced

and autotrophic denitrification (using elemental sulfur) results in 4.5 grams of $CaCO_3$ consumed per gram of NO_3^- reduced. The oyster shell contained within the denitrification region of the S:OS unit was expected to replace some of the alkalinity consumed during autotrophic denitrification. Through dissolution studies, Sengupta et al. (2007) found that the oyster shells rate of release of alkalinity was approximately 10 mg/L as CaCO3 per day. Total phosphorous removal was achieved in both of the bioretention units, which was most likely due to the sorption of phosphorous onto the media contained within the bioretention units (Evangelou, 1998). Approximately, 67% and 87% TP removal was achieved within the S:OS and Denyte bioretention units, respectively.

The main goal of both bioretention units was TN removal. However, Table 4.1 shows that lower than expected TN removal was achieved in both of the units during the first lab event. On an average basis, only 31% and 36% TN removal was achieved within the S:OS and Denyte bioretention units, respectively. Figures 4.1 and 4.2 shows the influent and effluent nitrogen speciation over time during Laboratory Event #1. The extent to which ammonification, nitrification and denitrification were carried out within the bioretention units can explain the low level of TN removal achieved. Excellent ammonification took place in both of the units since effluent TN was usually only comprised of NH_4^+ and NO_3^-. Moderate rates of nitrification occurred in both units, which can be concluded from the relatively low levels of NH_4^+ and elevated levels of NO_3^- in the effluent. The elevated levels of NO_3^- in the effluent of both units implies that denitrification was the process limiting the extent to which TN removal was achieved within the bioretention units.
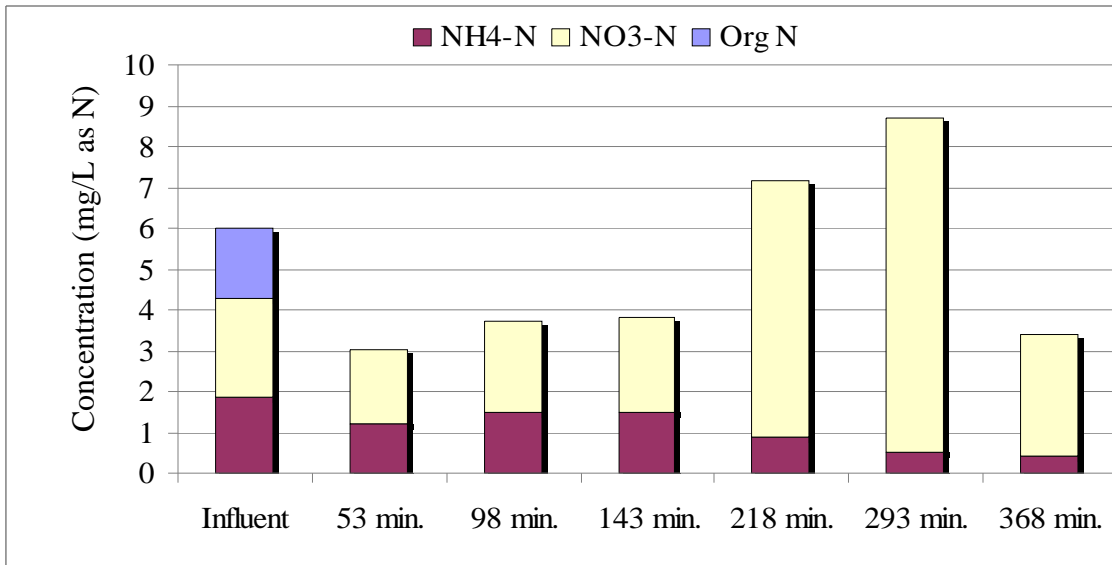
Figure 4.1: Average Influent and Effluent Nitrogen Species vs. Time for S:OS Unit During Laboratory Event #1. Org N Conc. Calculated by Difference Between TN and $NO_3^- + NH_4^+$.
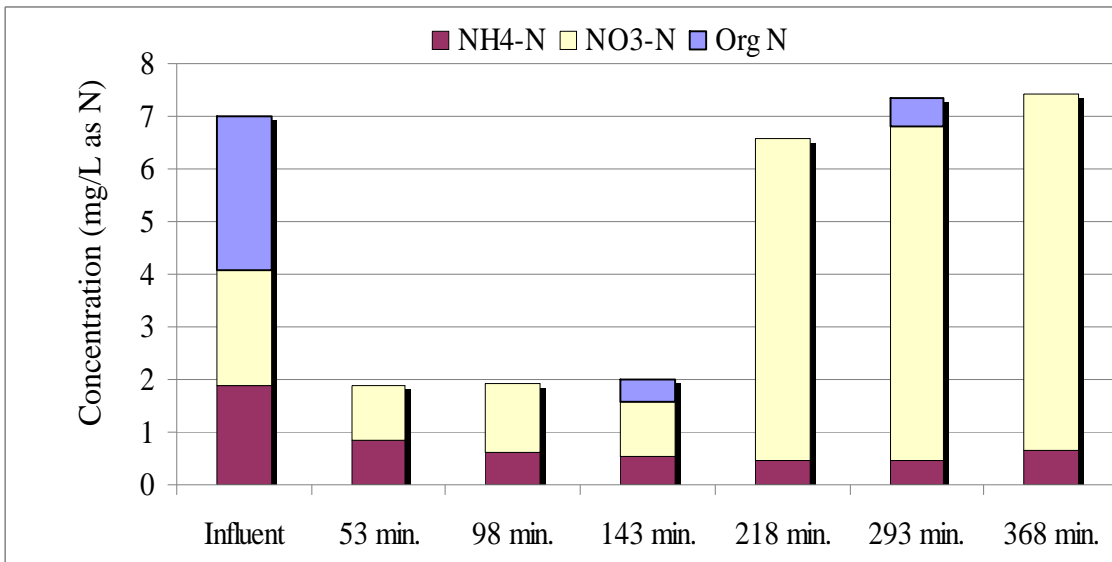
Figure 4.2: Average Influent and Effluent Nitrogen Species vs. Time for Denyte Unit During Laboratory Event #1. Org N Conc. Calculated by Difference Between TN and $NO_3^- + NH_4^+$.

Influent and effluent pH did not vary much from neutral, and therefore, no inhibition to the processes of nitrification and denitrification were expected due to pH. Instead, the nitrifying and denitrifying microbial communities were most likely not yet established enough to handle the nitrogen loading rate. From Figures 4.1 and 4.2, it can be concluded that initial TN removals were high in both units but then the TN removal declined rapidly and TN production was even observed. This can be explained by the initial flushing of the submerged denitrification region that contained water that remained in the denitrification region from the previous application. Following the initial flushing, the TN levels increased rapidly due to the influent nitrogen loading rate exceeding the capacities of the nitrifying and denitrifying microbial communities, especially the denitrifying microbial community.

Due to the poor TN removal achieved during Laboratory Event #1, approximately 20 liters of synthetic stormwater was applied to both units every 3 to 7 days for 5 weeks (total of 10 applications) to promote the establishment of the nitrifying and denitrifying microbial communities. Laboratory Event #2 was carried out on June 5, 2007. A total of two influent samples and thirteen effluent samples were taken during this event. Average influent and effluent concentrations for the various parameters are shown in Table 4.2. The standard deviations from the average values are shown in parentheses.

Table 4.2: Results of Laboratory Event #2

Analyte	Average Influent	Average S:OS Effluent	Average Denyte Effluent	Units
pH	6.7 (0.03)	7.0 (0.21)	6.3 (0.16)	
TN	7.6 (1.69)	0.8 (0.44)	1.4 (0.67)	mg/L as N
NO_3^-	1.4 (0.19)	< MDL	< MDL	mg/L as N
NH_4^+	2.0 (0.32)	0.7 (0.10)	0.2 (0.03)	mg/L as N
TP	0.6 (0.14)	0.3 (0.05)	0.1 (0.03)	mg/L as P
SO_4^{2-}	5.2 (0.19)	54.9 (32.71)	1.0 (1.43)	mg/L
Alkalinity	20.8 (2.47)	179.7 (61.20)	306.7 (121.71)	mg/L as $CaCO_3$
COD	4.1 (0.44)	82.0 (33.74)	124.5 (47.72)	mg/L
BOD_5	7.3 (1.89)	19.7 (15.14)	49.2 (27.46)	mg/L
TSS	0.7 (0.49)	2.2 (0.87)	20.7 (10.53)	mg/L
VSS	0.4 (0.14)	1.3 (1.10)	9.4 (2.42)	mg/L

*Standard Deviations given in ( ), see Appendix A for # of samples used to determine standard deviations.

As shown in Table 4.2, an increase in COD, BOD_5, TSS, VSS and alkalinity concentrations were observed in both of the bioretention units during Laboratory Event #2. These increases were most likely due to leaching of organic matter and SMP production, as discussed previously. Both bioretention units had similar TP removal rates as achieved in Laboratory Event #1. Approximately, 55% and 84% of the influent TP was removed within the S:OS and Denyte bioretention units, respectively. Figure 4.3 shows the effluent SO_4^{2-} concentrations over time in the S:OS unit effluent during Laboratory Event #2. Based on the stoichiometry of autotrophic denitrification using elemental sulfur, 92% of the effluent SO_4^{2-} production could be attributed due to sulfur oxidizing denitrification. The remainder of the SO_4^{2-} produced is most likely due to the utilization of O_2 as an electron acceptor, especially between synthetic storm events, when O_2 from the nitrification region can transfer into the denitrification region. This is confirmed by the initially high SO_4^{2-} concentrations observed due to the initial flushing of the denitrification region. Steady SO_4^{2-} concentrations were observed approximately 300 minutes (5 hours) following the start of

the influent application, as shown in Figure 4.3. A 50% decrease in effluent SO_4^{2-} concentration was observed approximately 200 minutes (3.3 hours) after the start of the influent application. The initial flushing of the denitrification region could be estimated from these results to be between 200 and 300 minutes. This estimate is reinforced by the increase in TN observed in the effluent of both units during laboratory Event #1 after 218 minutes, as shown in Figures 4.1 and 4.2.
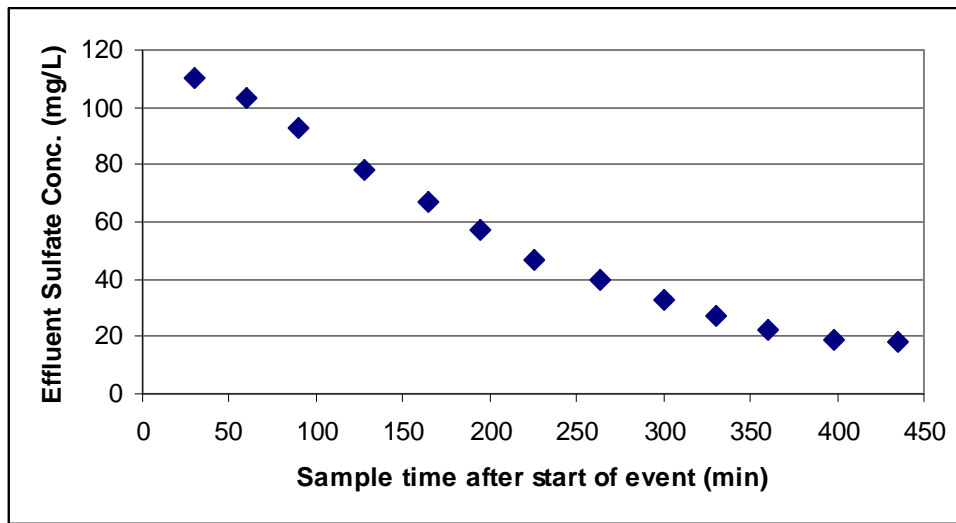
Figure 4.3: S:OS Effluent SO_4^{2-} Concentration vs. Time During Laboratory Event #2

High TN removals were observed in both of the bioretention units during Laboratory Event #2. On an average basis, 89% and 82% of the influent TN was removed by the S:OS and Denyte bioretention units, respectively. The increase in TN removal achieved during Laboratory Event #2 can be attributed to the establishment of the microbial community following Laboratory Event #1. Figures 4.4 and 4.5 show the influent and effluent nitrogen speciation over time during Laboratory Event #2. Relatively steady TN removal efficiencies were achieved in both bioretention units throughout the entire event. The rapid increase in effluent TN concentration following the initial flushing of the denitrification region that occurred during Laboratory Event

#1 did not occur during Laboratory Event #2. Towards the end of Event #2 there was a slight

increase in the TN concentration in the S:OS bioretention unit effluent.

Figure 4.4: Average Influent and Effluent Nitrogen Species vs. Time for S:OS Unit During Laboratory Event #2. Org N Conc. Calculated by Difference Between TN and $NO_3^- + NH_4^+$.

Figure 4.5: Average Influent and Effluent Nitrogen Species vs. Time for Denyte Unit During Laboratory Event #2. Org N Conc. Calculated by Difference Between TN and $NO_3^- + NH_4^+$.

As a result of the increased microbial activity within the bioretention units, it was decided not to apply synthetic stormwater to the bioretention units between Laboratory Event #2 and #3. Laboratory Event #3 was carried out on June 19, 2007 after an 18 day idle period. A total of two influent samples and eighteen effluent samples were taken during thi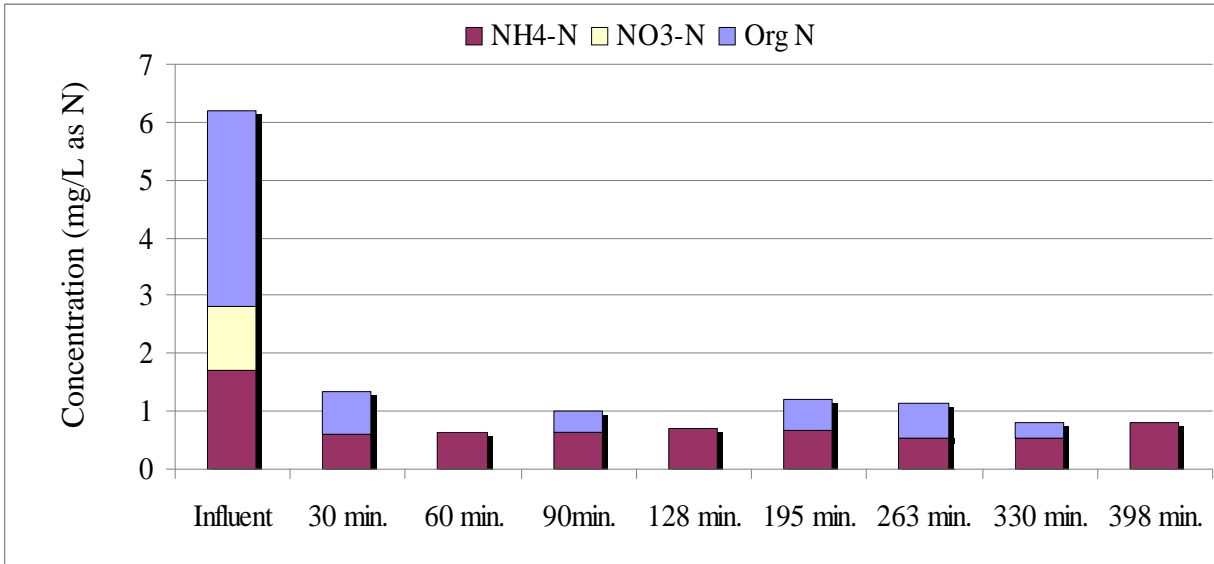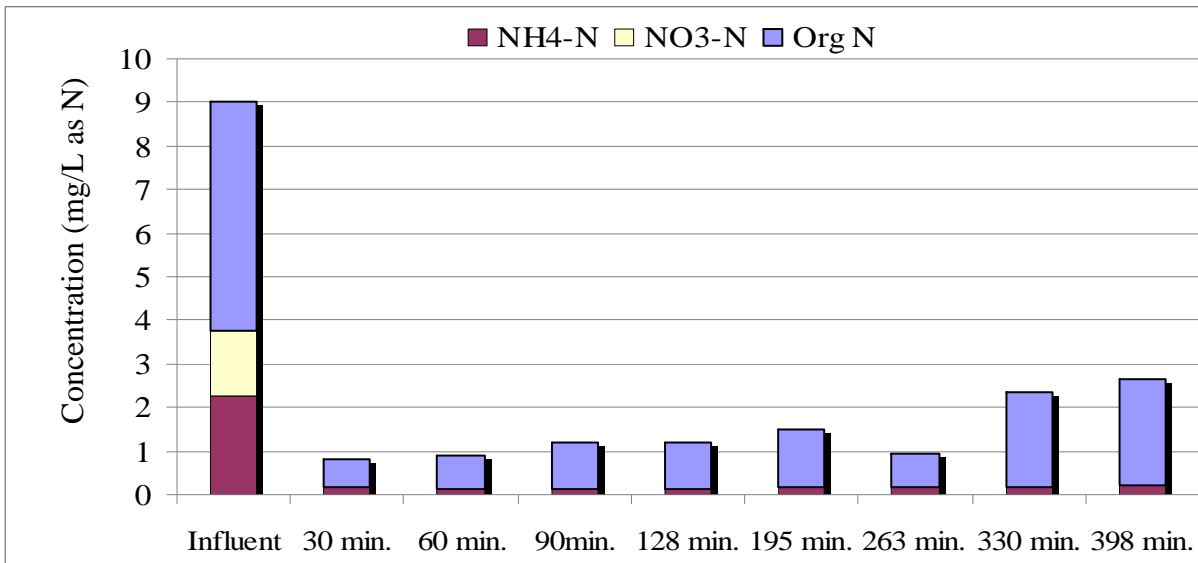s event. Average influent and effluent concentrations for the various parameters analyzed for are shown in Table 4.3. The standard deviations from the average values are shown in parentheses.

Table 4.3: Results of Laboratory Event #3

Analyte	Average Influent	Average S:OS Effluent	Average Denyte Effluent	Units
pH	7.0 (0.04)	7.6 (0.26)	6.7 (0.13)	
TN	7.6 (1.68)	0.6 (0.14)	0.9 (0.27)	mg/L as N
NO_3^-	1.5 (0.43)	< MDL	< MDL	mg/L as N
NH_4^+	2.1 (0.49)	0.43 (0.25)	0.3 (0.20)	mg/L as N
TP	0.6 (0.17)	0.2 (0.04)	0.1 (0.03)	mg/L as P
SO_4^{2-}	5.1 (0.36)	49.0 (30.09)	3.3 (1.17)	mg/L
Alkalinity	< MDL	163.3 (60.33)	280.0 (79.40)	mg/L as $CaCO_3$
COD	12.7(0.22)	60.6 (4.36)	87.5 (7.72)	mg/L
BOD_5	7.3 (1.90)	13.0 (10.13)	29.3 (13.93)	mg/L
TSS	0.8 (0.35)	2.5 (2.63)	14.4 (6.0)	mg/L
VSS	0.5 (0.35)	2.4 (2.63)	8.2 (0.84)	mg/L

*Standard Deviations given in ( ), see Appendix A for # of samples used to determine standard deviations.

An increase in COD, BOD_5, TSS, VSS and alkalinity concentrations was observed from both of the bioretention units during Laboratory Event #3. These increases can be explained for the same reasons as discussed previously with regards to the results of Laboratory Event #1. Laboratory Event #3 resulted in both bioretention units having similar TP removal rates as those achieved in Laboratory Event #1 and #2. Approximately, 63% and 89% of the influent TP was removed within the S:OS and Denyte bioretention units, respectively. The production of SO_4^{2-} within the

S:OS bioretention unit during Laboratory Event #3 was similar to that observed during Laboratory Event #2. Nearly 84% of the S:OS effluent SO_4^{2-} observed during Laboratory Event #3 could be attributed to the process of autotrophic denitrification.

Laboratory Event #3 resulted in higher TN removal in both of the bioretention units than that achieved in Laboratory Event #2. On an average basis, 92% and 88% of the influent TN was removed by the S:OS and Denyte bioretention units, respectively. The increase in the TN removal achieved during Laboratory Event #3 further reinforced that a robust microbial community of nitrifiers and denitrifiers had been established in both of the bioretention units. Figures 4.6 and 4.7 show the influent and effluent nitrogen speciation over time during Laboratory Event #3. Steady and excellent TN removal was achieved in both of the units throughout Event #3.
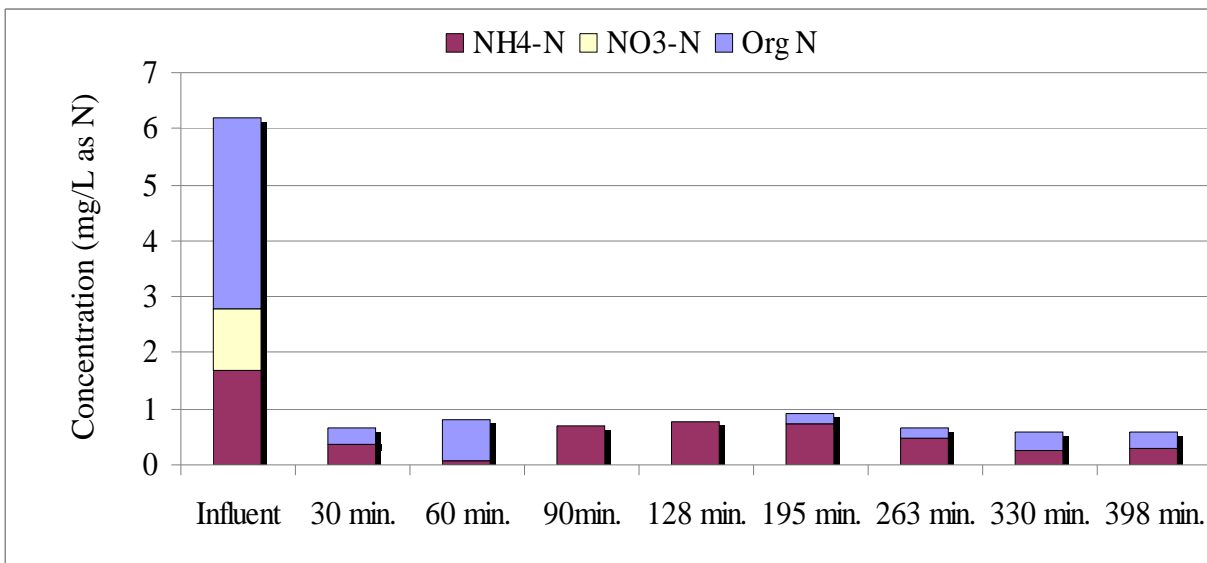
Figure 4.6: Average Influent and Effluent Nitrogen Species vs. Time for S:OS Unit During Laboratory Event #3. Org N Conc. Calculated by Difference Between TN and $NO_3^- + NH_4^+$.
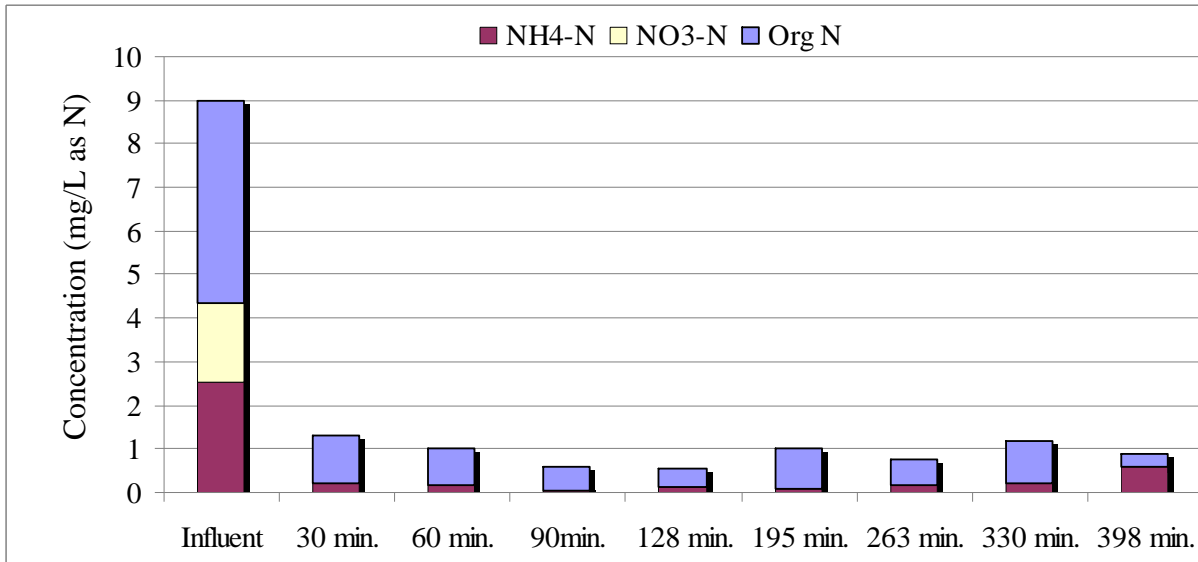
Figure 4.7: Average Influent and Effluent Nitrogen Species vs. Time for Denyte Unit During Laboratory Event #3. Org N Conc. Calculated by Difference Between TN and $NO_3^- + NH_4^+$.

The final Laboratory Event (#3) resulted in excellent nitrogen and phosphorous removal by both of the bioretention units. Davis et al. (2001) observed approximately 80% phosphorous removal, 65-75% TKN removal, 60-80% NH_4^+ removal and less than 20% NO_3^- removal during laboratory testing of conventional bioretention units. Laboratory Event #3 resulted in an average of 63% (S:OS) and 93% (Denyte) TP removal, 90% and 85% TKN removal, 80% and 88% NH_4^+ removal and >95% (S:OS and Denyte) NO_3^- removal. When compared to the results of Davis et al. (2001) it can be concluded that the bioretention units utilized during this project met or exceeded most of their removal efficiencies. The major difference in the results obtained in this project was the excellent NO_3^- removal compared to the poor NO_3^- removal of Davis et al. (2001). This difference is due to the fact that Davis et al. (2001) used a conventional bioretention system, which was not designed to carry out denitrification. The bioretention units in this project were modified in a manner similar to that proposed by Kim et al. (2003), in order to carry out denitrification.

Kim et al. (2003) conducted a series of laboratory tests to evaluate the performance of various electron donors for denitrification. During these laboratory studies, Kim et al. (2003) concluded that shredded newspaper out-performed the other electron donors, which included wood chips and elemental sulfur, the two electron donors utilized during this research project. During column studies, small sulfur particles (0.6 to 1.18 mm) resulted in 91% NO_3^- removal compared to only 30% NO_3^- removal when large sulfur particles (2 to 2.36 mm) were used. This is an interesting finding since this project observed >95% NO_3^- removal when using even larger sulfur particles (4 mm). Kim et al. (2003) utilized limestone as an alkalinity source within the denitrification region, where as this project utilized crushed oyster shell as an alkalinity source. Therefore, the difference in findings could be due to the different sources of alkalinity utilized. The careful acclimation of the bioretention units during this project could also have been a factor in the difference in results from those of Kim et al. (2003).

Kim et al. (2003) conducted pilot-scale studies utilizing shredded newspaper as the electron donor within the denitrification region. Kim et al (2003) observed 70 to 80% NO_3^- removal from the bioretention unit with shredded newspaper as the electron donor. Whereas, this research project observed >95% NO_3^- removal within pilot-scale bioretention units utilizing elemental sulfur and wood chips as electron donors. Similar testing procedures, with regards to the concentration of NO_3^-, flow rates and the application duration, were utilized by Kim et al. (2003) to those utilized during this research project. Therefore, the performance observed during this research project contradicts the findings of Kim et al. (2003) that shredded newspaper out performs elemental sulfur and wood chips when utilized as an electron donor.

As noted previously, tracer studies were also conducted during Phase II of this project. The tracer studies were conducted during Laboratory Event #2 and #3 in an effort to estimate the overall mean hydraulic residence times of both bioretention units. The first tracer study conducted during Laboratory Event #2 was not conducted in a manner that would allow for a particularly good estimate of the hydraulic residence times. The reason for poor results of the first tracer study is two-fold. First of all, the Br^- solution was not added soon enough following the start of Laboratory Event #2, which resulted in poor breakthrough of the tracer in the effluent during the duration of the event. Also, sampling of the effluent was not carried out for a long enough period of time to see the Br^- concentration in the effluent rise to a maximum and diminish. Therefore, it was decided to conduct another tracer study during Laboratory Event #3. However, this time the Br^- tracer pulse was introduced to both bioretention units earlier and the duration of effluent sampling was increased. These changes resulted in a better effluent Br^- breakthrough curve that rose to a peak concentration and diminished thereafter. Figure 4.8 illustrates both bioretention units' effluent Br^- concentration over time during Laboratory Event #3.
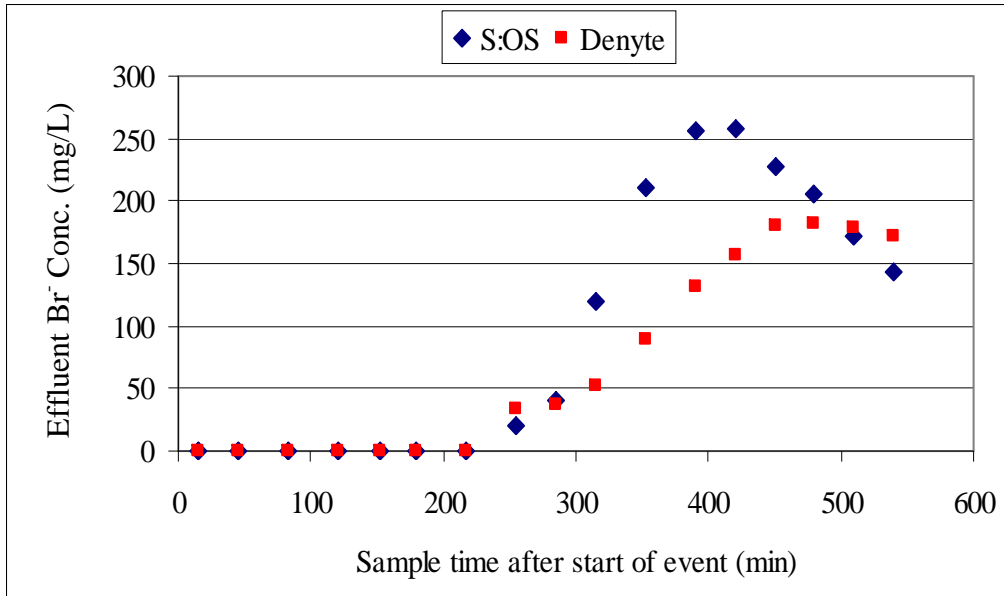
Figure 4.8: Effluent Br⁻ Concentration vs. Time During Laboratory Event #3

The results of the Br⁻ pulse input tracer study conducted during Laboratory Event #3 were analyzed following the exit age distribution method of Lawler and Benjamin (2006). This exit age distribution method allows for the estimation of the mean residence time of a hydraulic system. Based on the exit age distribution method, the overall mean hydraulic residence times were estimated to be approximately 6 hours and 4.3 hours for the S:OS and Denyte bioretention units, respectively. The difference in the hydraulic residence times is most likely due to the difference in denitrification media within the two bioretention units, since the rest of the media in the units were the same. Appendix A contains the full set of data and calculations utilized to achieve the mean hydraulic residence time estimations.

Figure 4.8 shows that the initial breakthrough of Br⁻ in the effluent took approximately 250 minutes. This would imply that the initial flushing of the submerged denitrification region takes approximately 250 minutes. The Br⁻ breakthrough coincides with the time it took for the SO_4^{2-}

effluent concentration to diminish and reach steady state (200 to 300 minutes as shown in Figure 4.3) as well as with the increase in effluent TN concentrations from both reactors observed in laboratory Event #1 (218 minutes as shown in Figures 4.1 and 4.2). Therefore, 250 minutes would be a good estimate for the time it takes to initially flush the submerged denitrification region.

Based on the stoichiometry of denitrification, the mass of substrate supplied within the denitrification regions and the amount of NO_3^- reduced per year the denitrification life expectancy of both units was estimated. The amount of substrate contained within the units denitrification region was estimated to be 2.6 kg of organic matter (cellulose) within the Denyte unit and 42.1 kg of sulfur within the S:OS unit. The amount of cellulose available was based on the methods of Germano-Presby et al. (2005) and the amount of sulfur available was determined by the volume of sulfur added to the S:OS unit. The amount of NO_3^- reduced per year was based on 80 rain events per year, which was the number of rain events used to determine the average storm for the Western MA region. Each rain event would input approximately 691 mg NO_3^- -N to the units. Based on the methods used by Germano-Presby et al. (2005), it was determined that the denitrifying life expectancy for the Denyte unit would be approximately 16.5 years, see Appendix C for calculations. Based on Equation 2.6, approximately 2.5 g of sulfur is consumed per gram of NO_3^- reduced and from this it was estimated that the denitrifying life expectancy of the S:OS unit would be approximately 305 years, see Appendix C for calculations. These estimates are solely based on denitrification abilities and do not reflect the actual sustainability of the units.

In reality, these units would most likely require some maintenance on an annual basis or even more frequently in order to maintain optimal performance. The type of maintenance that can be expected is the visual inspection of the top soil and mulch layer to check for erosion and inspection of the proper flow through the units during wet weather events to make sure water is flowing correctly into and out of the units. Major maintenance such as replacing material (top soil, sand, denitrification substrates, etc.) would most likely need to take place on a less frequent interval, such as every 5 to 10 years. The denitrification life expectancy estimates of 16.5 and 305 years for the Denyte and S:OS units, respectively, do not necessarily establish the time between replacement of these substrates since they are solely based on reduction of NO_3^-. In reality, these substrates most likely will break down and be unavailable for denitrification more rapidly, and therefore, will need to be replaced more frequently. Replacement of materials every 5 to 10 years is solely an estimate and the actual maintenance requirements should be based on the operation and performance of the units. The actual real-life sustainability of these units will not be completely established until full-scale bioretention units are installed and operated for an extended period of time.

4.2   Phase III Results

Water from a waste treatment lagoon at a dairy farm in Putnam, CT was supplied to the bioretention units during Phase III of this project. A total of seven field events were performed between August 2007 and May 2008. Influent and effluent samples were obtained during each field event in order to gain insight into the performance of the two bioretention units. The time

frame for Phase III allowed for the observation of the response of the bioretention units to seasonal changes. Full sets of experimental data for the field events are included in Appendix B.

The waste treatment lagoon exhibited much higher concentrations of nutrients, nitrogen and phosphorous, when compared to the concentrations applied to the units during Phase II. Samples obtained from the treatment lagoon revealed relatively high levels of COD, BOD_5 and suspended solids within the lagoon. Solids were not applied to the units during Phase II of this project. Therefore, the increased nutrient concentrations and the presence of high concentrations of organic material and solids made the waste treatment lagoon water a drastic change in influent for the bioretention units. The average composition of the waste treatment lagoon effluent during field testing of the bioretention units is shown in Table 4.4.

Table 4.4: Average Composition of Waste Treatment Lagoon during Phase III

Analyte	Average	Maximum	Minimum	Units
pH	7.8	7.9	7.4	-
TN	81.5	114.0	39.6	mg/L as N
NO_3^-	<MDL	3.8	-	mg/L as N
NO_2^-	<MDL	-	-	mg/L as N
NH_4^+	29.7	56.0	10.6	mg/L as N
TP	45.1	57.5	21.2	mg/L as P
PO_4^{3-}	23.5	30.1	10.1	mg/L as P
Alkalinity	687.2	925.0	372.5	mg/L as $CaCO_3$
COD	1759.4	3258.1	185.2	mg/L
BOD_5	185.2	291.3	113.1	mg/L
TSS	508.0	114.7	1,440.0	mg/L
VSS	461.3	1334.0	105.3	mg/L

A comparison between Tables 4.4 and 2.2 shows that the waste treatment lagoon had similar characteristics to anaerobic lagoons operated at other dairy farms. This is likely due to the lack of aeration of the treatment lagoon at the dairy farm where Phase III was carried out.

During Field Event #1, the waste treatment lagoon water was applied for only 3 hours instead of the usual 6 hours. This was done to promote the initial acclimation of both bioretention units to the change in influent from Phase II to Phase III. During Field Event #3, the influent was applied to the units for an extended period to observe their response to a continuous application of influent. For the rest of the field events the waste treatment lagoon water was applied to both bioretention units for 6 hours at a flowrate of 4ml/sec. Detailed results from each field event will not be presented within the text of this document, but can be viewed in Appendix B. The results of a field event, following the acclimation carried out in Field Event #1 and prior to the freezing of the units in the winter, will be presented to show the typical field performance of both bioretention units. The response of the units to freezing will be presented through the discussion of results obtained during the spring 2008 field events.

The results from Field Event #2, which was carried out on August 15, 2007, will be presented to illustrate the typical performance of the bioretention units during the field events conducted in the late summer and fall of 2007. The average results of Field Event #2 are summarized in Table 4.5.

Table 4.5: Results of Field Event #2 – Typical Performance during Summer/Fall 2007 Events

Analyte	Influent	Average S:OS Effluent	Average Denyte Effluent	Units
pH	7.9	7.0	6.5	
TN	82.8	37.6	48.2	mg/L as N
NO_3^-	< MDL	< MDL	< MDL	mg/L as N
NO_2^-	< MDL	< MDL	< MDL	mg/L as N
NH_4^+	21.8	8.4	9.3	mg/L as N
TP	51.6	16.6	19.8	mg/L as P
PO_4^{3-}	28.8	< MDL	< MDL	mg/L as P
SO_4^{2-}	27.1	441.4	22.4	mg/L
Alkalinity	891.0	469.7	615.2	mg/L as $CaCO_3$
COD	1,215.8	694.7	789.8	mg/L
BOD_5	143.7	49.7	95.2	mg/L
TSS	252.0	31.3	67.8	mg/L
VSS	222.0	25.2	54.7	mg/L

From Table 4.5 it can be seen that the influent water had high alkalinity and a decrease in alkalinity was observed in the effluent from both bioretention units. Based on the stoichiometry, approximately, 245 mg/L and 50 mg/L of the alkalinity (as $CaCO_3$) consumed within the S:OS and Denyte units, respectively, was due to the processes of nitrification and denitrification (see Appendix C for calculations). The remainder of the alkalinity consumed within both bioretention units was most likely due to changes of the influent carbonate system within the units.

SO_4^{2-} measurements were taken in order to gain insight into the levels of SO_4^{2-} being produced within the S:OS denitrification region. During Field Event #2 the S:OS effluent SO_4^{2-} concentration declined over time, most likely due to the initial flushing of the denitrification region as discussed previously with regards to the results of the laboratory events. However, the field event effluent SO_4^{2-} concentrations were much higher than those observed during the laboratory events. On and average basis, only 37% of the SO_4^{2-} observed in the effluent could be attributed to the process of autotrophic denitrification within the S:OS bioretention unit. The remainder of

the SO_4^{2-} produced was most likely due to the utilization of O_2 as an electron acceptor, especially between events when O_2 in the nitrification region could transfer into the denitrification region. This is confirmed by the initial higher SO_4^- concentrations observed due to the flushing of the denitrification region.

The S:OS bioretention unit removed an average of 88% and 89% of the influent TSS and VSS, respectively. The Denyte unit achieved an average of 73% and 75% of the influent TSS and VSS. Total suspended solids have been reported to be reduced by 90% in conventional bioretention units (PGDER, 1993). Both bioretention units exhibited fairly constant TSS and VSS removal throughout the entire 6 hour duration of Field Event #2. TSS and VSS removal in the bioretention units is due to the media filtering out solids. The top soil region most likely retained the majority of the solids due to the relatively low permeability of this region.

Field Event #2 resulted in an average of 68% (S:OS) and 62% (Denyte) TP removal and greater than 99% removal of PO_4^{3-} in both bioretention units. PO_4^{3-} removal accounts for approximately 82% and 90% of the TP removal observed from the S:OS and Denyte bioretention units, respectively. Approximately 15% and 14% of the TP removal was estimated to be due to VSS removal within the S:OS and Denyte units, respectively. This estimate was made by assuming that $C_5H_7O_2N_1P_{0.1}$ was the chemical formula for VSS (Rittmann and McCarty, 2001). From these results, it can be concluded that adsorption of PO_4^{3-} and filtration of VSS removal are the two major removal mechanisms of TP within the bioretention units.

Table 4.5 shows that COD and BOD_5 concentrations in the waste treatment lagoon were

relatively high. The S:OS unit removed an average of 43% and 65% of the influent COD and

BOD_5, respectively. The Denyte unit removed an average of 35% and 34% of the influent COD

and BOD_5, respectively. Approximately 54% and 56% of the COD removal was estimated to be

due to VSS removal within the S:OS and Denyte units, respectively. The BOD_5 removed by the

bioretention units was due to the biological decomposition of organic matter. Figure 4.9 (S:OS)

and Figure 4.10 (Denyte) show the concentrations of COD and BOD_5 in the influent and effluent

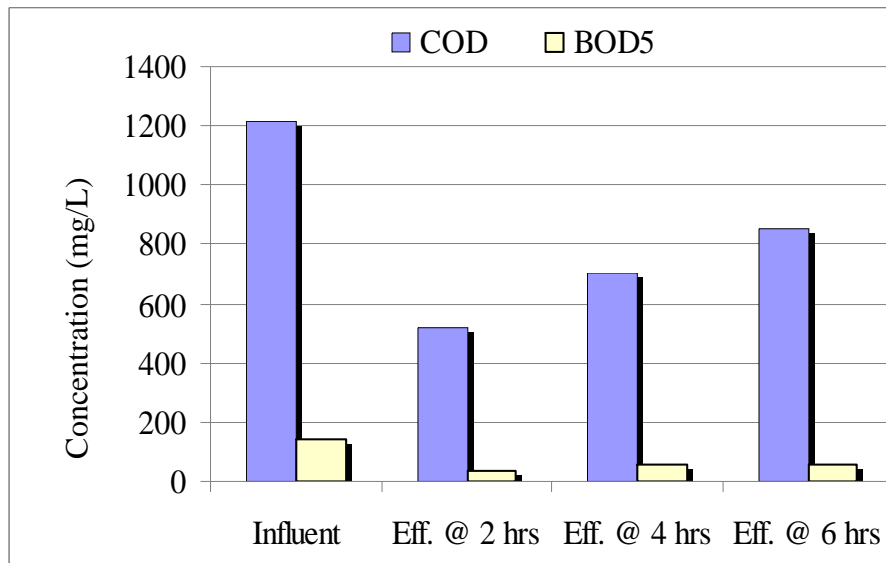samples collected during Field Event #2.

Figure 4.9: S:OS COD and BOD_5 during Field Event #2
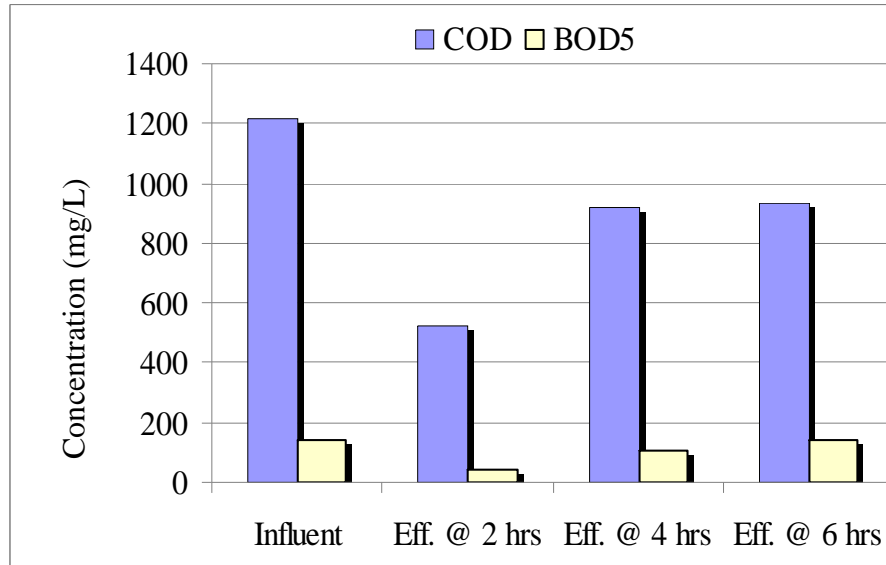
Figure 4.10: Denyte COD and BOD_5 during Field Event #2

Figures 4.9 and 4.10 show that the effluent COD concentration from both bioretention units increased over time. The lower initial COD concentration was most likely due to the flushing of the submerged denitrification region containing the water from the previous influent application. The water retained between events had an extended period for biological treatment to occur. The same trend over time occurs for BOD_5, but not as drastically did for the COD. This is probably due to the fact that the BOD_5 fraction of COD is generally readily biodegradeable. Therefore, the removal of BOD_5, throughout the entire field event, remains relatively constant due to the biodegradation occurring within the units.

The mediocre removal of COD and BOD_5 observed during Field Event #2 could have been due to the low BOD_5 to COD ratio of the influent. Ratios less than 0.3 are often associated with wastewater that can be difficult to treat biologically (Metcalf and Eddy, 2003). The waste treatment lagoon exhibited a ratio of approximately 0.1, and therefore, implies that biological treatment could be difficult.

Moderate removal of nitrogen was accomplished by the bioretention units. On an average, the mass removal rate was approximately 0.13 mg/L-min and 0.10 mg/L-min of nitrogen removed by the S:OS and Denyte units, respectively. The S:OS and Denyte units achieved an average TN removal of 55% and 42%, respectively. The removal of NH_4^+ accounts for 30% and 36% of the TN removal attained by the S:OS and Denyte units, respectively. Approximately, 53% and 59% of the TN removal was estimated to be due to VSS removal within the S:OS and Denyte units, respectively, by assuming an empirical chemical formula for VSS of $C_5H_7O_2N_1P_{0.1}$. Figure 4.11 (S:OS) and Figure 4.12 (Denyte) illustrate the speciation of nitrogen in the influent and effluent samples taken during Field Event #2. NO_3^- and NO_2^- were below the method detection limit for all samples collected during Field Event #2, and therefore, are not included in Figures 4.11 and 4.12.

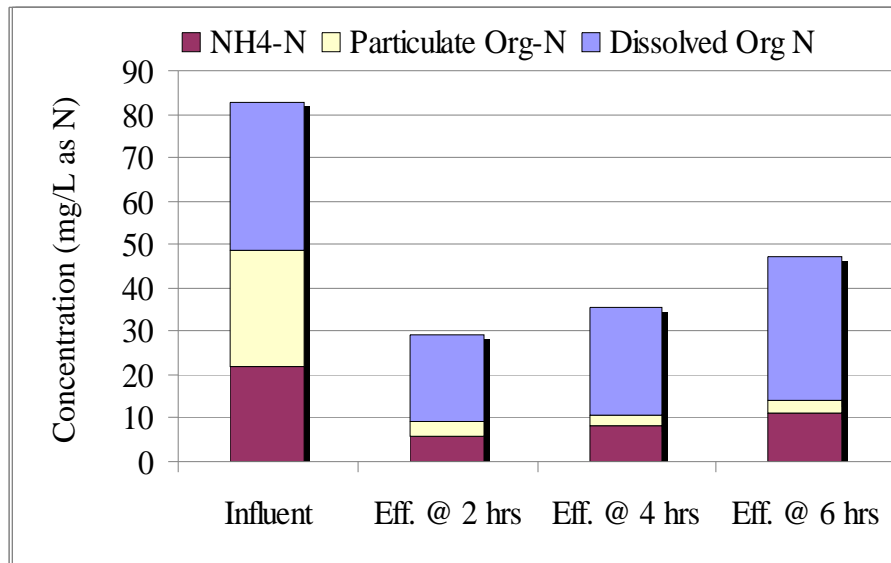Figure 4.11: S:OS Nitrogen Speciation during Field Event #2. Particulate + Dissolved Org N Conc. Calculated by Difference Between TN and NO_3^- + NH_4^+. Particulate Org N Fraction Determined by Assuming an empirical formula of $C_5H_7O_2N_1P_{0.1}$ for VSS.
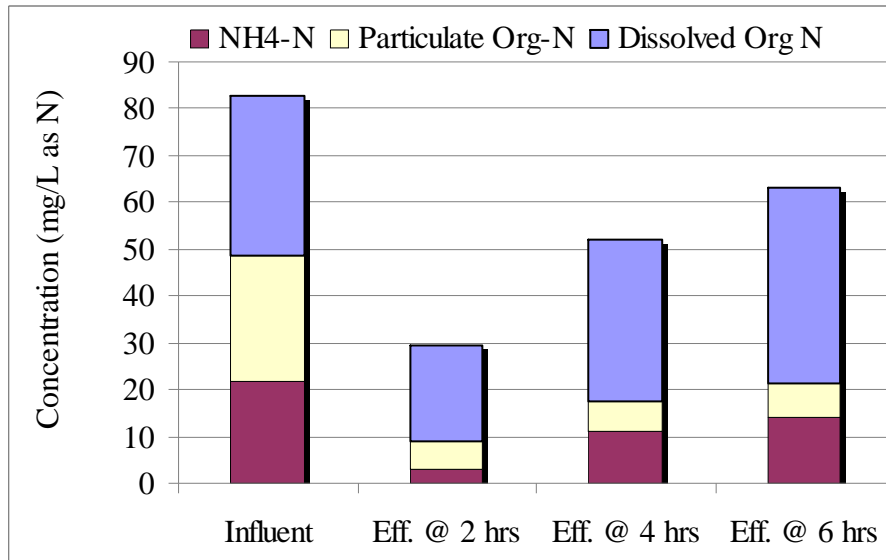
Figure 4.12: Denyte Nitrogen Speciation during Field Event #2. Particulate + Dissolved Org N Conc. Calculated by Difference Between TN and $NO_3^- + NH_4^+$. Particulate Org N Fraction Determined by Assuming an empirical formula of $C_5H_7O_2N_1P_{0.1}$ for VSS.

Figures 4.11 and Figure 4.12 show that effluent TN concentrations from both units increased over time. The lower initial TN concentration is most likely due to the flushing of the submerged denitrification region containing the water from the previous influent application. The water retained between events has had an extended period for biological treatment to occur. Following the flushing of this water, the TN concentration increases, possibly due to the nitrogen levels entering the bioretention units overwhelming the nitrifying and denitrifying microbial communities. The lack of NO_3^- and NO_2^- in the effluent suggests that excellent denitrification occurred in both units. The presence of NH_4^+ in the effluent implies complete nitrification did not occur in the units. Influent and effluent pH values did not vary much from neutral pH, and therefore, no inhibition to the processes of nitrification and denitrification were expected due to pH. Figures 4.11 and 4.12 show that effluent NH_4^+ concentrations did not make up the majority of the effluent TN concentration. This implies another factor most likely controlled the extent to which the bioretention units could remove TN.

The fraction of particulate and dissolved Org N in the influent and effluent samples suggest that the transformation of Org N to NH_4^+ (ammonification) most likely limited the extent of TN removal. Ammonification must occur prior to nitrification, and therefore, if it does not occur the Org N cannot be removed through the process of denitrification. Ammonification occurs either through hydrolysis of Org N, in the form of urea, or through heterotrophic decomposition of organic matter, as discussed in Section 2.2. During Field Event #2, the TN contained in most samples was composed of 77% to 79% Org N. Therefore, these high fractions of Org N imply that the extent to which the processes of hydrolysis and/or heterotrophic decomposition of organic matter occurred within the bioretention units was limited.

The limited ammonification occurring within both bioretention units led to the mediocre TN removal observed during Phase III of this project. Currently, Umass Dartmouth students are investigating pretreatment of the waste treatment lagoon water prior to application to the bioretention units. The goal of the pretreatment process is to remove organic carbon through methanogenesis and to promote the process of ammonification. Pretreatment is expected to increase the extent to which TN removal can be achieved by the bioretention units. Results from Umass Dartmouth have not yet been generated at this time, and therefore, are not included in this Thesis.

As noted previously, the influent was left on for an extended period during Field Event #3 to observe the response of the units to continuous application of influent over an extended storm event. Field Event #3 was initially carried out in the same fashion as the other field events,

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sampling over 6-hour period. After the usual 6-hour field event, the influent was left on for two

additional days. Influent and effluent samples were obtained after two days, a total of 55 hours

after the initial start of Field Event #3. Table 4.6 summarizes the results with regard to TN

concentration.

Table 4.6: Results of Extended Influent Application – Field Event #3

Sample	Sample Time After Start of Event (hr)	Total Nitrogen Concentration (mg/L as N)	
		S:OS	Denyte
Influent #1	6	90.3	
Influent #2	55	79.0	
Effluent #1	2	22.8	12.1
Effluent #2	4	31.3	26.8
Effluent #3	6	41.0	35.5
Effluent #4	55	58.0	66.0

Table 4.6 shows that a decrease in TN removal was observed when the influent was applied for an

extended period. The effluent TN concentration from both units after 55 hours was higher than

the effluent concentrations observed after 6 hours. These results demonstrate that under the field

testing conditions, the bioretention units perform better when the influent is intermittently applied

to the units. Allowing the units to be idle between influent applications permits further treatment

of the water contained within the submerged denitrification region, resulting in better average TN

removal from both of the bioretention units.

Figure 4.13 illustrates the influent and effluent average TN concentrations observed during each

field event conducted during Phase III of this project. It should be noted that Field Event #1 was

only carried out for 3 hours rather than the usual 6 hours. Also, no field events could be

conducted between September 12, 2007 and November 2, 2007 due to an extended dry period,

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which caused the water level of the waste treatment lagoon to fall below the intake pipe. The results of Field Event #4 show that both bioretention units performed well after this 50 day dormant period. An increase in TN removal was observed between Field Event #2 and Field Event #4. This increase in performance is most likely due to the further acclimation of the microbial communities to the waste treatment lagoon effluent. Field Event #4 resulted in the best average TN removal, with approximately 76% and 74% achieved from the S:OS and Denyte units, respectively. Field Event #5 resulted in a decrease in performance from both bioretention units. This is most likely due to a decrease in microbial activity due to the lower temperature at which this field event was conducted. The waste treatment lagoon froze over following Field Event #5. Field testing of the bioretention units resumed in the Spring of 2008 when the waste treatment lagoon thawed.
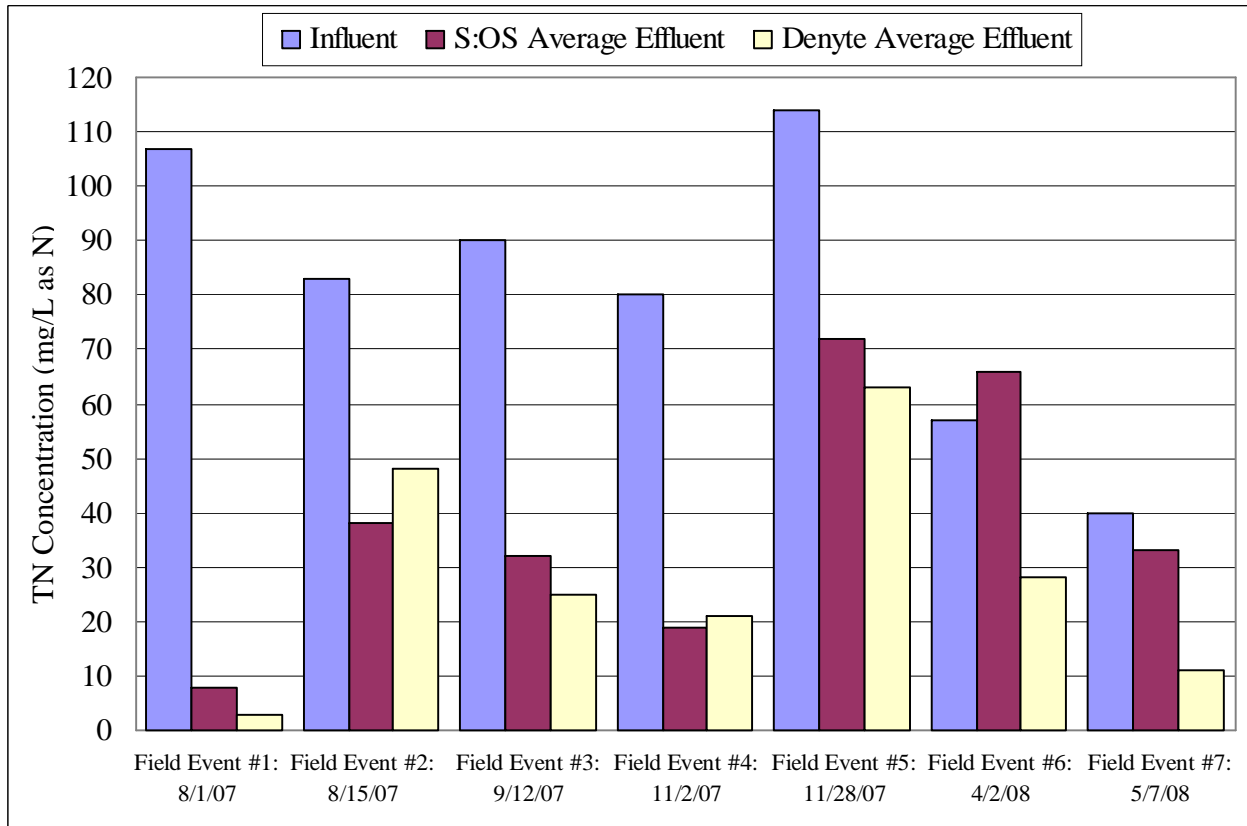
Figure 4.13: Summary of Average TN Removal during Phase III

Figure 4.13 shows a decrease in the influent TN concentration following Field Event #5. This can be explained by an operational change at the dairy farm where Phase III of this project was conducted. A new cattle barn and waste handling system was constructed at the dairy farm and cattle were no longer kept within the barnyard shown in Figure 3.3. Therefore, the waste treatment lagoon stopped receiving the concentrated barnyard runoff, which it did during the first five field events.

Despite the decrease in influent TN concentration, the average effluent TN concentration from the S:OS unit was higher than the influent TN concentration during Field Event #6. Moderate TN removal was observed from the Denyte unit during Field Event #6. The poor performance of the

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bioretention units compared with the Summer and Fall 2007 events was most likely due to the freezing of the bioretention units during the winter months.

The microbial communities within the bioretention units most likely were detrimentally affected due to the freezing of the units. Therefore, the extent to which biological denitrification occurred decreased within the bioretention units after thawing. In addition, the freezing and subsequent thawing of the media within the units could have caused "cracking" within the media structure, creating short-circuits within the units. This is reinforced by high solids concentrations observed in the effluent from the S:OS unit during Field Event #6, which could explain the S:OS effluent TN concentration being higher than the influent TN concentration. Short-circuiting would allow for the flushing of solids contained within the S:OS from previous field events, with higher influent TN concentration, being flushed from the units and in turn resulting in higher effluent TN concentrations than those in the influent. The solids contained in the effluent of the Denyte unit during Field Event #6 were not abnormally high, and therefore, could explain the TN removal achieved.

Figure 4.13 shows that the second field event following the winter months, Field Event #7, had an increase in TN removal both bioretention units when compared with Field Event #6. This is most likely explained by the re-acclimation of the microbial communities within the bioretention units. In addition, the solids contained in the S:OS effluent decreased from Field Event #6, implying that the short-circuiting affect decreased. During Field Event #6 and #7, the Denyte unit out performed the S:OS unit. This suggests that heterotrophic denitrifiers survive freezing and rebound better than autotrophic denitrifiers.

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Overall, it appeared that the Denyte bioretention unit performed better than the S:OS bioretention unit when treating the waste treatment lagoon effluent during Phase III. Of the seven field events conducted, five resulted in the Denyte unit achieving better TN removal than the S:OS unit. The Denyte unit also outperformed the S:OS unit following the winter months, implying that the Denyte unit is less affected by seasonal changes.

Due to the reduced performance observed from the units during Phase III, the denitrification life expectancy was not estimated for the units. The maintenance requirements previously discussed with regards to the laboratory testing would also be necessary under field conditions. Full-scale testing of the units under real-life conditions should be carried out so that the actual life expectancy and maintanence requirements can be established for the bioretention units.

CHAPTER 5:   CONCLUSIONS

The overall objective of this research was to develop a robust and efficient bioretention system to control non-point sources of nitrogen. Specifically, the design, acclimation, operation and performance under various conditions were investigated. Two pilot-scale denitrifying bioretention systems were investigated, one was used to carry out autotrophic denitrification (S:OS unit) and the other was used to carry out heterotrophic denitrification (Denyte unit). The experimental program was performed in three phases. Phase I and II took place in a laboratory setting and Phase III took place under field conditions.

During Phase I the nitrifying and denitrifying microbial communities were acclimated in the two bioretention units. The acclimation of the denitrification and nitrification regions took approximately 23 days and 45 days, respectively. In Phase II, a synthetic stormwater intended to mimic nitrogen levels contained in runoff from agricultural croplands, was used as the influent. Water from a waste treatment lagoon at a dairy farm in Northeastern CT was used as the influent during Phase III.

Excellent performance was observed in both bioretention units during Phase II. The final laboratory event resulted in an average of 63% (S:OS) and 93% (Denyte) TP removal, 92% and 88% TN removal, 90% and 85% TKN removal, 80% and 88% NH_4^+ removal and >95% (S:OS and Denyte) NO_3^- removal. The level of nitrogen removal observed from both bioretention units exceeded those observed in similar studies. The high level of nitrogen removal observed during Phase II was most likely due to the proper design of the units and the careful acclimation of the microbial communities within the units. The mean hydraulic residence times were estimated based

on data from a tracer test as 6 hours and 4.3 hours for the S:OS and Denyte bioretention units, respectively.

Moderate removals of TN, TP, solids and organic material were observed during Phase III of this study. A typical field event (Event #2) resulted in 55% (S:OS) and 42% (Denyte) TN removal, 68% and 62% TP removal, 88% and 73% TSS removal, 89% and 75% VSS removal, 43% and 35% COD removal, and 65% and 34% BOD_5 removal. Ammonification appeared to limit the extent to which TN removal could be achieved, due to the presence of high Org N concentrations observed in the effluent from both bioretention units. Currently, the UMass Dartmouth team is investigating pretreatment of the influent prior to application of the bioretention units to remove organic carbon and promote ammonification. Pretreatment is expected to increase the extent to which TN removal can be achieved by the bioretention units.

Phase III demonstrated that the bioretention systems operated better when the influent was intermittently applied rather than applied for an extended period. Idle time in between events permits further treatment of the water in the submerged denitrification region, resulting in better average TN removal.

The time frame in which Phase III was carried out allowed for observations of the response of the units to seasonal changes. Both bioretention units performed well after a 50 day dormant period induced by dry weather. During cold temperatures, a decrease in the performance was observed, which was most likely due to reduced microbial activity within the units. Freezing of the bioretention units over the winter negatively affected their performance during the Spring. This

could be due to detrimental affects to the microbial communities. Also, due to elevated levels of solids in the effluent from the bioretention units it is expected that the freezing and subsequent thawing of the media within the units could have caused "cracking" of the media structure, creating short-circuiting within the S:OS bioretention unit. However, the bioretention units showed an improvement in performance in the second field event conducted during the Spring of 2008. This implies that the bioretention units can re-acclimate themselves after freezing during the winter months.

Overall, the results of this research project demonstrate that bioretention units can be used to achieve total nitrogen removal from stormwater runoff. However, the characteristics of the stormwater runoff will dictate the performance of the bioretention units. Phase II showed that bioretention units can achieve excellent TN removal from runoff that is characteristic of agricultural croplands. Phase III showed that the treatment of high strength runoff from dairy farm waste treatment lagoons was challenging for the bioretention units.

In comparison, the S:OS and Denyte bioretention units performed similarly during Phase II. However, the Denyte unit appeared to perform better than the S:OS unit during Phase III. The Denyte unit achieved higher average TN removals than the S:OS in most of the field events. The Denyte unit also outperformed the S:OS unit following the winter months, implying that the Denyte unit was less affected by low temperatures.

Suggestions for further research include:

- Observe the performance of both bioretention units when the pretreatment step, being investigated by UMass Dartmouth, is carried out at the dairy farm in Putnam, CT.

- Conduct full-scale experiments of a bioretention unit used to treat runoff from agricultural lands with manure applied. Due to the challenges observed during Phase III of this project it would not be recommended to attempt treatment of such high strength waste with a full-scale bioretention unit. Since the Denyte unit outperformed the S:OS unit it would be recommended to use organic matter as the denitrification substrate in the full-scale unit rather than sulfur.

- Carry out full-scale experiments for a long enough period to get an idea of the actual life expectancy of the units and the timeline for which maintenance and replacement of media is required.

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APPENDICES

APPENDIX A: Laboratory Results

Laboratory Event #1 Results

Laboratory Event #2 Results

Laboratory Event #3 Results

APPENDIX B: Field Results

Field Event #1 Results

Field Event #2 Results

Field Event #3 Results

Field Event #4 Results

Field Event #5 Results

Field Event #6 Results

Field Event #7 Results

APPENDIX C: Sample Calculations

Calculation of Flowrate:

Bioretention Surface Area = 2' X 1.5' = 3 ft^2

Bioretention Area is 5% of Drainage Area → Drainage Area = 3 ft^2 / 0.05 = 60 ft^2

Rational Method Runoff Coefficient = 0.15 (grassed lands)

Therefore Actual Drainage Area of Bioretention Units are 60 ft^2 / 0.15 = 400 ft^2

With Above information the flowrate was calculated as follows:

Average Storm Total = 0.6" ; Storm Duration = 6 hours

400 ft^2 X 0.15 X (0.6/12)' = 3 ft^3 or 22.5 gallons → runoff volume from drainage area

Flowrate = 22.5 gallons / 6 hours = 3.75 gallons/hour or **~ 0.063 gpm or ~ 4 ml/min**

Field Event #2 TN, TP and COD removals due to VSS Removal:

Data for Field Event #2:

	Average VSS (mg/L)	Average TN (mg/L as N)	Average TP (mg/L as P)	Average COD (mg/L)
Influent	222	82.75	51.56	1215.8
S:OS Effluent	25.2	37.55	16.59	694.7
Denyte Effluent	54.7	48.2	19.77	789.8

Average Removals:

	VSS (mg/L)	TN (mg/L as N)	TP (mg/L as P)	COD (mg/L)
S:OS	196.8	45.2	34.97	521.1
Denyte	167.3	34.55	31.79	426

Using the following assumptions I calculated how much COD, TN and TP removal was due to VSS removal:

1) VSS Chemical Formula = $C_5H_7O_2NP_{0.1}$ (From Rittmann and McCarty)
2) 1.42 mg COD/ mg VSS

Calculated removals due to VSS removal:

	TN (mg/L as N)	TP (mg/L as P)	COD (mg/L)
S:OS	23.8 (52.7%)	5.1 (14.6%)	279.4 (53.6%)
Denyte	20.2 (58.5%)	4.3 (13.5%)	237.5 (55.8%)

Example Calculations:

For S:OS TN removal: (196.8 mg C5H7O2NP0.1/L) * (14 g N/116 g C5H7O2NP0.1) = 23.8 mg/L of N removed from VSS removal

For S:OS TP removal: (196.8 mg C5H7O2NP0.1/L) * (30*0.1 g P/116 g C5H7O2NP0.1) = 5.1 mg/L of P removed from VSS removal

For S:OS COD removal: (222 mg COD - 25.2 mg COD) * (1.42 g COD/ g VSS) = 279.4 mg/L of COD removed from VSS removal

Lab Event #3 and Field Event #2 Sulfate Production Due to Denitrification:

Based on
Stoichiometry:
7.54 g SO4 produced / g NO3 reduced

<u>Lab Event #3:</u>
Inf. TN =   6.1 $\Longrightarrow$ 5.46 mg NO3 reduced/L
Avg. Eff TN =   0.64

Therefore: 5.46 * 7.54 = 41.1 g SO4 produced/L

$\Longrightarrow$ ~84% due to
Actual Average SO4 = 48.9 mg/L   denitrification

<u>Field Event #2:</u>
Inf. TN   82.8
Avg. Eff TN   37.6
                                $\Longrightarrow$ ~21.4 mg NO3
TN Removal From VSS = 23.8   reduced/L

Therefore: 21.4 * 7.54 = 161.2 g SO4 produced/L

$\Longrightarrow$ ~37% due to
Actual Average SO4 = 440 mg/L   denitrification

Field Event #2 Alkalinity Change due to Nitrification/Denitrification

Based on Stoichiometry:
For Nitrification: 7.07 mg CaCO3 consumed / mg NH4 oxidized
For Heterotrophic Denitrification: 3.57 mg CaCO3 produced / mg NO3 reduced
For Autotrophic Denitrification: 4.5 mg CaCO3 consumed / mg NO3 reduced

Field Event #2:
S:OS had a removal of 21.2 mg N/L removed by Nit/Denit
Denyte had a removal of 14.2 mg N/L removed by Nit/Denit

TN removal was from NH4 going to NO3 going to N(gas).

Therefore:
Nitrification:
21.2 * 7.07 = 150 mg CaCO3 consumed/L in S:OS unit
14.2 * 7.07 = 100 mg CaCO3 consumed/L in Denyte unit
Denitrification:
21.2 * 4.5 = 95.4 mg CaCO3 consumed/L in S:OS unit
14.2 * 3.57 = 50.7 mg CaCO3 produced/L in Denyte unit

Net CaCO3:
S:OS: -150 + -95.4 = -245.4 mg CaCO3/L
Denyte: -100 + 50.7 = -49.3 mg CaCO3/L

⇩

Overall S:OS Alk declined by 421.3 and therefore ~58% due to Nit/Denit
Overall Denyte Alk declined by 275.8 and therefore ~18% due to Nit/Denit

Calculation of Denitrification Life Expectancy:

Nitrate reduced per event = 691.2 mg, found by 8mg NO_3/L reduced * 86.4 L per event
# of events per year = 80 (western MA average)
Nitrate reduced per year = 691.2 * 80 = 55.3 g NO_3

Denyte Unit:
Based on methods of Germano-Presby et al. (2005) it was determined that 0.915 kg of NO_3 can be reduced by mass of cellulose contained in denitrification region.

Therefore: 915 g NO_3 / (55.3 g NO_3 per year) = **16.5 years**

S:OS Unit:

Mass of sulfur contained in denitrification region is about 42.1 kg
From Eq. 2.6 found that 2.5 g sulfur consumed per g NO_3 reduced
Per event: 0.6912 g NO_3 reduced * 2.5 g Sulfur consumed per g NO_3 reduced = 1.728 g sulfur consumed per event
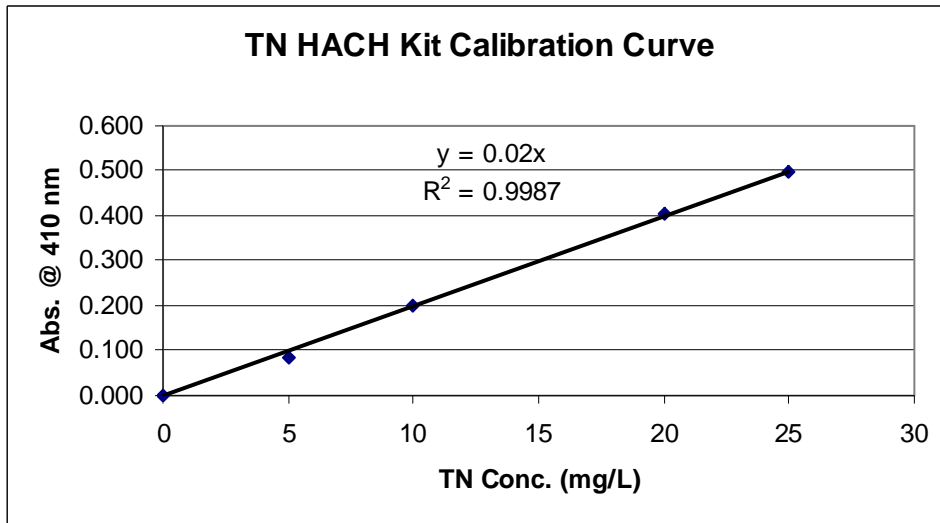Per Year: 1.728 * 80 events = 138 g sulfur consumed per year

Therefore: 42,100 g Sulfur / (138 g sulfur consumed per year) = **304.5 years**

APPENDIX D: Calibration Curves

TN Calibration Curve:

Standard Conc. (mg/L as N)	Abs. @ 410 nm	Correction
0	0.047	0.000
5	0.132	0.085
10	0.246	0.199
20	0.450	0.403
25	0.547	0.500

TN HACH Kit Calibration Curve

$y = 0.02x$

$R^2 = 0.9987$

Abs. @ 410 nm vs. TN Conc. (mg/L)

TN MDL Analysis:

Sample	Abs. @ 410 nm	Correction	Conc. (mg/L as N)
Blank	0.059	0	0.000
1	0.068	0.009	0.450
2	0.067	0.008	0.400
3	0.068	0.009	0.450
4	0.07	0.011	0.551
5	0.07	0.011	0.551
6	0.069	0.01	0.501
7	0.075	0.016	0.801

	average	std dev
	0.529	0.132

			mg/L as N
MDL = std dev * 3.14	=	**0.41**	N

*Sample Target Concentration was 0.5 mg/L as N

COD Calibration Curve:

Standard Conc. (mg/L)	Abs. @ 420 nm	Correction
0	0.786	0
5	0.766	0.02
50	0.627	0.159
100	0.478	0.308
125	0.385	0.401

COD Calibration Curve

$y = 0.0032x$

$R^2 = 0.999$

Abs. @ 420 nm vs. COD (mg/L)
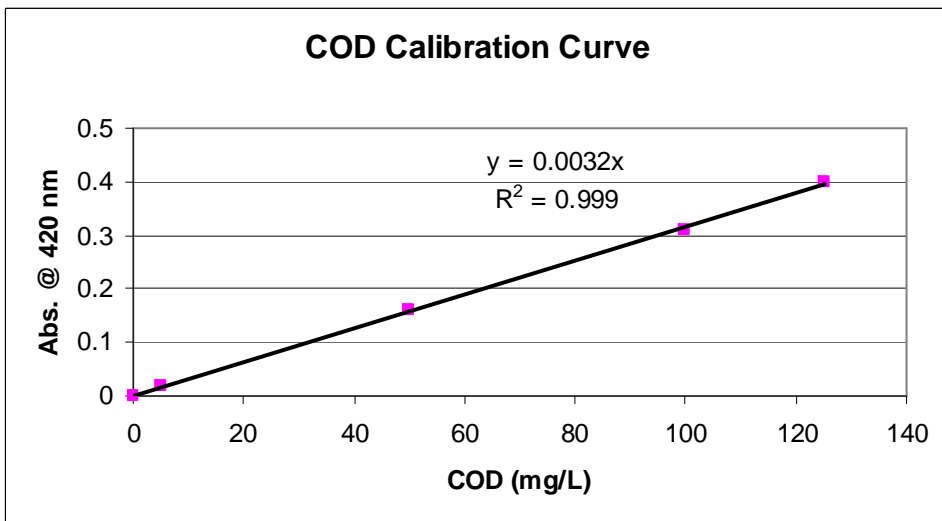
TP Calibration Curve:

Standard Conc. (mg/L as P)	1st Abs. @ 880 nm	2nd Abs. @ 880 nm	2nd-1st	Correction
0	0.089	0.114	0.025	0
0.1	0.089	0.175	0.086	0.061
0.3	0.091	0.27	0.179	0.154
0.6	0.09	0.44	0.35	0.325
1	0.09	0.671	0.581	0.556

TP-P Calibration Curve

$y = 0.5502x$

$R^2 = 0.9989$

Abs. @ 880 nm vs. TP (mg P/L)
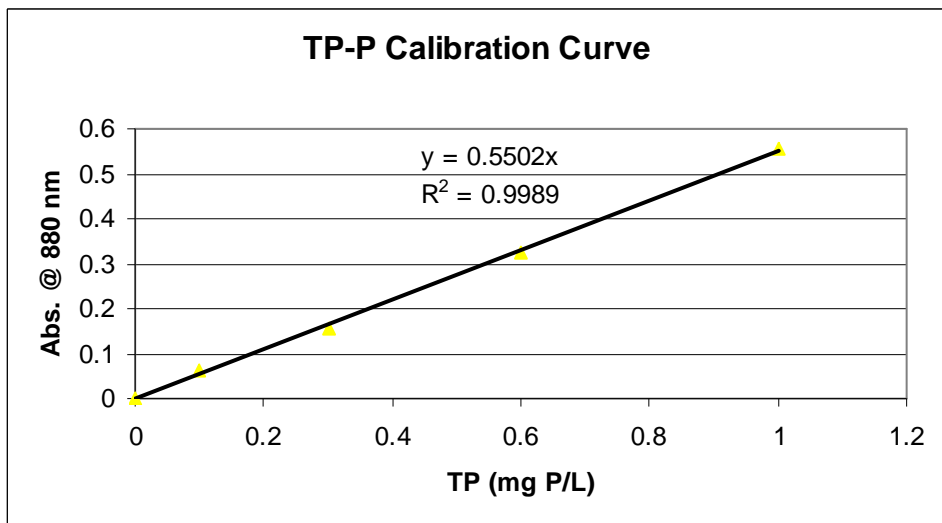
NO3-N Calibration Curve - HACH Kit:

Standard Conc. (mg/L as N)	Abs. at 507nm	Correction
0	0.005	0
0.5	0.01	0.005
1	0.017	0.012
2	0.04	0.035
4	0.076	0.071
8	0.132	0.127

NO3-N Calibration Curve - HACH Kit

$y = 0.016240x$

$R^2 = 0.993491$

Abs. @ 507nm

NO3-N COnc (mg/L)
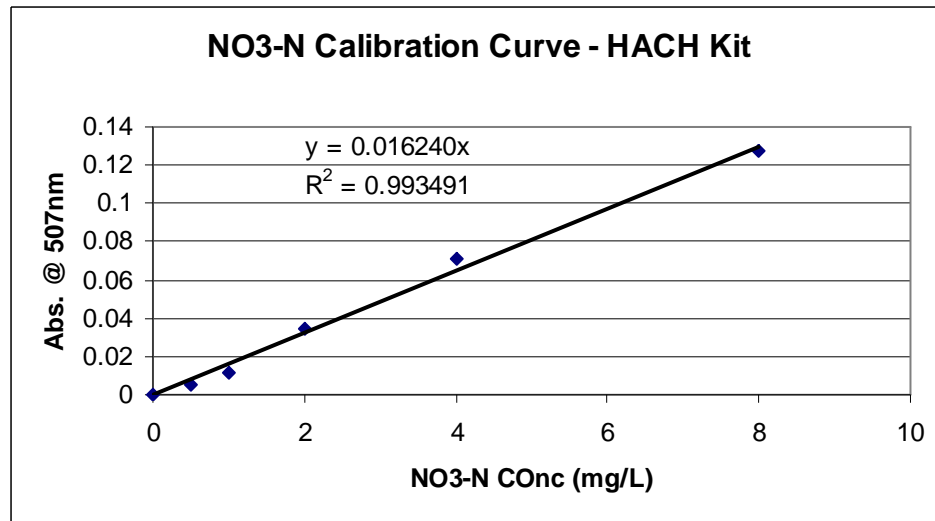
Ammonia Electrode Calibration Curve Example

Concentration (mg/L as N)	Readout (mV)
4.0	200.1
2.0	218.4
1.0	237.5

**Separate Calibration Curve Carried out for each Lab and Field Event due to operator manual suggestion. Standards used generally in this range, however, sometimes slightly different depending on the expected concentrations.

Ammonia Calibration Curve - ISE Meter

$y = -26.978397 Ln(x) + 237.366667$

$R^2 = 0.999848$

(X-axis: Concentration (mg/L as N), Y-axis: ISE Meter Readout (mV))
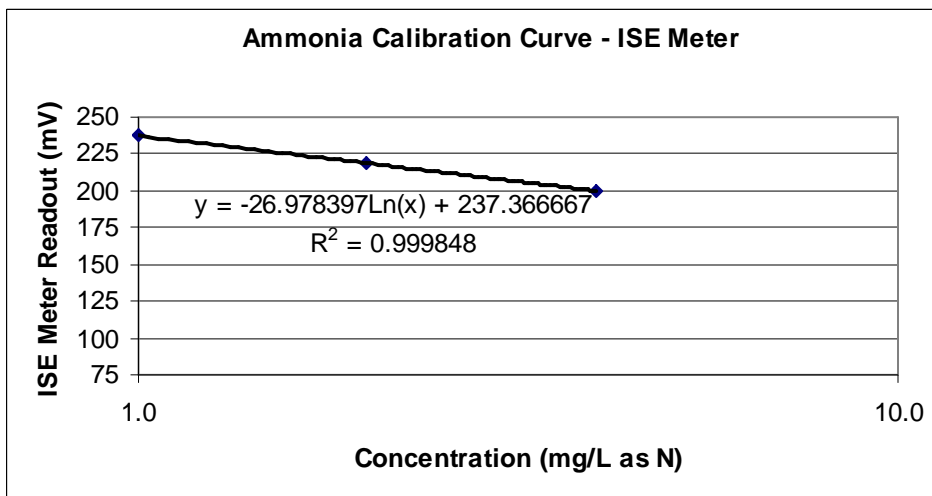
APPENDIX E: Quality Assurance/Quality Control

Quality Assurance/Quality Control

For each analytical batch of samples processed, the following steps were followed as close as possible as part of Quality Assurance/Quality Control procedures and to assure defensibility of analytical results:

(a) Recovery of known additions:

The recovery of known additions will be part of regular analytical protocol.   This will be used to verify the absence of matrix effects or the amount of interference.   The sum of duplicates and known additions will be greater than 20% of the samples.   The known addition will be between 1 and 10 times the ambient level. The procedure would not be used above the demonstrated linear range of the method.   As part of this method, concentrated solutions will be used so that volume change in sample is negligible.

(b) Analysis of duplicates:

Duplicate samples will be processed on a routine basis.   A duplicate sample is a sample that will be processed exactly as the original sample, including preparation and analysis.   The duplicate samples will be used to determine precision.   The sum of duplicates and known additions will be greater than 20% of the number of samples.

(c) Analysis of reagent blanks:

Reagent blanks will be analyzed whenever new reagents will be used or 5% of the sample load, whichever is greater.   This will monitor purity of reagents and the overall procedural blank.   A reagent blank will be run after any sample with a concentration greater than that of the highest standard or that might result in carryover from one sample to the next.

(e) Calibration with standards:

As a minimum, three different dilutions of the standard would be measured when an analysis is initiated.   Reportable analytical results would be those within the range of the standard dilutions used.   Values above the highest standard would not be reported unless an initial demonstration of greater linear range has been made and the value is less than 1.5 times the highest standard.   If a blank is subtracted, the result will be reported even if it turns out to be negative.