Nitrogen fluxes into, out of, and within a Virginia permaculture livestock farm

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Abstract

Nitrogen (N) is necessary for food production, but when N in excess of crop-plant requirements enters the environment, it creates a number of detrimental impacts.

Alternative agricultural practices, such as pasture-based livestock production, are often suggested as possible strategies for minimizing negative environmental impacts of modern agriculture. To evaluate the potential for these practices to decrease N losses to the environment, this thesis quantifies the influxes and effluxes of N from an alternative livestock farm (beef, pork, poultry, eggs) in central Virginia and evaluates the role of a farm pond in influencing the effluxes.

The majority of the N brought into Timbercreek Farm ($5,300 - 8,100 \text{ kg N year}^{-1}$) is not exported as product ($750 - 2,300 \text{ kg N year}^{-1}$). On an annual scale, farm N use efficiency (output as product/total input) is $14 - 28\%$, which lead to N surpluses (inputs minus outputs) of $28 - 35 \text{ kg N ha}^{-1} \text{ year}^{-1}$. Total dissolved N (TDN) flux *via* stream water into the farm is similar to TDN flux out of the farm ($1140 \pm 120 \text{ kg N year}^{-1}$ and $1370 \pm 150 \text{ kg N year}^{-1}$, respectively). Therefore, the farm has a surplus of N, over what is needed for livestock production, but the majority of the excess N is not exported in the farm's streams. The farm pond is a small sink of N ($100 \pm 60 \text{ kg N year}^{-1}$) and denitrification and/or burial in sediment are the likely fates of the N. During high flows and over short time scales, the pond is also a sink for N ($3 - 40 \text{ kg N per storm}$). However, relative to other fluxes, the magnitude of the N sink represented by the pond is small ($1 - 3\%$ of surplus N on the farm).

Timbercreek Farm N use efficiencies are similar to conventional farm efficiencies, but, in contrast to conventional farms, spread surplus N over a larger area.

On-site biogeochemical processes store and/or transform surplus N and prevent it from being exported in the streams. Relative to conventional agriculture, alternative livestock practices, such as those at Timbercreek Farm, have the potential to reduce negative environmental impacts on the farm scale, but are not likely to address the larger issue of inefficient resource use.

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1. Introduction

Conventional food production has had a profound impact on human and environmental health. Industrial methods have helped to feed a growing human population, but these same production practices have caused widespread harm to the environment, particularly the hydrosphere. As the impacts of conventional agriculture are more fully understood, research has shifted to focus on practices that have the potential to mitigate negative environmental outcomes. Pasture-based livestock is one alternative production practice that some suggest as a possible solution; however, the environmental impacts of grazing systems are still being quantified. To evaluate the potential for alternative agricultural practices to mitigate the environmental impacts of conventional production, we need a more robust understanding of nutrient fluxes within these systems and a broader perspective on how these fluxes compare to conventional production.

The overarching objective of this thesis was to quantify the nitrogen fluxes on an alternative livestock farm and to evaluate the potential for these practices to reduce negative environmental impacts from excess reactive nitrogen. This study uses a nested model of nitrogen fluxes to evaluate on-farm efficiency, nitrogen losses to surface waters, and the role of a pond in influencing nitrogen export *via* surface stream water.

1.1 The nitrogen challenge

Nitrogen (N), in some form, is required for all life. While it is one of the most globally abundant elements, N is mostly found as N₂, a non-reactive form that can only be used by fewer than 100 known species (Dos Santos et al. 2012). Reactive nitrogen (Nr) refers to all of the forms of N that are biologically usable, radiatively active, and

chemically available including ammonia (NH_3), ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), organic N, and others (Galloway et al. 2003). Some form of Nr is necessary for crop and animal production (primarily, NH_4^+ , organic N and NO_3^- , depending on the species). Through the Haber-Bosch process, industrial fixation yields NH_4^+ that is incorporated into synthetic fertilizer for use in agricultural production (Galloway et al. 2007). In the last 75 years, anthropogenic Nr has helped to support a growing human population by increasing agricultural yields dramatically (Erisman et al. 2008).

For the farmer, any nutrient, including Nr that does not end up in the crops or meat is considered a loss from a “cost of production” viewpoint, and most of the Nr used in agriculture is lost to the environment during the food-production process (Galloway et al. 2007). As the lost Nr moves through the N cycle, it creates a cascade of detrimental environmental impacts including smog, acid rain, eutrophication, climate change and stratospheric ozone depletion (Galloway et al. 2003). A single atom of N can be transported through and transformed within the atmosphere, hydrosphere and biosphere and create these impacts in sequence (Galloway et al. 2003). The challenge with respect to N, therefore, is to maximize the food-production benefits of Nr while minimizing losses to the atmosphere and the hydrosphere.

1.2 Conventional agriculture

More than 95% of the food grown and raised in the United States (US) is produced through conventional methods (USDA 2012). Conventional crop agriculture typically is characterized by intensive, monoculture production that requires high inputs of synthetic fertilizer, pesticides and irrigation water, but produces high yields (USDA

2012). Conventional animal production relies heavily on concentrated animal feeding operations (CAFOs) and processed feed (i.e., corn, soybeans, etc.) consumption (USDA 2012). CAFOs are large-scale, high density production systems that raise livestock in an enclosed area and that do not rely on forage crops (USDA 2012).

The intensive methods that characterize conventional agriculture, including greater synthetic N use (+300% since the 1960s), have led to dramatic increases in food production globally (+20% between 1985 and 2005, and +56% between 1965 and 1985) with only small increases in land used for food production (+3% increase between 1985 and 2005) (Foley et al. 2011, Bouwman et al. 2013, Erisman et al. 2008). These increases in production per unit of land have helped to support a growing human population (from 3.3 billion in 1965 and to 6.7 billion in 2008) (Erisman et al. 2008).

Advances in conventional production of livestock, in particular, have led to more efficient conversion of feed to animal products (Bouwman et al. 2013). At the same time, demand for animal products has increased, and the total number of livestock globally has more than doubled (Godfray et al. 2010). Including both pasture land and crop land used to grow feed crops, livestock production accounts for the largest of all anthropogenic land uses globally (Herrero and Thornton 2013) and occupies more than 75% of all agricultural land (Foley et al. 2011).

The intensification of conventional agriculture, particularly of animal agriculture, has created a system that is 1) very resource intensive and 2) relatively inefficient (Foley et al. 2011). Animal agriculture adds a significant amount of Nr (6-7 Tg N year⁻¹) to the environment (through excess fertilizer used to produce feed crops and manure from the

animals) and is a key driver of the human alteration of the N cycle (Bouwman et al. 2013, Galloway et al. 2003, EPA 2011).

Only $0.5 \text{ T N year}^{-1}$, or 5% of all animal production globally, comes from grazing livestock (Herrero et al. 2015), but these systems account for 3.4 billion ha, or 90% of the land used for animal agriculture globally (Foley et al. 2011). Pasture-based animal production has the potential to increase the food available for humans when land not suitable for growing food crops is grazed, but may also decrease available food for humans when high value agricultural land is used to grow feed crops (Foley et al 2011).

1.3 Increased demand for animal products

Global projections indicate that demand for animal products will rise in the future because of 1) a growing human population and 2) changing diets. By 2050, the earth's population will reach 8 – 10 billion (UN 2009). At the same time, as developing nations grow wealthier, demand for meat products will increase (Godfray et al. 2010). To meet these growing demands, total food production needs to double by 2050 (Godfray et al. 2010, Foley et al. 2011, Tilman et al. 2011) and it is predicted that the total number of livestock will also double (Bouwman et al. 2013). Increased production of crop and animal products (without changes in agricultural practices) will lead to dramatic increases in N_r losses to the environment over the high levels currently observed (Pelleteir and Tyedmers 2010, Bouwman et al. 2013).

The challenge of meeting increasing demand for food while decreasing environmental impacts will require changes to current food production practices (Godfray et al. 2010) and further evaluation of the environmental impacts of diverse production

practices (Tilman et al. 2011). Many studies have focused on the environmental impacts of meat production (Pelletier and Tyedmers 2010), but more data are needed on potential sustainable solutions that are specific to animal production (Herrero and Thornton 2013). Such ‘sustainable intensification’ practices, have the potential to reduce Nr pollution while producing sufficient quantities of food (Godfray et al. 2010).

1.4 Alternative agriculture

Sustainable agriculture is often suggested as a possible strategy for minimizing the negative environmental impacts of conventional agriculture (Youngberg and DeMuth 2013). While difficult to define, ‘sustainable’ agriculture refers to an ideal type of agriculture that can efficiently produce food for humans while balancing ecological functioning (Harwood 1990). It is difficult to determine what, if any, agricultural systems can be considered ‘sustainable’, and more research is needed on alternative farming practices to determine the extent that they may be considered ‘sustainable’. In particular, very little is known about the Nr losses to the environment that result from alternative livestock production practices.

From a historical perspective, alternative agricultural practices including grass-fed beef, free range chickens, and other pasture-based livestock production practices are not new. Indeed, before the advent of modern, conventional practices, these were the *only* methods of livestock production. In this sense, the modern revitalization of ‘alternative farming practices’ can instead be considered a neoclassical approach to food production and a reaction against the industrialization of farming.

Organic farming, one alternative method of agricultural production, may result in lower N_r losses per unit land (Cambardella et al. 2015, Kramer et al. 2006, Hansen et al. 2000). However, because organic systems have lower production (Seufert et al. 2012), N_r losses may be similar when measured as a function of the product produced (Mondelaers et al. 2009, Tuomisto et al. 2012). Additionally, organic production relies heavily on existing N_r (manure, crop residues, etc.) and has the potential to introduce less new N_r (from BNF or Haber-Bosch) relative to conventional production (Cattell Noll et al. 2016). Conventional animal production is slightly more efficient than organic production, but because pasture-based livestock systems are used more widely in organic production, N losses per unit land may be less (Dalgaard et al. 1998).

Alternative livestock production practices, such as ‘grass-fed beef’ and ‘free range chickens’, are typically inefficient relative to conventional production. Feed conversion ratios (FCR) for pasture-based cattle are 6 - 11 kg dry matter intake (DMI) kg gain⁻¹ (Fernandez and Woodward 1999, Cho et al. 2009, Lee et al. 2009). FCRs for pasture-based poultry and pig meat are typically lower than beef; 2 – 3 kg DMI kg gain⁻¹ for poultry (Fanatico et al. 2009, Moritz et al. 2005) and 2 – 4 kg DMI kg gain⁻¹ for pig meat (Grela et al. 2012, Strudsholm and Hermansen 2005). However, conventional livestock production is comparably inefficient (Cattell Noll et al. 2016). FCR for conventional beef, poultry and pig meat are typically 5 – 10 kg DMI kg gain⁻¹, 1 - 3 kg DMI kg gain⁻¹, and 1 – 5 kg DMI kg gain⁻¹, respectively (Leach et al. 2016).

Lower livestock densities in non-conventional animal production can lead to fewer losses on a per unit land basis (Mondelaers et al. 2009, Hansen et al. 2000, Cederberg and Mattsson 2000, Dalgaard et al. 1998). However, alternative practices

require more land to produce the same amount of meat and it is unclear whether there is enough land globally to meet food demands through alternative production (Badgley et al. 2007). To evaluate the potential for alternative livestock systems to maximize food production, while minimizing losses, we need a more robust understanding of Nr fluxes within these systems.

1.5 Research objectives

The overarching objective of this thesis was to quantify the N fluxes on an alternative livestock farm and to evaluate the potential for these practices to reduce Nr losses to the environment. Using a budget approach, N movements into, out of, and within the farm were quantified. Additionally, this study focuses on the role of a pond in influencing N fluxes in surface waters of the farm. These overarching objectives were addressed through three specific objectives:

- 1) Calculate a farm N budget for 2014 and 2015
 - a. Quantify the farm product inputs and outputs of N
 - b. Quantify the farm stream inflows and outflows of N
- 2) Calculate an annual N budget for the farm pond
- 3) Determine the effect of storm events on pond N fluxes

By extending the farm N budget (which began in 2012, see Section 2.1.3 below), objective 1 will assess the efficiency of the current farm practices. Quantification of intentional inputs and outputs (e.g., feed, hay, meat, etc.) and stream inflows and outflows will determine if the farm is a source or a sink of N. An annual N budget for the farm pond (objective 2) and a determination of the effect of storm events on pond N

fluxes (objective 3), will provide insight into how the pond influences the N fluxes in the surface waters of the farm. These N fluxes are connect and will provide a comprehensive picture of the N fluxes into, out of, and within Timbercreek Farm (Figure 1).

Figure 1. Conceptual diagram of nested N_r fluxes into, out of and within Timbercreek Farm. The black box represents the farm property. Waterways (blue lines) are stylized for simplicity; arrows show direction of flow. Numbers correspond to the objective that seeks to quantify that flux. Arrows show direction of flux. Figure is not to scale. All fluxes were evaluated on an annual scale, except Objective 3 fluxes (shown above as rain drops), which were evaluated at the scale of storm events (hours to days). Results are given as annual fluxes (kg N year^{-1}) and annual fluxes per unit area ($\text{kg N ha}^{-1} \text{ year}^{-1}$). Pasture BNF includes all cultivated biological nitrogen fixation on the farm.

1.6 Site description

Timbercreek Farm, the alternative livestock farm used as the field site for this research, is located in Albemarle County, Virginia, USA (38.0975°N , 78.5612°W , elevation of 146 - 213 m, Figure 2). The farmer describes the alternative agricultural

practices as ‘approaching permaculture’ (Zach Miller, personal communication).

Permaculture farming strives to replicate natural ecosystem processes and utilize the natural cycling of nutrients (Mollison 1988). Typical practices include, combined crop-animal production, rotational grazing, composting, agroforestry (the integration of food production and forestry) and others (Mollison 1988).

Timbercreek Farm raises pigs, cattle, laying chickens, broiler chickens, and other seasonal livestock on a total of 165 ha of pasture and forest land (Zach Miller, personal communication). Approximately 30% of the property is pasture, 19% is silvopasture (land used to grow trees and graze animals), 40% is forested and 11% has other land uses (Leach 2014, Figure 3). Timbercreek Farm began producing livestock in 2011, and on-site research has been conducted since 2013 (Leach 2014). The farm imports only a modest amount of feed, and the livestock graze or forage for a significant percentage of their diet (Leach 2014). This study defines the farm system bounds as all agricultural production taking place on Timbercreek Farm property. Full details on production practices can be found in Leach 2014.

Figure 2. Map of the eastern United States with Timbercreek Farm marked at 38.1° N, 78.6°W. *From Leach 2014.*

The farm has three first order streams; the central stream originates on the farm, while the other two flow onto the farm from adjoining lands (Figure 3). The central stream is dammed to provide a pond for the farm. The three streams meet in the southern end of the property then drain into Little Ivy Creek which feeds the Rivanna River, a tributary of the James River. The watershed of this small tributary (marked in red in

Figure 3. Timbercreek farm property (dark red line), watershed (bright red line), land use (green for forest, tan and orange for agriculture and gray for developed) and waterways. The farm is a total of 165 ha and the watershed is 216 ha (101 ha are on farm property).

Figure 3) is 216 ha, of which 101 ha are on the farm property (Kozuch 2014). The Soil Survey indicates that the soils are in the mesic Typic Hapludults taxonomic class which

denotes a classic, somewhat weak ultisol that is typical for the Virginia piedmont region (USDA – NRCS 2011). Average temperatures in this region range seasonally from 3°C to 23°C, with average annual precipitation of about 100 cm (NOAA 2016).

A nested conceptual model of Nr fluxes (Figure 1) shows how the farm property, farm streams and farm pond relate to each other. Arrows depict the movement of N and the numbers associated with each indicate the objective that seeks to quantify each flux. All fluxes were estimated on a yearly timescale, except for Objective 3 (noted in the figure as a raindrop), which was evaluated on shorter timescales based on the duration of each storm (hours to days). Following this introduction, the thesis is divided into four sections; the first three address each of the three objectives. The last section is an integrated discussion that covers all three objectives.

2. Objective 1: Calculate a farm N budget for 2014 and 2015

2.1 Background

2.1.1 Nitrogen budgets

Nutrient budgets are one way of evaluating the potential sustainability of different management practices. In particular, N budgets quantify the N entering and leaving a defined system and use the difference between the two to make inferences about N losses and transformations. Nitrogen budgets have been applied to a wide range of scales (local, regional, global) and systems (farms, countries, watersheds, lakes, marine, etc.) (Leach 2014, David et al. 2006, Oenema et al. 2006).

Farm N budgets are based on black-box models that quantify the inputs to a farm (fertilizer, feed, hay, purchased animals, etc.) and outputs from a farm (crops, meat, animal products, slaughter waste, etc.) (Leip et al. 2011, Watson and Atkinson 1999, Oenema et al. 2003). Typically, these farm budgets are from the farmer's perspective; that is, an N loss is anything that does not end up in product or by-product. A whole-farm N use efficiency (NUE) can be estimated by dividing the outputs ($\text{kg N ha}^{-1} \text{ year}^{-1}$) by the inputs ($\text{kg N ha}^{-1} \text{ year}^{-1}$). Individual animal type NUEs can also be calculated. From the farmer's perspective, an NUE of 1 indicates a perfectly efficient system, while an NUE of <1 indicates that a farm is either losing N to the environment (denitrification, leaching to groundwater, export *via* streams, etc.) or storing it on site (in soil, plant mass etc.). Similarly, an NUE greater than one suggests to a farmer that the farm is exporting more

N than they are importing, a situation which is ultimately unsustainable (Robertson and Swinton 2005).

Since individual-animal and whole-farm estimates of NUE using a farm N budget are normalized to production outputs, they can be used to compare farms that are of different spatial or production scales and/or that have different management practices (Oenema 2006, Nielsen and Kristensen 2005). Nitrogen budgets are used for scientific inquiry, as metrics for producers, and to inform policy decisions (Oenema et al. 2003). Different studies may use different system bounds (e.g., whole farm vs. individual animal) which may have a substantial influence on the results (Oenema et al. 2003). Therefore, it is important to ensure that system bounds are clearly defined.

N budgets that are focused on the impact of production practices often distinguish between intentional and unintentional N inputs and outputs (Leach 2014). Intended N inputs include any N that is brought onto the farm by the farmer, purchased by the farmer or encouraged by the farm (as in the case of cultivated biological N fixation). Unintended inputs include N deposition and biological N fixation that is not the result of agricultural practices (i.e., in forests or uncultivated meadows). Intended outputs from the farm include all products (meat, eggs, etc.) and by-products (slaughter waste that is used for other purposes or composted). Unintended N outputs include all N loss pathways (leaching, volatilization, denitrification, etc.) and on-site N storage (in soils, plants, etc.). In addition to the inputs and outputs discussed above, this N budget also includes inflows and outflows *via* surface waters.

2.1.2. Nr transport via the hydrologic cycle

One potential unintended N input to and output from the farm is Nr fluxes through surface waters. The hydrologic cycle is a key driver of Nr loss to the environment and surface waters in particular are sites of significant Nr transport and transformation (Carpenter et al. 1998, Seitzinger et al. 2002). Streams with watersheds that are dominated by agricultural land uses often transport significant amounts of N because N application rates are so high (Howden et al. 2011, Buda and DeWalle 2009). During base flows, N transport *via* the hydrologic cycle is typically in the form of NO_3^- , which is highly soluble (Howden et al. 2011). Nr may also be transported in the form of NH_4^+ , dissolved organic N (DON), or particulate N (PN), which can include both organic and inorganic forms. Particulate N flux is typically only important during storm events, and preliminary data collected confirmed that PN flux was small (based on 27 samples, the average PN flux was 1% of TN flux).

Decades of intensive agriculture have led to increased NO_3^- concentrations in groundwater (Burow et al. 2010, Canter 1996); in turn, this has led to increased NO_3^- concentrations in base flows (that are primarily supplied by groundwater) (Tesoriero et al. 2009). N in groundwater represents a long-term Nr reservoir (Howden et al. 2011) with residence times that are typically on the order of years to decades (McGuire et al. 2005). This ‘legacy’ N is likely to continue to impact stream water quality in agricultural catchments for decades to come (Tesoriero et al. 2013).

2.1.3 Previous on-site research

Previous research at Timbercreek Farm estimated that for 2012, intended N inputs were $32 \pm 7 \text{ kg N ha}^{-1}$ and intended N outputs were $5 \pm 0.7 \text{ kg N ha}^{-1}$ (Leach 2014). For

2013, intended N inputs were $49 \pm 10 \text{ kg N ha}^{-1}$ and intended N outputs were $14 \pm 2 \text{ kg N ha}^{-1}$. By balancing this N budget, Leach (2014) determined that the farm had an N surplus of 32-39 kg N ha^{-1} annually.

The N surplus is either a) lost to the environment *via* leaching, volatilization, or denitrification and/or b) stored in the on-farm biomass, soil, groundwater or surface water. The exact magnitude and relative importance of each potential fate/flux is unknown, but preliminary research has estimated that approximately 20 kg N/ha/year is leached into groundwater at Timbercreek Farm (Kozuch 2014). Additionally, preliminary data from 2013 - 2014 estimated that the dissolved inorganic N (DIN) flux into the farm *via* stream water was similar to the DIN flux out of the farm *via* stream water (both were 5-10 mg N s^{-1}), but DON inputs and outputs were not quantified (Leach 2014).

2.2 Methods

2.2.1 Farm N budget

Leach (2014) created a N budget for Timbercreek Farm for 2012-2013 (Figure 4). The present analysis extends that record by the addition of two more years, and further characterizes the inter-annual variability of the N budget. The N budget includes intended N inputs (feed, fertilizer, purchased livestock, bedding, hay, electricity use, and pasture BNF), unintended N inputs (N deposition, forest BNF) and intended outputs (meat, meat products, meat by-products, primarily slaughter waste, livestock sold to auction) (Figure 4). Collected data were used to calculate annual N fluxes (kg N year^{-1}) for each of the budget components (See Leach (2014) for complete calculation details) (Table 1).

Using these data, N use efficiency (NUE) was calculated:

$$NUE = \frac{\text{Intended Outputs}}{\text{Intended Inputs}} \quad (1)$$

where intended outputs is sum of all of the intended outputs ($\text{kg N ha}^{-1} \text{ year}^{-1}$), intended inputs is the sum of all intended inputs ($\text{kg N ha}^{-1} \text{ year}^{-1}$), and NUE is unitless.

N surplus ($\text{kg N ha}^{-1} \text{ year}^{-1}$) was calculated as:

$$N \text{ Surplus} = \text{Intended Inputs} - \text{Intended Outputs} \quad (2)$$

where all variables are previously defined.

Figure 4. Conceptual diagram of farm N budget for Timbercreek Farm. The black box represents the farm property, which are also the system bounds. Inputs are in green and outputs are in orange. Intended inputs and outputs are shown with solid arrows, while unintended inputs and outputs are shown with dotted arrows. On farm storage is not shown, but is represented by the area inside the box. Unintended outputs (leaching, volatilization, denitrification) are not quantified. *From Leach 2014.*

Table 1. Data collected for the farm nitrogen budget (2012-2015). *Adapted from Leach 2014.*

N Budget Category	N Budget Component	Data Types Collected	Data Source
N inputs: intended	Feed	<ul style="list-style-type: none"> • lbs of corn, soybeans, oats, etc • N content of corn, soybeans, oats, etc. 	<ul style="list-style-type: none"> • Timbercreek Farm (TCF) • International Plant Nutrition Initiative, 2010
	Hay	<ul style="list-style-type: none"> • number of hay bales • mass of hay bales • N content of hay 	<ul style="list-style-type: none"> • TCF • VA Department of Agriculture, 2013
	Fertilizer	<ul style="list-style-type: none"> • lbs of purchase fertilizer • N content of fertilizer 	<ul style="list-style-type: none"> • TCF
	Bedding	<ul style="list-style-type: none"> • lbs of purchased sawdust • N content of sawdust 	<ul style="list-style-type: none"> • TCF • Pennsylvania State University Extension, 1997
	Purchased Livestock	<ul style="list-style-type: none"> • lbs of purchased livestock (or number of livestock purchased and average weight) • N content of live animal 	<ul style="list-style-type: none"> • TCF • Food and Agriculture Organization (FAO), 2011
	Pasture BNF	<ul style="list-style-type: none"> • % cover of legumes • Estimates of N fixation ($\text{kg N ha}^{-1} \text{ legumes year}^{-1}$) 	<ul style="list-style-type: none"> • TCF • Gorsky 2016 • Anglade et al 2014
	Energy Use	<ul style="list-style-type: none"> • Fuel use, electricity use etc. • Emissions factors 	<ul style="list-style-type: none"> • TCF • Leach et al 2012
N inputs: unintended	N Deposition	<ul style="list-style-type: none"> • Estimates of N deposition ($\text{kg N ha}^{-1} \text{ year}^{-1}$) 	<ul style="list-style-type: none"> • National Atmospheric Deposition Program, 2014
	Forest BNF	<ul style="list-style-type: none"> • Field survey and literature 	<ul style="list-style-type: none"> • Leach 2014
N outputs: intended	Meat	<ul style="list-style-type: none"> • lbs of meat sold • N content of meat 	<ul style="list-style-type: none"> • TCF • FAO, 2011
	By-products	<ul style="list-style-type: none"> • lbs of meat sold • yield ($\text{kg meat kg live animal}^{-1}$) • N content of live animal 	<ul style="list-style-type: none"> • TCF • T&E Meats, 2011 • FAO, 2011
	Animal Products	<ul style="list-style-type: none"> • number of eggs sold • N content of eggs 	<ul style="list-style-type: none"> • TCF • FAO, 2011
	Livestock sold to auction	<ul style="list-style-type: none"> • lbs of live animal sold (or number of livestock sold and average weight) • N content of live animal 	<ul style="list-style-type: none"> • TCF • FAO, 2011

Production practices at Timbercreek Farm have evolved over time and several key changes in production have been implemented. System bounds and N flows in livestock

production for 2012 – 2015 are shown in detail in Figures 5 and 6. Key changes in production for 2014 and 2015 included:

- Eggs – In 2014, there was limited on-site egg production, but due to high layer morality, all remaining layers were sold at auction and egg production was contracted to a partner farm. In 2015, there was no onsite production of eggs.
- Broilers – In 2014 and 2015, some broilers were produced onsite at Timbercreek Farm and some were produced offsite at a partner farm. Feed for all broilers was brought to Timbercreek Farm before being sent either to the partner farm or to the fields to feed onsite broilers. All of the chickens are still slaughtered onsite and slaughter waste is composted.
- Cattle – In 2014 and 2015, the farm began breeding and raising cattle for sale as calves at livestock auctions (typical age, 6 months).
- Produce – In 2015, Timbercreek Farm began producing a small amount of fresh fruits and vegetables onsite. The garden is amended with compost from the farm.

To make each year comparable to one another, the present study defines the system bounds as production taking place on Timbercreek Farm property. Therefore, this analysis does not include eggs, broilers, cattle or any other product produced off the farm (even if it was slaughtered-onsite or was sold as part of the Timbercreek Farm business).

For the 2014 and 2015 calculation, estimates of pasture BNF were updated using a robust pasture survey, legume sample analysis (using an elemental analyzer) and equations relating legume N content to rates of N fixation (Gorksy 2016, Anglade et al. 2015). The pasture survey included sampling every meter along three 50-m transects (locations were determined using 3 randomly selected points in each field and a random

direction). Legume samples were collected (three per field), sorted (leaf materials, stem, roots), dried (at 60° for 24 hours or until a constant mass was reached), ground, and analyzed to estimate N content. Fixation was estimated as a function of stem N content (Anglade et al. 2015). See Gorsky (2016) for full details.

Figure 5. Nitrogen inputs, outputs and system bounds for farm budget for Timbercreek Farm 2012 and 2013. Arrows show inputs to the farm and outputs from the farm. Dotted line shows system bounds which is equivalent to system bounds shown as a solid line in Figure 4. Only difference is purchased calves were an input in 2012 and not in 2013.

Figure 6. Nitrogen inputs, outputs and system bounds for farm budget for Timbercreek Farm 2014 and 2015. Arrows show inputs to the farm and outputs from the farm. Dotted line shows system bounds which is equivalent to system bounds shown as a solid line in Figure 4. Key differences are discussed in Section 2.2.1.

2.2.2 *N inputs to and outputs from the farm via surface water*

To calculate N fluxes into and out of the farm *via* surface waters, samples were collected every other week from 2013-2016 (n=55). Sampling sites included an on-site

spring (Site A), two inflowing streams (Site D, Site E) and two outflowing streams (Site F, Site G) (Figure 7).

A Marsh-McBirney flow meter and the mid-section velocity method (Rantz 1982) were used to estimate instantaneous discharges at each of the stream locations (Figure 7). Stream samples were collected concurrent with gauging, including duplicates at each site and one blank per sampling date. Samples were collected in 125-mL polyethylene Nalgene bottles that were acid washed in a 1% HCL solution. Blanks were empty bottles that were 1) acid washed in the same way as sample bottles, 2) opened in the field at the exact same time as a stream sample was collected, 3) filled with deionized water in the lab and 4) processed/analyzed in exactly the same manner as samples. Blanks were used to determine if there was any source of contamination of samples at any point in sample collection, processing or analysis.

Within 48 hours, samples were filtered through a 47-mm diameter, 0.45- μ m pore size membrane filter (Fisher 09-719-2E) and transferred to 125-mL polyethylene Nalgene bottles that were acid washed as described above. Samples were stored at 40°C in a refrigerator. Within six months of filtering, water samples were analyzed *via* spectrophotometry using a Lachat QuickChem 8500 Series Flow-Injection Autoanalyzer (Lachat) to measure $\text{NO}_3^-/\text{NO}_2^-$ and NH_4^+ . Dissolved inorganic N is the sum of $\text{NO}_3^-/\text{NO}_2^-$ and NH_4^+ . A subset of samples (n=4, one from each season between Fall 2015 and Summer 2016) was also analyzed for DON. A persulfate digestion was used to oxidize all dissolved N to NO_3^- ; 5mL of sample and 0.5mL of persulfate oxidizing agent were sealed in glass ampules and then autoclaved for 40 mins at 120°C and 12psi (Wells 2014). Processed samples were run through the autoanalyzer to determine the resultant

Figure 7. Map of Timbercreek Farm stream sampling sites. Farm inflow sites are Site A, Site E and Site D. Farm outflow sites are Site F and Site G. Pond inflow is Site H. The pond itself is Site B. Pond outflow is Site J. The farm property is shown as the dark red line. Surface waters are shown in blue.

NO_3^- , which represented total dissolved N (TDN) in the original samples (Wells 2014). Dissolved organic N was estimated as TDN minus DIN. Because preliminary data collected to help define the analyses indicated that, during base flow conditions, PN was negligible, only TDN was considered in this study.

2.3 Results

2.3.1 Farm N budget

Between 2012 and 2015, Timbercreek Farm imported 32 - 49 kg N ha⁻¹ year⁻¹ (Figure 8, Table 2, Table 3). Feed was the largest input for all 4 years, ranging from 16 to 46 kg N ha⁻¹ year⁻¹. Smaller but still important inputs included hay (3 – 11 kg N ha⁻¹ year⁻¹), pasture BNF (2 – 7 kg N ha⁻¹ year⁻¹), purchased livestock (1 – 6 kg N ha⁻¹ year⁻¹) and atmospheric deposition (4 kg N ha⁻¹ year⁻¹). Inputs from bedding (0.2 – 0.4 kg N ha⁻¹ year⁻¹) and energy use (0.1 kg N ha⁻¹ year⁻¹) were very small (both less than 1% of total inputs). Estimates of pasture BNF and atmospheric deposition were relatively constant over time (partially because of data inputs were constant over all years), whereas feed, hay and purchased livestock inputs vary over time (Figure 8, Table 2). This reflects the multi-year timescale of livestock production and shows that there is some inter-annual variability in inputs.

Outputs from Timbercreek Farm from 2012 – 2015 totaled 5- 14 kg N ha⁻¹ year⁻¹ (Figure 8, Table 2, Table 3). Meat was the largest output in each of the four years, ranging from 2 - 11 kg N ha⁻¹ year⁻¹. By-products (primarily slaughter waste, but also products not suitable for human consumption, but used for other purposes) were also

important exports for all four years ($1 - 5 \text{ kg N ha}^{-1} \text{ year}^{-1}$). No livestock were sold to auction in 2012 or 2013, but livestock sales were important outputs for 2014 and 2015 (2.1 ± 0.3 and $1.3 \pm 0.2 \text{ kg N ha}^{-1} \text{ year}^{-1}$ respectively). Produce was a very small output ($0-1 \text{ kg N year}^{-1}$) and was considered negligible.

Table 2. Nitrogen inputs and outputs for Timbercreek Farm 2012 – 2015. Data from 2012 and 2013 are from Leach et al 2014. Summary data and efficiency metrics are shown in Table 3. All units are $\text{kg N ha}^{-1} \text{ year}^{-1}$. Ranges are based on ranges of N content of input or output.

		2012	2013	2014	2015
Inputs	Feed	19 ± 2.9	40 ± 6.2	34 ± 6.1	23 ± 5.5
	Hay	3.9 ± 1.1	4.1 ± 1.2	4.4 ± 1.3	8.0 ± 2.3
	Legume BNF	4.2 ± 2.3	4.2 ± 2.3	3.8 ± 2.3	3.8 ± 2.3
	Livestock	4.7 ± 0.8	0.6 ± 0.1	1.2 ± 0.3	1.5 ± 0.2
	Bedding	0.2 ± 0.02	0.4 ± 0.04	0.2 ± 0.02	0.2 ± 0.02
	Energy Use	0.1	0.1	0.1	0.1
	Slaughter Waste	-	-	0.5 ± 0.03	0.9 ± 0.1
	Atmospheric Deposition	4.2	4.2	4.2	4.2
Outputs	Meat	2.9 ± 0.4	11 ± 1.3	6.5 ± 1.0	5.9 ± 1.0
	Slaughter Waste	1.6 ± 0.2	4.7 ± 0.8	1.1 ± 0.1	1.1 ± 0.1
	Livestock	-	-	2.1 ± 0.3	1.3 ± 0.2
	Produce	-	-	-	0.004

Table 3. Total intended N inputs/outputs, nitrogen use efficiency (NUE) and N surplus ($\text{kg N ha}^{-1} \text{ year}^{-1}$) for Timbercreek Farm 2012-2015. Data from 2012 and 2013 is from Leach 2014.

	Intended N Inputs ($\text{kg N ha}^{-1} \text{ year}^{-1}$)	Intended N Outputs ($\text{kg N ha}^{-1} \text{ year}^{-1}$)	Nitrogen Use Efficiency (Intended N Inputs Intended N Outputs ⁻¹)	N Surplus ($\text{kg N ha}^{-1} \text{ year}^{-1}$)
2012	32	5	0.14	28
2013	49	14	0.28	35
2014	44	10	0.22	34
2015	38	8	0.22	29

Timbercreek Farm production was lowest in 2012 (when the farm was still ramping up its operation) and greatest in 2013 (Figure 8, Table 3). These data also showed the changing nature of the production, with a shift towards livestock production

(that is, the sale of calves born on-site) in 2014 and 2015 and away from on-site meat production (which peaked in 2013). The changing mix of animal products (Figure 9) shows a clear shift away from egg production and towards pork production. Whole farm estimates of NUE ranged from 0.14-0.28 and the N surplus was estimated to be between 28 and 35 kg N ha⁻¹ year⁻¹ (Table 3, Figure 9).

Figure 8. Timbercreek Farm N budget 2012 - 2015. All units are kg N ha⁻¹ year⁻¹. Error bars represent high and low estimates based on ranges of N content of inputs and outputs. Dashed line shows the division between inputs (to the left of dashed line) and outputs (to the right of dashed line). Data shown in Table 2 with summary data in Table 3.

2.3.2 N inputs to and outputs from the farm via surface water

Dissolved inorganic N flux into Timbercreek Farm *via* stream water ranged from 7 – 100 mg N s⁻¹ or 0.05 – 1 mg N ha⁻¹ s⁻¹ (Figure 10, Appendix B). DIN flux out of

Timbercreek Farm *via* stream water ranged from $5 - 120 \text{ mg N s}^{-1}$ or $0.02 - 0.5 \text{ mg N ha}^{-1} \text{ s}^{-1}$. These data showed a strong seasonal pattern, with greater DIN fluxes in the wintertime and lower DIN fluxes in the summertime. On a yearly basis, total DIN fluxes were nearly equal, indicating little or no net yearly N flux from the farm. However, DIN fluxes per ha were consistently greater into the farm, indicating that N loading on the farm was less than N loading into the farm. The different patterns between absolute and per ha DIN fluxes are due to the differences in area of the watersheds of the inflow (A, D and E) and outflow sites (F and G) (Table 4).

Figure 9. Mix of animal production at Timbercreek Farm 2012 – 2015 with NUE. Eggs were not produced on site in 2015. *From Leach et al. 2016.*

When plotted against each other (Figure 11), total DIN fluxes have a clear 1:1 linear slope. On a per ha basis, DIN fluxes into the farm were consistently less than DIN fluxes out of the farm. Instantaneous net DIN fluxes (Figure 12) indicate that on the majority of days sampled, more N was leaving the farm than entering it. However, when calculated per ha, the same data indicate that N loading into the farm commonly exceeds N loading from the farm. Again, this pattern is due to the differences in watershed area.

Figure 10. Dissolved inorganic N fluxes into and out of Timbercreek Farm *via* surface waters from 2013 - 2016. Top panel shows DIN fluxes in terms of mg N s⁻¹. Bottom panel shows DIN fluxes in terms of mg N ha⁻¹ s⁻¹ (calculated based on area of watershed, 107 ha for inflow and 211 for outflow). Inflow sites (A, E, D) and outflow sites (F, G) are marked in Figure 7). Figure includes samples from 55 days.

Table 4. Watershed area and land uses for Timbercreek Farm stream sampling sites. Site A, D and E are inflows to the farm. Sites F and G are outflows from the farm. See Figure 7 for site locations.

Site	Area (ha)	Agricultural (%)	Forest (%)	Developed (%)	Open Water (%)
A	16	59	22	19	0
D	27	84	10	6	0
E	64	41	42	17	0
F	94	42	46	12	0
G	117	61	30	9	0.2

The stream sites' contributing watershed areas ranged from 16 to 117 ha (Table 4). The majority land uses in the watersheds for Site A, D and G were all agricultural, while land uses in areas draining to Sites E and F were an even mix of agriculture and forest. In all cases, developed land was less than 20% of the watersheds. Preliminary data on DON fluxes into and out of the farm indicate that they likely represent an important flux (Figure 13). Depending on the sample date and the location, DON as a percentage of TDN ranged from 0-80%. There appears to be some seasonality to the importance of DON, but this limited data set is not complete enough to describe this pattern.

Figure 11. Dissolved inorganic N flux (mg N s^{-1}) into and out of Timbercreek farm *via* surface waters. The panel on the left shows flux as mg N s^{-1} . The panel on the right shows flux as $\text{mg N s}^{-1} \text{ha}^{-1}$. Dotted line indicates 1:1 relationship. Samples were conducted on 55 days.

2.4 Discussion

The continuation of the farm N budget for Timbercreek Farm shows a similar pattern as previous research (Leach 2014), but expands our knowledge of inter-annual variability and highlights the impact of changing production. Intended N inputs greatly exceed intended N outputs, with feed and meat dominating fluxes. Additionally, stream water fluxes indicate that DIN inflows are similar to DIN outflow, but data on fluxes per unit ha and on DON show a more complicated picture. Together, these data suggest that the farm is losing N to the environment, but that it is not being exported as DIN *via* stream water. If data on DON fluxes were included, the results may be different.

Figure 12. Net DIN flux, calculated as DIN flux out of the farm minus DIN flux into the farm, from 2013 – 2016. The top figure shows fluxes as mg N s^{-1} . The bottom figure shows fluxes as $\text{mg N ha}^{-1} \text{s}^{-1}$. Negative values indicate that more DIN was entering the farm than leaving it. Positive values indicate that more DIN was leaving the farm than entering it. Fluxes are instantaneous and were collected on 55 sampling days between June 2013 and July 2016.

2.4.1 Farm N budget 2012 – 2015

The intended N inputs to Timbercreek Farm were dominated by feed (Figure 8). Compared to conventional production, Timbercreek Farm is a relatively low input agricultural system (Leach 2014). Since the farm uses no fertilizer, consumption of feed and production of manure (by chickens and pigs) is the primary mechanism by which soil amendments are applied. These additions of N to the pasture are important because grazing cattle remove N from the pasture (by eating the grass/legume mix) that is then exported off the farm as meat and/or livestock. The shift towards increased pork production (Figure 9) means that relatively more feed is being brought onto the farm; suggesting that N amendments to pasture (relative to livestock density of cows on pasture) increased during the study period. Intended outputs of N were dominated by meat; however, as production practices at Timbercreek Farm changed, export of livestock became increasingly important (Figure 8).

Figure 13. Dissolved organic N as a portion of TDN for four sampling dates (one for each season between Fall 2015 and Summer 2016). Site locations are marked in Figure 7. TDN is equal to DON plus dissolved inorganic nitrogen (DIN). DIN includes nitrate/nitrite and ammonium.

In all years, the farm NUE indicates that 70-80% of N inputs were not being exported in product; instead they were either being stored on site or lost to the environment. Inter-annual variability in NUE is driven primarily by the mix of livestock types and their respective efficiency at converting N in feed to N in live animal. Egg production was relatively inefficient at Timbercreek Farm, since layers were subject to significant predation (Zach Miller, personal communication). For 2012, the large portion of egg production could partially account for the low NUE. Similarly, Timbercreek Farm production was still ramping up in 2012 and inputs of N in purchased livestock were greatest that year (Figure 8), which was likely driving down the NUE for that year. The N in the pasture was not directly quantified in this analysis and therefore was treated as ‘free N’; this is consistent with Leach (2014). In 2013, the share of beef production was largest (Figure 9) and therefore drove the NUE that year to its highest level (28%). NUE on conventional livestock farms ranges from 30% to 60% and on organic livestock farms ranges from 10% to 140% (Leach 2014). Overall, Timbercreek Farm is inefficient, but not more so than most alternative livestock farms and some conventional livestock farms.

The N surplus for Timbercreek Farm (Table 3) is significant relative to the inputs to the farm, but low ($28 - 35 \text{ kg N ha}^{-1} \text{ year}^{-1}$) compared to N surpluses for conventional farms, which are typically on the order of hundreds of $\text{kg N ha}^{-1} \text{ year}^{-1}$ (Leach 2014). N loading to conventional agricultural lands ($\text{kg N ha}^{-1} \text{ year}^{-1}$) is typically high enough to lead to N leaching into groundwater, N export *via* streams and N volatilization to the atmosphere (Burow et al. 2010, Tesoriero et al. 2009). However, in low N input agricultural systems, like Timbercreek Farm, surplus N does not seem to have the same impacts on local waterways (Cambardalla et al. 2015). Production on low input farms is

typically spread over a larger area (hence, inputs and outputs per ha are lower). In these cases, excess N may be spread over a large enough area that it does not exceed the potential for primary production uptake or storage in soils. Hence, low input farms may be less likely to have elevated stream N (e.g., Cambardalla et al. 2015).

2.4.2 N flux into and out of the farm via surface waters – 2012 – 2016

Total DIN flux into the farm is estimated to be similar to total DIN flux out of the farm, however, when compared on an areal basis, DIN flux into the farm was greater than DIN flux out of the farm (Figure 10); this difference is due to the difference in watershed area for the farms inflows and outflows (Table 4). On an absolute basis, the farm exports about the same amount of DIN as it imports (*via* stream water), but DIN loading ($\text{kg N ha}^{-1} \text{ year}^{-1}$) out of the farm is less than DIN loading ($\text{kg N ha}^{-1} \text{ year}^{-1}$) into the farm. This is consistent with the farmer's knowledge of the practices of neighboring farms; several upstream properties use synthetic fertilizer on their pastures (Zach Miller, personal communication). Indeed, DIN fluxes in the surface water at Timbercreek Farm ($0.02 - 1 \text{ mg N ha}^{-1} \text{ s}^{-1}$) are similar to those found in other pasture based systems ($0.1 - 1.2 \text{ mg N ha}^{-1} \text{ s}^{-1}$) (Hooda et al. 2000), but somewhat less than those found in watersheds dominated by conventional agriculture ($0.5 - 2.5 \text{ mg N ha}^{-1} \text{ s}^{-1}$) (Vanni et al. 2001). DIN fluxes had a clear seasonal pattern. Fluxes peaked during winter when primary production is low and stream discharges are typically higher. Winter was also when the difference between inflows per ha and outflows per ha was greatest (Figure 10).

Plotted against each other, instantaneous N fluxes (mg N s^{-1}) show a slight bias towards DIN flux out of the farm (Figure 11). This is consistent with the observation

above that these fluxes are comparable, but, on an absolute basis, slightly larger in the outflow. Per ha however, the relationship between DIN flux in and DIN flux out, is skewed towards DIN fluxes out (Figure 11). This is consistent with the conclusions above; the N loading on the farm is lower than N loading off the farm.

Net DIN fluxes (Figure 12) are reflective of the pattern described for instantaneous DIN fluxes; on an absolute basis, N flux out of the farm is slightly greater than N flux into the farm. This suggests that the Timbercreek Farm is adding a small amount of N to the stream (probably through groundwater). On a per ha basis, though, N flux out of the farm is typically lower than N flux into the farm. This suggests that within the farm inflows of N to the stream have a low concentration of DIN relative to inflows from off the farm. The net fluxes, when expressed as flux per hectare, imply that, relative to its neighbors, Timbercreek Farm contributes little N to surface waters.

This analysis does not quantify N leaching from farm practices to groundwater, which eventually determines water quality during base flows. However, legacy N in groundwater at Timbercreek Farm, which has been under agricultural management for decades (and perhaps centuries), is expected to be high. It is unknown whether current agricultural practices are increasing the N concentrations in groundwater. However, these data suggest that current concentrations of N in groundwater at the farm are lower than N concentrations in stream waters flowing from off-site.

This analysis currently considers site A as a farm inflow (Figure 1, Figure 7), even though it is a site that is within the farm's borders. It is the first easy to sample location after the spring that is the beginning of the stream. The N moving through this site comes from three different sources:

1. current, off-site farming practices (since a portion of the watershed is not on the farm property)
2. historic farming practices (that is, all of the farming that occurred before 2011, when Timbercreek Farm, LLC was formed)
3. current farming practices

There is not a clear way to separate these inputs and the relative impact of each source is unknown. It is possible that the majority of the N at this site is legacy N left from generations of farms (Burow et al. 2010). If so, then this N represents a true input to the farm (since the system bounds are the current farm and the goal is to evaluate the current farming practices). Additionally, if the majority of the N is from the neighboring farm, that is known to use synthetic N fertilizer and graze cattle on the pastures (Zach Miller, personal communication), then this N represents another true input to the farm. However, if the majority of N is from current farm practices (such as cattle grazing the fields uphill from the site, or chicken slaughtered nearby at the farm's barn), then this N does not represent a true N input. The most likely answer is that the N flux through site A comes from a combination of these sources; therefore, it is likely that this analysis is over-estimating the true N inputs *via* streams (however, the magnitude of this error is unknown).

DON is a variable, but significant, portion of TDN moving into and out of the farm (Figure 13). Insufficient DON data were collected to draw conclusions about how DON fluxes impact N inflows to or outflows from the farm, but they suggest that 1) a more robust analysis needs to include estimates of DON, 2) there may be some spatial variability in DON fluxes on the farm, and 3) there may be some temporal variability in

DON fluxes on the farm. If DON was included in the farm inflows and outflows, the net impact of these N fluxes into and out of the farm may be different.

2.4.3 Potential pathways for N surplus

The farm has a surplus of N, but it is not being exported from the farm *via* surface waters. This begs the question, what is happening to this excess N? It could be 1) stored on-site, 2) volatilized to the atmosphere (NH_3) or 3) denitrified to the atmosphere (N_2 , N_2O). Recent research has suggested that N accumulation in agricultural soils can account for a significant portion of the surplus N that is not exported *via* streams (Van Meter et al. 2016); the researchers estimated that cropland soils can accumulate 25 – 70 $\text{kg N ha}^{-1} \text{ year}^{-1}$. In some alternative agricultural systems, accumulation of soil organic matter (and associated N) has been well documented (Drinkwater et al. 1998, Torstensson et al. 2006). Therefore, the surplus N at the Timbercreek Farm could be stored in the soil rather than truly ‘lost’ from the system. Accounting for changes in soil N content (which this study does not do), may increase estimates of NUE relative to conventional systems (Lin et al. 2016).

In pasture-based livestock systems, volatilization of NH_3 from manure can account for 3 – 12 % of all N excreted annually and, during summertime, up to 30% of N excreted (Bussink and Oenema 1998). Depending on stocking rate, N_r fluxes to the atmosphere range from 3 – 80 $\text{kg N ha}^{-1} \text{ year}^{-1}$ (Oenema 2006, Watson and Atkinson 1999). A simple calculation based on cattle manure production and the above volatilization rates suggests that, at Timbercreek Farm, 3 – 15 $\text{kg N ha}^{-1} \text{ year}^{-1}$ (or 10 –

60% of surplus N) could be volatilized to that atmosphere. A soil N budget could be used to estimate volatilization or direct measurements could be made (Leach 2014).

Denitrification is a potential N loss pathway in terrestrial and aquatic systems. Farm N budgets have estimated that total on-farm denitrification can account for 2 – 40 kg N ha⁻¹ year⁻¹ (Oenema 2006, Watson and Atkinson 1999). Surface waters, including streams and lakes, can be sites of significant denitrification. In streams with agricultural watersheds, denitrification typically accounts for up to 5 - 30% of N removal and, in some cases, can account for up to 75% of N removal (Mulholland et al. 2008).

Small agricultural impoundments, like the one at Timbercreek Farm (Figure 7), can be important sites for controlling N fluxes (Powers et al. 2015). Farm ponds can store N (either through burial in sediment or primary producer uptake) or can denitrify it to the atmosphere. Previous research at the Timbercreek Farm concluded that the pond may play a key role in accounting for the surplus N that is not exported *via* streams (Leach 2014). N fluxes into and out of the farm pond are explored in depth in Sections 3 and 4.

2.5 Summary

The continuation of the farm N budget, including (a) intended inputs and outputs and (b) stream inflows and outflows, indicates that much of the N brought onto the farm is not exported in product. This is typical of both conventional and alternative livestock farms. Despite the N surplus, the farm is not exporting a significant amount of DIN *via* surface water; however, if DON fluxes were included, N fluxes both into and out of the farm may be higher. N is being lost to the environment on the farm, but that it is not being transported in the farm's streams. Other potential significant N fates and flows

include: 1) on-site storage, 2) volatilization to the atmosphere and 3) denitrification to the atmosphere. Timbercreek Farm is as inefficient as other farms, but on-site biogeochemical processes are preventing excess N from impacting stream water quality.

3. Objective 2: Calculate an annual N budget for the farm pond

3.1. Background

To inform an understanding of the Nr dynamics that result from alternative agricultural practices, I established a N budget that evaluates the role of the farm pond in influencing N fluxes in the surface water. Only a few studies have characterized the potential for Nr transport through, and transformation within, surface and subsurface waters on alternative agricultural farms (e.g., Cambardella et al. 2015). Indeed, the role of lentic and lotic systems in controlling Nr export from lands under conventional agricultural management is still being determined (Powers et al. 2015, Mulholland et al. 2008, Boyer et al. 2006).

N that is applied to agricultural land (i.e., fertilizer or manure), or that is deposited from the atmosphere, can intersect the hydrological cycle through leaching to groundwater or stormwater runoff. Nitrogen that is leached into groundwater can advect into riparian zones (Williams et al. 2014) and enter streams slowly during base flow (Howden et al. 2011). In areas that have been used for agriculture for many years, groundwater can be contaminated with N and account for a significant portion of N flux into streams (Canter 1996, Howden et al. 2011, Ator and Denver 2015). Because of the long residence time of groundwater, N from decades ago advects into streams today (Hamilton 2012) and will continue to do so for a long time, even if N application immediately ceased. This lag-time between agricultural management practices and changes in stream water quality presents a problem for quantifying the impacts of

alternative agriculture (which is likely to be a relatively new practice) on N fluxes in surface waters.

Lotic systems, including creeks, streams and rivers, transport significant quantities of N from agricultural regions to downstream ecosystems (Sobota et al. 2013, Boyer et al. 2006). N loading from land to streams represents a major threat to water resources and human and environmental health (Carpenter et al. 1998). However, there is great temporal and spatial variability of N export *via* rivers (Boyer et al. 2006, Van Drecht et al. 2005) and the linked hydrologic and biogeochemical processes that create this variability are a topic of investigation.

3.1.1. N transport through and transformation within lentic systems

Biogeochemical cycling within freshwater lentic systems, including lakes, reservoirs, and ponds systems, can modify and/or delay N export *via* surface waters (Hamilton 2012). Naturally occurring lakes are a significant N sink (Seitzinger et al. 2002, Mulholland et al. 2008, Goodman et al. 2011). Like lakes, reservoirs are also N sinks (Powers et al. 2014); however, because the physical parameters of impoundments, primarily lake morphology and residence time, make them distinct from natural lakes (Thornton et al. 1990), the magnitude and relative importance of N pathways may be different.

Biological N fixation (BNF), or the conversion of N₂ gas to NH₃, is a key biogeochemical process that adds N to lakes and reservoirs. In aquatic systems, BNF is most commonly carried out by cyanobacteria, and is highly seasonally and spatially variable (Marcarelli and Wurtsbaugh 2009, Patoine et al. 2006). N fixation typically

peaks in late summer when inflows are lowest, light availability is greatest and water temperature is highest (Marcarelli and Wursbaugh 2009).

Natural lentic systems remove a variable, but often significant, percentage of N inputs (Harrison et al. 2009, Saunders and Kalff 2001). Biogeochemical processes that remove N from lentic systems include volatilization and denitrification. Volatilization, or the conversion of aqueous NH_4^+ to gaseous NH_3 , is strongly controlled by pH and is negligible when pH is less than 7 (Hargreaves et al. 1998). Denitrification, or the reduction of NO_3^- by microorganisms (typically heterotrophic bacteria) to N_2O and then to N_2 , occurs under anoxic conditions (Davids et al. 2006). Denitrification removes N from the environment and converts it to a non-reactive form (N_2), however N_2O is emitted also. Denitrification represents a nearly permanent sink of N (to the atmosphere) while short-term sinks include N burial in sediment, and N uptake by primary producers.

Reservoirs, of all sizes, accumulate sediment (Downing et al. 2008, Smith et al. 2002) and organic matter (Brainard and Fairchild 2012), along with associated PN (Powers et al. 2013). N burial in reservoir sediments prevents N export from agricultural regions, but, because of the potential for flushing of PN during storms, burial may not represent a long-term sink (Brainard and Fairchild 2012). Additionally, organic matter at the sediment surface may undergo mineralization, or the decomposition of organic N to NH_4^+ (Hargreaves 1998); the newly mobile DIN may be an additional source of N over short time scales.

Primary production in lakes and reservoirs is typically limited by N or P availability (Vitousek and Howarth 1991). Therefore, immobilization, or the biological conversion of DIN to biomass (i.e., plants, microorganisms), is an important N process in

lentic systems, where hydraulic residence times are long enough and light availability is high enough to allow significant primary production (Carpenter et al. 1998). The uptake of DIN by plants and microbes in a lentic system represents a short-term (days to months) storage of N, because these organisms die and are mineralized, which eventually converts organic matter (which includes both dead plant and animal remains and the bacteria that are working to decompose them) back to DIN.

In addition to these biogeochemical transformations of N, lentic systems alter other water quality parameters that impact N cycling. On a seasonal cycle, lakes and reservoirs undergo temperatures changes, which in turn affect dissolved oxygen (DO), reaction rates, and biological uptake (Gooseff et al. 2005). These changes in water quality impact N biogeochemical processes (e.g., denitrification rates increase under higher temperatures and low DO values (Inwood et al. 2005)). The magnitude of the impact on water quality is dependent on residence time, age of impoundment, water quality in the inflow, and other variables (Fairchild and Velinsky 2006). Residence time is a particularly key variable; longer residence times lead to greater N uptake by biomass (Davids et al. 2006), larger denitrification rates (Davids et al. 2006), and increased N retention (Seitzinger et al. 2002).

3.1.2. N transport and transformation in small, agricultural impoundments

N cycling in natural lakes and large reservoirs has been the focus of research for decades, but relatively few studies have characterized the hydrologic and biogeochemical controls on N transport through and transformation within small agricultural impoundments (Powers et al. 2015, Fairchild and Velinsky 2006). Remote sensing

techniques have recently revealed that small impoundments are more numerous than previously thought, cover a greater surface area, and are likely to be concentrated in agricultural areas (McDonald et al. 2012, Verpoorter et al. 2014), pointing to a clear need to understand their impact on N cycling.

Farm ponds, which number in the hundreds of thousands in the US (Downing et al. 2006, McDonald et al. 2012), are so dense in heavily agricultural areas, that they are likely to have a substantial impact on biogeochemical cycles (Fairchild and Velinksey 2006, Smith et al. 2002). Indeed, there is some evidence that small agricultural ponds can retain significant amounts of N (Fairchild and Velinksy 2006) and reduce NO_3^- export in streams (Ignatius and Rasmussen 2015). However, research is needed to further characterize the magnitude and relative importance of N dynamics in these systems.

3.1.3 Previous on-site research

Previous research at Timbercreek Farm concluded that more N is imported to the farm than is exported in product and that inflows and outflows of N *via* surface water are similar (see Section 2.1.3 and Leach 2014). Taken together, these data suggest that Timbercreek Farm has a surplus of N_r , but that there are on-site processes that are mitigating N export *via* surface water. Biogeochemical processes may be mitigating these N losses thorough conversion to long-term sinks (denitrification to the atmosphere) or short-term sinks (storage in sediment or biomass). As a site where biogeochemical cycling of N may be potentially significant, the farm pond may play a key role in controlling N export *via* surface water (Leach 2014). To begin to characterize the role of

the pond, my objective was to establish and construct an annual N budget for the farm pond.

Previous research at Timbercreek Farm used a mass balance approach to calculate an annual water budget for the farm pond for April 2015 – April 2016 (Suhling 2016). The analysis included every other week measurements of inflow and outflow, estimates of precipitation and evaporation using meteorological data from the Charlottesville-Albemarle airport and ArcGIS estimates of the pond's volume over time based on a bathymetric map and regular surface elevation readings (Suhling 2016). Outflows were approximately 11% larger than inflows (Table 5) and a simple calculation suggests that groundwater inflow (which was not directly measured) could account for the majority of this difference (Suhling 2016). However, estimating groundwater by difference creates some uncertainty in our estimate of net groundwater flux.

Table 5. Timbercreek Farm pond water budget components on an annual timescale. Stream inflows and outflows were measured every other week from April 2015 – April 2016. Outflows exceed inflows by about 11%. A simple calculation suggests that groundwater inflow could account for much of this difference. *Adapted from Suhling 2016.*

Category	Flow Type	Flow ($\text{m}^3 \text{ year}^{-1}$)
Inflows	Stream	1.6×10^5
	Precipitation	4.6×10^3
Outflows	Stream	1.8×10^5
	Evaporation	3.1×10^3
Net	Groundwater?	2.0×10^4

3.2 Methods

Between April 2015 – June 2016, data were collected on and near the Timbercreek Farm pond (Figure 7) including quarterly data on the pond's physical and chemical parameters (Section 3.2.1), and data on N inputs and outputs (Section 3.2.2 –

3.2.5). These data were used to estimate an annual pond N budget (Section 3.2.6).

Blanks, duplicates and independent standards were used to determine data quality (Section 3.2.7).

3.2.1. Physical and chemical characteristics of the pond water and sediment

A depth sounder and a handheld GPS unit were used to determine the depth of the pond at 64 sites. ESRI ArcGIS 10.2 was used to create a digital bathymetric map and to locate and estimate the pond's maximum depth, maximum length and maximum breadth. Additionally, ESRI ArcGIS 10.2 and a digital elevation model from the National Elevation Data set (USGS 2007) were used to delineate the catchment area of the pond's inflow, the catchment area of the pond's outflow, the pond's area and the length of the pond's shoreline. Using these measurements, the pond's volume, mean depth, depth ratio, shoreline development, and development of volume were calculated (Table 6). The depth ratio compares the mean depth to the max depth. Shoreline development compares the length of the shoreline to the perimeter of a circle and is a measure of the irregularity of the shore. Development of volume compares the volume of the lake to the volume of a cone with the same max depth; it is a measure of the regularity of the lake bottom.

Aquatic N cycle reactions are highly dependent on the chemical parameters of the water (Vitousek et al. 1997). To quantify these conditions, a YSI 600SM Sonde was used to measure the temperature (°C), dissolved oxygen (%), and pH at 0.5- m depth intervals in the water column at 12 sites in the pond (Figure 14). To capture seasonal changes, sonde measurements were taken quarterly (August 2015, November 2015, December 2015 and April 2016). Additionally, water samples from the same 12 sites in the pond

were collected quarterly (October 2015, February 2016, April 2016 and June 2016).

Surface samples were collected by hand in a row boat and depth samples were collected every 0.5 m *via* a Van Dorn sampler. Water samples were collected, processed, stored and analyzed for DIN and DON as described in Section 2.2.2.

Table 6. Summary of pond morphometric characteristics and approaches. Analysis was conducted using a depth sounder, handheld GPS unit and ArcGIS.

	Parameter	Variable	Instrument/Equation
Measurements	Depth (at 64 sites)	Z	Depth Sounder, GPS Unit
	Maximum Depth	$Z_{\max}$	Depth Sounder
	Maximum Length	$L_{\max}$	ArcGIS 10.2
	Maximum Breadth	$B_{\max}$	ArcGIS 10.2
Estimates	Catchment Area of Inflow	A_{Inflow}	ArcGIS 10.2
	Catchment Area of Outflow	A_{Outflow}	ArcGIS 10.2
	Pond Area	A	ArcGIS 10.2
	Shoreline Length	L	ArcGIS 10.2
	Pond Volume	V	ArcGIS 10.2
Calculations	Mean Depth	$\bar{Z}$	$\bar{Z} = \frac{V}{A}$
	Depth Ratio	D_{ratio}	$D_{\text{ratio}} = \frac{\bar{Z}}{Z_{\max}}$
	Shoreline Development	D_L	$D_L = \frac{L}{\sqrt{2A\pi}}$
	Development of Volume	D_V	$D_V = \frac{3\bar{Z}}{Z_{\max}}$

Using a Ponar® dredge clamshell grab sampler, samples of the surface sediment were collected at the same 12 sites in the pond where water samples were collected. Samples were collected in October 2015, February 2016, April 2016 and June 2016. Sediment samples were oven dried at 60 °C for 24h or until a constant mass was reached, then ground using a mortar and pestle. A small amount of dried and ground sediment (20 – 30 mg) was analyzed for total C and total N in a C:N analyzer (Thermo Scientific Flash 2000) (CE Instruments 2016). Instrument blanks, sample blanks and soil standards were used to ensure data quality. These data, showing spatial and temporal variability in Nr concentrations in the pond's water and sediment, provided context for interpreting flux results.

Figure 14. Timbercreek Farm Pond with the pond's inflow (site H), outflow (site J) and within pond sampling locations marked. The primary outflow is a stand pipe which travels under the dam. The secondary outflow is an overflow channel that rejoins the main channel before the outflow sampling site. On a quarterly basis, data was collected at sites 1 - 12 every 0.5 m in depth on temperature ($^{\circ}\text{C}$), dissolved oxygen (%), and pH. Additionally, quarterly water samples (every 0.5 m in depth) and sediment samples were collected at these sites and analyzed for N content. See section 3.2 Methods for details.

3.2.2 Pond N budget inputs and outputs

Total inputs of N to the pond were determined as:

$$Nr\ Inputs = NFlux_{Site\ H} + NFlux_{Groundwater} + NFlux_{Direct\ Loading} + NFlux_{BNF} + NFlux_{Direct\ Atmo.\ Deposition} \quad (3)$$

where, $NFlux_{Site\ H}$ is the TN flux into the pond *via* surface water, $NFlux_{Groundwater}$ is the TN flux into the pond *via* subsurface flow, $NFlux_{Direct\ Loading}$ is the TN flux into the pond *via* overland flow, $NFlux_{BNF}$ is the TN flux into the pond *via* BNF and

$NFlux_{Direct\ Atmo.\ Deposition}$ is the TN flux into the pond *via* direct atmospheric deposition.

N outputs from the pond were calculated as:

$$Nr\ Outputs = NFlux_{Site\ J} + NFlux_{Groundwater} + NFlux_{Volatilization} + NFlux_{Denitrification} \quad (4)$$

where $NFlux_{Site\ J}$ is the TN flux out of the pond *via* surface water, $NFlux_{Groundwater}$ is the TN flux out of the pond *via* subsurface flow, $NFlux_{Volatilization}$ is the TN flux out of the pond *via* volatilization to the atmosphere and $NFlux_{Denitrification}$ is the TN flux out of the pond *via* denitrification to the atmosphere. Note, not all N inputs and outputs were quantified; they are included here for completeness. See Section 3.2.6 for details.

3.2.3 Stream inflow and outflow

The primary inputs to and outputs from reservoirs are surface waters (Thornton et al. 1990). To calculate instantaneous N fluxes in the surface waters, water samples were collected at the pond inflow (Site H) and outflow (Site J) on a biweekly basis (Figure 14) over the period April 2015 – April 2016. Site H is the only surface water inflow to the pond. The pond has two outflows: 1) a standard standpipe that drains under the constructed dam and 2) an overflow channel which flows intermittently. Site J is located just after the primary outflow channel and the overflow channel join back together. Data from Site J were used to estimate the TN flux out of the pond (Equation 4).

A Marsh-McBirney flow meter and the mid-section velocity method (Rantz 1982) were used to estimate instantaneous stream-discharge readings at these sites. Stream samples were collected in parallel with gauging, including duplicates at each site and one

Table 7. Data needed, approach and calculations for the farm pond nitrogen budget. TN = Total Nitrogen, TPN = Total Particulate Nitrogen, DON = Dissolved Organic Nitrogen, TDN = Total Dissolved Nitrogen.

	Data	Approach	Data Calculations
N Inputs	N flux in surface water	<ul style="list-style-type: none"> Stream gauging and sample collection every other week Analyze samples for $\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$, DON and TPN 	$\text{TN} = \text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+ + \text{DON} + \text{TPN}$ $\text{NFlux} = \text{Discharge} * \text{TN}$
	N flux in groundwater	<ul style="list-style-type: none"> Water budget Analyze spring samples for $\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$, DON and TPN 	$\text{TN} = \text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+ + \text{DON} + \text{TPN}$ $\text{NFlux} = \text{Discharge} * \text{TN}$
	N flux from direct loading	<ul style="list-style-type: none"> Assumed to be negligible 	
	BNF in pond	<ul style="list-style-type: none"> Exploratory sampling and microscopic analysis 	
	Direct Atmospheric deposition	<ul style="list-style-type: none"> Estimate surface area of pond Literature values for N deposition 	$\text{N Deposition} = \text{Area}_{\text{Pond}} * \text{Average N Deposition}$
N Storage	N in Biomass	<ul style="list-style-type: none"> Collect quarterly samples of pond water at multiple depths Analyze for TPN 	$\text{N Storage} = \frac{\text{TPN}_{\text{Initial}} - \text{TPN}_{\text{Final}}}{\Delta \text{Time}}$
	N in Pond water	<ul style="list-style-type: none"> Collect quarterly samples of pond water at multiple depths Analyze samples for $\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$ and DON 	$\text{TDN} = \text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+ + \text{DON}$
	N in Sediment	<ul style="list-style-type: none"> Collect monthly sediment samples, at surface and depth, quarterly Analyze samples for TN 	$\text{N Storage} = \frac{\text{TN}_{\text{Initial}} - \text{TN}_{\text{Final}}}{\Delta \text{Time}}$
N Outputs	N flux in surface water	<ul style="list-style-type: none"> Stream gauging and sample collection every other week Analyze samples for $\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$, DON and TPN 	$\text{TN} = \text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+ + \text{DON} + \text{TPN}$ $\text{NFlux} = \text{Discharge} * \text{TN}$
	N flux in groundwater	<ul style="list-style-type: none"> Water budget Analyze spring samples for $\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$, DON and TPN 	$\text{TN} = \text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+ + \text{DON} + \text{TPN}$ $\text{NFlux} = \text{Discharge} * \text{TN}$
	Volatilization	<ul style="list-style-type: none"> ph < 6.3, assumed NH_3 volatilization is trivial 	
	Denitrification	<ul style="list-style-type: none"> Estimate from balanced N budget 	

blank per sampling date. Water samples were collected, processed, stored and analyzed for DIN and DON as described in Section 2.2.2. Particulate N was not quantified. Total N flux (mg TN s^{-1} and $\text{mg TN ha}^{-1} \text{ s}^{-1}$) into and out of the pond *via* surface waters was calculated using these chemical and hydrologic data, and then scaled to an annual basis.

3.2.4 Net groundwater flow

Previous research at Timbercreek Farm used a water budget approach to estimate that a net positive inflow of groundwater accounts for 11% of the water budget (Suhling 2016). Total dissolved N concentrations of groundwater were approximated by sampling and analyzing (as described above) water from the stream's source (a spring located approximately 300 m upstream of the pond). Net groundwater flux (mg N s^{-1}) was estimated using the balance of the water budget and TDN concentrations.

3.2.5 Other N inputs and outputs

Direct atmospheric N deposition to the pond was estimated based on literature values and the area of the pond. N inputs to the pond *via* overland flow were assumed to be negligible. Exploratory sampling and microscopic analysis of the pond water indicated that cyanobacteria were not present at significant concentrations (none were found in 6 surface samples collected from around the pond); therefore, BNF inputs were assumed to be negligible. Over four sampling dates, 12 sampling sites, and multiple depths per site, the vast majority (95%) of pH readings were acidic than 6.3; therefore, N outputs *via* NH_3 volatilization were assumed to be negligible.

Figure 15. Conceptual N budget for the pond at Timbercreek Farm. Dotted arrows indicate fluxes that are assumed to be negligible (N in overland flow, BNF in pond, volatilization). Dashed lines indicate a flux that is not measured directly but inferred from the balanced N budget (denitrification). See table 7 for detailed description of how inputs/outputs will be measured or estimated.

3.2.6 Constructing the pond N budget

A mass balance approach suggests that if pond inputs are greater than outputs, the system is a net sink. Conversely if outputs are greater than inputs, the system is a net source. This study quantified all of the N inputs and outputs with the exception of N flux to the atmosphere *via* denitrification as:

$$NFlux_{Site\ H} + NFlux_{Direct\ Atmo.\ Deposition} - NFlux_{Site\ J} \pm NFlux_{Groundwater} = N_{Storage} + NFlux_{Denitrification} \quad (5)$$

where, $N_{Storage}$ is the mass of total nitrogen (TN) accumulating in the pond over time (either in sediment or in biomass); all other variables are previously defined. Note that variables previously declared to be negligible were excluded from this equation (Figure 15).

3.2.7 Quality assurance and error estimates

Each water sampling event included a blank (see Section 2.2.2 for details). Additionally, every time samples were analyzed, a subset of samples was run as same-day duplicates. Same day duplicate samples were taken from the same sample bottle, but analyzed separately. These results were used to determine the precision of the analysis. If duplicates were more than 10% different, samples were analyzed again. Additionally, independent standards (made by an independent lab and not used to establish the standard curve) were analyzed with each sample batch to evaluate procedural and instrumental accuracy. A subset of samples were analyzed as storage duplicates (analyzed twice, six weeks apart to confirm that sample storage was not significantly altering N species composition).

Error around discharge readings was estimated by collecting discharge data seven times at both the inflow and outflow (in sequence) and using the resulting estimates to calculate standard error. The standard error around discharge was scaled to estimate a range for the N flux data. The assumption is that error around discharge was greater than error around sample collection and analysis for chemical composition.

3.3 Results

3.3.1 Quality assurance

Nitrate concentrations in blanks were consistently less than 1% of the average NO_3^- concentration for that sample date (Table 8). Ammonium concentrations in blanks (as a percentage of average NH_4^+ concentrations) were somewhat higher (up to 7%), but

still averaged 2%. DON concentrations in blanks (as a percentage of average concentrations) were greater (9 – 10%), but are based on a small number of blanks.

Overall, there is little evidence of contamination in the sample blanks.

Table 8. Nitrogen concentrations of sample blanks. Blanks were used to determine if there was any source of contamination at any point in sample collection, processing or analyzing. Data on blanks below include the concentration found for each species and the percent of the average sample for that day that this concentration represents. The detection limit for NO_3^- , NH_4^+ and DON was $0.005 \text{ mg N L}^{-1}$.

	Date	NO_3^-		NH_4^+		DON	
		mg N L^{-1}	%	mg N L^{-1}	%	mg N L^{-1}	%
Blanks	3/16/15	0.00	0%	0.000	0%	-	-
	4/6/15	0.01	1%	0.000	0%	-	-
	4/13/15	0.00	0%	0.001	5%	-	-
	4/20/15	0.01	1%	0.000	0%	-	-
	4/27/15	0.00	0%	0.002	7%	-	-
	6/30/15	0.00	0%	0.002	7%	-	-
	10/6/15	0.00	0%	0.000	0%	0.03	9%
	2/8/16	0.00	0%	0.000	0%	0.04	10%
	4/4/16	0.00	0%	0.000	0%	-	-
	5/23/16	0.00	0%	0.000	0%	-	-
	Average	0.00	0%	0.001	0.02	0.03	9%

Same-day duplicates show that procedural and instrumental precision is within 1% (or 0.01 mg N L^{-1}) for NO_3^- and within 3% (or $0.001 \text{ mg N L}^{-1}$) for NH_4^+ (Table 9). N concentrations from independent standards indicated that procedural and instrumental accuracy is within 3% (or 0.02 mg N L^{-1}) for NO_3^- , 2% (or $0.005 \text{ mg N L}^{-1}$) for NH_4^+ and 9% (or 0.04 mg N L^{-1}) for DON (Table 10). Storage had little impact on NO_3^- concentrations (less than 10% difference, on average 2% difference). Storage had some impact on the relative importance of NH_4^+ and DON, but TDN remained steady over time (Table 11).

Table 9. Nitrogen concentrations as absolute and percent difference for same-day duplicates. Same day duplicates were used to determine the precision of the instrumentation and accompanying standards/reagents; data on same day duplicates below includes the difference in concentration between each duplicate and the percentage difference relative to the average of the duplicates.

	Date	NO ₃ ⁻		NH ₄ ⁺		DON	
		mg N L ⁻¹ diff.	% Diff.	mg N L ⁻¹ diff.	% Diff.	mg N L ⁻¹ diff.	% Diff.
Same Day Duplicates	3/16/15	0.00	0%	0.000	0%	-	-
	3/31/15	0.00	0%	0.000	0%	-	-
	4/6/15	0.02	2%	0.001	1%	-	-
	4/13/15	0.03	3%	-0.001	-3%	-	-
	4/20/15	-0.12	-12%	-0.005	-9%	-	-
	4/27/15	0.01	1%	0.000	0%	-	-
	5/4/15	0.00	0%	-0.001	-1%	-	-
	5/12/15	0.00	0%	-0.001	-15%	-	-
	5/28/15	0.00	0%	0.001	6%	-	-
	6/2/15	0.00	0%	0.000	0%	-	-
	6/9/15	0.00	0%	-0.001	-1%	-	-
	6/16/15	-0.01	-1%	-0.001	-9%	-	-
	6/23/15	0.00	0%	-0.001	-8%	-	-
	7/14/15	0.00	0%	-	-	-	-
	7/28/15	0.00	0%	-	-	-	-
	8/4/15	0.01	1%	-	-	-	-
	8/18/15	0.00	1%	-	-	-	-
	Average	0.00	-0.3%	-0.001	-3%	-	-

For the pond's inflow, one standard error of the mean for discharge readings was 0.0004 m³ s⁻¹. For the pond's outflow, one standard error of the mean for discharge readings was 0.0006 m³ s⁻¹. Relative to typical water fluxes, this instrument and/or measurement error represents 5% and 6%, respectively.

Table 10. Nitrogen concentrations as absolute and percent difference for independent standards. Independent standards were mixed by an independent laboratory and independent laboratory staff; data on independent standards below includes the difference between the concentration found and the target concentration and the percentage difference relative to the target.

	Date	NO ₃ ⁻		NH ₄ ⁺		DON	
		mg N L ⁻¹ diff.	% Diff.	mg N L ⁻¹ diff.	mg N L ⁻¹ diff.	% Diff.	mg N L ⁻¹ diff.
Independent Standards	7/1/15	-	-	0.000	0%	-	-
	7/1/15	-	-	0.004	1%	-	-
	7/1/15	-	-	0.000	0%	-	-
	7/8/15	0.00	-2%	-	-	-	-
	7/8/15	0.01	4%	-	-	-	-
	7/8/15	0.04	6%	-	-	-	-
	7/8/15	0.04	6%	-	-	-	-
	7/8/15	0.02	1%	-	-	-	-
	7/8/15	-0.09	-5%	-	-	-	-
	7/29/15	0.04	2%	-0.023	-10%	-	-
	8/3/15	-	-	-	-	-0.05	-12%
	8/3/15	-	-	-	-	-0.08	-19%
	8/3/15	-	-	-	-	-0.07	-17%
	8/3/15	-	-	-	-	-0.05	-12%
	8/5/15	0.14	12%	-	-	0.01	2%
	8/5/15	-	-	-	-	0.04	9%
	4/22/16	-	-	-	-	-0.04	-9%
	4/22/16	-	-	-	-	-0.04	-9%
	4/22/16	-	-	-	-	-0.04	-10%
	Average	0.02	3%	-0.005	-2%	-0.04	-9%

3.3.2 Physical and chemical characteristics

The physical and chemical characteristics of the pond water and sediment indicate that the pond is generally a well-mixed reservoir that exhibits some seasonal patterns in composition and volume. The bathymetric map (Figure 16) illustrates that the northern portion of the pond (where the inflow enters) is relatively shallow (less than 0.5 m), while the southern end (where the standpipe is located) is relatively deep (more than 2 m).

Table 11. Nitrogen concentrations as absolute and percent difference for storage duplicates. Storage duplicates were used to assess the impact of storage on samples (since not all samples were stored for the same length of time); data on storage duplicates below includes the difference between the first and second analysis and the percentage difference relative to the average of the results.

	Date	NO ₃ ⁻		NH ₄ ⁺		DON	
		mg N L ⁻¹ diff.	% Diff.	mg N L ⁻¹ diff.	mg N L ⁻¹ diff.	% Diff.	mg N L ⁻¹ diff.
Storage Duplicates	6/9/15	-0.07	-4%	0.000	7%	-	-
	6/9/15	0.02	4%	0.000	0%	-	-
	6/9/15	0.02	4%	0.002	5%	-	-
	6/9/15	0.02	4%	-0.001	-87%	-	-
	6/9/15	0.00	1%	0.000	-2%	-	-
	6/9/15	0.01	4%	0.010	37%	-	-
	6/9/15	0.03	5%	-0.004	-17%	-	-
	6/9/15	-0.15	-10%	0.007	29%	-	-
	6/9/15	0.03	5%	-0.004	-4%	-	-
	6/9/15	0.03	5%	0.000	0%	-	-
	6/9/15	0.03	6%	-0.004	-5%	-	-
	6/9/15	0.03	6%	0.000	1%	-	-
	1/13/16	-	-	-	-	0.15	57%
	1/13/16	-	-	-	-	0.18	42%
	2/1/16	-	-	-	-	-0.42	-89%
	2/1/16	-	-	-	-	-0.35	-90%
	2/22/16	-	-	-	-	0.23	53%
	2/22/16	-	-	-	-	0.21	47%
	Average	0.00	2%	0.001	-3%	0.00	3%

The pond's surface area was 6400 m² and the pond's volume was 6800 m³ (although over the course of the year the volume varied substantially) (Suhling 2016, Table 8). Morphometric measurements (Table 12) indicate that the Timbercreek Farm pond is a shallow pond that has a relatively regular shape (i.e., oblong and conical).

Figure 16. Bathymetric map of the Timbercreek Farm pond based on depth readings and GPS coordinates from 64 sites within the pond. The ponds inflow is in the north portion of the pond and the outflow is in the center of the south portion of the pond. Compare to Figure 14 for details.

Temperatures in the pond varied seasonally from 20-30 C° in summer to 6-10 C° in wintertime (Appendix A). The difference between surface temps and temperatures at depth was greatest in the summer (7-10 C° difference) and spring (4-8 C° difference) relative to the fall (1-2 C° difference) and winter (3-4 C° difference). The pH of the water ranged from 5.3 to 7.8, with most values falling between 6.5 and 6.7. The lowest pH values were found at Sites 1, 2, 8 and 9, which are in the shallow northern portion of the

farm pond (Figure 14). The median percent saturation of dissolved oxygen was 88%, but varied dramatically between 2% and 680% (Appendix A).

Table 12. Summary of pond morphometric characteristics. Analysis was conducted using a depth sounder, handheld GPS unit and ArcGIS. See table 6 for approaches.

Parameter	Variable	Estimate	Units
Maximum Depth	$Z_{\max}$	2.8	m
Maximum Length	$L_{\max}$	150	m
Maximum Breadth	$B_{\max}$	60	m
Catchment Area of Inflow	A_{Inflow}	46	ha
Catchment Area of Outflow	A_{Outflow}	54	ha
Pond Surface Area	A	6400	m^2
Shoreline Length	L	350	m
Pond Volume	V	6800	m^3
Mean Depth	$\bar{Z}$	1.1	m
Depth Ratio	D_{ratio}	0.38	-
Shoreline Development	D_L	1.7	m m^{-2}
Development of Volume	D_V	1.1	-

The N concentration of water samples varied over time (Figure 17, Appendix A). Nitrate concentrations were low in the summer ($0.1 - 1.3 \text{ mg N L}^{-1}$) compared to the fall ($1.1 - 1.3 \text{ mg N L}^{-1}$), winter ($1.3 - 1.8 \text{ mg N L}^{-1}$) and spring ($0.6 - 2.4 \text{ mg N L}^{-1}$). Ammonium concentrations were low throughout the year relative to NO_3^- (ranging from $0.01 - 0.4 \text{ mg N L}^{-1}$), with median concentrations between $0.04 - 0.2 \text{ mg N L}^{-1}$. DON concentrations were an important component of TDN throughout the year, and were highest in summer (as high as $0.3\text{-}0.5 \text{ mg N L}^{-1}$). TDN concentrations varied seasonally, but within each sample date the range was small. The exception are the data from the April 2016 sample date, which had high spatial variability in TDN and DON; this variability may have been due to laboratory error.

Figure 17. Box and whisker plots showing seasonal variability of N species in the pond. Plots show median (dark line), Quartile 1 and Quartile 3 (box) and min and max values (error bars).

Figure 18. Box and whisker plots showing spatial variability of N species in the pond by sample site. Site numbers are on y-axis. See Figure 14 for site locations. Plots show median (dark line), Quartile 1 and Quartile 3 (box) and min and max values (error bars).

The TDN content of pond water samples varied very little ($0.5 - 1 \text{ mg N L}^{-1}$) horizontally (among surface samples) (Figure 18) and vertically (over depths) (Figure 19), although the exact composition of N species changed. Across the 12 sampling sites within the pond (Figure 14), NO_3^- concentrations and NH_4^+ concentrations change little relative to DON ($0.5 - 1.5 \text{ mg N L}^{-1}$ and $0.05 - 0.2 \text{ mg N L}^{-1}$, respectively) (Figure 18). In contrast, DON concentrations were relatively higher at shallow sites (Sites 1, 7 and 8) as compared to deeper sites (Sites 4, 9, 10). In terms of N contents at different depth, NO_3^- and TDN were relatively constant (Figure 19). However, median NH_4^+ and DON concentrations increased slightly ($+0.02 \text{ mg N L}^{-1}$ and $+0.01 \text{ mg N L}^{-1}$, respectively) at the deepest depth (2 m).

N contents (%), carbon contents (%) and C:N ratios of sediment samples were relatively constant over space and time (Figure 20, Table 13). N was typically $0.4 - 0.5\%$ of total dried mass of sediment, while C was $4 - 5\%$ of total dried mass of sediment. Therefore, C:N ratios were between 9 and 15; similar to the expected ranges for soils ($8 - 15$) (Batjes 1996) and for impoundment sediments ($7 - 14$) (Dean and Gorham 1998).

Figure 19. Box and whisker plots showing spatial variability of N species in the pond by depth. Plots show median (dark line), Quartile 1 and Quartile 3 (box) and min and max values (error bars).

Figure 20. Box and whisker plots showing seasonal variability of sediment N, C and C:N mass ratios. Plots show median (dark line), Quartile 1 and Quartile 3 (box) and min and max values (error bars).

Table 13. Seasonal and spatial variability of C and N in sediment samples collected from the Timbercreek Farm in October 2015 and June 2016. See Figure 14 for map of sampling sites within the pond.

Date	Site	C Content (%)	N Content (%)	C:N ratio
10/12/15	1	6.34	0.50	12.8
10/12/15	2	4.65	0.42	11.0
10/12/15	3	4.71	0.47	10.1
10/12/15	4	4.67	0.50	9.4
10/12/15	5	4.47	0.48	9.3
10/12/15	6	5.05	0.56	9.0
10/12/15	7	4.12	0.38	10.9
6/1/16	1	1.80	0.16	12.1
6/1/16	2	2.06	0.18	11.2
6/1/16	3	4.34	0.36	11.8
6/1/16	4	4.79	0.43	9.7
6/1/16	5	4.81	0.41	11.0
6/1/16	6	4.75	0.49	11.5
6/1/16	7	4.07	0.37	11.8
6/1/16	8	7.69	0.67	15.0
6/1/16	9	4.09	0.35	12.1
6/1/16	10	2.35	0.16	9.4
6/1/16	11	4.28	0.35	10.0
6/1/16	12	4.92	0.52	10.1

3.3.3 Pond inflow and outflow

Instantaneous discharge data from the pond indicate that the inflow ($0.002 - 0.02 \text{ m}^3 \text{ s}^{-1}$) and outflow ($0.004 - 0.03 \text{ m}^3 \text{ s}^{-1}$) were comparable, but not equal (Figure 21).

Over the course of the year, more water left the pond than entered it *via* stream flow; the 11% difference was attributed to a net positive groundwater inflow (Suhling 2016). Due to a failing standpipe, on two occasions the water level in the pond dropped by about as much as 1 m resulting in a 50% decrease in the pond volume. In both cases, the pond later filled back up to previous levels within a few weeks. For example: in Figure 21, it

can be clearly seen that on sampling data 11/9/15 the pond was draining (given the large outflow as compared with the inflow), but that on 12/22/15, 1/13/16 and 2/1/16 the pond was consistently filling back up.

Figure 21. Discharge data from the ponds inflow (Site H) and outflow (Site J). Data was collected on 30 sampling days (approximately biweekly) between April 2015 and April 2016. Error bars show one standard deviation in both the positive and negative direction based on repeated measurements ($n=7$) in quick succession at each site.

3.3.4 *N* concentrations in inflow and outflow waters

Nitrogen in the inflowing waters was consistently dominated by NO_3^- ($0.9 - 1.6 \text{ mg N L}^{-1}$), but DON was also important ($0.1 - 0.9 \text{ mg N L}^{-1}$) (Figure 22). Ammonium concentrations ($0.001 - 0.05 \text{ mg N L}^{-1}$) were small relative to other N species.

Outflowing waters showed a clear seasonal pattern with NO_3^- dominating in winter and spring (ranging from $0.6 - 1.2 \text{ mg N L}^{-1}$) but declining in importance in summer and fall (ranging from $0.2 - 0.6 \text{ mg N L}^{-1}$) (Figure 23). DON concentrations were variable over the year, but they were relatively more important during summer and fall (ranging from

Figure 22. Nitrogen concentrations in the pond inflow collected at Site H. Nitrate concentrations are consistently greater than both DON and NH_4^+ concentrations. Dissolved organic N is an important component of TDN. Ammonium concentrations are small compared to the other N species. *Adapted from Chaffin 2016.*

0.2 – 0.6 mg N L⁻¹). Ammonium concentrations in the outflow were relatively small (ranging from 0.006 – 0.2 mg N L⁻¹), but greater than in the inflowing waters. On all dates samples TDN concentrations were greater in the inflow (ranging from 1.2 – 2 mg N L⁻¹) than in the outflow (ranging from 0.35 – 1.9 mg N L⁻¹) (Figure 24). The difference between the TDN concentration in the inflow and outflow was greatest in the summer and smallest in the winter.

The TDN flux into and out of the pond *via* surface waters were comparable but not equal. On 77% of sampling days, the TDN flux in the inflow was greater than the TDN flux in the outflow (Figure 25). This was especially true in the summer time (5/12/15 through 7/18/15) when N flux into the pond was greater than N flux out of the pond for 9 straight sampling days. On a per ha basis, this difference is even greater. The

net TDN flux into and out of the pond (mg N s^{-1}) shows the magnitude of these differences and highlights the seasonal pattern (Figure 26).

Figure 23. N concentrations in the pond outflow collected at Site J. Nitrate concentrations are relatively higher in winter and spring relative to summer and fall samples. Dissolved organic nitrogen concentrations are variable over the year, but relatively more important in summer and fall. Ammonium concentrations are small compared to the other N species, but greater than in the pond inflow. *Adapted from Chaffin 2016.*

3.3.5 Annual pond N budget

On an annual basis, the stream inflow adds 490 ± 22 kg N into the pond, net ground water adds 76 ± 76 kg N and direct deposition contributes 3 kg N (no error was estimated for N deposition) (Figure 27). Note that the uncertainty around the groundwater flux creates some uncertainty in the net ground water input of N; this may be as high as 152 kg N year⁻¹ or as low as 0 kg N year⁻¹. On a per ha of watershed basis, stream inflow and net groundwater estimates are 11 ± 0.5 kg N ha⁻¹ and 9.5 ± 9.5 kg N ha⁻¹, respectively. Total inputs are 570 ± 98 kg N year⁻¹ or 11 ± 1.8 kg N ha⁻¹. Stream outflow

exports 410 ± 23 kg N from the pond or 7.6 ± 0.4 kg N ha⁻¹. The balance of the N budget suggests that 160 ± 120 kg N year⁻¹ (or 3.0 ± 1.4 kg N ha⁻¹ year⁻¹) are either accumulating in the pond (in either the sediment or biomass) and/or denitrifying to the atmosphere.

Figure 24. Total dissolved N concentrations in the pond inflow (Site H) and outflow (Site J). Total dissolved N concentrations in the inflow was consistently greater than TDN concentrations in the outflow with a more pronounced difference in the summer.

3.4 Discussion

The pond is a sink for N, but it is unknown whether this N is being denitrified (with emission of N₂ and N₂O) to the atmosphere or stored in the pond. The magnitude of the sink is modest (30% of inputs) and, because the uncertainty around N flux in groundwater, somewhat uncertain. The physical and chemical characteristics of the pond's water and sediment over space and time indicate that while conditions may be conducive to denitrification, residence times may limit the potential for significant N removal.

Figure 25. Instantaneous TDN fluxes in inflow (Site H) and outflow (Site J) for 30 sampling dates from April 2015 – April 2016. Top figure shows TDN flux as mg N s^{-1} . Bottom figure shows TDN flux as $\text{mg N s}^{-1} \text{ ha}^{-1}$. On 77% of days when sampling occurred, N flux into the pond via surface waters exceeded N flux out of the pond via surface waters. Differences were greatest in May 2015 – July 2015 and December 2015 – February 2016.

3.4.1 N fluxes into and out of the pond via surface waters

Surface waters dominate the N fluxes into and out of the farm pond (Figure 27). Discharge, both in and out of the pond, is highly variable (Figure 21) while TDN concentrations are relatively steady over time (Figure 24), such that N fluxes in surface waters are more strongly driven by discharge as opposed to N concentrations. However, the composition of N species in the inflow and outflow waters changes with time (Figure 22 – 23) and provides insights into the biogeochemical processes that may be affecting N in the water and sediment of the pond.

Figure 26. Net TDN flux calculated as TDN flux into the pond minus TDN flux out of the pond. On 75% of days sampled N flux into pond was greater than N flux out of pond. From April 2015 through April 2016, the total net flux was 80 kg N.

Nitrate concentrations were lower in the outflow relative to the inflow (10-80% less NO_3^-) (Figure 22-23). Other studies have found that small ponds retain 11 – 80% of inflowing NO_3^- (Fairchild and Velinsky 2006, Cunha et al. 2014) and that this change is

often most pronounced in watersheds dominated by agriculture relative to forested or developed watersheds (Ignatius and Rasmussen 2015). In the Timbercreek Farm pond, NO_3^- concentration changes in the outflow were most pronounced in the summer (55-80% less NO_3^- in the outflow than in the inflow) as compared to winter (10-30% less). A similar seasonal pattern was observed in small agricultural ponds in Pennsylvania (Fairchild and Velinsky 2006), in a mature impoundment in Wisconsin (Powers et al. 2013) and a large agricultural reservoir in Illinois (David et al. 2006). Seasonal retention of NO_3^- suggests that biological uptake of DIN may be a short term (seasonal) sink for N in the pond.

Ammonium concentrations were 2-10 times greater in the pond's outflow relative to the inflow (Figure 22-23). Similar NH_4^+ concentration increases were also observed in small agricultural ponds in Pennsylvania (Fairchild and Velinsky 2006) and Georgia (Ignatius and Rasmussen 2015). Increases in NH_4^+ in the outflow were most pronounced in spring (Figure 23); these increases may be due to higher temperatures and lower stream flows (Ignatius and Rasmussen 2015) that are likely to encourage mineralization in sediment (Hargreaves 1998). Sediments may be an internal source of NH_4^+ to the pond and, therefore responsible for the increased NH_4^+ concentrations in the outflow relative to the inflow. However, NH_4^+ concentrations were consistently 1-2 orders of magnitude less than NO_3^- and DON, and so can be considered negligible.

Dissolved organic N concentrations were variable over time at both the inflow (Figure 22) and the outflow (Figure 23), but neither exhibited a clear pattern. Naturally occurring lakes are often sinks of DIN, but sources of DON (Goodman et al. 2011). DON fluxes into and out of agricultural impoundments are often highly variable (Powers et al.

2013). The relative importance of DON in the Timbercreek Farm pond's outflow changed seasonally; in the winter, DON was 10-30% of the TDN flux and in the summer and fall, 40-50% of the TDN (Chaffin 2016). A similar study found that both dissolved organic matter and DON increased in a pond's outflow in the summer (Goodman et al. 2011). This seasonal pattern suggests that primary production (and subsequent decomposition) is important in controlling DON:DIN ratios in the pond's outflow (Chaffin 2016).

Total dissolved N concentrations were consistently lower in the pond's outflow relative to the inflow (5-70% less TDN) (Figure 24). A study in the mid-western US that compared reservoir outflows to unimpeded streams found that flows contained 20% less TDN after traveling through a reservoir (Powers et al. 2015). Decreased TDN concentrations in outflow streams may be due to dilution (if, inflows of groundwater or precipitation have a lower N content), decreases in the total mass of N within the water body (denitrification, volatilization) or storage within the pond (biological uptake of N or burial in sediment) (Powers et al. 2015). In the case of both the inflow and outflow, TDN concentrations were relatively steady over time and much of the variability seen in NO_3^- and DON concentrations cancels itself out (Figure 24).

Discharge from the pond's inflow and outflow (Figure 21) has a strong seasonal pattern with low flows in the late summer and higher flows in the winter and spring. High flows in fall 2015 were due to a tropical storm on October 2nd – 3rd (NWS 2016). The inflow and outflow are comparable over the year, but these data indicate that over short timescales (days-weeks) the pond may not be at steady state. In some cases, this difference is due to the flood routing function of the reservoir (that is, its ability to

storage water temporarily to reduce flooding downstream). However, on at least two occasions, the non-steady state nature of the pond was due to a significant drainage; the pond's stand pipe failed twice and the pond drained by about 50%, before refilling in the following weeks. Over the course of the year, more surface water left the pond than entered it (Figure 21), but the pond's total volume was the same (Suhling 2016). These results suggest that other inflows to the pond (groundwater fluxes) are also important (Suhling 2016).

Instantaneous TDN fluxes in the surface waters indicate that the majority of the time, more N is moving through the inflow site than through the outflow site, especially when compared on a per ha basis (Figure 25 - 26). The instantaneous TDN flux is strongly controlled by the stream discharge. Therefore, instantaneous TDN fluxes in the inflow and outflow exhibit a seasonal pattern similar to discharge with lower fluxes in the summer and greater fluxes in the winter and spring (Figure 21). TDN-flux data for large reservoirs indicates that inflow N fluxes often exceed outflow N fluxes (Powers et al. 2015). The present data suggest that small agricultural ponds may exhibit a similar pattern.

3.4.2 Annual pond N budget

When accounting for all inflows and outflows, more N enters the pond than leaves it (Figure 27); therefore, the pond can be considered a sink for N. Inputs of N to the pond are dominated by the surface inflow (87%), but groundwater inputs are also important (13%). In contrast, direct deposition is a negligible input (<1%).

On an annual basis, large reservoirs are known to be TDN sinks (Powers et al. 2015), and there is some evidence that small agricultural ponds may also be TDN sinks (Fairchild and Velinsky 2006). N balance data from the literature suggests that in small agricultural ponds N sink pathways are likely to be denitrification, burial in sediment and biomass uptake (Powers et al. 2015). Previous text (Section 3.4.1) discussed how N concentration data provide insights into the relative importance of these potential sink pathways. An important distinction needs to be made however between short-term and long-term N sinks; denitrification represents a long-term (nearly permanent) sink of N to the atmosphere, while biomass uptake represents a short-term (days-years) sink of N and burial in sediment represents a medium-term sink (months-decades). The importance and magnitude of these sinks is a function of residence time (Rueda et al. 2006).

Figure 27. Annual N budget for the Timbercreek Farm pond for April 2015 – April 2016. All units are in kg N year^{-1} . N in stream inflows, stream outflows and net groundwater are based on discharge data and N content of waters. Ranges represent uncertainty around discharges readings that have been scaled up to N flux (no uncertainty in N content was determined). The balance of the N budget is assumed to be storage in the pond sediment or N losses via denitrification.

The pond N budget is strongly controlled by water fluxes; greater streamflow means increased fluxes and *vice-versa*. There is some evidence that N retention in reservoirs may increase in dry years (Powers et al. 2015), but with only one year of data, this analysis cannot determine if this is true for the Timbercreek Farm pond. The uncertainty around the pond water budget creates uncertainty about net groundwater fluxes and indicates the important role that N flux in groundwater has on the pond N budget. This analysis was based on a water budget (Suhling 2016) that estimated groundwater flows by difference. Direct measurements of groundwater fluxes could confirm these estimates of subsurface flow.

3.4.3 Potential for denitrification

The conditions required for denitrification may be present in the pond. Dissolved oxygen was consistently low in the deepest portions of the pond (Appendix A), especially in summer, when DO saturation was only 2-10%. Combined with the high temps recorded that same day (25 – 30 °C), these data indicate that rates of denitrification could be significant (Jansson et al. 1994, Inwood et al. 2005). Indeed, the conditions that allow for denitrification (anoxia, NO_3^- , carbon, etc.) are likely to exist in shallow littoral sediments (Bruesewitz et al. 2012) and on the bottom of ponds (Inwood et al. 2005). In larger agricultural ponds and lakes, denitrification rates can be significant, typically on the order of 10 - 100 mg N m² day⁻¹ (Davids et al. 2006, Seitzinger 1988). Therefore, based on the area of the pond, denitrification could account for 20 – 200 kg N year⁻¹ (or 10 – 100% of the pond N sink).

Hydraulic residence time of a lentic system is one of the factors that controls the potential for denitrification (Rueda et al. 2006). Therefore, it is possible that small ponds, like the Timbercreek Farm pond, simply do not retain water long enough for denitrification to occur to the same magnitude as it does in larger ponds (even though the rates may be similar) (Fairchild and Velinsky 2006). Additionally, longer residence times lead to increased water temperatures (during summertime), which increases the rate of denitrification (Gooseff et al. 2005). There is some evidence that when residence times in the Timbercreek Farm pond were larger, TDN removal was also larger, however, this was a weak correlation (Figure 28). Regardless, the short residence times of the Timbercreek Farm pond (4-20 days) are less than residence times of other agricultural impoundments (14 – 300 days) (Powers et al. 2015) and may be limiting the potential for N removal *via* denitrification.

Figure 28. Total dissolved nitrogen removal as a function of residence time. TDN removal (%) is calculated as TDN in the inflow minus TDN in the outflow divided by TDN in the inflow. Residence time was calculated based on weekly pond levels (scaled to volume using ArcGIS) and outflow discharges. These data show a weak correlation.

3.5 Summary

Over an annual timescale, the Timbercreek Farm pond is a sink for N; denitrification and/or storage are the likely fates. Surface water fluxes are the major components of the pond N budget; however, groundwater fluxes are also important. Nitrate concentrations were lower in the outflowing waters relative to the inflowing waters, but NH_4^+ concentrations were greater in the outflow. DON concentrations were variable, but relatively more important in the outflow during the summer. Inflowing waters had consistently larger TDN concentrations relative to outflowing waters. TDN in inflow and outflow waters is relatively steady over time, therefore weekly changes in N flux are driven by changes in discharge. The physical and chemical conditions that are conducive to denitrification may exist in the pond, but residence times may limit the potential for N removal. The Timbercreek Farm pond is an active system that is both removing N from the surface waters and changing the composition of N species.

4. Objective 3: Determine the effect of storm events on pond N fluxes

4.1 Background

N fluxes during base flows provide valuable information about N transport and transformation in lentic systems. However, these fluxes (whether instantaneous or annual) do not tell the whole story; there is increasing evidence that nutrient fluxes during short-term storm events can be important inputs to and outputs from lentic systems (Carpenter et al. 2015). Extreme storm events can be responsible for 10 - 50% of annual N loads from agricultural watersheds (e.g., Royer et al. 2006). Therefore, the objective of this section is to determine the effect of storm events on N fluxes into and out of the Timbercreek Farm pond.

4.1.1 Changes in discharge during storm events

Dependent on antecedent conditions, precipitation events (or storms) can increase stream discharge. Since discharge is a key driver of N flux (Section 3.4.1), rain events can lead to increased N fluxes in surface waters. During storm events, flow pathways from agricultural lands to streams include 1) infiltration excess overland flow 2) saturation excess overland flow 3) shallow subsurface flow and 4) groundwater flow (Biggs et al. 2006). Stormflow is typically dominated by pre-event water (Orlowski et al. 2015) and subsurface flow can be a primary pathway (Buda and DeWalle 2009).

Many agricultural lands have tile drains that effectively act as macropores delivering significant preferential flow during storm events (Cambardella et al. 2015). In non-tile drained catchments, preferential subsurface flow may still be important (Weiler and McDonnell 2007). Additionally, overland flow may be important in agricultural

catchments. Compared to forests, pastures have greater soil compaction (Greenwood and McKenzie 2001) and an increased likelihood of infiltration-excess overland flow (Biggs et al. 2006, Elsenbeer et al. 1999).

Hillslope topography plays a key role in controlling storm flow magnitudes and pathways (Ocampo et al. 2006). Steep hillslopes have the potential to transport pre-event and event water to streams over short time periods and, in these cases, important transport mechanisms may include unsaturated flow and/or flow through a perched water table (McGuire and McDonnell 2010). However, there is still some uncertainty as to the exact processes that control stormflow from hillslopes to streams (McGuire and McDonnell 2010), especially in heavily agricultural catchments (Biggs et al. 2006).

Reservoirs are important hydrologic controls on floods; they store storm water over short time scales (minutes to days) and mitigate peak flows downstream (Smith et al. 2002). In this way, reservoirs route storm water and control storm flows. Farm ponds, even though they may not have been built for this purpose, also mitigate storm flows.

The storage of water in reservoirs and the change in velocity of the streamflow may allow for sedimentation (Verstraeten and Poesen 2000). However, the percentage of suspended sediment in the inflow that is deposited as sediment on the bottom of a pond is dependent on many variables including sediment particle size, residence time, inflowing discharge, physical parameters of the pond and other characteristics (Verstraeten and Poesen 2000). Over time, sedimentation decreases pond volume and therefore, shortens pond residence times (which is a function of volume) (Powers et al. 2015). A mature impoundment may accumulate sediment to the point where no further deposition occurs (Powers et al. 2015).

4.1.2 Changes in N concentrations during storm events

In addition to increased streamflow, storms are also important because they can change the TN concentration in surface waters and/or change the mix of N species within TN. TDN concentrations have been found to increase with storm flow in forested catchments (Campbell et al. 2000) and agricultural catchments (Vanni et al. 2001). However, more recent data has indicated that the relationship between N concentration and discharge is more complicated than previously thought.

Storm flows can flush N out of watersheds, resulting in initial increases in N concentrations followed by later decreases (Rusjan et al. 2008), although the exact mechanisms are still being determined (Weiler and McDonnell 2006). The N concentration/discharge relationship often reveals a pattern of hysteresis when plotted (Chanat et al. 2002). The pattern of this relationship is a function of the relative importance of different flow pathways as well as the N concentrations of water flowing from each source (Chanat et al. 2002). Since storm flows may mobilize previously stored N (either in soils, or sediments at the bottom of streams, lakes, etc.), N sources during storm events may be different than during base flows (Buda and DeWalle 2009).

Hysteresis of the NO_3^- /discharge relationship is common in agricultural catchments (Oeurng et al. 2010) and forested catchments (Chanat et al. 2002, Rusjan et al. 2008). Analysis of the pattern of hysteresis can give some clues into N sources. A clockwise pattern (greater N concentrations in rising limb of hydrograph) suggests rapid N mobilization during storms (Bowes et al. 2009). While a counter-clockwise pattern

(greater N concentrations in falling limb of hydrograph) suggests a later mobilization of water with a higher N content (Bowes et al. 2009).

Since storm flows may have flow pathways that are distinct from base flow pathways, they may therefore have a unique mix of N sources. This unique mix of N sources can change the mix of N species within stream water TN concentrations.

Overland flow during storms can deliver significant loads of PN to streams (Kemp and Dodds 2001); so PN may be an important component of N flux during storms, even if it is not important during base flows. Shallow sub-surface flow in agricultural catchments can mobilize and increase NO_3^- concentrations (Buda and Dewalle 2009). DON and NH_4^+ can be transported *via* overland flow, although not to the extent of PN (Kemp and Dodds 2001). Changes in the N concentrations of individual species can provide insight into the sources of N in the stream (N stored in groundwater, N stored in soils, etc.), the flow pathways that resulted in those N concentrations (shallow sub-surface flow, overland flow, etc.) and the transformational processes that might occur along different pathways (mineralization, nitrification, etc.).

In forested catchments, NO_3^- concentrations in streams are often highly sensitive to storm events, while in developed catchments (including those with agricultural land uses), NO_3^- concentrations are typically more constant over time (Basu et al. 2010).

Another study found that in agricultural streams, N sources during storms are similar to N sources during base flows (Buda and Dewalle 2009). Together, these data suggest that increased groundwater discharge (or mobilization of old water) is an important potential mechanism for storm flows in agricultural watersheds. In catchments that have been used for agriculture for decades, groundwater often has elevated NO_3^- concentrations (Burrow

et al. 2010). If this same water is mobilized to streams during storms, N concentrations in streams may also increase.

4.1.3 Changes in N flux during storms

Nitrogen fluxes in streams typically increase during storm events (Gu et al. 2008). A significant portion of N export from agricultural lands to waterways occurs during storm events (Pionke et al. 1999), with the subsurface flows acting as the primary transport mechanism (Biggs et al. 2006). In agricultural catchments, much of the increased stream N flux during storms is due primarily to increased discharge (as opposed to change in N concentrations) (Royer et al. 2006). In some cases, the majority of annual N loads can be during storm events (Vanni et al. 2001). Indeed, discharges above median values can mobilize N that is being stored in agricultural streams, causing them to become sources of N (Royer et al. 2006). However antecedent conditions (moisture, temperature, etc.) partly control the magnitude of storm discharges (Fang and Pomeroy 2016) and, therefore, can increase or decrease the likelihood of N export.

Lentic systems can also become sources of N during storm events (Wurtsbaugh et al. 2005). Nitrogen burial in reservoir sediment during base flows can be mobilized by high flows and result in N export over short time scales (hours to days) (Hirsch 2012).

4.1.4 Previous on-site research

Previous research at Timbercreek Farm indicates that high flows may be responsible for significant N export. On the majority of days (77%) sampled DIN flux *via* surface water into the farm was greater than DIN flux out of the farm *via* surface water

(Leach 2014), suggesting that the surface waters on the farm are a sink for N. However, when these data were averaged over the course of one year, DIN flux *via* stream water into the farm was comparable to DIN flux out of the farm, both 200 – 2000 kg N/year (Leach 2014). Thus, most of the time Timbercreek Farm is a sink for N coming into the farm *via* the stream, but when N does leave the farm in the stream water, it does so in large enough amounts to negate any storage during the rest of the year. These data suggest that high flow events may flush N out of the pond (perhaps *via* remobilization of sediment) and, that over short time scales the pond may be a source of N.

4.2 Methods

4.2.1 Pond N fluxes during storm events

To determine the impact of storm events on the pond N fluxes, water samples were collected during storm events with a flow-actuated ISCO sampler. Water samples were collected, processed, stored and analyzed for DIN and DON as described in Section 2.2.2. Masses of total suspended solids (TSS) (mg TSS L^{-1}) were recorded in the filtering and drying phase. Before filtering, filters were oven dried at 60 °C for 24h or until a constant mass was reached; after filtering, sediment samples (and accompanying filters) were oven dried again. The difference in filter weight pre- and post-filtering was used to estimate TSS (mg TSS L^{-1}). A subset of samples was analyzed for total N and total C in a C:N analyzer (Thermo Scientific Flash 2000) (CE Instruments 2016). N contents (%) were similar to estimates from pond sediment samples (Section 3.3.2, Table 13) and an average value was used to calculate PN (mg N L^{-1}). The assumption is that the dynamic variation in TSS was greater than any variation in N content.

Figure 29. Stilling well design. Stilling wells and pressure transducers were installed at the pond's inflow (Site H) and outflow (Site J) to measure stage (m) every 6 minutes. See Figure 15 for site locations. Design and drawing by Aaron Mills.

Two gauging stations were installed at the pond's inflow (Site H) and outflow (Site J) to capture changes in stage (*via* a pressure transducer) during storm events

(Figure 14, Figure 19). Instantaneous discharge readings (using a Marsh-McBirney flow meter and the mid-section velocity method) and stage data from the pressure transducer were used to create a rating curve for the pond's inflow and outflow (Figure 14). Daily rainfall data (mm day^{-1}) from the Charlottesville-Albemarle Airport as reported by the National Weather Service were used to construct a hyetograph (rainfall over time).

Data on NO_3^- , NH_4^+ , DON and PN concentrations and stream discharge were used to calculate the total N flux into and out of the pond *via* surface waters over short time scales. Stormflow pathways were not quantified and this analysis did not include hydrograph separation. Instead, the focus was on N fluxes during storm events and how the N flux in the pond's inflow and outflow changed during storm events.

Figure 30. Rating curve for the pond inflow (Site H) based on discharge readings ($\text{m}^3 \text{s}^{-1}$) collected using a Marsh McBirney flow meter and stage readings (m) from a pressure transducer. Note the log scale on y-axis. See Figure 14 for site location.

4.3 Results

Hydrograph stage data were collected from July 2015 – June 2016. Instantaneous discharge readings were collected on 22 dates during that time and used to create rating curves for the pond's inflow (Figure 30) and outflow (Figure 31). Stage is more predictive of discharge at the inflow site ($r^2=0.79$) relative to the outflow site ($r^2=0.40$); these data indicated that there is greater uncertainty around the estimate of the outflow as compared to the inflow.

Figure 31. Rating curve for the pond outflow (Site J) based on discharge readings ($\text{m}^3 \text{s}^{-1}$) collected using a Marsh McBirney flow meter and stage readings (m) from a pressure transducer. Note the log scale on the y-axis. See Figure 14 for site locations.

Between July 2015 and June 2016, flow-actuated ISCO samples were collected on 8 occasions. Of these sampling dates/times, data from four storms were considered to be of high quality because they included samples from both the inflow and the outflow and

Figure 32. Hyetograph, inflow hydrograph and outflow hydrograph for September 2015 – February 2016. Hyetograph shows daily precipitation data from Charlottesville-Albemarle Airport as reported by the National Weather Service. Note that inflow and outflow hydrographs have different scales on the y-axis. Storms #1-4 are labeled in figures. Dots on hydrographs show points in time when samples were collected.

covered a significant portion of the stormflow. Examination of the hyetograph (Figure 32) indicates that these storms include 4 of the 6 largest rainfall events, as measured by total precipitation, between September 2015 and February 2016. The inflow hydrograph shows that these four storms include the two largest peak flows during this time (Figure 32). The outflow hydrograph shows that these four storms do not include the largest peak flow during this time, but do include 4 out of the 6 largest flows (Figure 32). Overall, storm 1 was the largest, followed by storm 4. Storm 2 and 3 were moderate storms. Streamflow during storm 4 included some rainfall, but, since a significant amount of snow was on the ground the day of the storm and temperatures were well above freezing (41 - 55°C), it is likely that streamflow also included some snowmelt (National Weather Service 2016, McCabe et al 2007).

As expected, the hydrograph from storm 1 (10/1/15 – 10/6/15) indicate that the inflow discharge peaked higher and sooner than the outflow discharge, but both display a similar pattern (Figure 33). In both the inflow and the outflow, NO_3^- concentrations went up during storm 1. Additionally, in the inflow, PN initially increased before declining, DON declined over time and NH_4^+ concentrations remained small. In the outflow, both PN and NH_4^+ concentrations remained low over time, while DON increased slightly before falling back to pre-storm levels. Instantaneous N flux data indicate that more N entered the pond than left it during storm 1.

During storm 2 (10/28/15 – 10/29/15), the inflow discharge peaked twice (both moderate relative to storm 1), while the outflow discharge did not display a clear peak but did increase relative to base flows (Figure 34). In the inflow, NO_3^- concentrations increased during storm 2, while DON declined. Again, PN showed an initial increase in

Figure 33. Concentration, discharge and N flux data from Storm 1 (10/1/15 – 10/6/15) from A) the pond's inflow (Site H), B) the pond's outflow (Site J) and C) N Flux from both. Note that y-axes are different between the graphs.

Figure 34. Concentration, discharge and N flux data from Storm 2 (10/28/15 – 10/29/15) from A) the pond's inflow (Site H), B) the pond's outflow (Site J) and C) N Flux from both. Note that y-axes are different between the graphs.

concentration before declining rapidly and NH_4^+ concentrations remained low. In the outflow, NO_3^- and DON concentrations were variable, but generally NO_3^- increased during the storm and DON decreased. Initially, PN was an important component of the outflow (about 0.5 mg N L^{-1}) but then declined to $0.001 \text{ mg N L}^{-1}$ over time. Ammonium concentrations remained small in the outflow during storm 2. Instantaneous N flux data indicate that more N entered the pond than left it during storm 2.

During storm 3 (11/19/15 – 11/20/15), inflow discharge peaked twice and the outflow discharge peaked once at a much lower rate; again exhibiting an expected pattern (Figure 35). Nitrate concentrations in the inflow increased during the storm, DON was relatively constant (except for a later peak), PN was variable but relatively more important earlier in the storm and NH_4^+ concentrations remained low throughout the storm. In the outflow, PN was initially important before declining, while NO_3^- increased during storm 3. By contrast, DON and NH_4^+ concentrations were relatively steady over time with the former being relatively more important. Instantaneous N flux data indicate that more N entered the pond than left it during storm 3.

Discharge peaks in storm 4 (2/3/16 – 2/4/16) were higher as compared with the other storms examined, and, as observed in all the storms, the inflow discharge exceeded the outflow discharge (Figure 36). N concentration data were not collected during peak flow, but coverage does include the falling limb of the hydrographs. N concentrations were relatively steady over time; NO_3^- was consistently the largest component of TN, while PN, DON and NH_4^+ were relatively less important. In the outflow, PN was initially important, but declined over time, while NO_3^- concentrations remained high. DON and NH_4^+ in the outflow were relatively constant over time, with DON being relatively more

Figure 35. Concentration, discharge and N flux data from Storm 3 (11/19/15 – 11/20/15) from A) the pond's inflow (Site H), B) the pond's outflow (Site J) and C) N Flux from both. Note that y-axes are different between the graphs.

Figure 36. Concentration, discharge and N flux data from Storm 4 (2/3/16 – 2/4/16) from A) the pond's inflow (Site H), B) the pond's outflow (Site J) and C) N Flux from both. Note that y-axes are different between the graphs.

important. Instantaneous N flux data indicate that more N entered the pond than left it during storm 4.

During storm events the pond retained water and N. Total inflows and outflows of water indicated that 500 – 10,000 m³ of water is stored (temporarily) in the pond (Table 14). N fluxes into the pond during storm events ranged from 4.1 – 49 kg N per storm, while N fluxes out of the pond during storm events ranged from 1.9 – 6.0 kg N. The pond was a sink of 2.2 – 40 kg of N per storm event.

Table 14. Magnitude of water (m³) and N (kg) fluxes per storm event. Note each storm duration was unique; see the date/time ranges given for each storm.

	Date/Time	Flux	Water (m ³)	N (kg)
Storm #1	10/2/15 21:00 – 10/6/15 14:00	Inflow	13000	49
		Outflow	3000	6.0
		Retained in Pond	10000	43
Storm #2	10/28/15 9:00 – 10/29/15 8:00	Inflow	2500	6.6
		Outflow	1100	1.9
		Retained in Pond	1400	4.7
Storm #3	11/19/15 5:00 – 11/20/15 2:00	Inflow	1500	4.1
		Outflow	970	1.9
		Retained in Pond	530	2.2
Storm #4	2/3/16 16:00 – 2/4/16 15:00	Inflow	1700	5.3
		Outflow	950	2.1
		Retained in Pond	750	3.2

4.4 Discussion

During the measured storm events at Timbercreek Farm, 1) inflow hydrographs peaked sooner and higher than outflow hydrographs, indicating short term (hours – days) storage of water in the pond, 2) NO₃⁻ concentrations increased during high flows, 3) PN was an important component of TN concentrations, especially early in storm hydrographs, and 4) DON and NH₄⁺ concentrations were relatively unaffected by storm events. During storms, the pond stored N, however the duration of this storage is unknown.

4.4.1 Discharge and flood routing

Inflow and outflow discharge indicate that the pond is storing water during storm events. As expected, outflow discharges peaked later and lower than inflow discharges (Figures 33 - 36). The farm pond was effectively controlling floodwaters by storing the water temporarily and then slowly releasing it into the outflow stream; indeed, this is one of the primary functions of many reservoirs (Smith et al. 2002). Over short time scales (mins to days), this means that the farm pond was gaining in volume, before losing volume later (hours to days). This expected pattern is most apparent in storm 1 (for which the longest time scale is included) (Figure 33). The temporary storage of water increases residence time (relative to a stream), which may allow additional time for biogeochemical processes to convert N to a long-term sink (denitrification to atmosphere) or a short-term sink (burial in sediment or uptake by primary producers).

4.4.2 N concentrations during storms

During all four storms, NO_3^- concentrations in the inflow increased during high flows (Figure 33 - 36). This suggests that storm water mobilizes N from the watershed and exports it to the stream within a short time-frame (minutes to hours). Shallow sub-surface flow can mobilize N stored in agricultural catchments and caused elevated NO_3^- concentrations (Buda and Dewalle 2009). Additionally, streamflow during storm events is most often “old water” (Bazemore et al. 1994), so elevated NO_3^- concentrations could indicate a rapid influx of groundwater that is enriched in NO_3^- (typical in an area with a long history of agriculture).

Nitrate concentrations in the outflows also increased during storms, but less so than for the inflows (Figure 33 - 36). Water stored in the pond from base flows before the storm may have diluted the NO_3^- rich water in the storm inflow resulting in a more dilute peak flow. Additionally, in-pond processes, such as uptake by primary producers, could be another reason that NO_3^- in the outflow is never quite as high as the NO_3^- concentrations in the inflow (also observed during base flows, Section 3.3.4). As noted above, the temporary storage of water in the pond allows time for these processes to occur.

During storm 1 and storm 2, PN is an important component of the pond's inflow (Figure 33 – 36). The mobilization of sediment from watersheds and/or streambanks during storm flows (Hirsch 2012), likely explains the pattern of greater concentrations initially, that decline later. Indeed, rainfall events play an important role in PN transport from catchments to streams and also within streams. Sediment that is mobilized in a stream during a storm, may settle out in a reservoir (Hirsch 2012). Therefore, the PN that enters the pond during storms may be stored there, however the exact time scale of this storage is unknown.

In contrast to the above data on inflows, PN was an important component of the pond's outflow during storm 3 and storm 4. In both cases, PN concentrations started high initially before declining rapidly (Figure 33 – 36). Therefore, high flows may initially flush PN out of the pond, while later lower flows, allow time for PN to settle out of the water column. It is notable that PN in the outflow is important during the storms that occur in late fall (November) and winter (February), but not in the mid fall (October). In storm 3 and storm 4, PN may have been mobilized because of seasonal changes (e.g., less

primary production, influx of fall leaf litter, higher base flows, etc.). Lastly, storm 4 was a rain event that occurred while snow was on the ground. Rain onto snow storm flow pathways may be different than typical storm flow pathways (McCabe et al. 2007) and could be responsible for the increased PN loading.

During all storms, DON and NH_4^+ concentrations were variable, and did not display a clear trend (Figure 33 -36). These data suggest that storm flows are not important components of total annual DON and NH_4^+ fluxes through streams. Instead, NH_4^+ is more likely to be controlled by water chemistry (i.e., pH) (Hargreaves et al. 1998). DON concentrations are likely more strongly controlled by seasonal patterns in primary producer uptake and subsequent decomposition (Chaffin 2016) than by storm flows.

TDN concentrations increased for the pond's inflow and outflow during all storm events (Figure 36 - 36). Other studies have found similar increases in magnitude in TDN in an agricultural watershed (3.5 mg N L^{-1} to 8.5 mg N L^{-1}) (Vanni et al.) and in forested watersheds (Buffam et al. 2001, Wondzell and Swanson 1996).

4.4.3 Relationship between discharge and TN concentration

When TN concentrations and discharges are plotted against each other for the inflow and outflow of storms 1-3, there is some evidence of hysteresis (Figure 37). During storm 1, the inflow was relatively high in TN initially, before declining later. This pattern highlights the importance of PN, which dominated TN early in the storm and then later decreased dramatically (Figure 33). During the same storm, the outflow displayed a pattern of lower TN concentrations in the rising limb of the hydrograph, relative to TN concentrations in the falling limb of the hydrograph. This suggest that N mobilization in

Figure 37. Total N concentrations vs discharge for storms 1 – 3 for the pond inflow and outflow. In cases where patterns were observed, arrows are added to show the direction of time. Note storm #4 was not included because samples were not collected on the rising limb of the hydrograph. Note that the y and x-axes have different scales.

the outflow was later in the storm; this is consistent with the discharge data which suggest that the pond is temporarily storing water and later releasing it to the outflow. This later water may be elevated in TN relative to the water stored in the pond before the storm; this would explain the pattern observed during storm 1.

4.4.4 Effect of storm events on pond N fluxes

N fluxes during storm events for both the inflow and outflow were greater than base flow N fluxes by 1-2 orders of magnitude (Figures 33 - 36, Section 3.3). These data highlight the importance of discharge in controlling N flux in surface waters. Data on N fluxes during storms indicate that more N is entering the pond during storms than leaves the pond during storms. This represents a sink of N, over short time scales. Farm ponds that act as sinks for N are effectively behaving as retention basins, an important storm water best management practice (Weiss et al. 2007).

However, these storm data do not include storms from spring or summer, when these N fluxes may be different. Nitrogen fluxes in springtime tend to be greater than fluxes during other times of the year (driven by high base flows) and therefore, storm flows in springtime may display a different pattern of N fluxes. Additionally, these storm data (in most cases) do not extend through the full duration of the stormflow; that is, samples were not collected for the full length of time required for the outflow to return to base flow. If these additional data had been collected, results may have been different. However, when N fluxes were calculated for an extended period of time after the storm (samples were collected for 8 days after storm 1), N fluxes into the pond continued to exceed N fluxes out of the pond.

4.5 Summary

Storms events play an important role in influencing N fluxes into and out of the Timbercreek Farm pond. Stream water fluxes during storms are 1-2 orders of magnitude greater than base flows. In the inflow waters, NO_3^- concentrations during high flows were greater than during base flows; suggesting rapid mobilization of NO_3^- from the watershed to the stream. PN was an important component of TN concentrations into the pond during storm events, especially in the inflow. During high flows and over short time scales, the pond is a sink for N. Sedimentation of PN, temporary storage of water in the pond and NO_3^- uptake by primary producers in the pond are three processes that likely account for the N sink during storms.

5. Synthesis

Modern agriculture presents a challenge: how can N be used to maximize food production, while minimizing losses to the atmosphere and hydrosphere? Alternative agricultural practices, such as pasture-based livestock, are often suggested as a potential strategy for reducing negative environmental impacts; but that suggestion is made with little understanding of N fluxes on alternative livestock farms. This thesis quantifies the N fluxes on one alternative livestock farm and evaluates the potential for the practices used on that farm to reduce N losses to the environment. Particular focus is given to the role of the pond in influencing N fluxes in the surface water. These results are then interpreted within the broader framework of N fluxes on the farm as conceptualized in the nested model presented in the introduction (Figure 1). The overall model includes annual N fluxes into and out of the farm, and both annual and short term (days to weeks) N fluxes in the surface waters. Specifically, the objectives of this thesis were:

- 1) Calculate a farm N budget for 2014 and 2015
 - a. Quantify the farm product inputs and outputs of N
 - b. Quantify the farm stream inflows and outflows of N
- 2) Calculate an annual N budget for the farm pond
- 3) Determine the effect of storm events on the pond N fluxes

5.1 Nested model of N fluxes

The results presented in Sections 2 – 4 represent N fluxes into, within and out of Timbercreek Farm. When calculated on an annual basis, these data give a snapshot of the movement of N on an alternative livestock farm (Figure 38, Figure 39). Including all

Figure 38. Nested model with N fluxes into, out of and within Timbercreek Farm. Most fluxes are shown on an annual timescale (kg N year⁻¹), but storm N flux data are over short timescales (mg N s⁻¹). Note that farm stream inflows and outflows are based on DIN concentrations only. N budget data are averaged over the four years of data collected (2012 – 2015). Farm inflow and outflow stream N data are from 2013 – 2016 Pond inflow and outflow stream N data are from 2015 – 2016.

Figure 39. Nested model with N fluxes into, out of and within Timbercreek Farm on a per ha basis. Most fluxes are shown on an annual timescale ($\text{kg N ha}^{-1} \text{ year}^{-1}$), but storm N flux data are over short timescales ($\text{mg N ha}^{-1} \text{ s}^{-1}$). Note that farm stream inflows and outflows are based on DIN concentrations only. N budget data are averaged over the four years of data collected (2012 – 2015). Farm inflow and outflow stream N data are from 2013 – 2016 Pond inflow and outflow stream N data are from 2015 – 2016. Catchment areas are in Table 4 and Table 9. The farm inputs and outputs are over the farm's area (165 ha – Figure 3).

quantified N fluxes, influxes are dominated by N imported for livestock production, most notably feed (57% of total N inputs) which is an order of magnitude greater than any other input. Other farm-specific inputs, like hay, pasture BNF, livestock and bedding, combine to account for another 22% of inputs. However, unintended N inputs, including N deposition and N in stream inflows into the farm, are also important and together make up 22% of inputs.

Important N fluxes out of the farm include the products of livestock production, including meat and animal products (33% of outputs) and by-products (12% of outputs) (Figure 38). The sale of livestock to auction also represents an important N output (9%). As noted previously, the magnitude of stream inputs to and outputs from the farm are similar (950 ± 110 kg N year⁻¹ for inflows and $1,100 \pm 120$ kg N year⁻¹ for outflows), but, since total outputs are less than inputs, stream outputs make up a greater percentage of the total outputs (46%).

The farm pond is a sink of N over annual time scales, but this sink (100 ± 60 kg N) is small relative to the fluxes into and out of the farm (Figure 38). During storms, much more N entered the pond than left the pond (difference of 3 – 40 kg N per storm), suggesting that the pond was a larger sink of N during storm flows than during base flows (Figure 38). The nested model shows that inflow and outflows of N *via* surface waters represent important fluxes within the context of an alternative livestock farm, especially during storm events.

5.2 Farm N budget

The majority (70-85%) of N intentionally brought onto the farm does not end up in a product; this analysis assumes that the balance of N is lost to the environment (e.g., stored in soil, denitrified, etc.). The whole farm NUE (14 – 28%) is similar to NUE estimates from conventional farms (20 – 30% for beef and 30 – 60% for pig/poultry) (Section 2.4.1). Therefore, this analysis estimates that permaculture livestock farming is similarly inefficient as compared to conventional livestock farming. This excess N is stored on site or lost to the environment. The N loss pathways were not directly quantified, but may include denitrification to the atmosphere (e.g., N_2 , N_2O), leaching to groundwater (e.g., NO_3^-) and/or volatilization (e.g., NH_3).

On an annual basis, N fluxes into the farm *via* stream water ($950 \pm 110 \text{ kg N year}^{-1}$) are comparable to N fluxes out of the farm *via* stream water ($1100 \pm 120 \text{ kg N year}^{-1}$) (Figure 38). Therefore, N export from the farm *via* streams is not a significant N loss pathway. Annual N loads in the streams flowing out of Timbercreek Farm ($5.0 \pm 1.3 \text{ kg N ha}^{-1} \text{ year}^{-1}$) are less than those typically found on conventional farms (50 – 200 $\text{kg N ha}^{-1} \text{ year}^{-1}$, Section 2.4.2). Therefore, N export *via* streams is not a significant N losses pathway for this permaculture farm.

5.3 Pond N budget

Over the course of a year, the pond is a sink for N (Figure 38, Figure 39). However, relative to the balance of the farm N budget (Section 2.4), this sink is small (1 – 2 % of N surplus). The nested model suggests that N transformations in the pond (denitrification to the atmosphere and/or burial in sediment) are too small to account for

the large N losses from the farm. Farm ponds can effectively remove N in stream water, however, regular pond maintenance is necessary to maximize their potential to store N and/or convert N_r to a non-reactive form. Additionally, agricultural stream-pond networks are sensitive to changes in land use and management (Powers et al. 2015) so the importance of the pond may change as Timbercreek Farm expands their on-site production.

5.4 Potential N loss pathways not quantified

The farm has a surplus of N, but that the majority of this excess N is not being exported *via* streams, and only a small amount is being denitrified or stored in the farm pond. This begs the questions; what is happening to the rest of the excess N? Taken together, data on the farm N budget and the pond N budget suggest that onsite biogeochemical processes are storing N (e.g., in the soils, uptake by primary producers) and/or transferring N (e.g., volatilization of NH_3 to the atmosphere). These processes prevent the majority of the excess N from being transported to the farm's surface waters and therefore, prevent it from being exported from the farm *via* the streams. However, if this N surplus builds up over time it could start to 'leak' into groundwater and/or surface waters.

Additional research is needed to further quantify these fluxes and their relative importance at Timbercreek Farm. Specifically, future work could include 1) ongoing analysis of the farm N budget and stream water fluxes 2) quantification of pasture N fluxes, 3) estimates of spatial and temporal patterns in N in the soil and 4) estimates of N volatilization from manure.

5.5. *N losses per unit land vs. per unit product*

N losses per unit land from alternative agricultural farms may be lower than conventional farms (Cambardella et al. 2015, Kramer et al. 2006, Hansen et al. 2000). For conventional livestock farms, N surplus estimates are typically on the order of 100 – 300 kg N ha⁻¹ year⁻¹ (Leach 2014, Dalgaard et al. 1998). For alternative livestock farms (including organic), N surplus estimates are typically on the order 50 – 200 kg N ha⁻¹ year⁻¹ (Leach 2014, Dalgaard et al. 1998). But alternative farms typically generate less product per unit land (Seufert et al. 2014) than conventional operations, and, therefore, N losses expressed on a per unit of product basis may be comparable (Cattell Noll et al. 2016).

N inputs and outputs per ha from Timbercreek Farm are less than those found in conventional farms, but N surplus per ha estimates are also less (28 – 35 kg N ha⁻¹ year⁻¹) (Table 3). The N budgets suggests that there are N losses from Timbercreek Farm, but that they are spread over a large enough area to prevent N export *via* streams. Therefore, the Timbercreek Farm system can be described as low efficiency and low intensity. Additionally, the location of N losses (pastures) relative to the streams and forest may impact the potential for N transport from the land to the streams (Creed and Band 1998). Soil characteristics also help to determine N leaching to groundwater (which flows to streams) and may therefore mitigate nutrient export from pastures (Heckrath et al. 1995, Steinheimer et al. 1998).

Current Timbercreek Farm practices and resulting N losses are spread across a large enough area that there is little to no impact on N concentrations in stream water.

Increasing production has the potential to pass some unknown threshold, above which a farm would start to add N to the stream water. Therefore, in pasture-based livestock systems, increases in production per unit land (i.e., larger stocking rates) should be carefully considered and such changes should be implemented incrementally and in concert with a stream-monitoring program.

5.6 Conclusions

Nitrogen use should maximize food production while minimizing losses. Little is known about N fluxes on alternative livestock farms, like Timbercreek Farm, but some of their practices (e.g., pasture-based livestock) are suggested as potential ways of reducing N losses to the environment. A nested model of Nr fluxes at Timbercreek Farm suggests that 1) the farm is as N inefficient as conventional production, 2) current practices contribute little N to surface waters, 3) the pond is a sink for N, but relative to these other fluxes this sink is small and 4) storm events are an important component of N fluxes on the farm. Further research is needed to quantify the fate of excess N on the farm.

Timbercreek Farm NUEs are similar to conventional farm efficiencies, but, as a low intensity system, spread these losses over a larger area. On-site biogeochemical processes store and/or transform surplus N and prevent it from being exported in the streams. Relative to conventional agriculture, alternative livestock practices, such as those at Timbercreek Farm, have the potential to reduce negative environmental impacts on the farm scale, but are not likely to address the larger issue of inefficient resource use.

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APPENDIX A

Temporal and spatial variability of Timbercreek Farm pond water chemistry.

Table A1. YSI Sonde (600SM) readings from quarterly analysis. Over four sampling dates, data was collected at 12 sites in the pond (Figure 14) every 0.5 m depth. Dashes indicated missing data.

Date	Site	Depth	Temperature (C°)	Dissolved Oxygen (%)	pH
8/13/15	1	0	31	70	5.3
8/13/15	2	0	28	35	5.9
8/13/15	3	0	28	38	6.2
8/13/15	3	1	24	32	6.3
8/13/15	4	0	26	37	6.6
8/13/15	4	1	24	25	6.5
8/13/15	5	0	29	46	6.7
8/13/15	5	1	24	37	6.6
8/13/15	5	2	23	10	6.0
8/13/15	6	0	30	50	6.4
8/13/15	6	1	24	34	6.3
8/13/15	7	0	31	52	7.5
8/13/15	8	0	30	38	7.2
8/13/15	9	0	30	36	7.2
8/13/15	10	0	29	41	6.9
8/13/15	10	1	24	32	6.8
8/13/15	11	0	29	35	7.3
8/13/15	11	1	24	26	7.0
8/13/15	11	2	23	10	6.6
8/13/15	12	0	30	39	7.8
8/13/15	12	1	24	2	7.0
11/17/15	1	0	10	-	6.2
11/17/15	2	0	10	-	6.4
11/17/15	3	0	10	-	6.5
11/17/15	3	0.5	10	-	6.5
11/17/15	3	1	10	-	6.6
11/17/15	4	0	10	-	6.6
11/17/15	4	0.5	10	-	6.6
11/17/15	4	1	10	-	6.6
11/17/15	4	1.5	10	-	6.6
11/17/15	5	0	10	-	6.7
11/17/15	5	0.5	10	-	6.7
11/17/15	5	1	10	-	6.7
11/17/15	5	1.5	10	-	6.7
11/17/15	5	2	10	-	6.6
11/17/15	6	0	10	-	6.7
11/17/15	6	0.5	10	-	6.7
11/17/15	6	1	10	-	6.7
11/17/15	6	1.5	10	-	6.7

11/17/15	6	2	10	-	6.5
11/17/15	7	0	11	-	6.8
11/17/15	8	0	12	-	6.4
11/17/15	9	0	11	-	6.6
11/17/15	9	0.5	11	-	6.5
11/17/15	10	0	10	-	6.7
11/17/15	10	0.5	10	-	6.7
11/17/15	10	1	10	-	6.7
11/17/15	10	1.5	10	-	6.7
11/17/15	11	0	10	-	6.8
11/17/15	11	0.5	10	-	6.7
11/17/15	11	1	10	-	6.7
11/17/15	11	1.5	10	-	6.7
11/17/15	11	2	10	-	6.7
11/17/15	12	0	10	-	6.8
11/17/15	12	0.5	10	-	6.8
11/17/15	12	1	10	-	6.7
11/17/15	12	1.5	10	-	6.7
12/22/15	1	0	8.3	77	6.4
12/22/15	2	0	8.3	83	6.6
12/22/15	3	0	8.3	88	6.5
12/22/15	3	0.5	7.4	82	6.5
12/22/15	3	1	7.3	77	6.5
12/22/15	4	0	8.5	82	6.6
12/22/15	4	0.5	7.3	78	6.4
12/22/15	4	1	7.0	75	6.4
12/22/15	4	1.5	7.0	74	6.4
12/22/15	5	0	7.9	84	6.6
12/22/15	5	0.5	7.3	78	6.4
12/22/15	5	1	7.0	77	6.4
12/22/15	5	1.5	6.8	72	6.4
12/22/15	6	0	7.8	89	6.6
12/22/15	6	0.5	7.4	80	6.5
12/22/15	6	1	7.0	76	6.4
12/22/15	6	1.5	6.7	69	6.4
12/22/15	7	0	7.7	88	6.6
12/22/15	8	0	9.1	86	6.6
12/22/15	9	0	8.6	86	6.6
12/22/15	9	0.5	7.5	83	6.6
12/22/15	10	0	7.9	86	6.6
12/22/15	10	0.5	7.2	82	6.6
12/22/15	10	1	7.0	76	6.5
12/22/15	10	1.5	6.8	71	6.4
12/22/15	11	0	8.0	88	6.6
12/22/15	11	0.5	7.3	81	6.5
12/22/15	11	1	6.9	75	6.4
12/22/15	11	1.5	6.7	72	6.4
12/22/15	11	2	6.7	63	6.4
12/22/15	12	0	8.0	87	6.6

12/22/15	12	0.5	7.3	78	6.5
12/22/15	12	1	6.9	70	6.4
4/11/16	2	0	18	111	6.5
4/11/16	3	0	15	100	6.6
4/11/16	3	0.5	15	99	6.5
4/11/16	4	0	15	99	6.7
4/11/16	4	0.5	14	97	6.8
4/11/16	4	1	11	84	6.5
4/11/16	5	0	14	98	6.8
4/11/16	5	0.5	13	94	6.7
4/11/16	5	1	11	94	6.7
4/11/16	5	1.5	11	82	6.6
4/11/16	6	0	14	98	6.7
4/11/16	6	0.5	13	94	6.6
4/11/16	9	0	18	103	6.6
4/11/16	10	0	15	100	6.7
4/11/16	10	0.5	15	100	6.7
4/11/16	10	1	14	91	6.7
4/11/16	11	0	15	100	6.7
4/11/16	11	0.5	14	99	6.7
4/11/16	11	1	12	89	6.7
4/11/16	11	1.5	10	76	6.4
4/11/16	12	0	14	99	6.8

Table A2. Nitrogen concentrations (mg N L^{-1}) in pond water samples collected on four dates between Fall 2015 and Summer 2016. Samples were collect, processed and analyzed as described in Section 3.2.1. Site locations are shown in Figure 14.

Date	Site	Depth (m)	NO3 (mg N L^{-1})	NH4 (mg N L^{-1})	DON (mg N L^{-1})	TDN (mg N L^{-1})
10/12/15	1	0	1.22	0.29	0.41	1.91
10/12/15	2	0	1.25	0.33	0.16	1.75
10/12/15	2	0.5	1.23	0.15	0.27	1.66
10/12/15	3	0	1.18	0.19	0.36	1.72
10/12/15	3	0.5	1.20	0.17	0.33	1.70
10/12/15	3	1	1.22	0.23	0.32	1.77
10/12/15	4	0	1.24	0.18	0.30	1.73
10/12/15	4	0.5	1.28	0.15	0.24	1.67
10/12/15	4	1	1.24	0.19	0.24	1.67
10/12/15	4	1.5	1.29	0.18	0.16	1.62
10/12/15	5	0	1.25	0.18	0.21	1.65
10/12/15	5	0.5	1.26	0.14	0.24	1.64
10/12/15	5	1	1.11	0.25	0.43	1.79
10/12/15	5	1.5	1.32	0.18	0.06	1.56
10/12/15	6	0	1.20	0.19	0.35	1.75
10/12/15	6	1	1.24	0.25	0.34	1.83
10/12/15	6	2	1.19	0.21	0.34	1.74
10/12/15	7	0	1.24	0.18	0.30	1.72
10/12/15	7	0.5	1.19	0.18	0.27	1.65
10/12/15	8	0	1.25	0.20	0.26	1.72
10/12/15	9	0	1.25	0.20	0.18	1.64
10/12/15	9	0.5	1.25	0.27	0.23	1.76
10/12/15	10	0	1.28	0.17	0.20	1.65
10/12/15	10	0.5	1.25	0.22	0.22	1.69
10/12/15	10	1	1.25	0.20	0.14	1.59
10/12/15	10	1.5	1.24	0.19	0.07	1.50
10/12/15	11	0	1.23	0.13	0.20	1.56
10/12/15	11	1	1.23	0.17	0.36	1.77
10/12/15	11	2	1.26	0.18	0.30	1.74
10/12/15	12	0	1.23	0.23	0.25	1.71
10/12/15	12	0.5	1.19	0.14	0.28	1.61
10/12/15	12	1	1.23	0.22	0.25	1.71
10/12/15	12	1.5	1.24	0.25	0.20	1.69
2/22/16	3	0	1.60	0.13	0.11	1.84

2/22/16	3	0.5	1.54	0.16	0.19	1.89
2/22/16	4	0	1.59	0.14	0.09	1.82
2/22/16	4	1.5	1.34	0.31	0.07	1.72
2/22/16	5	0	1.59	0.12	0.15	1.86
2/22/16	6	0	1.60	0.09	0.19	1.88
2/22/16	8	0	1.80	0.00	0.20	1.99
2/22/16	9	0	1.68	0.07	0.01	1.76
2/22/16	9	0.5	1.55	0.17	0.08	1.79
2/22/16	10	0	1.58	0.13	0.07	1.78
2/22/16	10	0.5	1.57	0.14	0.17	1.88
2/22/16	11	1	1.60	0.20	0.24	2.05
2/22/16	12	0.5	1.57	0.16	0.16	1.89
2/22/16	12	1	1.57	0.16	0.22	1.95
2/22/16	12	1.5	1.57	0.19	0.12	1.89
4/25/16	2	0	1.98	0.24	-0.64	1.58
4/25/16	3	0	0.88	0.03	-1.13	-0.22
4/25/16	3	0.5	2.39	0.02	0.09	2.50
4/25/16	4	0	0.88	0.03	-1.33	-0.43
4/25/16	4	0.5	1.88	0.03	0.04	1.95
4/25/16	4	1	0.80	0.05	-0.91	-0.07
4/25/16	5	0	0.87	0.03	0.14	1.04
4/25/16	5	0.5	1.37	0.02	0.00	1.39
4/25/16	5	1	1.11	0.02	-0.43	0.70
4/25/16	6	0	1.08	0.01	-0.18	0.90
4/25/16	9	0	1.94	0.08	-0.01	2.01
4/25/16	10	0	0.87	0.02	-1.11	-0.22
4/25/16	10	0.5	0.86	0.02	0.07	0.95
4/25/16	10	1	0.58	0.06	0.12	0.76
4/25/16	11	0	0.83	0.02	0.38	1.23
4/25/16	11	0.5	0.84	0.02	0.13	0.99
4/25/16	11	1	0.86	0.03	0.16	1.05
4/25/16	11	1.5	0.67	0.13	0.07	0.87
4/25/16	12	0	0.80	0.02	0.16	0.97
6/1/16	1	0	0.43	0.07	0.34	0.84
6/1/16	2	0	0.43	0.08	0.31	0.82
6/1/16	2	0.5	0.38	0.08	0.30	0.76
6/1/16	3	0	0.43	0.01	0.35	0.79
6/1/16	3	0.5	0.50	0.01	0.28	0.79
6/1/16	3	1	0.82	0.06	0.18	1.06

6/1/16	4	0	0.82	0.01	-0.09	0.75
6/1/16	4	0.5	0.79	0.03	0.11	0.93
6/1/16	4	1	0.66	0.02	0.29	0.97
6/1/16	4	1.5	0.60	0.11	0.24	0.94
6/1/16	5	0	0.48	0.02	0.35	0.85
6/1/16	5	0.5	0.52	0.02	0.27	0.81
6/1/16	5	1	0.79	0.03	0.29	1.12
6/1/16	5	1.5	0.08	0.45	0.45	0.97
6/1/16	5	2	0.06	0.41	0.36	0.83
6/1/16	6	0	0.49	0.02	0.32	0.83
6/1/16	6	0	0.47	0.04	0.30	0.81
6/1/16	6	1	0.52	0.03	0.29	0.84
6/1/16	7	0	0.48	0.02	0.28	0.78
6/1/16	8	0	0.42	0.07	0.29	0.77
6/1/16	9	0	0.49	0.02	0.32	0.82
6/1/16	9	0.5	0.48	0.03	0.28	0.79
6/1/16	10	0	0.49	0.02	0.28	0.79
6/1/16	10	0.5	0.51	0.04	0.27	0.82
6/1/16	10	1	0.69	0.02	0.26	0.97
6/1/16	10	1.5	0.36	0.28	0.35	0.99
6/1/16	11	0	0.53	0.02	0.26	0.81
6/1/16	11	0.5	1.11	0.02	-0.28	0.85
6/1/16	11	1	0.78	0.01	0.29	1.09
6/1/16	11	1.5	0.60	0.03	0.24	0.87
6/1/16	11	2	0.15	0.35	0.32	0.82
6/1/16	12	0	0.52	0.02	0.26	0.80
6/1/16	12	0.5	1.32	0.03	-0.51	0.83
6/1/16	12	1	0.67	0.03	0.10	0.80
6/1/16	12	1.5	0.40	0.06	0.30	0.76

APPENDIX B

Discharge, N species and DIN flux data by site and date for Timbercreek Farm inflows and outflows.

Table B1. Discharge measurements ($\text{m}^3 \text{s}^{-1}$) for Timbercreek Farm inflows (Site A, D and E) and outflows (Site F and G). See Figure 7 for site locations. Dashes indicate missing data.

	Site A	Site D	Site E	Site F	Site G
6/26/13	0.003	0.009	0.008	0.018	0.013
7/10/13	0.008	0.006	0.007	0.010	0.008
7/16/13	0.006	0.008	0.011	0.021	0.011
7/24/13	0.004	0.014	-	-	0.013
8/8/13	0.002	0.009	0.004	0.018	0.018
8/14/13	0.004	0.003	0.009	0.008	0.011
8/21/13	0.005	0.006	0.009	0.017	0.016
9/3/13	0.007	0.004	0.015	0.022	0.022
9/10/13	0.007	0.007	0.013	0.016	0.013
9/24/13	0.005	0.006	0.007	0.016	0.015
10/1/13	0.012	0.004	0.008	0.010	0.005
10/8/13	0.005	0.008	0.010	0.014	0.011
10/22/13	0.007	0.025	0.010	0.034	0.025
11/5/13	0.002	0.021	0.015	0.021	0.017
2/7/14	0.019	0.013	0.019	0.040	0.023
3/21/14	0.008	0.019	0.013	0.052	0.032
4/25/14	0.007	0.008	0.013	0.028	0.028
6/17/14	0.014	0.008	-	0.032	0.058
7/1/14	0.006	0.011	0.027	0.013	0.031
7/25/14	0.006	0.008	0.019	0.016	0.017
8/7/14	0.003	0.005	0.006	0.015	0.026
8/20/14	0.014	0.005	0.009	0.007	0.035
9/4/14	0.023	0.009	-	0.013	0.023
9/16/14	0.036	0.005	-	0.027	0.051
9/30/14	0.025	0.004	-	0.032	0.062
10/21/14	0.024	0.018	-	0.022	-
11/4/14	0.015	0.016	-	0.018	0.043
11/25/14	0.008	0.015	0.037	0.016	0.080
12/9/14	0.011	0.020	0.022	0.073	0.034
12/22/14	0.044	0.008	0.011	0.034	0.034
1/19/15	0.009	0.023	0.016	0.032	0.065

2/2/15	0.007	0.017	0.018	0.021	0.047
3/2/15	0.012	0.013	0.030	0.029	0.038
3/16/15	0.015	0.020	0.026	0.035	0.057
3/31/15	0.006	0.016	0.020	0.016	0.046
4/13/15	0.027	0.012	0.020	0.026	0.054
4/27/15	0.025	0.018	0.017	0.031	0.091
5/12/15	0.009	0.006	0.013	0.019	0.023
5/28/15	0.005	0.004	0.009	0.012	0.026
6/2/15	0.007	0.008	0.055	0.022	0.025
6/9/15	0.007	0.009	0.014	0.015	0.017
6/16/15	0.011	0.014	0.011	0.013	0.028
6/23/15	0.005	0.006	0.010	0.016	0.016
6/30/15	0.004	0.006	0.010	0.013	0.025
7/14/15	0.004	0.002	0.006	0.011	0.015
7/21/15	0.008	0.007	0.006	0.007	0.010
7/28/15	0.003	0.003	0.009	0.008	0.006
8/4/15	0.007	0.006	0.005	0.009	0.017
8/11/15	0.003	0.006	0.009	0.008	0.012
8/18/15	0.003	0.003	0.004	0.002	0.007
8/31/15	0.001	0.003	0.003	0.002	0.011
9/14/15	0.005	0.003	0.004	0.006	0.007
9/28/15	0.003	0.004	0.007	0.005	0.010
10/19/15	0.008	0.008	0.021	0.013	0.027
10/26/15	0.007	0.009	0.018	0.014	0.016
11/9/15	0.016	0.019	-	0.024	0.034
11/23/15	0.011	0.009	0.051	0.018	0.028
12/7/15	0.010	0.004	-	0.017	0.030
12/22/15	0.013	0.006	0.017	0.026	0.035
1/13/16	0.002	0.005	0.002	0.023	0.037
2/22/16	0.011	0.005	0.015	0.023	0.056
3/9/16	0.004	0.012	0.008	0.008	0.016
3/21/16	0.002	0.004	0.010	0.014	0.017
4/4/16	0.003	0.003	0.013	0.012	0.024
4/18/16	0.002	0.008	0.008	0.009	0.016
5/23/16	0.008	0.012	0.030	0.034	0.028
6/13/16	0.003	0.005	0.006	0.016	0.012
7/1/16	0.002	0.002	0.006	0.009	0.012

Table B2. Nitrate concentrations (mg N L⁻¹) for Timbercreek Farm inflows (Site A, D and E) and outflows (Site F and G). See Figure 7 for site locations. Dashes indicate missing data.

	Site A	Site D	Site E	Site F	Site G
6/26/13	0.49	0.26	0.18	0.10	0.21
7/10/13	0.52	0.40	0.16	0.15	0.26
7/24/13	1.72	1.22	0.30	0.37	0.96
8/8/13	1.62	1.06	0.32	0.33	0.84
8/14/13	1.60	0.98	0.31	0.31	0.82
8/21/13	1.66	0.94	0.26	0.31	0.78
9/3/13	1.60	1.08	0.35	0.38	0.90
9/10/13	1.45	0.92	0.37	0.34	0.79
9/24/13	1.60	0.97	0.30	0.31	0.77
10/1/13	1.58	0.95	0.37	0.22	0.85
10/8/13	1.44	0.78	0.24	0.14	0.51
10/22/13	1.60	0.72	0.32	0.23	0.94
11/5/13	1.57	0.96	0.28	0.23	0.77
1/27/14	1.67	1.74	0.60	0.48	1.56
2/7/14	2.42	1.55	0.55	0.50	1.58
3/21/14	2.45	2.27	0.43	0.36	1.96
4/25/14	2.39	0.63	0.31	0.28	1.14
6/17/14	1.79	0.93	-	0.35	0.85
7/1/14	1.75	0.94	0.37	0.33	0.83
7/25/14	1.86	0.61	0.36	0.34	0.60
8/7/14	1.53	0.60	0.32	0.31	0.60
8/20/14	1.86	0.59	0.39	0.32	0.60
9/4/14	1.84	0.59	-	0.16	0.57
9/16/14	1.89	0.61	-	0.11	0.59
9/30/14	1.87	0.61	-	0.06	0.58
10/21/14	1.86	0.59	-	0.04	0.57
11/4/14	1.79	0.60	-	0.03	0.57
11/25/14	1.96	1.00	0.22	0.21	0.93
12/9/14	2.25	1.07	0.26	0.25	-
12/22/14	2.00	1.23	0.29	0.30	1.15
1/19/15	2.07	1.26	0.31	0.31	1.27
2/2/15	2.01	1.24	0.30	0.29	1.28
3/2/15	2.03	1.23	0.30	0.30	1.24
3/16/15	2.02	1.13	0.52	0.46	1.31

3/31/15	2.18	1.15	0.38	0.33	1.28
4/13/15	1.73	0.62	0.21	0.15	0.89
4/27/15	1.92	1.03	0.28	0.27	1.00
5/12/15	1.86	0.59	0.22	0.25	0.98
5/28/15	1.86	0.58	0.05	0.16	0.62
6/2/15	1.88	0.58	0.02	0.08	0.55
6/9/15	1.87	0.58	0.05	0.18	0.62
6/16/15	1.77	0.57	0.05	0.19	0.89
6/23/15	1.87	0.53	0.04	0.17	0.56
6/30/15	2.71	0.52	0.04	0.00	0.55
7/14/15	1.83	0.53	0.04	0.15	0.58
7/21/15	1.77	0.50	0.04	0.16	0.57
7/28/15	1.71	0.48	0.04	0.15	0.59
8/4/15	1.79	0.50	0.04	0.17	0.52
8/11/15	1.30	0.47	0.03	0.13	0.51
8/18/15	1.50	0.57	0.05	0.12	-
8/31/15	2.22	0.22	0.04	0.12	0.51
9/14/15	2.39	0.46	0.04	-	0.50
9/28/15	1.47	0.48	0.04	0.03	0.53
10/19/15	1.85	0.55	0.07	0.14	0.94
10/26/15	1.76	0.78	0.01	0.10	0.93
11/9/15	1.81	0.78	-	0.27	0.91
11/23/15	1.86	0.90	0.36	0.35	0.97
12/7/15	1.94	0.94	-	0.46	1.11
12/22/15	1.86	0.85	0.46	0.43	1.07
1/13/16	1.93	0.98	0.60	0.54	1.19
2/22/16	2.12	-	0.80	0.67	1.31
3/9/16	1.97	0.97	0.60	0.47	1.31
3/21/16	2.15	0.99	0.64	0.27	1.12
4/4/16	1.81	0.95	0.27	0.15	1.06
4/18/16	1.83	0.82	0.17	0.16	0.96
5/23/16	1.81	0.69	0.21	0.26	0.66
6/13/16	1.82	0.76	0.04	0.22	0.85
7/1/16	1.70	0.71	0.12	0.26	0.78

Table B3. Ammonium concentrations (mg N L⁻¹) for Timbercreek Farm inflows (Site A, D and E) and outflows (Site F and G). See Figure 7 for site locations. Dashes indicate missing data.

	Site A	Site D	Site E	Site F	Site G
6/26/13	0.011	0.157	0.045	0.010	0.012
7/10/13	0.016	0.111	0.039	0.014	0.013
7/24/13	0.000	0.172	0.050	0.001	0.009
8/8/13	0.003	0.013	0.004	0.002	0.009
8/14/13	0.011	0.004	0.030	0.002	0.006
8/21/13	0.004	0.008	0.025	0.000	0.004
9/3/13	0.006	0.151	0.034	0.009	0.029
9/10/13	0.000	0.001	0.011	0.000	0.005
9/24/13	0.015	0.011	0.035	0.010	0.018
10/1/13	0.002	0.006	0.015	0.000	0.000
10/8/13	0.002	0.002	0.020	0.001	0.009
10/22/13	0.002	0.006	0.022	0.003	0.002
11/5/13	0.005	0.005	0.012	0.004	0.005
1/27/14	0.000	0.001	0.008	0.002	0.005
2/7/14	0.003	0.022	0.004	0.008	0.012
3/21/14	0.016	0.000	0.014	0.001	0.015
4/25/14	0.017	0.013	0.019	0.000	0.010
6/17/14	0.015	0.007	-	0.008	0.016
7/1/14	0.014	0.013	0.023	0.012	0.018
7/25/14	0.000	0.002	0.004	0.002	0.005
8/7/14	0.005	0.007	0.002	0.012	0.000
8/20/14	0.002	0.000	0.012	0.005	0.010
9/4/14	0.020	0.005	-	0.004	0.007
9/16/14	0.008	0.013	-	0.008	0.009
9/30/14	0.007	0.008	-	0.009	0.009
10/21/14	0.000	0.000	-	0.000	0.000
11/4/14	0.000	0.000	-	0.000	0.000
11/25/14	0.016	0.005	0.031	0.004	0.007
12/9/14	0.006	0.005	0.013	0.021	0.015
12/22/14	0.002	0.001	0.014	0.008	0.040
1/19/15	0.000	0.000	0.000	0.000	0.000
2/2/15	0.000	0.000	0.000	0.000	0.000
3/2/15	0.006	0.004	0.004	0.029	0.009
3/16/15	0.004	0.002	0.010	0.003	0.006

3/31/15	0.005	0.001	0.012	0.000	0.022
4/13/15	0.010	0.000	0.015	0.000	0.001
4/27/15	0.002	0.000	0.058	0.002	0.004
5/12/15	0.018	0.002	0.053	0.010	0.010
5/28/15	0.020	0.010	0.018	0.021	0.024
6/2/15	0.015	0.007	0.014	0.005	0.017
6/9/15	0.005	0.002	0.028	0.026	0.020
6/16/15	0.021	0.014	0.024	0.029	0.027
6/23/15	0.012	0.003	0.046	0.009	0.009
6/30/15	0.002	0.019	0.010	0.002	0.020
7/14/15	0.000	0.000	0.003	0.000	0.000
7/21/15	0.000	0.000	0.001	0.000	0.000
7/28/15	0.000	0.000	0.005	0.000	0.000
8/4/15	0.000	0.000	0.018	0.000	0.000
8/11/15	0.00	0.00	0.01	0.00	0.00
8/18/15	0.000	0.000	0.000	0.000	0.000
8/31/15	0.005	0.008	0.004	0.005	0.001
9/14/15	0.001	0.009	0.016	-	0.022
9/28/15	0.005	0.006	0.018	0.032	0.033
10/19/15	0.006	0.006	0.086	0.025	0.011
10/26/15	0.004	0.004	0.061	0.004	0.001
11/9/15	0.000	0.003	-	0.020	0.020
11/23/15	0.000	0.000	0.005	0.000	0.000
12/7/15	0.000	0.000	-	0.000	0.000
12/22/15	0.000	0.000	0.000	0.000	0.000
1/13/16	0.000	0.000	0.000	0.000	0.005
2/22/16	0.000	-	0.000	0.012	0.031
3/9/16	0.002	0.000	0.016	0.000	0.035
3/21/16	0.016	0.000	0.079	0.000	0.043
4/4/16	0.000	0.010	0.012	0.009	0.018
4/18/16	0.001	0.000	0.006	0.027	0.011
5/23/16	0.026	0.001	0.068	0.034	0.014
6/13/16	0.010	0.012	0.038	0.026	0.020
7/1/16	0.015	0.008	0.070	0.039	0.022

Table B4. Dissolved inorganic nitrogen flux (mg N s^{-1}) for Timbercreek Farm inflows (Site A, D and E) and outflows (Site F and G). See Figure 7 for site locations. Dashes indicate missing data.

	Site A	Site D	Site E	Site F	Site G
6/26/13	1.62	3.92	1.82	2.01	2.92
7/10/13	4.17	2.99	1.33	1.54	2.26
7/24/13	7.03	19.20	0.00	0.00	12.59
8/8/13	3.86	9.73	1.38	5.98	14.89
8/14/13	6.92	3.26	2.93	2.64	8.86
8/21/13	7.80	5.97	2.48	5.21	12.41
9/3/13	11.73	5.37	5.72	8.57	20.02
9/10/13	10.17	6.29	5.09	5.35	10.58
9/24/13	8.52	5.50	2.19	5.03	12.06
10/1/13	18.89	3.66	3.16	2.18	4.41
10/8/13	7.63	6.12	2.75	1.98	5.52
10/22/13	10.39	18.39	3.32	7.92	23.44
11/5/13	3.19	20.48	4.32	4.81	13.32
1/27/14	0.00	0.00	0.00	0.00	0.00
2/7/14	45.97	20.55	10.36	20.36	36.48
3/21/14	18.66	43.29	5.83	18.63	63.09
4/25/14	16.59	5.19	4.34	7.93	32.50
6/17/14	25.33	7.39	-	11.68	50.56
7/1/14	10.89	10.25	10.49	4.46	26.40
7/25/14	10.78	4.89	7.01	5.59	10.13
8/7/14	5.17	3.30	1.93	4.80	15.80
8/20/14	25.93	2.80	3.45	2.22	21.45
9/4/14	43.67	5.06	-	2.18	13.12
9/16/14	69.24	3.14	-	3.15	30.30
9/30/14	47.21	2.72	-	2.12	36.75
10/21/14	45.65	10.73	-	0.92	0.00
11/4/14	26.66	9.70	-	0.62	24.53
11/25/14	16.35	14.80	9.40	3.33	74.76
12/9/14	24.24	21.26	6.11	20.09	96.68
12/22/14	87.98	10.19	3.43	10.38	40.31
1/19/15	19.41	28.73	5.07	10.00	82.86
2/2/15	13.91	21.43	5.60	6.18	59.64
3/2/15	23.85	16.44	9.02	9.49	47.46
3/16/15	29.99	22.57	13.80	16.06	75.28

3/31/15	12.55	18.15	7.91	5.33	59.99
4/13/15	47.26	7.25	4.44	3.75	48.23
4/27/15	47.44	18.97	5.87	8.39	91.25
5/12/15	17.27	3.69	3.56	5.05	23.03
5/28/15	10.36	2.59	0.62	2.09	16.43
6/2/15	13.32	4.86	2.04	1.85	14.12
6/9/15	12.57	5.50	1.04	2.99	11.03
6/16/15	19.13	7.86	0.87	2.90	25.39
6/23/15	8.84	3.39	0.87	2.73	8.93
6/30/15	10.82	3.47	0.51	-	14.06
7/14/15	6.87	1.30	0.25	1.61	8.54
7/21/15	14.60	3.49	0.26	1.12	5.50
7/28/15	4.73	1.31	0.47	1.13	3.62
8/4/15	11.69	2.90	0.33	1.54	8.66
8/11/15	4.46	2.57	0.36	1.04	6.30
8/18/15	4.24	1.61	0.20	0.20	-
8/31/15	2.99	0.78	0.16	0.25	5.50
9/14/15	11.68	1.19	0.20	-	3.84
9/28/15	3.80	1.83	0.39	0.29	5.39
10/19/15	14.46	4.64	3.13	2.16	26.01
10/26/15	11.51	6.99	1.31	1.44	14.60
11/9/15	29.63	15.17	-	7.06	31.06
11/23/15	20.45	8.24	18.64	6.31	27.03
12/7/15	20.18	3.54	-	8.00	33.38
12/22/15	24.15	5.16	7.75	10.86	37.33
1/13/16	4.25	5.09	0.93	12.14	44.58
2/22/16	23.82	-	12.27	15.91	75.47
3/9/16	7.99	11.25	4.74	3.85	21.51
3/21/16	5.39	4.03	7.16	3.79	20.05
4/4/16	6.15	3.03	3.60	1.94	25.84
4/18/16	3.14	6.64	1.45	1.73	15.57
5/23/16	15.56	8.42	8.42	9.84	18.66
6/13/16	5.49	3.92	0.49	3.86	10.34
7/1/16	2.58	1.32	1.08	2.62	9.60